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Effect of circular flow on single-molecule cross-mode correlations in liquid water

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In a molecular-dynamics computer simulation of liquid water, a circular field of force is applied to a central region of about 250 molecules out of a total of 500 molecules. This is achieved by dividing the molecular-dynamics sample into an outer cube subject to periodic boundary conditions, and an inner cube, whose side is 0.75 of that of the outer cube. The inner cube (containing roughly half the molecules on average) can therefore be seen as subject to natural or thermal boundary conditions for the circular flow set up there. The effect of this circular flow on the molecular dynamics of all 500 molecules is then studied by means of autocorrelation and cross-correlation functions in the laboratory frame, and in the moving frame defined by the principal moment of inertia axes of the water molecule. The results are compared with equivalents in 500 molecules of liquid water at equilibrium, and the effects of rotational flow on the symmetry of various single-molecule cross-mode coupling tensors are discussed in detail.

I. INTRODUCTION

The studies in two dimensions of linear flows recently initiated by Clementi and co-workers have revealed the ability of molecular-dynamics computer simulation to reproduce the classical phenomena of hydrodynamics from the classical Hamiltonian.[1-3] Thus molecular dynamics, with the simplifying assumption of pairwise additivity in the (model) pair potential, can produce eddies and vortices of hydrodynamics through the intermediary of computer simulation in two dimensions, using up to 160 000 interacting disks.

In this article an attempt is made to explore the effect of an external circular field of force on liquid water in three dimensions. It is important to understand how far computer simulation can go at present towards building up the elementary flow phenomena of water and also to understand the effect of circular and linear flow on the symmetry[4] of cross-mode coupling at the single-molecule level. These would be the first steps towards linking molecular dynamics and hydrodynamics in water and aqueous environments. Ultimately, the technique of computer simulation on the parallel processors now in the course of rapid evolution at IBM Kingston and elsewhere would hope to tackle problems of aqueous flow of importance to engineering.

Cross-mode coupling on the single-molecule level is affected by the presence of circular force fields applied to the water sample under consideration. Cross-mode coupling can be investigated statistically by means of time cross-correlation functions provided that the segment over which the running-time average is constructed finds the sample in a statistically stationary condition. In the present work a constant circular force field is applied to a central region of the sample containing on average about half the molecules in the complete molecular-dynamics cube of 500 molecules subject to periodic boundary conditions. The inner region is confined to the molecules inside a cube, concentric with the outer, whose side is 0.75 of that of the outer cube, and whose volume is therefore half that of the complete sample. The inner cube is not subject to periodic boundary conditions, so that the effects of the circular field, applied in this inner region only, are shielded from any artifacts introduced by periodicity.

The statistics of the complete sample are then analyzed in detail with a range of laboratory and moving frame time correlation functions introduced recently for isotropic molecular dynamics by Evans and co-workers.[5-10] The symmetry properties of the cross-correlation functions then provide ample scope to distinguish between the properties of water at thermal equilibrium and subject to a constant external circular flow field. It is seen that the symmetry rules governing the existence of cross-correlation functions in both frames no longer apply in the presence of circular flow because the sample is no longer isotropic in the x, y, and z axes of the laboratory frame. This allows many new cross-correlation functions (ccf's) to appear in the presence of flow. It may then be inferred that in the region of an aqueous vortex (or whirlpool) such ccf's would characterize the hydrodynamic vortex phenomenon in terms of single-molecule cross-mode coupling in liquid water. Similar considerations would apply to linear flow in liquid water, where a different set of time ccf's might be expected to appear with different tensor symmetries on the single-molecule level.

