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Role of linear velocity in "rotational" diffusion

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By considering afresh the three-dimensional diffusion of an asymmetric top molecule, new statistical cross-correlation functions are reported using computer simulation. Off-diagonal elements exist *directly* in the *laboratory frame (x,y,z)*, of the tensor cross-correlation function between a molecule's Coriolis acceleration, $2\boldsymbol{\omega}\times\mathbf{v}$ at time t and *its own* angular velocity $\boldsymbol{\omega}$ at $t=0$. Here $\mathbf{v}$ is the molecule's center-of-mass *linear* velocity. This is the first clear evidence that the historically popular theory of rotational diffusion is in need of development at a fundamental level to involve *directly* the linear velocity $\mathbf{v}$.

INTRODUCTION

This Rapid Communication presents firm evidence that the historically popular theory of rotational diffusion[1] is fundamentally incomplete when applied to the diffusional dynamics of dipolar molecular liquids. It is incomplete because there exists, directly in the laboratory frame of reference (x,y,z), a large number of different statistical cross correlations involving the angular velocity $\boldsymbol{\omega}$ of the diffusing dipolar molecule, and its own linear velocity $\mathbf{v}$, i.e., that of the molecule's own center of mass. This Rapid Communication establishes the nature of these direct, laboratory-frame correlations using molecular dynamics computer simulation[2] of the liquid-state three-dimensional diffusion of the dipolar asymmetric top, dichloromethane. The existence is also established for the first time of a large number of other types of hitherto unknown cross-correlation functions involving the diffusing molecule's position vector $\mathbf{r}$, $\mathbf{v}$ $(=\dot{\mathbf{r}})$, and $\boldsymbol{\omega}$ both in frame (x,y,z) and a moving frame $(1,2,3)$, defined by the principal molecular moments of inertia. These cross-correlation functions show that the widely used purely rotational approach is fundamentally incomplete and is not, therefore, a valid approximation in any frame.

ANALYTICAL

The existence of these cross-correlation functions can be deduced by using a rotating frame of reference $(1,2,3)'$ in which to write the translational Langevin equation.[1] This frame has its origin fixed at that of the laboratory frame (x,y,z), but rotates at an angular velocity $\boldsymbol{\omega}$, that of the diffusing asymmetric top. In this frame, the translational Langevin equation becomes[3,4]

$$[\dot{\mathbf{v}}+2\boldsymbol{\omega}\times\mathbf{v}+\dot{\boldsymbol{\omega}}\times\mathbf{r}+\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})]_{(1,2,3)'} + \beta_v(\mathbf{v}+\boldsymbol{\omega}\times\mathbf{r})_{(1,2,3)'}=[\dot{\mathbf{W}}]_{(1,2,3)'} \; , \qquad (1)$$

where β_v is the scalar translational friction coefficient which is the same in any frame of reference, and $[\dot{\mathbf{W}}]_{(1,2,3)'}$ is a statistical process generated from the laboratory-frame Wiener process[1] $[\dot{\mathbf{W}}]_{(x,y,z)}$ by the frame transformation $(x,y,z)\rightarrow(1,2,3)'$.

The angular velocity $\boldsymbol{\omega}$ is the same in frames (x,y,z) and $(1,2,3)'$ (because it is the angular velocity of one frame with respect to the other) and also driven in the frame $(1,2,3)$ of the principal moments of inertia by the standard Euler-Langevin equations[5]

$$\begin{aligned} I_1\dot{\omega}_1-(I_2-I_3)\omega_2\omega_3+I_1\beta_1\omega_1&=I_1\dot{W}_1 \; ,\\ I_2\dot{\omega}_2-(I_3-I_1)\omega_3\omega_1+I_2\beta_2\omega_2&=I_2\dot{W}_2 \; ,\\ I_3\dot{\omega}_3-(I_1-I_2)\omega_1\omega_2+I_3\beta_3\omega_3&=I_3\dot{W}_3 \; . \end{aligned} \qquad (2)$$

