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Symmetry of cross-correlation tensors in molecular dynamics: Rotation and translation in condensed matter

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The three-dimensional diffusion of an asymmetric-top molecule is described in terms of the linked translational and rotational Langevin equations both written in the moving frame of reference. The terms appearing in these equations suggest the existence of cross-correlation tensors in the moving frame (1,2,3) and in the laboratory frame (x,y,z). Their existence has been confirmed by molecular-dynamics computer simulation both in the absence and presence of a strong external electric field of force. The symmetry group to which the cross-correlation tensors belong depends on the variables being correlated, and changes when the field is applied. The latter is capable of generating cross-correlations which otherwise have no existence, and may therefore be used experimentally to isolate the cross-correlation functions from the ever-present autocorrelation functions which form the "background" to the ensemble molecular dynamics. It is shown that some off-diagonal elements exist in frame (x,y,z) in the absence of the field, thus invalidating the basic hypothesis of the theory of rotational diffusion.

I. INTRODUCTION

The rotational diffusion in three dimensions of the asymmetric-top molecule can be described in terms of a Langevin equation.[1] This is written[2] in the moving frame (1,2,3) of the molecular principal moments of inertia, because in that frame there is a linear relation between the angular velocity and momentum. However, when the center of mass of the rotating molecule is also translating in the laboratory frame (x,y,z), the problem arises of how to write down and solve the appropriate Langevin equations. In this paper progress is made toward obtaining such a solution by use of a digital computer simulation.[3]

A translational Langevin equation is written in this paper in a rotating frame of reference $(1,2,3)'$ by making a transformation from the laboratory frame (x,y,z). It is then straightforward to derive the moving-frame translational Langevin equation in which the molecular angular velocity appears as a natural variable. This variable is also driven by the standard[2] Euler-Langevin equation for rotational diffusion so the two equations, translational and rotational, are linked analytically. This procedure produces six equation in six unknowns and computer simulation can be used to establish which terms in these equations are correlated statistically and which are not. Correlation tensors between these terms can then be computed and their symmetry studied.[4]

II. THE LANGEVIN EQUATIONS

Consider a coordinate system $(1,2,3)'$ whose origin coincides with that of the laboratory frame (x,y,z) but which rotates with respect to the latter at the angular velocity $\boldsymbol{\omega}$, defined as being the molecular angular velocity. It follows from elementary dynamics[5,6] that

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

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

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

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

The subscripts in these equations mean that every vector on the right-hand side (rhs) or left-hand side (lhs) is defined with respect to that frame of reference. The vector $\mathbf{r}$ defines the position of the molecular center of mass; $\mathbf{v}$ is the center-of-mass linear velocity and $\boldsymbol{\omega}$ the molecular angular velocity in either frame of reference, being defined as the angular velocity of one frame with respect to the other. If a moving frame, (1,2,3), is now defined as that of the three principal molecular moments of inertia, and therefore with origin at $\mathbf{r}$ in frames (x,y,z) or $(1,2,3)'$, then

$$[\mathbf{r}]_{(1,2,3)'}\equiv[\mathbf{0}]_{(1,2,3)}\ , \tag{5}$$

$$[\mathbf{v}+\boldsymbol{\omega}\times\mathbf{r}]_{(1,2,3)'}\equiv[\mathbf{v}]_{(1,2,3)}\ , \tag{6}$$

$$[\dot{\mathbf{v}}+2\boldsymbol{\omega}\times\mathbf{v}+\dot{\boldsymbol{\omega}}\times\mathbf{r}+\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(1,2,3)'}\equiv[\dot{\mathbf{v}}+2\boldsymbol{\omega}\times\mathbf{v}]_{(1,2,3)}\ , \tag{7}$$

$$[\dot{\mathbf{W}}]_{(1,2,3)'}\rightarrow[\dot{\mathbf{W}}]_{(1,2,3)}\ . \tag{8}$$

Note that the root-mean-square components of $\mathbf{v}$ in frame (1,2,3) are not the same on the average, i.e.,

$$\langle v_1^2\rangle^{1/2}\neq\langle v_2^2\rangle^{1/2}\neq\langle v_3^2\rangle^{1/2}\ , \tag{9}$$

in contrast to

$$\langle v_x^2\rangle^{1/2}=\langle v_y^2\rangle^{1/2}=\langle v_z^2\rangle^{1/2}\ , \tag{10}$$

the usual laboratory-frame result for an isotropic liquid. It follows from Eq. (9) that the translational friction coefficient in the moving frame of reference is not a scalar, but a tensor with three differential diagonal components,

β_1, β_2, and β_3. This means that the translational Langevin equation in frame (1,2,3) is

$$[\dot{\mathbf{v}}+2\boldsymbol{\omega}\times\mathbf{v}+\boldsymbol{\beta}\mathbf{v}=\dot{\mathbf{W}}]_{(1,2,3)}\ , \tag{11}$$

or, in component form,

$$\dot{v}_1+2(\omega_2 v_3-\omega_3 v_2)+\beta_1 v_1=\dot{W}_{1v}\ , \tag{12}$$

$$\dot{v}_2+2(\omega_3 v_1-\omega_1 v_3)+\beta_2 v_2=\dot{W}_{2v}\ , \tag{13}$$

$$\dot{v}_3+2(\omega_1 v_2-\omega_2 v_1)+\beta_3 v_3=\dot{W}_{3v}\ . \tag{14}$$

In Eqs. (12)—(14) it can be seen that the angular velocity $\boldsymbol{\omega}$ is present as a natural component of the Coriolis acceleration $[2\boldsymbol{\omega}\times\mathbf{v}]_{(1,2,3)}$ with respect to frame (1,2,3). The angular velocity $[\boldsymbol{\omega}]_{(1,2,3)}$ in frame (1,2,3) is also driven by a rotational Langevin equation in this frame, which can be written as[2]

$$I_1\dot{\omega}_1-(I_2-I_3)\omega_2\omega_3+I_1\hat{\beta}_1\omega_1=I_1\dot{W}_1\ , \tag{15}$$

$$I_2\dot{\omega}_2-(I_3-I_1)\omega_3\omega_1+I_2\hat{\beta}_2\omega_2=I_2\dot{W}_2\ , \tag{16}$$

$$I_3\dot{\omega}_3-(I_1-I_2)\omega_1\omega_2+I_3\hat{\beta}_3\omega_3=I_3\dot{W}_3\ . \tag{17}$$

In Eqs. (15)—(17), I_1, I_2, and I_3 are the three principal molecular moments of inertia; $\hat{\beta}_1$, $\hat{\beta}_2$, and $\hat{\beta}_3$ are the three rotational friction coefficients of the Euler-Langevin equation[2] and W_1, W_2, and W_3 are the three rotational Wiener processes.