II. COMPUTER SIMULATION METHODS

The circular flow is induced in the inner cube through a force field of the type

$$\mathbf{F}=F_y\hat{\mathbf{j}}-F_x\hat{\mathbf{i}} , \tag{1}$$

$$F_x=F_0y/(x^2+y^2)^{1/2} , \tag{2a}$$

$$F_y=F_0x/(x^2+y^2)^{1/2} \tag{2b}$$

which is a function of the radius vector of each molecule's center of mass and propels all the molecules in the inner cube on to a circular track about the z axis of the laboratory frame. At the edges of the inner cube the individual flowing water molecules encounter those in the outer-cube region not directly subjected to the externally applied circular force field. The molecules in the inner cube are not, however, directly subject to periodic boundary conditions, which would otherwise impair the counter clockwise symmetry of the flow in the inner cube. The molecules in the outer-cube region thus shield those in the inner cube from periodicity, and for this reason, the inner cube may be looked upon as subject to thermal, or natural, boundary conditions. Eventually the flow set up in the inner cube may be expected to propagate in the outer-cube region, but experience with the two-dimensional simulations has shown[1-3] that this might occur, but would need several picoseconds, and for water this means a 100 000 timesteps or more.

The introduction of the external field of force of type (1) into the forces loop of the constant volume computer simulation algorithm used for this work causes an increase both in the translational and rotational kinetic energy (equivalent to + 20 kJ/mole). The temperature in a computer simulation at constant volume is usually set proportional to the mean rotational and translational kinetic energies over all the molecules in the sample at each timestep and the mean over the complete run computed at the end. This is a satisfactory procedure for samples at thermal equilibrium, but an external field of force of any type, whether mechanical, as in this paper, or electric, as in some previous work by Evans[10-15] causes the thermal temperature to be supplemented artificially by the kinetic energy introduced by the field. In this work this effect is countered by a temperature rescaling method which forces the temperature back to the input value of 293 K approximately every 50 timesteps. This is the same method as that used in previous work with electric fields.

The water-water molecular pair potential was modeled with a sum over site-site outeractions consisting of three Lennard-Jones atom-atom terms supplemented by partial charges on the hydrogen atoms and on the lone pair electrons. The complete pair potential has been tested for its thermodynamic and structural behavior as described fully elsewhere.[16,17]

The results in the presence of the circular field were compared with those in field-free equilibrium water using the same number of records, taken from 1000 configurations of 500 molecules each. All configurations were generated on the experimental 1CAP1 system at IBM Kingston, which allows implementation of parallel processing with up to 10 FPS array processors attached to a powerful IBM host computer. The configurations were stored on disks, and filter algorithms were prepared to translate the data into a form suitable for the construction of running-time averages in the core of the host processor. This allowed all auto and cross-correlation functions to be computed in about a minute each of real time. As with all the correlation calculations, the noise level increases the further out from the time origin and becomes significant only in the tails of the cross-correlation functions studied here.

III. THERMODYNAMIC AVERAGES

As this is one of the biggest samples of water simulated using the potential developed by Evans, it is of interest to compute some field-free averages and to note any sample size effect in comparison with previous results on 108 molecules only. For an input temperature of 293 K and an input molar volume of 1.8×10^{25} Å^3 the following thermodynamic averages were obtained over a segment of 1000 configurations: mean translational temperature = 309.1 K; mean rotational temperature = 325.4 K; mean pressure = −662 bar; mean potential energy = −34.93 kJ/mole; mean total energy = −27.02 kJ/mole.

In each case there are no statistically significant changes from the 108 molecule simulations carried out previously by Evans *et al.* and reported elsewhere.[16,17] This is ample evidence that sample effects are negligible for these quantities. It turns out that the same is also true of the dynamical time correlation functions, such as the autocorrelation functions in water at equilibrium and the ccf's.

IV. RESULTS AND DISCUSSION

A. Single-molecule cross-mode correlation

Cross-mode correlation is compared, item by item, for field-on and field-off segments, each of 1000 configurations and 500 molecules total. In the field-on case the averaging is carried out over all 500 molecules, for consistency of comparison with the field-off case, but the field is applied, as mentioned already, only to those molecules in the inner cube. The cross-mode correlation is measured through a number of different ccf's, in the laboratory frame (x,y,z) and in the moving frame (1,2,3) of the water molecule's principal moment of inertia axes. Any dynamical quantity A can be transformed into the frame (1,2,3) from the frame (x,y,z) with the frame transformation relations

