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The Discovery and Classification of New Laboratory Frame Cross Correlation Functions

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Abstract

The discovery is reported of numerous new cross correlation functions in the laboratory frame of reference (x,y,z) which are invariant by parity and reflection symmetry operations. These are obtained systematically by repeated differentiation of coordinates and momenta in a rotating, or dynamically non-inertial, frame of reference. In principle, these cross correlation functions can all be used to analyze the nature of molecular dynamics in a computer simulation, and therefore greatly add to the methods already available for dynamical correlation.

I. Introduction

The recent introduction[1-7] of the rotating frame of reference has improved our understanding of molecular dynamics by increasing the number of cross correlation functions available for the statistical correlation of dynamical quantities in a molecular dynamics computer simulation. That work resulted in the discovery[1-3]

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and implementation[4-7] of several different types of *single particle* cross correlation function in the moving frame of reference defined by the principal molecular moments of inertia. However, none of the new cross correlation functions established by these means existed in the laboratory frame of reference (x,y,z), which is a handicap to their eventual experimental determination. In this paper systematic use is made of the rotating frame of reference to establish the rules by which the existence of laboratory frame cross correlation functions (c.c.f's) may be determined analytically. The rotating frame is defined as in previous work[1-3] as the frame (1,2,3)′ which rotates with the angular velocity of the molecule with its origin fixed at that of the lab. frame (x,y,z). It should therefore be carefully distinguished from the moving frame of the molecular principal moments of inertia (1,2,3) which both rotates and translates with the molecule. This letter shows that the systematic differentiation with time of dynamical quantities in the frame (1,2,3)′ and subsequent back transformation into (x,y,z) produces a set of symmetry rules by which to anticipate the existence of c.c.f's direct in frame (x,y,z). As far as we are aware this is the first time that the laboratory frame c.c.f's have been explicitly *shown to exist, i.e., a set of c.c.f's is derived analytically, each member of which survives the tests*[8-10] *of* parity and reflection symmetry in frame (x,y,z). This implies that these c.c.f.'s can be utilized for the analysis of molecular dynamics using the lab. frame directly, previous analyses along these lines having been restricted to frame (1,2,3) and therefore to computer simulation. The only previous report[11] of a non-vanishing laboratory frame c.c.f. has been in the presence of a strong uni-axial electric field which destroys the symmetry invariance to parity reversal of the classical hamiltonian.

II. Analytical Theory

If the frame (1,2,3)′ rotates with respect to (x,y,z) at the angular velocity $\vec{\omega}$ the differential operator, $\frac{d}{dt} \equiv \hat{D}_f$, in frame (x,y,z) is equivalent to

$$[\hat{D}_m + \vec{w}x]_{(1,2,3)'} \tag{1}$$

in frame (1,2,3)′ by a basic theorem of classical dynamics.[12] *(The following analysis has its full quantum* mechanical equivalent.) If the position of the molecular center of mass is $\vec{r}$ then $\hat{D}_f$ operates on $\vec{r}$ to produce the linear center of mass velocity $\vec{v}$. A further operation produces the acceleration and so on as usual. In Eqn. (1) the operator $\hat{D}_m$ is implied to act in frame (1,2,3)′, the rotating frame, to produce the velocity and acceleration with respect to frame (1,2,3)′. With these definitions we obtain the reciprocal relations

$$[\vec{v}]_{(x,y,z)} \equiv [\vec{v} + \vec{\omega}x\vec{r}]_{(1,2,3)'} \tag{2}$$

$$[\vec{v}]_{(1,2,3)'} \equiv [\vec{v} - \vec{\omega}x\vec{r}]_{(x,y,z)} \tag{3}$$

In these equations everything within the square brackets on one side is equivalent to the contents on the other side, i.e., in the other frame of reference. Accordingly the linear center of mass velocity $\vec{v}$ in frame (x,y,z) is equivalent to the sum of two terms in frame (1,2,3)′, known in the literature as the 'inertial' velocity $\vec{v}$ and the 'non-inertial' velocity $\vec{\omega}x\vec{r}$. Newton's laws of motion apply to 'inertial' frames, and do not apply to rotation superimposed on translation, or to 'non-inertial' frames. It is of course well known that classical molecular dynamics are 'non-inertial', the rotational motion being represented[13] by Euler equations or through Hamilton's quaternions. However, the effect of this basic everyday behavior on statistical cross correlation in ensembles of N molecules is unknown in frame (x,y,z) and is the subject of this analysis. The accelerations equivalent to the velocities in Eqns. (2) and (3) are generated by two differential operations:

$$\hat{D}_f(\hat{D}_f\vec{r}) \equiv (\hat{D}_m + \vec{\omega}x)((\hat{D}_m + \vec{\omega}x)\vec{r}) \tag{4}$$

$$\hat{D}_m(\hat{D}_m\vec{r}) \equiv (\hat{D}_f - \vec{\omega}x)((\hat{D}_f - \vec{\omega}x)\vec{r}) \tag{5}$$

producing the result

$$[\vec{v}]_{(x,y,z)} \equiv [\vec{v} + 2\vec{\omega}x\vec{v} + \vec{\omega}x\vec{r} + \vec{\omega}x(\vec{\omega}x\vec{r})]_{(1,2,3)'} \tag{6}$$

$$[\vec{v}]_{(1,2,3)'} \equiv [\vec{v} - 2\vec{\omega}x\vec{v} - \vec{\omega}x\vec{r} + \vec{\omega}x(\vec{\omega}x\vec{r})]_{(x,y,z)} \tag{7}$$