A. Special cases

When there is no rotation, then

$$[\boldsymbol{\omega}]_{(1,2,3)}=\mathbf{0}\ ,$$

and we recover the translational Langevin equation in frame (1,2,3):

$$[\dot{v}_i+\beta_i v_i=\dot{W}_{vi}]_{(1,2,3)}\quad (i=1,2,3)\ . \tag{18}$$

Similarly, when there is no translation, Eqs. (12)—(14) vanish, leaving Eqs. (15)—(17), the standard Euler-Langevin equations. Therefore the system (12)—(17) reduces to the correct translational and rotational limits.

B. Spherical top and perfect sphere

It is necessary to make a careful distinction between the perfect sphere and the molecular spherical top of T_d or O_h symmetry, for example. This is because there is no rotation to translation cross correlation in the perfect sphere,[7] but this is not necessarily true for the molecular spherical top, where

$$I_1=I_2=I_3\ . \tag{19}$$

C. A perfectly spherical body

In this case condition (19) is supplemented by

$$\begin{aligned}&\beta_1=\beta_2=\beta_3\ \ (=\beta)\ ,\\ &\hat{\beta}_1=\hat{\beta}_2=\hat{\beta}_3\ \ (=\hat{\beta})\ ,\end{aligned} \tag{20}$$

and by

$$\begin{aligned}&\omega_1=\omega_2=\omega_3\ \ (=\omega)\ ,\\ &v_1=v_2=v_3\ \ (=v)\ ,\end{aligned} \tag{21a}$$

so that the Coriolis terms in Eqs. (12)—(14) disappear, and the set of translational equations. (12)—(14) becomes fully independent of the rotational equations (15)—(17).

D. The molecular spherical top

A molecule of O_h or T_d symmetry is a nondipolar spherical top. It is also possible to approximate to condition (19) quite closely with a number of dipolar molecules. In this case condition (21) is not necessarily true. For example, in a T_d-symmetry molecule, such as CCl_4, resistance to the translating (1,2,3) frame in the C-Cl axis is not necessarily the same as that perpendicular to this axis, so

$$\begin{aligned}&v_1\neq v_2\neq v_3\ ,\\ &\beta_1\neq\beta_2\neq\beta_3\ .\end{aligned} \tag{21b}$$

Condition (21) means that the Coriolis term in Eqs. (12)—(14) is *finite* even when

$$\begin{aligned}&\omega_1=\omega_2=\omega_3\ \ (=\omega)\ ,\\ &\hat{\beta}_1=\hat{\beta}_2=\hat{\beta}_3\ \ (=\hat{\beta})\ .\end{aligned} \tag{22}$$

The three-dimensional roto-translational equations for the molecular spherical top are therefore

$$\dot{v}_1+2\omega(v_3-v_2)+\beta_1 v_1=\dot{W}_{1v}\ , \tag{23}$$

$$\dot{v}_2+2\omega(v_1-v_3)+\beta_2 v_2=\dot{W}_{2v}\ , \tag{24}$$

$$\dot{v}_3+2\omega(v_2-v_1)+\beta_3 v_3=\dot{W}_{3v}\ , \tag{25}$$

$$I\dot{\boldsymbol{\omega}}+I\hat{\beta}\boldsymbol{\omega}=I\dot{\mathbf{W}}\ , \tag{26}$$

where $\hat{\beta}$ is the scalar rotational friction coefficient, and W is the rotational Wiener process. The set of Eqs. (23)—(25) becomes completely decoupled from Eq. (26) only when

$$v_2=v_3=0\ , \tag{27}$$

i.e., when the translational motion is constrained to the I axis of the moving frame (1,2,3). This kind of motion can be visualized if the rotation is confined to a plane. In this special case there will be no correlation between the molecular angular velocity and the center of mass linear velocity perpendicular to the plane in which the molecule rotates.

In general, for the three-dimensional diffusion of the spherical top molecule there will be statistical correlation between the angular velocity and center-of-mass linear velocity in frame (1,2,3), according to Eqs. (23)—(26).

E. Linear, nondipolar molecule (the thin rod)

In this case,

$$I_1=I_2=I,\ \ I_3=0\ . \tag{28}$$

The purely geometrical constraint (28) is supplemented by additional constraints on the friction coefficients,

$$\beta_1=\beta_2=\beta\ ,\quad \beta_3=0\ , \tag{29}$$

$$\hat\beta_1=\hat\beta_2=\hat\beta\ ,\quad \hat\beta_3=0\ , \tag{30}$$

and on the angular velocity,

$$\omega_1=\omega_2=\omega,\ \ \omega_3=0\ . \tag{31}$$

The set of Eqs. (12)—(17) therefore reduces in complexity, but it is clear that its translational and rotational components remain interlinked in frame (1,2,3) so that certain types of statistical cross-correlation survive in this case too.

F. Rotational motion confined to a plane

In this case the angular velocity reduces to a scalar quantity, which can be written as

$$[\boldsymbol\omega]_{(x,y,z)}=[\boldsymbol\omega]_{(1,2,3)}=\dot\theta\ . \tag{32}$$

The moving frame (1,2,3) in this case spins around one axis, e.g., the *I* axis, which remains fixed in an axis of the laboratory frame (x,y,z). Equation (7), under this constraint, becomes

$$[\dot{\mathbf v}]_{(x,y,z)}=[\dot{\mathbf v}]_{(1,2,3)}-2\dot\theta v_3\mathbf e_2+2\dot\theta v_2\mathbf e_3\ , \tag{33}$$

where $\mathbf e_2$ and $\mathbf e_3$ are unit vectors in the 2 and 3 axes, respectively, of the frame (1,2,3). By definition,

$$\omega_1=\dot\theta\ ,\quad \omega_2=\omega_3=0\ , \tag{34}$$

and the set (12)—(17) simplifies to

$$\dot v_1+\beta_1 v_1=\dot W_{1v}\ , \tag{35}$$

$$\dot v_2-2\dot\theta v_3+\beta_2 v_2=\dot W_{2v}\ , \tag{36}$$

$$\dot v_3+2\dot\theta v_2+\beta_3 v_3=\dot W_{3v}\ , \tag{37}$$

$$\ddot\theta+\hat\beta\dot\theta=\dot W\ . \tag{38}$$

Equations (35)—(38) describe the Langevin diffusion of an asymmetric-top molecule whose rotational motion has been confined to a plane, but which is otherwise free to translate in three dimensions, i.e., its center of mass can move in any direction defined by the three axes 1, 2, and 3 of frame (1,2,3). Equations (35)—(38) show that cross-correlation between rotation and translation survives in this limit in frame (1,2,3). The cross-correlation vanishes when, for example, $v_2=v_3=0$, i.e., when the motion of the asymmetric top is such that its center of mass translates only in axis *I*, around which it is simultaneously constrained to rotate. (This conclusion is the same as that already reached for the spherical top.) In this very special limit,

$$\dot v_1+\beta_1 v_1=\dot W_{1v},\ \ \ddot\theta+\hat\beta\dot\theta=\dot W\ , \tag{39}$$

and there is no analytical link between the translational and rotational Langevin diffusion. The two equations in (39) are fully independent in frame (1,2,3). More generally, the two types of diffusion become independent when any two components of the linear velocity vanish in frame (1,2,3).

