Molecular correlation functions in inertial and noninertial frames of reference

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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) 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. This is because the theories depend fundamentally on approximations which lead out of consideration all single molecule cross correlations such as \( \langle \mathbf{v}(t) \mathbf{w}(0) \rangle \). This correlates the molecular center of mass velocity \( \mathbf{v} \) and the same molecule's angular approximations result in overparametrization and confusion about frames of reference.

The state of uncertainty was finally resolved in 1981 by Fyskaert et al. using computer simulation. This proved that the cross correlation \( \langle \mathbf{v}(t) \mathbf{w}(0) \rangle \) 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 same dependence of cross correlation functions (ccf) of this type was confirmed by Evans et al. for different molecular symmetries ranging from low symmetry chiral molecules to spherical types of P2-point symmetry.

In 1985 the discovery of the ccf of \( \langle \mathbf{v}(t) \mathbf{w}(0) \rangle \) direct in the laboratory frame was reported by Evans 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 of \( \langle \mathbf{v}(t) \mathbf{w}(0) \rangle \) or \( \langle \mathbf{v}(t) \mathbf{w}(0) \rangle \) of the ccf, which is not generally true in the laboratory frame (x, y, z).

Again the contemporary theoretical approach was not predict what the outcomes of these computer simulations because of the difficulties of overparametrization in essentially empirical description of molecular diffusion.

Papers in 1983 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, centrifugal, 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 ccf 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 the rotation of the 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 complete the trajectory of some point on the center of mass of the body.

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 the vehicle of an example of frame of reference (1,2,3) (Fig. 1) whose origin is fixed at the origin of (x, y, z) but which rotates with constant angular velocity \( \omega \). 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 \( \omega \) is a rigid angular velocity (t-
self. Therefore, \( u \) is a constant of frame transformation from 
\((x, y, z)\) to \((x', y', z')\) or vice versa.

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

\[
D_\tau r = (D_\tau u + u \times r) \bar{r} \tag{1}
\]

and conversely

\[
D_\tau u = (D_\tau \bar{r} - u \times \bar{r}) r. \tag{2}
\]

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

\[
\{v_{x,y,z} r\} = \{v + u \times r\} \bar{r} \tag{3}
\]

\[
\{v_{x',y',z'} r\} = \{v - u \times r\} \bar{r} \tag{4}
\]

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

Equation (5) reverses the process, and shows that the center of mass linear velocity \( v \) in frame \((x', y', z')\) 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 translational imparts the linear velocity \( u \times r \) to its translational center of mass motion in the laboratory frame \((x, y, z)\).

The vector difference \( \{v - u \times r\}_{x',y',z'} \) also exists in frame \((x', y', z')\), the frame of the principal molecular moments of inertia, through the transformation, for any vector \( A \):

\[
A_x = A_{r1} + A_{r2} + A_{r3}, \tag{5}
\]

\[
A_y = A_{r1} + A_{r2} + A_{r3}, \tag{6}
\]

\[
A_z = A_{r1} + A_{r2} + A_{r3}, \tag{7}
\]

where the subscripts refer to the axes of the appropriate frame and where the unit vectors \( e_1, e_2, \) and \( e_3 \) are in the principal moment of inertia axes \(1, 2, \) and \( 3 \). Thus, \( e_x \) is the \( x \) component in frame \((x, y, z)\) of \( e_x \) and so on.

Using Eq. (5), therefore,

\[
(u \times r)_x = (u \times r)_1 e_1 + (u \times r)_2 e_2 + (u \times r)_3 e_3 \tag{8}
\]

and so on for the other components \((u \times r)_y \) and \((u \times r)_z \).

Equation (5), therefore, defines the existence of the linear velocity in the frame \((x', y', z')\). 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 operator, giving

\[
D_\tau (D_\tau r) = (D_\tau u + u \times r) \{D_\tau r + u \times \bar{r}\} \tag{9}
\]

and conversely

\[
D_\tau (D_\tau u) = (D_\tau \bar{r} - u \times \bar{r}) \{D_\tau r - u \times \bar{r}\} \tag{10}
\]

in terms of velocities

\[
\{v_{x,y,z} r\} = \{v + 2u \times r + u \times (u \times r)\}_{x,y,z} \tag{11}
\]

\[
\{v_{x',y',z'} r\} = \{v - 2u \times r - u \times (u \times r)\}_{x',y',z'} \tag{12}
\]

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

Equation (9) shows the Newtonian linear acceleration \( v \) 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 \((x', y', z')\). They are:

(i) the Newtonian acceleration \( v \);
(ii) the Coriolis acceleration \(-2u \times v\);
(iii) the centripetal acceleration \(u \times (u \times r)\); and
(iv) the nonuniform acceleration \(-u \times r\).