$$A_1 = A_x e_{1x} + A_y e_{1y} + A_z e_{1z} \ , \tag{3}$$

$$A_2 = A_x e_{2x} + A_y e_{2y} + A_z e_{2z} \ , \tag{4}$$

$$A_3 = A_x e_{3x} + A_y e_{3y} + A_z e_{3z} \ . \tag{5}$$

The time ccf's in either frame take the general form

$$\mathbf{C}(t) = \langle \mathbf{A}(t)\mathbf{B}^T(0) \rangle \ , \tag{6}$$

where T denotes vector transposition. Therefore each ccf is a 3×3 matrix of time-correlation functions. As we shall see the symmetry of this matrix is changed in the presence of the rotating external flow field for several of the ccf's investigated here in both frames of reference. This is a key to detecting the presence of a vortex in terms of single-molecule cross-mode couplings of many different kinds. It may be shown analytically that there are an infinite number of possible laboratory frame ccf's which may be used for this purpose. All of these utilize the noninertial linear velocities, accelerations, and time derivatives as classified theoretically in some recent work by Evans.[18] All these laboratory frame ccf's survive the fundamental symmetry rules of time reversal, parity reversal, and reflection in the *xz*, *yz*, and *xy* planes of the laboratory frame in an isotropic liquid medium. (In the presence of circular flow these symmetry rules no longer apply.)

In the moving frame (1,2,3) the symmetry rules that apply in an isotropic environment are those of point group theory, and in this respect the 500-molecule simulation of the present work confirms in all respects the results found previously by Evans and co-workers with 108 molecules in a field-free isotropic aqueous medium.[16,17] Again in the presence of circular flow in the inner cube the overall isotropy of the sample vanishes, and this has the effect of making possible the appearance of new types of single-molecule cross-mode coupling in the vicinity of a vortex or whirlpool.

B. Laboratory frame ccf's

We confine ourselves to an illustration of the effect of circular flow on two only out of the set of laboratory frame ccf's derived analytically by Evans. These are

$$C_1^{ij}(t)_{xyz}=\frac{\langle[\mathbf{v}(t)\times\boldsymbol{\omega}(t)]_i[\mathbf{F}(0)\times\boldsymbol{\omega}(0)]_j\rangle}{\langle[\mathbf{v}(0)\times\boldsymbol{\omega}(0)]_i^2\rangle^{1/2}\langle[\mathbf{F}(0)\times\boldsymbol{\omega}(0)]_j^2\rangle^{1/2}} \tag{7}$$

and

$$C_2^{ij}(t)_{xyz}=\frac{\langle[\mathbf{v}(t)\times\omega(t)]_i[\mathbf{T}_q(0)\times\mathbf{v}(0)]_j\rangle}{\langle[\mathbf{v}(0)\times\boldsymbol{\omega}(0)]_i^2\rangle^{1/2}\langle[\mathbf{T}_q(0)\times\omega(0)]_j^2\rangle^{1/2}} \tag{8}$$

which are members of the general set of acf's

$$C_3(t)_{xyz}=\langle\,\mathbf{A}(t)\dot{\mathbf{A}}^T(0)\rangle\ . \tag{9}$$

Here $\boldsymbol{\omega}$ is the molecular angular velocity, $\mathbf{v}$ the molecular center of mass linear velocity, $\mathbf{F}$ the net force on a molecule, and $\mathbf{T}_q$ the net torque. Thus $2\mathbf{v}\times\boldsymbol{\omega}$ is the molecular Coriolis acceleration in the laboratory frame (x,y,z). Both these ccf's survive the symmetry constraints mentioned already. Figures 1 and 2 are comparisons of the nonvanishing elements with and without circular flow. In the absence of flow, in the isotropic water sample the diagonal elements of tensors (7) and (8) exist in the laboratory frame of reference, and for (8) reach values of about 0.6 from an initial zero value at $t=0$. The effect of the rotational flow on the overall symmetry of tensor (7) is as follows:

$$C_1(t)=\begin{bmatrix}+&0&0\\0&+&0\\0&0&+\end{bmatrix}_{(x,y,z)}\rightarrow\begin{bmatrix}+&+&0\\+&+&0\\0&0&+\end{bmatrix}_{(x,y,z)},$$

i.e., it promotes the existence directly in the laboratory frame of the off-diagonal (x,y) and (y,x) elements, which