Interestingly, the equations also decouple for *all* v_1 if $v_2=v_3$. This follows by setting $v_2=v_3$ in Eqs. (35)—(38) and then adding Eqs. (36) and (37), assuming $\beta_2=\beta_3$. This limit describes the motion of a perfect disk which is constrained to rotate around axis *I*, but whose center of mass can translate in the plane perpendicular to the *I* axis. In this limit there is no statistical correlation between the two types of diffusion, which therefore have no influence on each other. This explains, roughly speaking, why a spinning top will remain in one spot if its axis of rotation remains vertical, i.e., as long as it rotates in a plane. As soon as it is tilted out of that plane, the point of contact with the ground will move, or attempt to move, as the center of mass of the top attempts to translate.

If the molecule is not a perfect disk, then in the presence of the constraint $v_1=0$ the Langevin diffusion is described by

$$\dot v_2-2\dot\theta v_3+\beta_2 v_2=\dot W_{2v}\ , \tag{40}$$

$$\dot v_3+2\dot\theta v_2+\beta_3 v_3=\dot W_{3v}\ , \tag{41}$$

$$\ddot\theta+\hat\beta\dot\theta=\dot W\ , \tag{42}$$

and there is cross-correlation in frame (1,2,3).

The nature of this mutual influence of rotation upon translation can be shown clearly in the limit

$$\beta_2=\beta_3=\hat\beta=0\ , \tag{43}$$

i.e., when the frictional potential energy is removed from the Hamiltonian. The Langevin equations then become

$$\dot v_2-2\dot\theta v_3=0\ , \tag{44}$$

$$\dot v_3+2\dot\theta v_2=0\ , \tag{45}$$

$$\ddot\theta=0\ . \tag{46}$$

Rearranging Eqs. (44)—(46) gives

$$\ddot v_2+4\Theta^2 v_2=0\ , \tag{47}$$

which is Hooke's law, with

$$\Theta=\int_0^t\ddot\theta\,dt=\text{const}\ .$$

Similarly,

$$\ddot v_3+4\Theta^2 v_3=0\ . \tag{48}$$

Depending on the magnitude of the constant angular velocity, Θ, therefore, the translational velocity components v_2 and v_3 move in an oscillatory fashion. This type of motion is that of an asymmetric top initially set spinning in a plane about a point which is not its center of mass, and then left to translate free of any Langevin friction. Equations (47) and (48) [written as they are in the moving frame (1,2,3)] describe *modulations* of the center-of-mass velocity $[\mathbf{v}]_{(x,y,z)}$ due to the spinning motion, taking place with an angular velocity Θ, which is, of course, the same in both frames of reference. This simply means that the center of mass of the molecule will translate alternatively more quickly and more slowly in the laboratory frame (x,y,z) as the molecule continues its offset rotation. The autocorrelation functions (ACF's) of v_2 and v_3 from Eqs. (47) and (48) are

$$\langle v_2(t)v_2(0)\rangle = \langle v_2^2(0)\rangle \cos\Theta t \ , \tag{49}$$

$$\langle v_3(t)v_3(0)\rangle = \langle v_3^2(0)\rangle \cos\Theta t \ . \tag{50}$$

These clearly depend on Θ $[=\dot{\theta}(t)=\text{const}]$ and this illustrates how rotational motion can affect translation in one simple limit.

III. BACK-TRANSFORMATION INTO THE LABORATORY FRAME

Any of the moving-frame equations in the preceding section can be back-transformed into the laboratory frame (x,y,z) with the general relations[8] for any vector quantity $\mathbf{A}$:

$$A_1 = A_x e_{1x} + A_y e_{1y} + A_z e_{1z} \ , \tag{51}$$

$$A_2 = A_x e_{2x} + A_y e_{2y} + A_z e_{2z} \ , \tag{52}$$

$$A_3 = A_x e_{3x} + A_y e_{3y} + A_z e_{3z} \ , \tag{53}$$

where $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are unit vectors in the three principal molecular moments of inertia. The Coriolis acceleration $2\boldsymbol{\omega}(t)\times\mathbf{v}(t)$ also back-transforms as

$$(\boldsymbol{\omega}\times\mathbf{v})_1 = (\boldsymbol{\omega}\times\mathbf{v})_x e_{1x} + (\boldsymbol{\omega}\times\mathbf{v})_y e_{1y} + (\boldsymbol{\omega}\times\mathbf{v})_z e_{1z} \ , \tag{54}$$

$$(\boldsymbol{\omega}\times\mathbf{v})_2 = (\boldsymbol{\omega}\times\mathbf{v})_x e_{2x} + (\boldsymbol{\omega}\times\mathbf{v})_y e_{2y} + (\boldsymbol{\omega}\times\mathbf{v})_z e_{2z} \ , \tag{55}$$

$$(\boldsymbol{\omega}\times\mathbf{v})_3 = (\boldsymbol{\omega}\times\mathbf{v})_x e_{3x} + (\boldsymbol{\omega}\times\mathbf{v})_y e_{3y} + (\boldsymbol{\omega}\times\mathbf{v})_z e_{3z} \ . \tag{56}$$

The original translational Langevin equation in the laboratory frame is well known to be[1]

$$[\dot{\mathbf{v}}+\beta_v\mathbf{v}]_{(x,y,z)} = [\dot{\mathbf{W}}]_{(x,y,z)} \tag{57}$$

and, therefore, by back-transforming Eqs. (12)—(14) into frame (x,y,z) and comparing term by term its components with those of Eq. (57), we obtain

$$\dot{v}_x + \beta_v v_x \equiv \dot{v}_x(e_{1x}+e_{2x}+e_{3x}) + 2(\boldsymbol{\omega}\times\mathbf{v})_x(e_{1x}+e_{2x}+e_{3x}) + v_x(\beta_1 e_{1x}+\beta_2 e_{2x}+\beta_3 e_{3x}) \ , \tag{58}$$

$$\dot{v}_y + \beta_v v_y \equiv \dot{v}_y(e_{1y}+e_{2y}+e_{3y}) + 2(\boldsymbol{\omega}\times\mathbf{v})_y(e_{1y}+e_{2y}+e_{3y}) + v_y(\beta_1 e_{1y}+\beta_2 e_{2y}+\beta_3 e_{3y}) \ , \tag{59}$$

$$\dot{v}_z + \beta_v v_z \equiv \dot{v}_z(e_{1z}+e_{2z}+e_{3z}) + 2(\boldsymbol{\omega}\times\mathbf{v})_z(e_{1z}+e_{2z}+e_{3z}) + v_z(\beta_1 e_{1z}+\beta_2 e_{2z}+\beta_3 e_{3z}) \ . \tag{60}$$