The last two of this list require explicit use of the position vector \( r \) 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

\[
\{r(t)\} = 0 \tag{13}
\]

\[
\lim (\{r(t) - r(0)\}) = 0 \tag{14}
\]

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

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3. Derivatives of the linear accelerations

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

\[ [V]_{x,x} = [D]_x + \alpha \frac{\partial}{\partial x} \left( 1 + 2a_x x \right) \]

\[ + \omega \frac{\partial}{\partial x} \left( \omega \left( \omega \frac{\partial}{\partial x} \right) \right)_{x,x} \quad (13) \]

and

\[ [V]_{t,x} = [D]_t - \omega \frac{\partial}{\partial x} \left( \omega \left( \omega \frac{\partial}{\partial x} \right) \right)_{t,x} \]

\[ - \omega \frac{\partial}{\partial x} \left( \omega \left( \omega \frac{\partial}{\partial x} \right) \right)_{t,x} \quad (14) \]

Therefore, there are, by Eq. (14), seven additional linear acceleration time derivatives to the Newtonian term \([V]_{t,x,x}\), both in frames \((x,x,t)\) and by Eq. (5) is frame \((2,3,2)\).

Equations (13) and (14) illustrate that the set of linear velocities, linear accelerations, and their time derivatives, to order \(a_{2,3,2}\), is enough to consider all these terms by definition. With advanced computer architecture, such as the Kingston ICAP, 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 ccf 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,

\[ [\omega]_{x,x} = [\omega]_{x,x,x} \quad (15) \]

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 \(3,7,11,...(2,3,2)\). This was the flow ccf to be discovered by computer simulation, viz. \(\langle \psi(\omega)\rangle_{\omega} \quad (1,2,3)\).

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 cfs, which should exist and which should just be noise, i.e., vanish by symmetry.

For example, the ccf between the linear velocity \(\omega \cdot x \cdot x\) and the angular velocity \(\omega \cdot x \cdot x\):

\[ \langle \omega(t) \cdot x \cdot x \rangle(t) \]

vanishes for nearly all molecular symmetries in frame \((1,2,3)\) by group symmetry for all \(t\) and vanishes in frame \((x,x,t)\) by parity symmetry for all molecules. This has been checked independently by computer simulation,\(^{28}\) which gave the expected results for a simple as small as 108 molecule cell of \(C_6\) symmetry.

2. Angular acceleration

This is generated by the usual operators

\[ [a]_{x,x,x} = [D]_x + \alpha \frac{\partial}{\partial x} \left( [a]_{x,x} \right)_{x,x} \quad (16) \]

\[ [a]_{t,x} = [D]_t - \omega \frac{\partial}{\partial x} \left( [a]_{x,x} \right)_{t,x} \]

which again give the simple result

\[ [a]_{x,x,x} = [a]_{x,x,x} \quad (18) \]

Therefore, again, there are no nonisolated 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

\[ \langle \psi(\omega)\rangle_{\omega} \quad (1,2,3) \]

in frame \((1,2,3)\). All the other possible cfs between the three non-Newtonian linear accelerations and \(\omega \cdot x \cdot x\) by symmetry is both frames.\(^{28}\) Again this has been checked individually by computer simulation for a 108 molecule sample of \(C_6\) triatomic molecules.

3. Angular acceleration derivatives

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

\[ [a]_{x,x,x} = [D]_x + \alpha \frac{\partial}{\partial x} \left( [a]_{x,x} \right)_{x,x} \]

\[ = [D]_x + \alpha \frac{\partial}{\partial x} \left( [a]_{x,x} \right)_{x,x} \]

\[ + \omega \frac{\partial}{\partial x} \left( \omega \left( \omega \frac{\partial}{\partial x} \right) \right)_{x,x} \]

\[ = [D]_x + \alpha \frac{\partial}{\partial x} \left( [a]_{x,x} \right)_{x,x} \]

\[ = [D]_x + \alpha \frac{\partial}{\partial x} \left( [a]_{x,x} \right)_{x,x} \]

\[ (19) \]

\[ (20) \]

In total therefor there are 16 possible cfs between the linear and angular acceleration derivatives in frames \((x,x,t)\) 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

\[ \langle a(t) \cdot x \cdot x \cdot A^{(n)}(0) \rangle \]

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


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The omega patterns

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

\[
\langle \omega | x| A(t) | A(0) \rangle_{(1,2,3)}\]

(23)

\[
\langle \omega | x| [\omega| x| A(t) | A(0) \rangle_{(1,2,3)}\]

(24)

and so on.

The B, D, patterns

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

\[
\langle D_y A(t) | A(0) \rangle \neq 0 \text{ for } t > 0
\]

both in frames (x,\(\omega\),\(\tau\)) and (1,2,3).