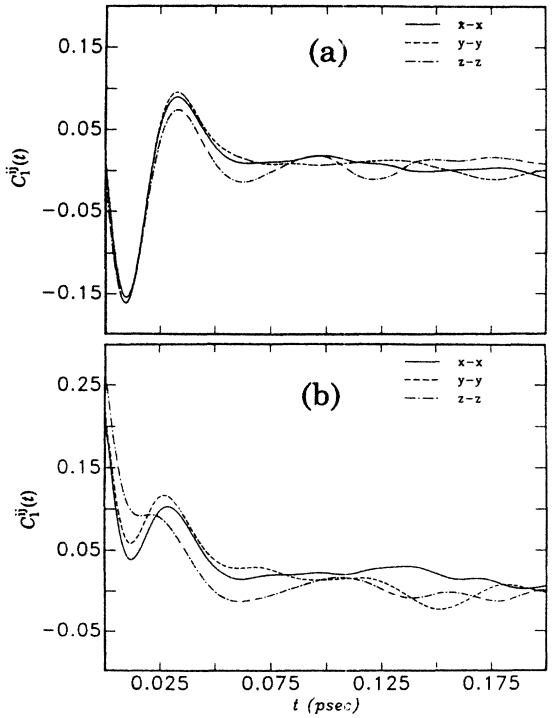

FIG. 1. Time dependence of the elements of the matrix $\mathbf{C}_1(t)$: (a) field-off results; (b) field-on results.

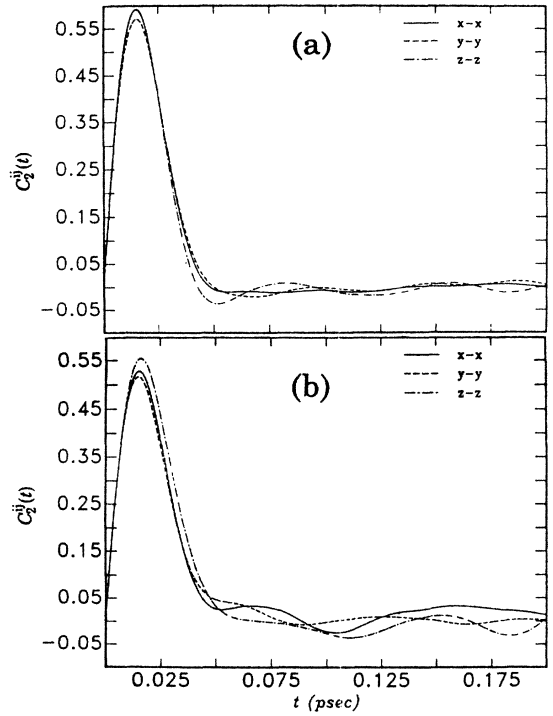

FIG. 2. Elements of the matrix $\mathbf{C}_2(t)$: (a) field-off results; (b) field-on results.

have the same time dependence within the noise. The rotational flow in the inner cube also changes considerably the time dependence of the diagonal elements, inducing a nonzero value at $t=0$ for (7); in the absence of flow each diagonal element vanishes at $t=0$ [Figs. 1(a) and 1(b)]. Therefore the properties of this tensor give ample scope for linking the presence of a rotational flow with single-molecule cross-mode coupling. In Fig. 2 the effect of the flow on the tensor $\mathbf{C}_2(t)$ is seen to be very much less pronounced, both in terms of the zero-time intercept and in time dependence. However in this case also there are signs of the appearance of off-diagonal (x,y) and (y,x) elements for rotational flow around the laboratory frame z axis.