These identities show that the original translational Langevin equation contains equivalent roto-translational components, namely the components $2(\boldsymbol{\omega}\times\mathbf{v})_x$, $2(\boldsymbol{\omega}\times\mathbf{v})_y$, and $2(\boldsymbol{\omega}\times\mathbf{v})_z$ of the Coriolis acceleration in the laboratory frame (x,y,z). (Confirmation of the existence of these terms in the laboratory frame is given later in this paper by computer simulation.) Therefore, as soon as consideration is taken of $\omega\neq 0$, the basic structure of the original translational Langevin equation itself is changed. In the limit $\omega=0$ (i.e., if, and only if, $\omega=0$) the structure of the original 1906 equation of Langevin is regained if we make the identities

$$e_{1x}+e_{2x}+e_{3x} \equiv 1 \ , \tag{61}$$

$$\beta_1 e_{1x}+\beta_2 e_{2x}+\beta_3 e_{3x} \equiv \beta_v \ . \tag{62}$$

Note that Eqs. (61) and (62) are not necessarily true for $\omega\neq 0$.

It is especially interesting to note the effect of an external electric field on a dipolar asymmetric top diffusing according to Eqs. (58) to (60). The electric field is known[1] to take effect through a torque $-\boldsymbol{\mu}\times\mathbf{E}$ on each molecule of the ensemble. If for the sake of argument the axis of $\boldsymbol{\mu}$, the net molecular dipole moment, coincides with the 1 axis of the principal molecular moment of inertia frame (1,2,3), and if the field $\mathbf{E}$ is applied in the z axis of the laboratory frame, then the average value of e_{1z} at time t over each molecule in the ensemble will increase. The distribution of components of orientation among Eqs. (58)—(60) is therefore changed. In contrast, it is not possible to say anything about the effect of an external electric field from the original Langevin equation (57), whereas it is known from computer simulation that certain cross-correlation functions (CCF's) between the molecular linear center-of-mass velocity v and its own angular velocity become directly visible in the laboratory frame (x,y,z) when the field is applied and the sample becomes anisotropic.[9]

IV. CROSS-CORRELATION FUNCTIONS

From the set of Eqs. (12)—(17), we can choose nine cross—fluctuation-dissipation terms

$$\begin{gathered}\langle \dot{W}_{1v}(t)\dot{W}_1(0)\rangle \ , \\ \langle \dot{W}_{2v}(t)\dot{W}_2(0)\rangle \ , \\ \langle \dot{W}_{3v}(t)\dot{W}_3(0)\rangle \ , \end{gathered} \tag{63}$$

$$\begin{gathered}\langle \dot{W}_{2v}(t)\dot{W}_1(0)\rangle \ , \\ \langle \dot{W}_{2v}(t)\dot{W}_3(0)\rangle \ , \\ \langle \dot{W}_{1v}(t)\dot{W}_2(0)\rangle \ , \end{gathered} \tag{64}$$

$$\begin{gathered}\langle \dot{W}_{1v}(t)\dot{W}_3(0)\rangle \ , \\ \langle \dot{W}_{3v}(t)\dot{W}_1(0)\rangle \ , \\ \langle \dot{W}_{3v}(t)\dot{W}_2(0)\rangle \ . \end{gathered} \tag{65}$$

In Langevin dynamics[1,2] each of these is proportional to a frequency-independent diffusion coefficient, which is the result both of translation and rotation. More generally, each is a time-dependent memory function.[1] Each can be expanded as a sum of cross-correlation functions in the moving frame (1,2,3) and these CCF's can be back-transformed into the laboratory frame (x,y,z). For example,

$$\langle \dot{W}_{1v}(t)\dot{W}_1(0)\rangle = \langle \{\dot{v}_1(t)+2[\omega_2(t)v_3(t)-\omega_3(t)v_2(t)]+\beta_1 v_1(t)\}[I_1\dot{\omega}_1(0)-(I_2-I_3)\omega_2(0)\omega_3(0)+I_1\hat{\beta}_1\omega_1(0)]\rangle \ . \tag{66}$$

The existence of statistical cross-correlation between the two Wiener processes in this equation can now be ascertained by calculating or computing each term on the rhs of Eq. (14), i.e., each CCF of time. This can be achieved by molecular-dynamics computer simulation.[10]

A. Computer-simulation algorithm and methods

The sample used in this simulation consisted of 108 CH_2Cl_2 molecules at 296 K with a molar volume of 8.0×10^{-5} m^3. The pair potential was a simple 3×3 site-site type with interaction parameters as follows:[3,9]

$$\epsilon(\text{Cl-Cl})/k = 173.5\ \text{K},\quad \epsilon(\text{CH}_2\text{-CH}_2)/k = 70.5\ \text{K}\ ,$$

$$\sigma(\text{CH}_2\text{-CH}_2) = 3.96\ \text{Å},\quad \sigma(\text{Cl-Cl}) = 3.35\ \text{Å}\ ,$$

$$q_{\text{Cl}} = -0.15\,|\,e\,|\,,\quad q_{\text{CH}_2} = 0.30\,|\,e\,|\ .$$

After equilibration the CCF's were calculated with the use of running-time averaging[11] using segments of about 2700 time steps each of 5.0×10^{-15} sec recorded every three time steps. Using two or more segments provided an estimate of the reliability of the computed CCF's. Using the field-on method of computer simulation, developed and described elsewhere,[1,9] the simulations were repeated in the presence of a z-axis electric field $\mathbf{E}$.

B. Cross-section functions from the computer simulations

Nearly all the different possible types of CCF which appear in the expansion of (63)–(65) were simulated in this way, both in frames (1,2,3) and (x,y,z). Note that these results *are not solutions* of the Langevin equations but computer simulations based on classical nonequilibrium statistical mechanics.[10]

In the moving frame, the following results were obtained (for all t):

$$\langle v_1(t)\omega_2(0)\omega_3(0)\rangle = 0\ , \tag{67}$$

$$\langle v_2(t)\omega_3(0)\omega_1(0)\rangle = 0\ , \tag{68}$$

$$\langle v_3(t)\omega_1(0)\omega_2(0)\rangle = 0\ , \tag{69}$$

$$\langle v_1(t)\omega_3(0)\omega_1(0)\rangle = 0\ , \tag{70}$$

$$\langle v_2(t)\omega_1(0)\omega_2(0)\rangle = 0\ , \tag{71}$$

$$\langle v_3(t)\omega_2(0)\omega_3(0)\rangle = 0\ , \tag{72}$$

$$\langle v_1(t)\omega_1(0)\omega_2(0)\rangle = 0\ , \tag{73}$$

$$\langle v_2(t)\omega_2(0)\omega_3(0)\rangle = 0\ , \tag{74}$$

$$\langle v_3(t)\omega_3(0)\omega_1(0)\rangle = 0\ . \tag{75}$$

Similarly, for all t,

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_1(t)\omega_2(0)\omega_3(0)\rangle = 0\ , \tag{76}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_2(t)\omega_3(0)\omega_1(0)\rangle = 0\ , \tag{77}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_3(t)\omega_1(0)\omega_2(0)\rangle = 0\ , \tag{78}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_1(t)\omega_3(0)\omega_1(0)\rangle = 0\ , \tag{79}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_1(t)\omega_1(0)\omega_2(0)\rangle = 0\ , \tag{80}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_2(t)\omega_2(0)\omega_3(0)\rangle = 0\ , \tag{81}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_2(t)\omega_1(0)\omega_2(0)\rangle = 0\ , \tag{82}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_3(t)\omega_2(0)\omega_3(0)\rangle = 0\ , \tag{83}$$

$$\langle (2\boldsymbol{\omega}\times\mathbf{v})_3(t)\omega_3(0)\omega_1(0)\rangle = 0\ . \tag{84}$$