In one sense the result

\[
\langle \omega| x| A(t) | A(0) \rangle_{(1,2,3)} = 0
\]

in frame (1,2,3) is a special case of Eq. (32), which vanishes in frame (x,\(\omega\),\(\tau\)) because of the parity symmetry difference imposed by the vector cross product \(\omega| x| A(0)\). Using the result (32), then both in frames (x,\(\omega\),\(\tau\)) and (1,2,3) the following patterns of nonvanishing higher order cross correlation functions emerge from inspection of Eqs. (21) and (22),

\[
\langle \omega| x| A(t) | A(0) \rangle_{(1,2,3)} = \langle \omega| x| [\omega| x| A(t) | A(0) \rangle_{(1,2,3)} = 0
\]

(32)

(33)

(34)

(35)

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

\[
\langle D_y A(t) | B^\dagger(0) \rangle
\]

(36)

\[
\langle D_y A(t) | C(0) \rangle
\]

(37)

\[
\langle D_y A(t) | D(0) \rangle
\]

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

\[
\langle \omega | x| [\omega| x| A(t) | A(0) \rangle_{(1,2,3)} = 0
\]

(25)

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

\[
\langle \omega | x| x| A(t) | A(0) \rangle_{(1,2,3)} = 0
\]

(26)

(27)

(28)

(29)

(30)

(31)

(32)

(33)

(34)

(35)

(36)

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

IV. DISCUSSION

The above classification schemes allowed the identification of nonvanishing higher order cfs 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 cfs 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 cfs 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 it is nearer to the Raman or far infrared. The implementation of single molecular cells of all types to monite these transitions is a task that is not yet accomplished. The cells that have been made up both of rotational and translational variables, together with the center of mass coordinates \( r \).

The various experimentally observed phases of ice and the ice-water transition itself present an interesting challenge because the intermolecular pair potential for water is known to increase strongly with increasing accuracy. Large molecular dynamics sam-

B. Representations of flow phenomena on a molecular level

Recent molecular dynamics simulations\(^2\) of two-dimensional flow around a circular obstruction, using up to 160,000 hard discs, 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 the aid of fast computers. With this, however, there is no scope for the investigation of cells of the type mentioned in this paper, because the angular motion of each individual disc is not accessible for it. Nevertheless, 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 flow of the eddy past the translation motion of the flow prior to its encounter with the obstacle is obviously transformed into rotational motion, clockwise in the eddy and counter clockwise in the other. In three-dimensional fully molecular systems the cef in the region of the eddy downstream of the cylindrical obstacles should be significantly different from those in a solid fluid 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 cells by running time averaging would have to depend implicitly on the fact that the flow is 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 obstacle 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 corotating external electric fields, or a circularly polarized electric field such as

\[
E_r = E_0 \cos(\omega t - \frac{2\pi r}{\lambda}), \quad (37)
\]

\[
E_\theta = E_0 \sin(\omega t - \frac{2\pi r}{\lambda}), \quad (38)
\]

which is assumed to generate a torque of the form

\[
\mu \times E = \mu (\mathbf{E}_r - \mathbf{E}_0) \times \mathbf{I} = \mu (\mathbf{E}_r - \mathbf{E}_0)
\]

\[
+ k (\mathbf{E}_r - \mathbf{E}_0), \quad (39)
\]

with

\[
\mathbf{E}_r = 0; \quad \mathbf{E}_\theta = E_0 \cos \mu \mathbf{r}; \quad \mathbf{E}_z = E_0 \sin \mu \mathbf{r}. \quad (40)
\]

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

\[
(\mu \times \mathbf{E}_r) = -\mu E_0 \sin(\mu, \mathbf{r} - \mu, \mathbf{j})
\]

\[
+ E_0 \cos(\mu, \mathbf{r} - \mu, \mathbf{k}). \quad (41)
\]

and the left polarized torque is

\[
(\mu \times \mathbf{E}_r) = -\mu E_0 \sin(\mu, \mathbf{r} - \mu, \mathbf{j})
\]

\[
+ E_0 \cos(\mu, \mathbf{r} - \mu, \mathbf{k}). \quad (42)
\]

If selected sample regions of the molecular dynamics cubes are irradiated in a computer simulation with fields of type (41) or (42) vortices will be set up in a clockwise or counter-clockwise direction. It would be interesting to check if the effect these vortices have on the rest of the sample, and to see if the subsequent effects could be monitored by computer simulation. If 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 strongly circularly polarized field would rotate the chiral molecule, causing subsequent translation of the center of mass. Larger 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/translational 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, energy absorption spectrum, 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 cef 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 ultra-high 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 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.

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