C. Moving frame ccf's

The simple ccf tensor between center of mass linear velocity and molecular angular velocity exists by symmetry for the water molecule in an isotropic or nonisotropic aqueous environment. In the isotropic (field-free) case the matrix is dominated by the (2,3) element of the (1,2,3) frame of the principal molecular moments of inertia. For 500 water molecules this reaches a maximum value of 0.13 when normalized by

$$C_4^{ij}(t)_{123}=\frac{\langle v_i(t)\omega_j(0)\rangle}{\langle v_i^2\rangle^{1/2}\langle \omega_j^2\rangle^{1/2}} \qquad (10)$$

which compares with a value of 0.15 for a sample of 108 field-free water molecules. Therefore again there is little or no statistically significant effect of sample size on this

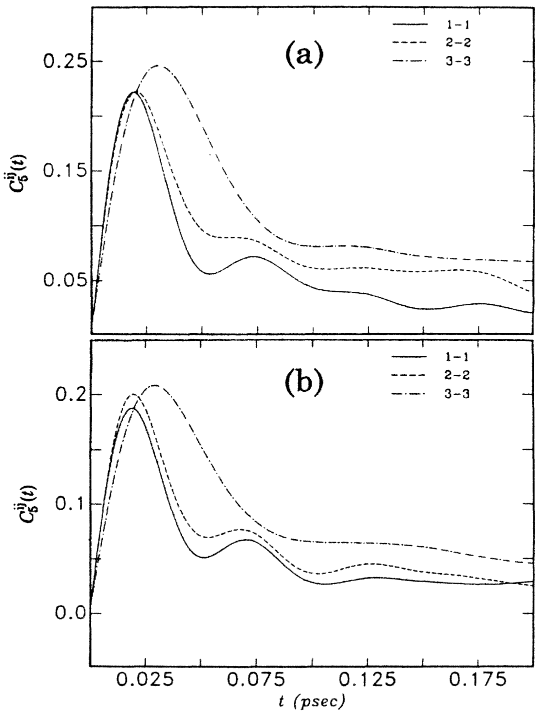

FIG. 4. Elements of the matrix $\mathbf{C}_5(t)$: (a) field-off results; (b) field-on results.

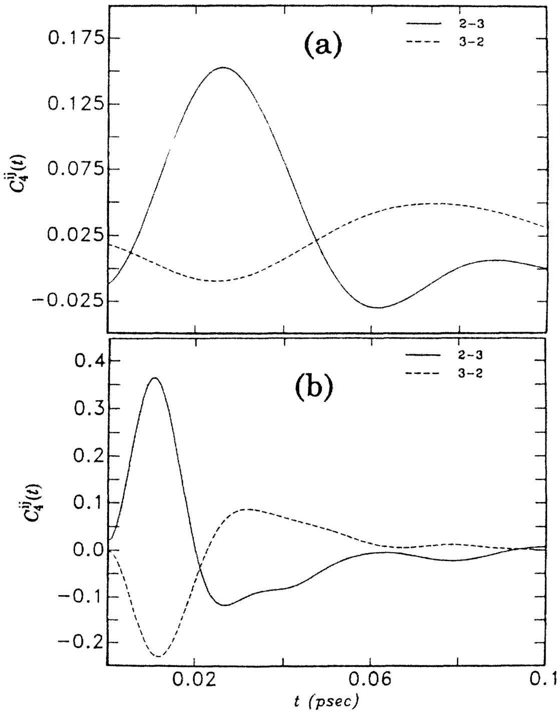

FIG. 3. Time dependence of the elements of the matrix $\mathbf{C}_4(t)$: (a) field-off results; (b) field-on results.

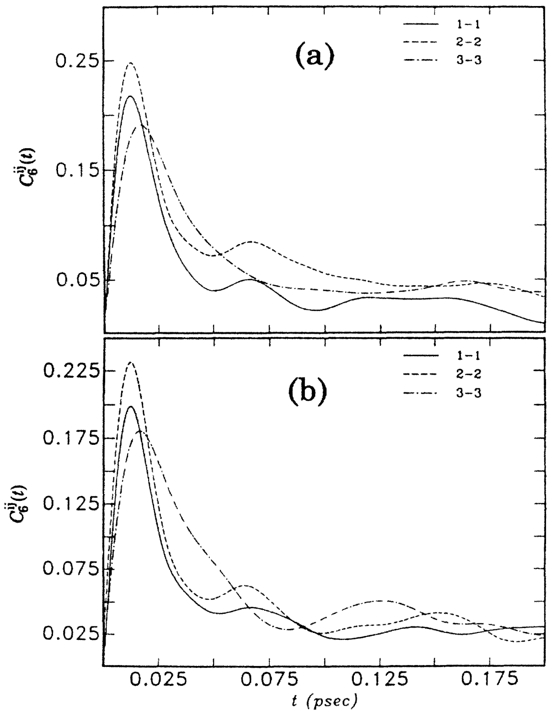

FIG. 5. Elements of the matrix $\mathbf{C}_6(t)$: (a) field-off results; (b) field-on results.