This reveals the existence of three non-inertial accelerations in both frames. In the laboratory frame (x,y,z) two of them are known traditionally as the Coriolis acceleration, $-2\vec{\omega}x\vec{v}$, and the centripetal acceleration, $\vec{\omega}x(\vec{\omega}xr)$.[12,13] The third exists whenever there is non uniform angular motion, so that the derivative of the angular velocity exists, i.e., whenever there are torques caused by intermolecular fields of force and torque. Applying the differential operator n times produces

$$[\vec{v}]^{(n+2)}_{(x,y,z)} = [\hat{D}_m + \vec{\omega}x]_{(1)}[\hat{D}_m + \vec{\omega}x]_{(2)}\cdots\cdots[\hat{D}_m + \vec{\omega}x]_{(n)}[\vec{v} + 2\vec{\omega}x\vec{v} + \vec{\omega}x\vec{r} + \vec{\omega}x(\vec{\omega}x\vec{r})]_{(1,2,3)'} \tag{8}$$

$$[\vec{v}]^{(n+2)}_{(1,2,3)'} = [\hat{D}_m - \vec{\omega}x]_{(1)}[\hat{D}_m - \vec{\omega}x]_{(2)}\cdots\cdots[\hat{D}_m - \vec{\omega}x]_{(n)}[\vec{v} - 2\vec{\omega}x\vec{v} - \vec{\omega}x\vec{r} + \vec{\omega}x(\vec{\omega}x\vec{r})]_{(x,y,z)} \tag{9}$$

so it becomes clear that the number of linear non-inertial terms rapidly increases with the order of differentiation. This is not an original result in itself, but the structure of Eqns. (8) and (9) is now used to provide a set of original rules by which to define the existence of new laboratory frame cross correlation functions in N molecule ensembles. These can be investigated by numerical computer simulation[14] in situations of experimental value and interest. Before proceeding to this the previous work in the moving frame (1,2,3) can be summarized very succinctly in terms of three sets of patterns of non-vanishing c.c.f.'s in this frame:

(1) The Omega Pattern: By inspection of the terms in the laboratory frame and by application of the standard rotation operation[15] into frame (1,2,3) from frame (x,y,z) for any dynamical vector it emerges that c.c.f's of the following type exist for $t > 0$ in frame (1,2,3):

$$<\vec{\omega}(t)x\vec{A}(t)\vec{A}^T(0)>_{(1,2,3)}. \tag{10}$$

This confirms the work already in the literature, which was produced by actual computation[1-7] of cross correlation functions. The omega pattern of Eqn. (10) contains the c.c.f's which were found to exist by computer simulation, thus confirming its validity.

(2) A subset of the ω pattern is $<\vec{\omega}(t)x\hat{D}_f\vec{A}(t)\vec{\omega}^T(0)>$, all members of which exist in frame (1,2,3) from inspection of the general Eqn. (9).

(3) Finally in frame (1,2,3) there exist patterns of c.c.f.'s made up of cross terms of the operator multiplications in Eqn. (9). None of these seems to have been actually explored yet for its time dependence from computer simulation, but each and every one is potentially useful for the statistical analysis of ensembles of molecules under all conditions of interest.

III. Non-Vanishing C.C.F.'s in the Laboratory Frame (x,y,z)

The basic condition for the existence of laboratory frame cross correlations is a very simple one, but when applied to linear non-inertial terms in Eqn. (9) it immediately produces a number of original results.

It is well known that laboratory frame c.c.f's of the type

$$< \dot{\vec{A}}(t) \bullet \vec{A}^T(0) >_{(x,y,z)} \tag{11}$$

exist for $t > 0$. Here the cross correlation is constructed between an inertial term such as the Newtonian linear center of mass velocity $\vec{v}$ and its time derivative. By applying the theorem (11) to linear non-inertial terms we come to the essence of this letter, for this process immediately produces the required patterns of non-vanishing c.c.f's involving both angular and linear molecular motions. These patterns may be summarized succinctly as follows , and emerge, as for frame (1,2,3), from an inspection of the general operator equation (9).