Essentially speaking, the original Debye theory of rotational diffusion only uses[6] Eq. (2) in describing the dynamical evolution of $\boldsymbol{\omega}$ in a spherical top $(I_1=I_2=I_3)$, leaving out the angular acceleration terms of the left-hand side (lhs) of Eq. (2). In this equation, I_1, I_2, and I_3 are the three principal molecular moments of inertia, and β_1, β_2, and β_3 are the rotational friction coefficients diagonalized in frame $(1,2,3)$ with the rotational Wiener processes[1,6] $\dot{W}_1$, $\dot{W}_2$, and $\dot{W}_3$. The theory is therefore incomplete because Eq. (1) is missing, and consequently $\mathbf{v}$ and $\mathbf{r}$ are undefined.

With contemporary analytical methods[6,7] Eqs. (1) and (2) are probably insoluble, but the technique of conventional computer simulation can be used to construct cross-correlation functions chosen by inspection from among the terms on the lhs of Eq. (1). These do not seem to have appeared in the literature of asymmetrical top diffusion, but are well known in elementary dynamics[3,4] to be (i) the Coriolis acceleration, $2\boldsymbol{\omega}\times\mathbf{v}$, (ii) the centripetal acceleration, $\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})$, (iii) the "nonuniform" acceleration, $\dot{\boldsymbol{\omega}}\times\mathbf{r}$, and (iv) the linear velocity $\boldsymbol{\omega}\times\mathbf{r}$.

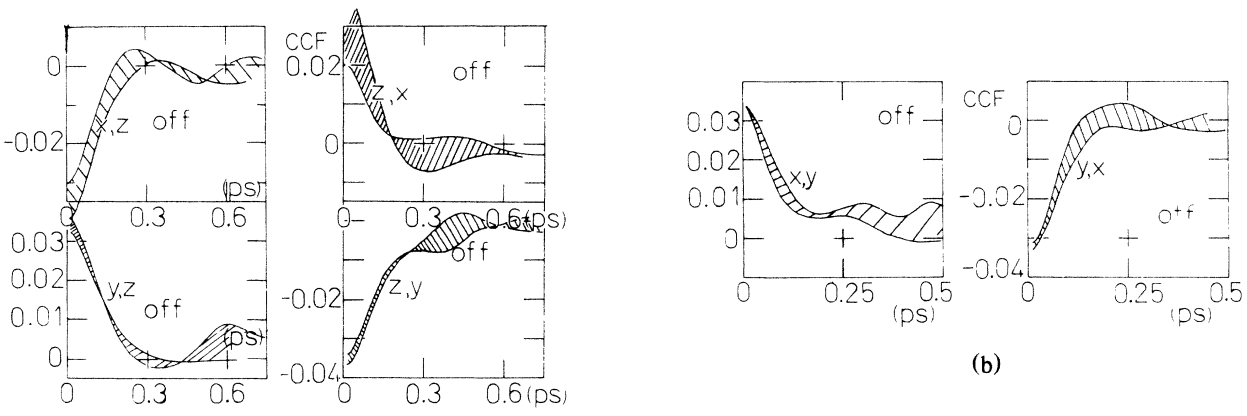
All these terms exist both in frame $(1,2,3)'$ *and* frame (x,y,z) because of the fully reversible nature of the frame transformations

$$(1,2,3)'\leftrightarrows(x,y,z) \; . \qquad (3)$$

The existence of these cross-correlation functions directly in the laboratory frame (x,y,z) is confirmed in this Rapid Communication by constructing tensor cross-correlation functions of time and, clearly, therefore, this also confirms the need to extend the theory of rotational diffusion with Eq. (1).