Results for some of the other types of CCF's are summarized in Table I, where a + sign denotes the existence of the CCF for $t>0$. The symbol δ means that none of the elements of the CCF could be detected above the computer noise. It can be seen, for example, that the diagonal elements of $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ [i.e., the three elements of $\langle \mathbf{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$] all vanish in the moving and laboratory frames, but some elements off the diagonal of the tensor CCF exist[1,4,8,12] in frame (1,2,3). The same is true for $\langle \dot{\mathbf{v}}(t)\dot{\boldsymbol{\omega}}^T(0)\rangle$, $\langle \dot{\mathbf{v}}(t)\boldsymbol{\omega}^T(0)\rangle$, and $\langle \mathbf{v}(t)\dot{\boldsymbol{\omega}}^T(0)\rangle$.

Therefore, there is enough information available from the computer simulation to show that all the CCF's on the rhs of Eq. (66) vanish for all t. This confirms, therefore, that every term in the expansion of $\langle \dot{W}_{1v}(t)\dot{W}_1(0)\rangle$ is separately zero, and similarly for $\langle \dot{W}_{2v}(t)\dot{W}_2(0)\rangle$ and $\langle \dot{W}_{3v}(t)\dot{W}_3(0)\rangle$. The cross-diffusion coefficients associated with Eq. (63) therefore all vanish:

$$\begin{aligned}&\langle \dot{W}_{1v}(t)\dot{W}_1(0)\rangle = 0\ ,\\ &\langle \dot{W}_{2v}(t)\dot{W}_2(0)\rangle = 0\ ,\\ &\langle \dot{W}_{3v}(t)\dot{W}_3(0)\rangle = 0\ .\end{aligned} \tag{85}$$

TABLE I. Some cross-correlation functions from the computer simulation.

Cross-correlation function	Frame (x,y,z)	 (1,2,3)
$\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\cdot\mathbf{v}(0)\rangle$	δ	+
$\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$	δ	+
$\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle$	δ	+
$\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$	+	δ
$\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$	δ	δ
$\langle \mathbf{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$	δ	δ

This means that the CCF of these Wiener processes in frame (1,2,3) contains only off-diagonal elements: in general, memory functions.[1] This result receives further confirmation from Eqs. (67)—(69), (76)—(78), and from Table I.

There is, however, clear evidence from the computer simulation for the existence of the cross-correlations in Eqs. (64) and (65) for $t>0$. These "cross-memory" functions are sums of the following CCF's which exist for $t>0$.

(i) Some off-diagonal terms of $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ already known in the literature.[1,4,8,12]

(ii) Some off-diagonal terms of $\langle \dot{\mathbf{v}}(t)\dot{\boldsymbol{\omega}}^T(0)\rangle$.

(iii) Some off-diagonal terms of $\langle \dot{\mathbf{v}}(t)\boldsymbol{\omega}^T(0)\rangle$ [and of $\langle \mathbf{v}(t)\dot{\boldsymbol{\omega}}^T(0)\rangle$].

Although this is not a direct solution of Eqs. (12)—(17) for these CCF's, their existence from computer simulation strongly suggests that the structure of these equations is correct, within the severe limits[1,2] of Langevin dynamics in general. It will probably take a technique akin to analogue circuit simulation[1,13,14] to solve the actual equations themselves, in the continued absence of suitable analytical methods.

It is especially interesting to note the effect of an electric field[1,9] on this type of CCF. The electric field promotes their appearance directly in the laboratory frame (x,y,z). This has been reported in full elsewhere.[9] Again, the electric field promotes the existence of two off-diagonal elements of $\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ in frame (1,2,3). In the absence of $\mathbf{E}$ it vanishes in frame (1,2,3) *but exists in the laboratory frame (x,y,z).* Its direct existence in the laboratory frame means that a description[2] of molecular diffusion in terms of pure rotation or translation is not suitable in any frame of reference, and that the "classical"