(1) *The* $\hat{D}_f$ *Pattern*: This is simply

$$< \hat{D}_f \vec{B}(t) \vec{B}^T(0) >_{(x,y,z)} \tag{12}$$

where in general the vector quantity $\vec{B}$ is a linear non-inertial dynamical variable. For example, one of the simplest applications of Eqn. (12) is

$$< \hat{D}_f (\vec{v}(t) - \vec{\omega}(t) \times \vec{r}(t))(\vec{v}(0) - \vec{\omega}(0) \times \vec{r}(0))^T > \tag{13}$$

which immediately shows the *possible*. existence of the six lab. frame cross correlation functions:

$$a. \quad < \dot{\vec{v}}(t) \vec{v}^T(0) >_{(x,y,z)} \tag{14a}$$

$$b. \quad < \dot{\vec{v}}(t) (\vec{\omega}(0) \times \vec{r}(0))^T >_{(x,y,z)} \tag{14b}$$

$$c. \quad < \dot{\vec{\omega}}(t) \times \vec{r}(t) \vec{v}^T(0) >_{(x,y,z)} \tag{14c}$$

$$d. \quad < \dot{\vec{\omega}}(t) \times \vec{v}(t) \vec{v}^T(0) >_{(x,y,z)} \tag{14d}$$

$$e. \quad < \vec{\omega}(t) \times \vec{v}(t) (\vec{\omega}(0) \times \vec{r}(0))^T >_{(x,y,z)} \tag{14e}$$

$$f. \quad < \dot{\vec{\omega}}(t) \times \vec{r}(t) (\vec{\omega}(0) \times \vec{r}(0))^T >_{(x,y,z)} \tag{14f}$$

The first of this group of six is the Newtonian (or linear inertial) c.c.f. The other five all contain the molecular angular velocity and are linear non-inertial in nature because of this. They vanish only when $\vec{\omega}$ vanishes and therefore distinguish molecular from atomic ensembles.

It is now easy to see that repeated application of the above procedure for more complex $\bar{B}$'s from inspection of the general equation (9) will produce very many new lab frame c.c.f.'s whose existences do not seem to be shown in the literature and whose explicit time dependences are unknown. Having taken the argument this far it is a small further step to obtain the actual time dependence by computer simulation. A second example will be sufficient illustration of the analytical argument. Applied to the $\bar{B}$ which is one of the terms in Eqn. (9), theorem (12) then produces the following cross correlation functions

$$< \hat{D}_f(\vec{\omega}(t)x(\vec{v}(t) - \vec{\omega}(t)x\vec{r}(t)))(\vec{\omega}(0)x(\vec{v}(0) - \vec{\omega}(0)x\vec{r}(0)))^T > \qquad (15)$$

which all exist in frame (x,y,z) and this time are all linear non-inertial in nature.

(2) The D_f pattern just described can be extended to certain cross terms from Eqn. (9) provided that the general symmetry remains that of Eqn. (12). These terms can be obtained easily from Eqn. (9) by inspection.

IV. Parity, Reflection Symmetry, and Time Reversal

Parity and reflection are well known symmetry operations[8-10] in frame (x,y,z) which apply for isotropic non-chiral ensembles in the absence of external force fields that may affect the invariance to these symmetry operations of the classical hamiltonian. They can be used to test the validity of the results obtained already in this letter. Since all the single particle correlations listed in Eqns. (14a-f) will not have any spatial dependence due to the homogeneity of the system, all these c.c.f.'s should therefore be invariant under the parity and reflection operations. This is indeed the case as can be easily checked out. Note that a c.c.f., such as $<\vec{\omega}(t)x\vec{v}(t)\vec{\omega}^T(0)>$, which does not fit into the general $\hat{D}_f$ pattern fails both symmetry tests. Another example is the simple c.c.f $<\vec{v}(t)\vec{\omega}^T(0)>$. This c.c.f. passes the reflection test but is not invariant under parity operation. This agrees with the pioneering work of Ryckaert *et al.* who were the first to detect the time dependence of this c.c.f. only in frame (1,2,3). Using the arguments of this letter this can now be classified as the simplest c.c.f between the linear inertial velocity $\vec{v}$ and the angular velocity $\vec{\omega}$, and thus belongs to a different pattern of c.c.f.'s because the c.c.f.'s considered in this work are always among linear terms of some kind, be these inertial or non-inertial in origin. For example, the centripetal and Coriolis accelerations are linear accelerations, although they are generated from cross products containing the angular velocity. So, when a discus is released by the thrower it has a linear trajectory as for a linearly propelled projectile such as a javelin.

All the c.c.f.'s in Eqn. (14) change sign under time reversal operation. That means if they do exist in the laboratory frame, they should be odd functions of t and vanish at $t=0$. Cross correlation functions of this type, for example $<\vec{\omega}(t)x\vec{v}(t)(\vec{\omega}(0)x\vec{v}(0))^T>$, have already been observed in our laboratory.

V. Discussion

The analytical arguments of this letter have revealed the existence in principle of cross correlation functions of many different kinds directly in the laboratory frame (x,y,z). The time dependences of these are unknown.

indeed the only lab frame c.c.f explored so far is one generated by an external electric field.[11] The new c.c.f.'s pass the appropriate symmetry tests and are all potentially useful as analytical tools for use in computer simulation. It would be particularly interesting to implement these new c.c.f.'s in the investigation by computer simulation of hydrodynamical flow phenomena, phase transitions, and likewise which need correlation criteria particularly sensitive to the interaction between rotational and translational motion in frames (x,y,z) and (1,2,3). Work in these directions is in progress in our laboratory.

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