COMPUTER SIMULATION METHODS

The dynamics of 108 CH_2Cl_2 molecules were simulated[8,9] at 296 K, molar volume of 5.0×10^{-8} m^3/mol for $\mathbf{E}\geqslant 0$, where $\mathbf{E}$ is a z-axis, uniaxial, electric field of force. At field-off equilibrium the correlation functions were calculated over segments of roughly 3000 time steps each (1000



(a)

(b)

FIG. 1. Normalized off-diagonal elements of the tensor cross-correlation function (CCF) $\mathbf{C}_3(t)$ in the laboratory frame (x,y,z). The symbol x,z, for example, denotes

$$C_3^{(x,z)}(t) \equiv \frac{\langle(\boldsymbol{\omega}(t)\times\mathbf{v}(t))_x\omega_z(0)\rangle}{\langle\omega_x^2(0)\rangle\langle v_x^2(0)\rangle^{1/2}} .$$

The hatching denotes the difference between results from two different segments of about 3000 time steps *each.* This is, therefore, a rough measure of the "computer noise." Note that the (x,z) and (z,x), (y,z) and (z,y), and (x,y) and (y,x) pairs seem to be mirror images.

records, each separated by three time steps of 5×10^{-15} sec each). The computation was repeated at field-on equilibrium, where the molecules are aligned by the field[10] so that the Langevin function is effectively saturated. In this condition, the overall Hamiltonian is no longer invariant to parity reversal,[11] and this affects the symmetry properties of the tensor cross-correlation functions.

CROSS-CORRELATION FUNCTIONS

By inspection, (1) and (3) reveal the existence of several possible vector cross-correlation functions typified by

$$C_1(t) = \langle 2\boldsymbol{\omega}(t)\times\mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$$

and

$$C_2(t) = \langle 2\mathbf{v}(t)\times\boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle .$$

The equivalent tensor cross-correlation functions[12,13] are, therefore,

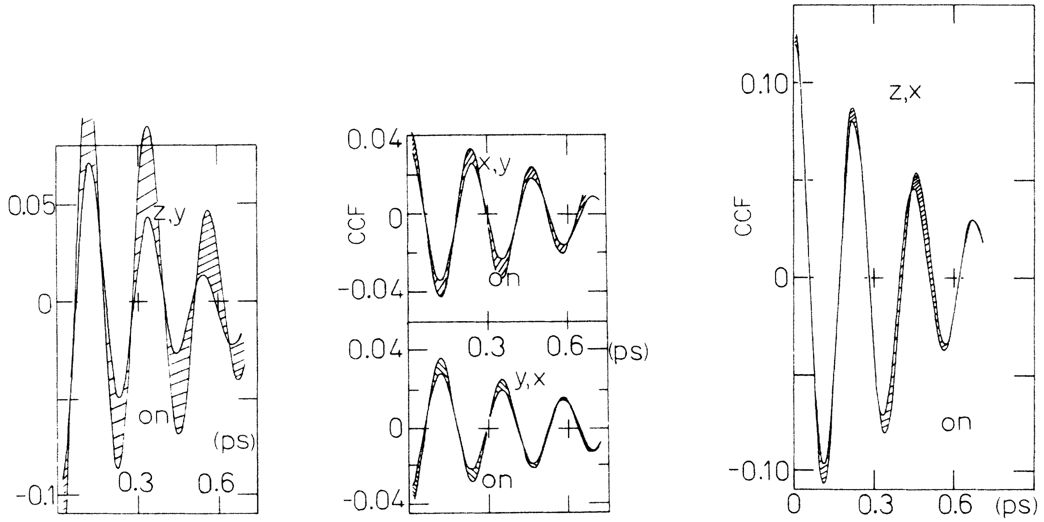
$$\mathbf{C}_3(t) = \langle 2\boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$$

and

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

where T denotes vector transposition.