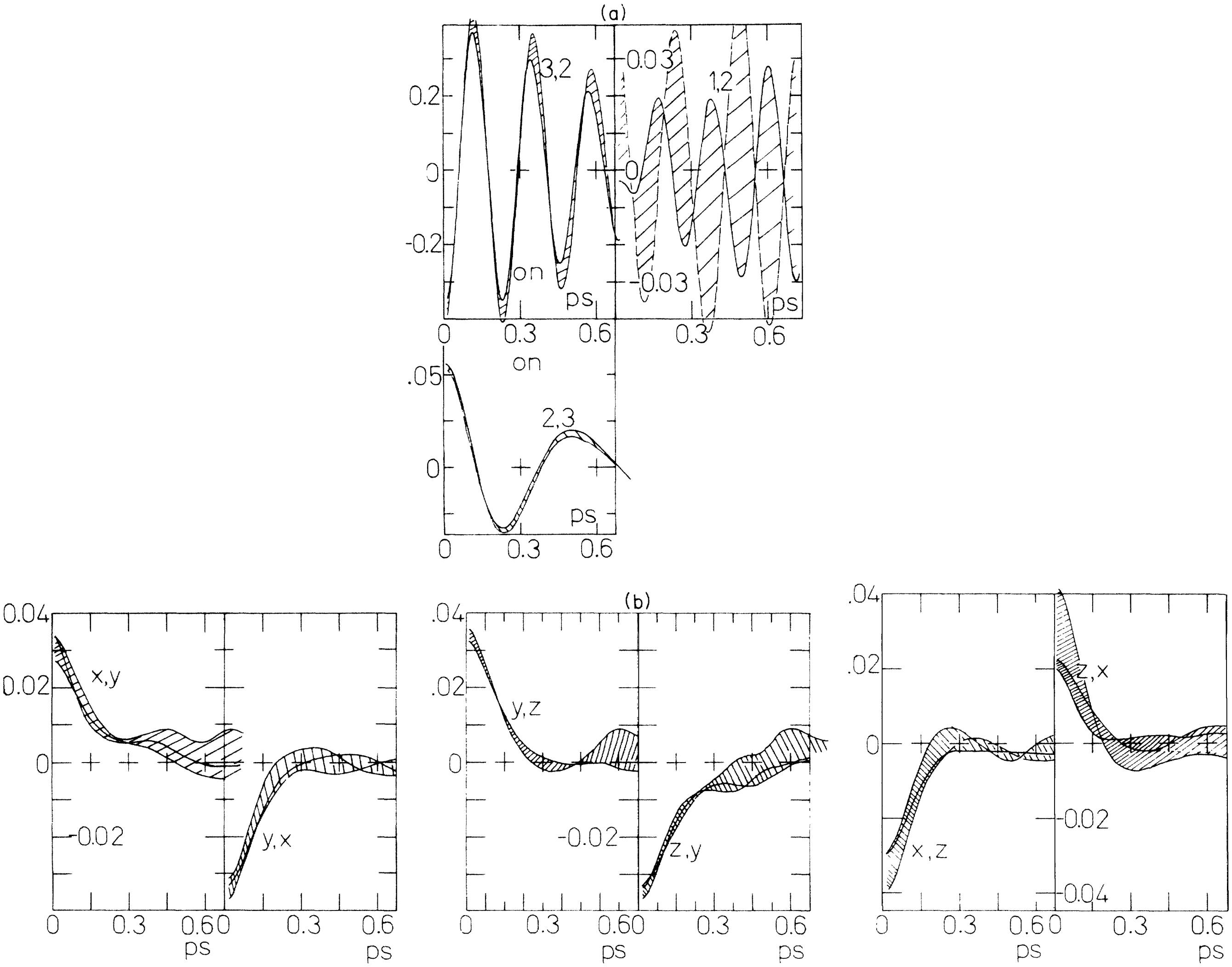

FIG. 1. (a) Illustrations of some of the elements of the cross-correlation tensor $\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ moving-frame, field on. The (3,2) and (2,3) elements exist, but the (1,2) element seems to be noise only. (b) The off-diagonal elements of

$$C_4(t)\equiv\frac{\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle}{\langle \omega^2(0)\rangle\langle v^2(0)\rangle^{1/2}}$$

for $\mathbf{E}=0$ *in the laboratory frame (x,y,z).* Each element is *triple*-checked with three nonconsecutive segments of 2700 time steps each.

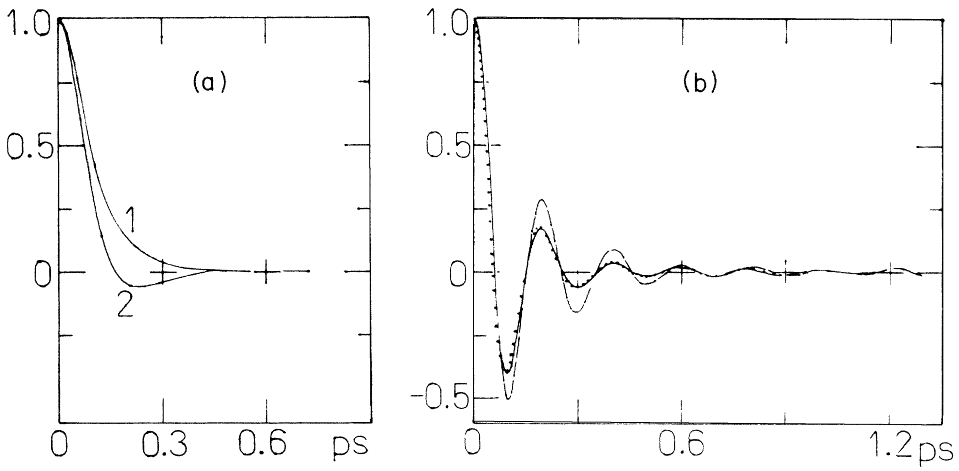

FIG. 2. Correlation functions of the Coriolis acceleration: (a) field off: 1, laboratory frame (x,y,z); 2, moving frame; (b) field on: laboratory frame (solid line); moving frame (dotted line): component ACF (Ref. 3) of the complete Coriolis acceleration (dashed line).

theory of diffusion is in need of extension along the lines suggested in this paper. Some illustrations of $\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ are given in Fig. 1 in the presence and absence of the field.[8] The existence of the ACF of the Coriolis acceleration[3] both in frame (x,y,z) and frame (1,2,3) is illustrated in Fig. 2.

V. USE OF THE ROTATING FRAME (1,2,3)′

The analysis can be extended considerably with a rotating frame (1,2,3)′ as defined in Sec. II of this paper, because this provides the opportunity to introduce into the translational Langevin equations the position vector $\mathbf{r}$ of the molecular center of mass as defined in Eqs. (2) and (4). The translational Langevin equation in frame (1,2,3)′ becomes[3]

$$[\dot{\mathbf{v}}+2\boldsymbol{\omega}\times\mathbf{v}+\dot{\boldsymbol{\omega}}\times\mathbf{r}+\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(1,2,3)'} +\underline{\beta}_v\cdot[\mathbf{v}+\boldsymbol{\omega}\times\mathbf{r}]_{(1,2,3)'}=[\dot{\mathbf{W}}]_{(1,2,3)'}\,, \qquad (86)$$

where the translational friction coefficient in frame (1,2,3)′ is, in general, a diagonal matrix, and the Wiener process $[\dot{W}]_{(1,2,3)'}$ is generated from $[\dot{\mathbf{W}}]_{(x,y,z)}$ by the frame transformation $(x,y,z)\rightarrow(1,2,3)'$.

The particular importance of Eq. (86) is that it introduces into the analysis the center-of-mass position vector $\mathbf{r}$ and therefore provides a link with equilibrium theories of liquid structure[15] and atom-atom pair distribution functions. It has been shown elsewhere[3] that ACF's of all the individual terms appearing on the lhs of Eq. (86) exist in the moving frame (1,2,3) and in the laboratory frame (x,y,z). Therefore the three frames provide us with a depth of insight to the inter-relation of liquid structure and dynamics[16] with the help of digital computer simulation.[10]

Again, this is especially interesting in the context of cross-correlation matrices such as (Figs. 3 and 4)