cross-correlation function. A third confirmation of its existence has recently been obtained[19] from an investigation using 343 water molecules and the flexible *ab initio* MCYL potential.[20] Similar checks in the field free case have been carried out for all the time correlation functions illustrated in this article.

The effect of the rotational flow in the inner sample is as illustrated in Fig. 3. The overall symmetry effect in frame (1,2,3) is as follows:

$$\mathbf{C}_4(t)=\begin{bmatrix}0&0&0\\0&0&+\\0&+&0\end{bmatrix}_{(1,2,3)}\rightarrow\begin{bmatrix}0&0&+\\0&0&+\\+&+&0\end{bmatrix}_{(1,2,3)},$$

i.e., the circular flow promotes the existence of more elements of the 3×3 correlation matrix in the moving frame (1,2,3). The (2,3) element itself is amplified to twice the field-free maximum by the rotational flow in the inner cube (Fig. 3) which also promotes the existence in frame (1,2,3) of the (3,2) element, reaching a negative maximum of -0.12. There are also signs of the existence of the (3,1) and (1,3) elements, but these are more noisy in appearance and smaller in amplitude.

In contrast to the behavior of the simple ccf tensor $\mathbf{C}_4(t)$ the effect of the field on the tensor

$$\mathbf{C}_5^{ij}(t)_{123}=\frac{\langle[\mathbf{r}(t)\times\boldsymbol{\omega}(t)]_i\mathbf{r}_j(t)\rangle}{\langle[\mathbf{r}(0)\times\boldsymbol{\omega}(0)]_i^2\rangle^{1/2}\langle\mathbf{r}_j^2(0)\rangle^{1/2}}\tag{11}$$

is to decrease the amplitude of the diagonal elements, with no effect on the off-diagonal elements as shown in Fig. 4. Different again is the behavior of the matrix

$$\mathbf{C}_6^{ij}(t)_{123}=\frac{\langle\{[\boldsymbol{\omega}(t)\times\mathbf{r}(t)]\times\boldsymbol{\omega}(t)\}_i[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]_j\rangle}{\langle\{[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]\times\boldsymbol{\omega}(0)\}_i^2\rangle^{1/2}\langle[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]_j^2\rangle^{1/2}},\tag{12}$$

where Fig. 5 shows virtually no change in amplitude or time dependence as a result of applying the field.

The overall symmetry behavior both of $\mathbf{C}_5(t)$ and $\mathbf{C}_6(t)$ is therefore:

$$\mathbf{C}_5(t)=\mathbf{C}_6(t)=\begin{bmatrix}+&0&0\\0&+&0\\0&0&+\end{bmatrix}_{(1,2,3)}\rightarrow\begin{bmatrix}+&0&0\\0&+&0\\0&0&+\end{bmatrix}_{(1,2,3)}$$

in contrast to the simple ccf matrix $\mathbf{C}_4(t)$. Further symmetry changes are induced by the rotational field in the ccf matrix

$$\mathbf{C}_7^{ij}(t)_{123}=\frac{\langle[\boldsymbol{\omega}(t)\times\mathbf{v}(t)]_iv_j(0)\rangle}{\langle[\boldsymbol{\omega}(0)\times\mathbf{v}(0)]_i^2\rangle^{1/2}\langle v_j^2(0)\rangle^{1/2}},\tag{13}$$

where the effect of rotation about the z axis in the inner cube may be summarized as

$$\mathbf{C}_7(t)=\begin{bmatrix}+&0&0\\0&+&0\\0&0&+\end{bmatrix}_{(1,2,3)}\rightarrow\begin{bmatrix}+&0&+\\0&+&+\\+&+&+\end{bmatrix}_{(1,2,3)}$$