The original result of this Rapid Communication is that the off-diagonal elements of the $\mathbf{C}_3(t)$ *are shown to exist*



(a)

(b)

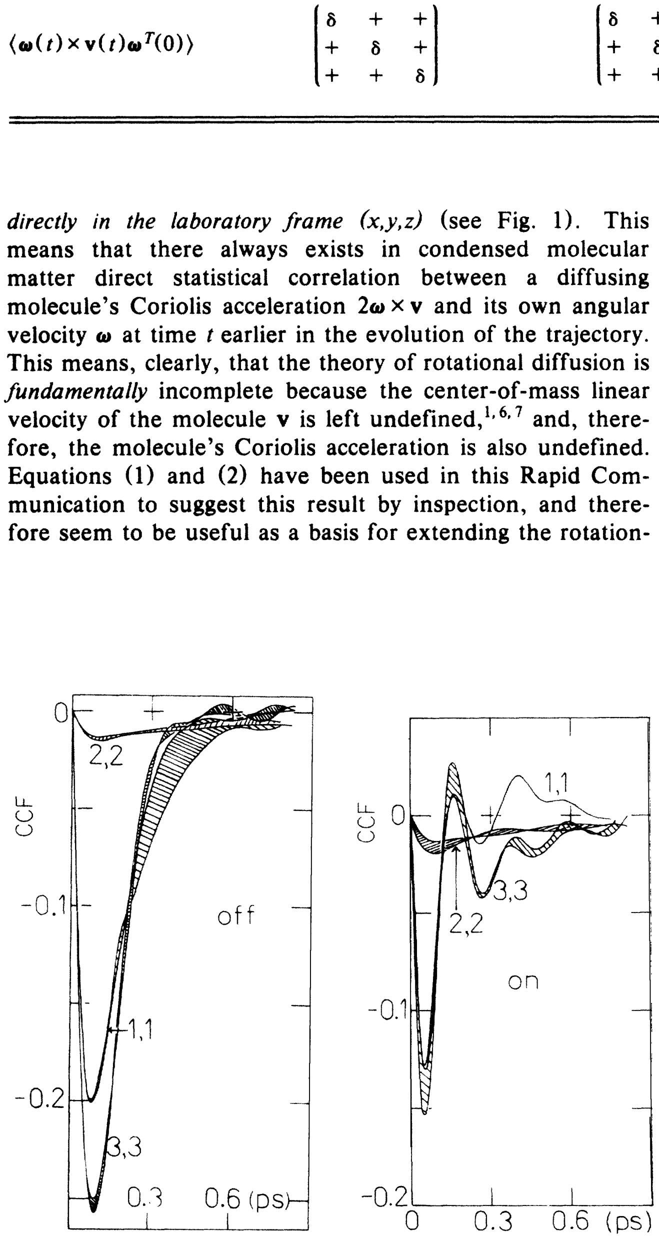
(c)

FIG. 2. As for Fig. 1 with a strong electric field **E** applied in the z axis of the (x,y,z) frame. The overall symmetry of $\mathbf{C}_3(t)$ is changed. (x,y) and (y,x) are still mirror images, but two elements, (y,z) and (x,z), have disappeared in the noise. In contrast (z,y) and (z,x) have increased in amplitude compared with Fig. 1.

TABLE I. Symmetry patterns for single molecule tensor cross-correlation functions.

Correlation matrix	Frame of reference (x,y,z)	$(x,y,z)+\mathbf{E}$	$(1,2,3)$	$(1,2,3)+\mathbf{E}$
$\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle$	$\begin{bmatrix}\delta&\delta&\delta\\\delta&\delta&\delta\\\delta&\delta&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&\delta&\delta\\\delta&\delta&\delta\\\delta&\delta&\delta\end{bmatrix}$	$\begin{bmatrix}+&\delta&\delta\\\delta&+&\delta\\\delta&\delta&+\end{bmatrix}$	$\begin{bmatrix}+&\delta&\delta\\\delta&+&\delta\\\delta&\delta&+\end{bmatrix}$
$\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$	$\begin{bmatrix}\delta&+&+\\+&\delta&+\\+&+&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&+&\delta\\+&\delta&\delta\\+&+&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&\delta&\delta\\\delta&\delta&\delta\\\delta&\delta&\delta\end{bmatrix}$	$\begin{bmatrix}\delta&\delta&\delta\\\delta&\delta&+\\\delta&+&\delta\end{bmatrix}$