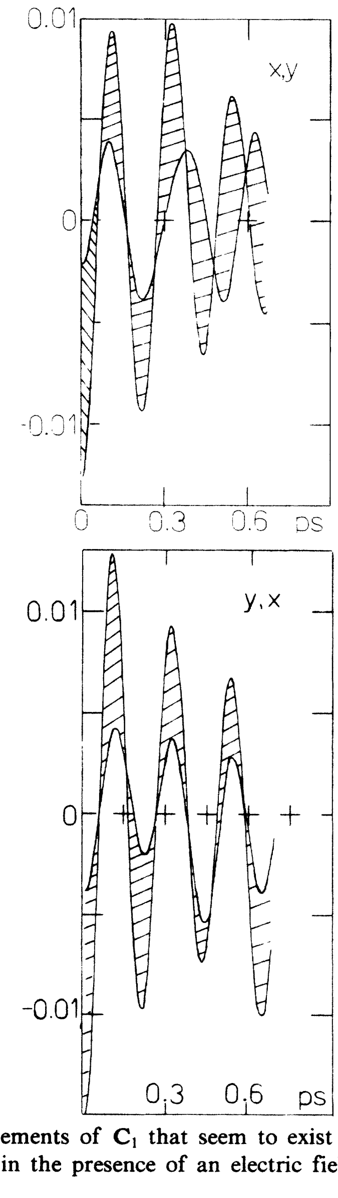

FIG. 3. Elements of $\mathbf{C}_1$ that seem to exist above the background noise in the presence of an electric field $\mathbf{E}$, laboratory frame.

$$\mathbf{C}_1(t) \equiv \frac{\langle \boldsymbol{\omega}(t) \times \mathbf{r}(t) \boldsymbol{\omega}^T(0) \rangle}{\langle \omega^2(0) \rangle \langle r^2(0) \rangle^{1/2}} , \tag{87}$$

and

$$\mathbf{C}_2(t) \equiv \frac{\langle \boldsymbol{\omega}(t) \times [\boldsymbol{\omega}(t) \times \mathbf{r}(t)][\boldsymbol{\omega}(0) \times \mathbf{r}(0)]^T \rangle}{\langle \omega^2(0) \rangle \langle \omega^2(0) \rangle^{1/2} \langle r^2(0) \rangle} , \tag{88}$$

computed both in the laboratory frame (x,y,z) and the moving frame (1,2,3). These CCF's deal with the interrelation between terms such as $\omega(t) \times \mathbf{r}(t)$, which appear in the translational equation (86) and the angular velocity $\boldsymbol{\omega}$ which appears in Eqs. (15)–(17).

The computer simulation provides the results summarized in matrix form in Table II. This table illustrates the different symmetries of the various cross-correlation matrices listed below. Out of the very many possible new CCF's suggested by the structure of the rotating-frame Langevin equations, ten are given below:

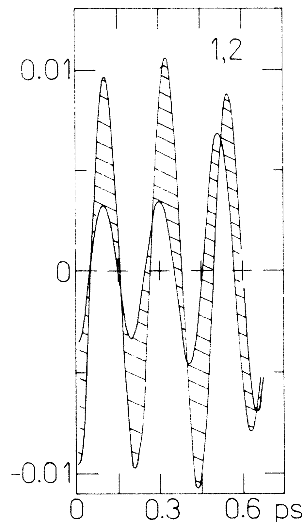

FIG. 4. As for Fig. 3, illustration of the field-on elements.

TABLE II. Symmetry of the CCF matrices.

Matrix	(x,y,z)			$(x,y,z)+E_z$			(1,2,3)			(1,2,3) + E_z		
$\mathbf{C}_1(t)$	δ	δ	δ	δ	+	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	+	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
$\mathbf{C}_2(t)$	δ	δ	δ	δ	δ	δ	+	δ	δ	+	δ	δ
	δ	δ	δ	δ	δ	δ	δ	+	δ	δ	+	δ
	δ	δ	δ	δ	δ	δ	δ	δ	+	δ	δ	+
$\mathbf{C}_3(t)$	δ	δ	δ	δ	δ	δ	+	δ	δ	+	δ	δ
	δ	δ	δ	δ	δ	δ	δ	+	δ	δ	+	δ
	δ	δ	δ	δ	δ	δ	δ	δ	+	δ	δ	+
$\mathbf{C}_4(t)$	δ	+	+	δ	+	δ	δ	δ	δ	δ	δ	δ
	+	δ	+	+	δ	δ	δ	δ	δ	δ	δ	+
	+	+	δ	+	+	δ	δ	δ	δ	δ	+	δ
$\mathbf{C}_5(t)$	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
$\mathbf{C}_6(t)$	δ	δ	δ	δ	δ	δ	+	δ	δ	+	δ	δ
	δ	δ	δ	δ	δ	δ	δ	+	δ	δ	+	δ
	δ	δ	δ	δ	δ	δ	δ	δ	+	δ	δ	+
$\mathbf{C}_7(t)$	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
$\mathbf{C}_8(t)$	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
$\mathbf{C}_9(t)$	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
$\mathbf{C}_{10}(t)$	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ
	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ	δ

$$\mathbf{C}_1(t),\quad \mathbf{C}_2(t)\,,$$

$$\mathbf{C}_3(t)\equiv\frac{\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle}{\langle v^2(0)\rangle\langle \omega^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_4(t)\equiv\frac{\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle}{\langle \omega^2(0)\rangle\langle v^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_5(t)\equiv\frac{\langle \boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{r}(t)]\boldsymbol{\omega}^T(0)\rangle}{\langle \omega^2(0)\rangle\langle \omega^2(0)\rangle^{1/2}\langle r^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_6(t)\equiv\frac{\langle \mathbf{r}(t)\times\boldsymbol{\omega}(t)\mathbf{r}^T(0)\rangle}{\langle r^2(0)\rangle\langle \omega^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_7(t)\equiv\frac{\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\mathbf{r}^T(0)\rangle}{\langle v^2(0)\rangle^{1/2}\langle \omega^2(0)\rangle^{1/2}\langle r^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_8(t)\equiv\frac{\langle \boldsymbol{\omega}(t)\times\mathbf{r}(t)\mathbf{v}^T(0)\rangle}{\langle \omega^2(0)\rangle^{1/2}\langle r^2(0)\rangle^{1/2}\langle v^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_9(t)\equiv\frac{\langle [\mathbf{v}(t)\times\boldsymbol{\omega}(t)]\{\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]\}^T\rangle}{\langle v^2(0)\rangle^{1/2}\langle \omega^2(0)\rangle^{1/2}\langle \omega^2(0)\rangle\langle r^2(0)\rangle^{1/2}}\,,$$

$$\mathbf{C}_{10}(t)\equiv\frac{\langle \dot{\boldsymbol{\omega}}(t)\times\mathbf{r}(t)\dot{\boldsymbol{\omega}}(0)\rangle}{\langle \dot{\omega}^2(0)\rangle\langle r^2(0)\rangle^{1/2}}\,.$$

The nine elements of each of these CCF's have been computed in both frames in the absence and presence of the *z*-axis electric field **E**. Here, **r** is the position vector of the molecular center of mass as defined already (see Appendix). It can be seen from Table II that few of the CCF's exist above the noise. In other words, the dynamics of cross correlation is highly selective in nature in both frames. From the perspective of Table II it can be seen that the effect of the electric field is to promote the existence of a number of off-diagonal elements, e.g., those of $\mathbf{C}_1(t)$ in the table in the laboratory frame and those of $\mathbf{C}_4(t)$ in the moving frame.

The following can be seen in Table II.