The field increases the amplitude of the diagonal components of this moving frame matrix to about twice the value in the field-free isotropic sample [Figs. 6(a) and 6(b)] and also promotes the existence, above the noise, of mirror image off-diagonal elements (1,3) and (3,1) and (2,3) and (3,2) which do not exist in the field-free matrix. In contrast to the field-induced off-diagonal elements in the laboratory frame the induced moving frame off-diagonal elements are mirror images in time dependence.

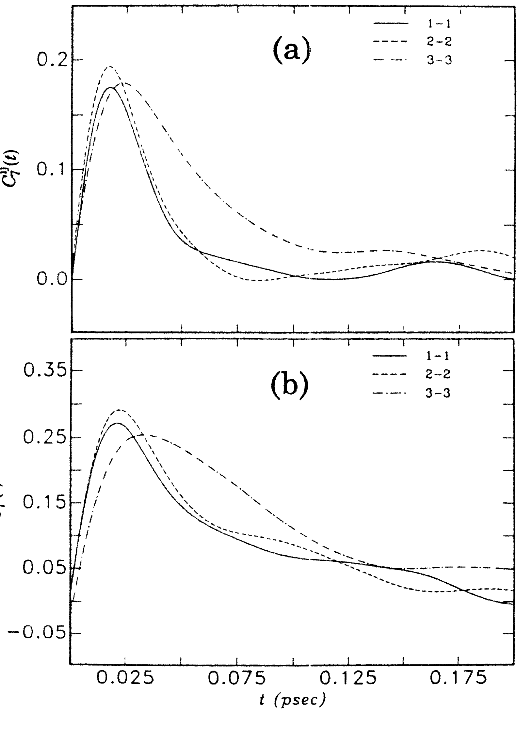

FIG. 6. Elements of the matrix $\mathbf{C}_7(t)$: (a) field-off results; (b) field-on results.

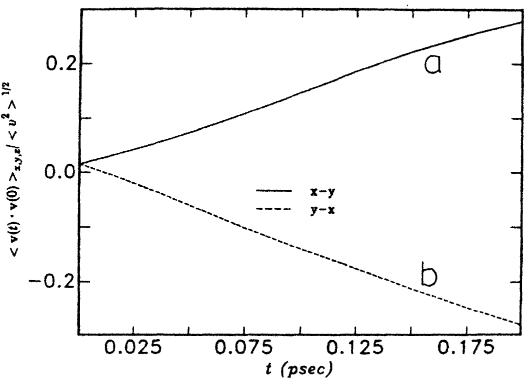

FIG. 7. Elements of the center of mass velocity autocorrelation matrix with field on.

D. Field induced laboratory frame acf's

The most direct effect of the induced rotational flow in the inner cube is seen in the (x,y) and (y,x) components of the 3×3 tensor acf of the laboratory frame center of mass linear velocity, as illustrated in Fig. 7. Within the noise, these off-diagonal elements have the same time dependence with a strong element of autocorrelation at $t=0$ between the x and the y components in the laboratory frame. This is caused by the nature of the circular field of force, (1) and (2), where there is a direct outer relation between the x and y components of force. Similarly the (y,z) and (z,y) components of this matrix seem to exist in the laboratory frame above the noise of the simulation. These off-diagonal elements vanish in the laboratory frame for an isotropic sample and are clearly therefore an effect of rotational flow on the single-molecule level.

Therefore there is considerable scope for the analysis of rotational flow and vortex effects in terms of single-molecule cross-mode coupling as measured through time cross-correlation functions as in this article. The same technique could be developed for the analysis of linear flow and for the interpretation of vortex and eddies in terms of phenomena on the single-molecule level.

The field-on cross correlations are inevitably accompanied by the appearance of flow induced birefrigence and are accessible by using computer simulation to interpret this phenomenon in terms of the same molecular-dynamical information used to describe the anisotropy of the laboratory frame orientational autocorrelation function.

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