directly in the laboratory frame (x,y,z) (see Fig. 1). This means that there always exists in condensed molecular matter direct statistical correlation between a diffusing molecule's Coriolis acceleration $2\boldsymbol{\omega}\times\mathbf{v}$ and its own angular velocity $\boldsymbol{\omega}$ at time t earlier in the evolution of the trajectory. This means, clearly, that the theory of rotational diffusion is *fundamentally* incomplete because the center-of-mass linear velocity of the molecule $\mathbf{v}$ is left undefined,[1,6,7] and, therefore, the molecule's Coriolis acceleration is also undefined. Equations (1) and (2) have been used in this Rapid Communication to suggest this result by inspection, and therefore seem to be useful as a basis for extending the rotational theory [essentially Eq. (2) alone] to include these new effects. It will be necessary to devise analytical (i.e., mathematical) methods for their complete solution.[5] A comparison can then be made with the computer simulation results, exemplified in Fig. 1.



(a) (b)

FIG. 3. The moving frame, (1,2,3), diagonal elements of $\mathbf{C}_4(t)$, normalized as in Fig. 1; (a) field-off and (b) field-on equilibrium. (a) and (b) are checks carried out with the vector (trace) CCF,

$$\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\cdot\mathbf{v}(0)\rangle/\langle v^2(0)\rangle\langle \omega^2(0)\rangle^{1/2}$$

computed *independently*. It can be seen that this exists in frame (1,2,3) but vanishes in frame (x,y,z) (see Table I).

The symmetry characteristics of $\mathbf{C}_4(t)$ are completely different in the laboratory frame (x,y,z). No elements of $\mathbf{C}_4(t)$ could be detected above the noise of two segments of the simulation. Therefore, no simple statistical correlation was found between the molecular Coriolis acceleration and the linear velocity $\mathbf{v}$ of the same molecule's center of mass.

In the moving frame (1,2,3) the symmetry characteristics of $\mathbf{C}_3(t)$ and $\mathbf{C}_4(t)$ are again different. In this case the diagonal elements of $\mathbf{C}_4(t)$ exist above the noise, but all the off-diagonal elements vanish. All the nine elements of $\mathbf{C}_3(t)$ vanish in frame (1,2,3).

In the laboratory frame (x,y,z) the symmetry of $\mathbf{C}_4(t)$ is unchanged when the field $\mathbf{E}$ is applied in the z axis of this frame. However, the nonvanishing elements of $\mathbf{C}_3(t)$ are significantly affected, and this is illustrated in Fig. 2. In the moving frame (1,2,3) the diagonal elements of $\mathbf{C}_4(t)$ become more oscillatory (Fig. 3), but the overall symmetry of the matrix is unaffected. The symmetry of $\mathbf{C}_3(t)$ is changed by the application of $\mathbf{E}$ in the z axis, in that the field promotes the existence of at least three off-diagonal elements of $\mathbf{C}_3(t)$ in frame (1,2,3).

These symmetry characteristics are summarized in Table I, where the symbol δ means that *no* "signal" (i.e., cross-correlation function) could be detected above the noise for $0 < t < \infty$. The symbol + means that a cross-correlation function *was* detected for $0 < t < \infty$.

Finally, a large number of other cross-correlation functions of this type can be constructed among the various terms of Eqs. (1) and (2). The existence of these new cross-correlation functions means that the theory of single-particle Brownian motion must be revised accordingly. Structures such as Eqs. (1) and (2) can be generalized to N-particle Brownian dynamics,[14] and also to involve memory functions[7] in an attempt to link them with basic equations of motion such as the Liouville equation.

ACKNOWLEDGMENT

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