(i) None of the off-diagonal elements can be observed in frame (1,2,3) for $\mathbf{E}=\mathbf{0}$.

(ii) CCF matrices of the type $\langle \mathbf{A}(t)\times\boldsymbol{\omega}(t)\mathbf{A}^T(0)\rangle$ [e.g., $\mathbf{C}_2(t)$, $\mathbf{C}_3(t)$, and $\mathbf{C}_6(t)$] belong to the same symmetry group and indeed behave similarly, in that only the diagonal elements of frame (1,2,3) exist for $\mathbf{E}\geq\mathbf{0}$. All the cross-correlation in this case is "concentrated" into these elements, which are, consequently, quite intense (Fig. 5).

(iii) As already mentioned, only $\mathbf{C}_4(t)$ in Table II exists for $\mathbf{E}=\mathbf{0}$ in frame (x,y,z), and then only the off-diagonal elements. These have been illustrated elsewhere[16] in full detail, and are summarized in Fig. 1(b). The existence of these interesting functions of time implies that a complete theory of molecular diffusion cannot be made purely rotational[17] or purely translational for the sake of mathematical convenience. Other off-diagonal elements of this type may exist[16] or other types of cross-correlation and this will be the subject of further work with different molecular symmetries.[17]

As for (ii), the CCF's $\mathbf{C}_1(t)$, $\mathbf{C}_4(t)$, and $\mathbf{C}_5(t)$ are the same type, $\langle \boldsymbol{\omega}(t)\times\mathbf{B}(t)\boldsymbol{\omega}^T(0)\rangle$, but for this group, elements of $\mathbf{C}_1$ and $\mathbf{C}_5$ do not seem to exist in the laboratory frame, or if they do, are so weak in intensity that they could not be detected above the noise of the simulation. These results, and others like them, cannot be explained easily on the grounds of parity inversion symmetry;[12] the symmetry argument becomes inapplicable in the presence of the electric field, because the classical Hamiltonian is then no longer invariant to parity reversal. This leaves computer simulation as the only available contemporary method of investigating single-molecule CCF's in the theory of diffusion. It is anticipated that analytical technique[1] and analogue circuit simulation[13,14] will soon develop to the stage where they could provide independent checks on the results presented in this paper.

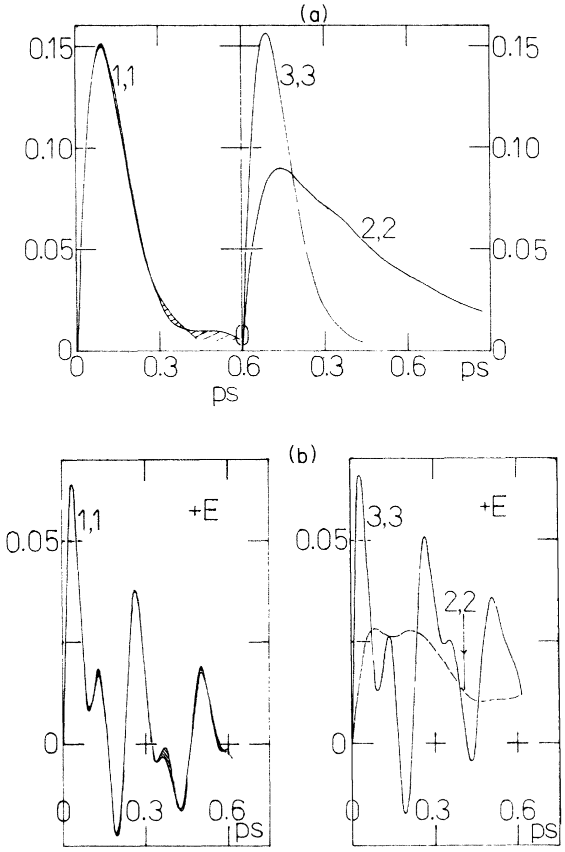

FIG. 5. Moving-frame, diagonal, elements of $\mathbf{C}_2(t)$: (a) field off; (b) field on.

Finally, we can identify the symmetry properties of $\mathbf{C}_1$ in the laboratory frame (x,y,z) with those of the matrix[9]

$$\mathbf{C}_{11}(t)=\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle\,.$$

Previous work has shown that the response of $\mathbf{C}_{11}$ to an electric field[9] is, in terms of symmetry, identical with that of $\mathbf{C}_1$, i.e., the (x,y) and (y,x) elements appear when the electric field **E** is applied in the *z* axis of frame (x,y,z). This is important from an experimental point of view, because spectral data in the presence of an electric field contain information on statistical cross-correlation which does not exist in the absence of the field. The application of an electric field to a molecular liquid promotes the existence of new cross-correlations. This finding invalidates theories, for example, of electric-field-induced birefringence based purely on rotational diffusion.[1] Note that the basic assumption of rotational diffusion theory itself[2] is incompatible with the existence of off-diagonal elements of $\mathbf{C}_4$ directly in the frame (x,y,z) in the *absence* of an electric field. This is another important finding of digital computer simulation if verified independently.

ACKNOWLEDGMENTS

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APPENDIX: DEFINITION OF THE POSITION VECTOR r IN FRAME (1,2,3)

For the purpose of computing the cross-section functions $\mathbf{C}_1(t)$ to $\mathbf{C}_{10}(t)$ in the text, the position vector $\mathbf{r}$ is defined for each of the 108 molecules by

$$r_1 = r_x e_{1x} + r_y e_{1y} + r_z e_{1z} \ , \tag{A1}$$

$$r_2 = r_x e_{2x} + r_y e_{2y} + r_z e_{2z} \ , \tag{A2}$$

$$r_3 = r_x e_{3x} + r_y e_{3y} + r_z e_{3z} \ . \tag{A3}$$

These three equations define a frame rotation from the laboratory frame (x,y,z) to the frame of the principal molecular moments of inertia. Equations (A1)–(A3) are a special case of Eqs. (51)–(53) of the text with $\mathbf{A} \equiv \mathbf{r}$.

Note that there is an apparent contradiction between Eq. (5) and (A1)–(A3). The explanation of this is that Eq. (5) always refers to an origin at *each molecule's* center of mass (where the axes of the three principal moments of inertia intersect), whereas in definitions (A1)–(A3) one takes $\mathbf{r}$ for each molecule as first defined *with respect to an origin in the laboratory frame (x,y,z)* and *then* projects the laboratory frame on to the principal moment of inertia axes *of each molecule in the ensemble* at each time step.

The moving-frame translational Langevin equation (11) and the well-known moving-frame rotational Euler-Langevin equations[2] (15)–(17) contain no explicit term in $\mathbf{r}$ because they are not explicitly defined with respect to any fixed point in the laboratory space. Equation (11) does, however, contain r *implicitly* through the extra equation

$$[\mathbf{v}]_{(x,y,z)} = [\dot{\mathbf{r}}]_{(x,y,z)} \ . \tag{A4}$$

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