New Langevin Equations for a Translating and Simultaneously Rotating Asymmetric Top

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By the writing of the translational Langevin equation in a rotating frame of reference $(1,2,3)'$ and the rotational equation in the usual moving frame (1,2,3), it is shown that the statistical correlation between the angular and linear center-of-mass motion of a diffusing asymmetric top can be described naturally and in detail. Computer simulation is used to illustrate the symmetry class and time dependence of many new types of autocorrelation and cross-correlation functions suggested by the structure of these equations.

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This Letter shows that the diffusion in three dimensions of an asymmetric top molecule requires adequate consideration of the translational diffusion of the center of mass superimposed[1-8] on the molecule's own rotation. If this is not taken into account, a great deal of statistical information is lost, and the theory of molecular diffusion is then unable to explain the numerical results now available.[9-11]

Computer simulation is used in this Letter to provide a variety of new cross-correlation functions. By writing the Langevin equations for rotation and translation in the appropriate frames of reference, I show in this Letter that certain new types of cross-correlation exist both in the laboratory frame (x,y,z) and in the moving frame of reference (1,2,3) of the principal molecular moments of inertia. Others exist in the frame (1,2,3) only; still others vanish in both frames, and so on.

Consider a frame of reference $(1,2,3)'$ whose origin is the same as that of the laboratory frame (x,y,z) but which rotates at an angular velocity $\boldsymbol{\omega}$. This is taken to be the same as the resultant angular velocity of the diffusing molecule defined with respect to frame (x,y,z), so that

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

The frame $(1,2,3)'$ is the *rotating* frame of reference, as distinct from the *moving* frame (1,2,3), which both rotates and translates with the frame of the principal molecular moments of inertia.[12-15]

An observer rotating in frame $(1,2,3)'$ would see only the resultant *translational* motion of a molecule that is also rotating with angular velocity $\boldsymbol{\omega}$. The observer and the molecule are always rotating, however, at the same rate, and the observer cannot, therefore, be aware of the molecule's resultant rotation [known to be discernible in frame (x,y,z)]. To an observer in frame $(1,2,3)'$, the molecule's diffusion seems, therefore, to be governed by a translational Langevin equation. The first step in the analysis consists of writing this in frame $(1,2,3)'$, which is a "noninertial" frame of reference with respect to (x,y,z), the static laboratory frame. From elementary dynamics[16] it follows that

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

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

On the right-hand side of these equations all the vectors are defined with reference to frame $(1,2,3)'$. On the left-hand side they are defined in frame (x,y,z). In these equations $\mathbf{r}$ is the position vector of the molecular center of mass, defined by

$$[\dot{\mathbf{r}}]_{(1,2,3)'} = [\boldsymbol{v}]_{(1,2,3)'}. \tag{4}$$

The translational Langevin equation in frame (x,y,z) is well known[12] to be

$$[\dot{\boldsymbol{v}} + \beta_v \boldsymbol{v}]_{(x,y,z)} = [\dot{\mathbf{W}}]_{(x,y,z)}, \tag{5}$$

where β_v is the translational friction coefficient, a scalar invariant to any frame transformation, and $\dot{\mathbf{W}}$ is a Wiener process.[12] Therefore, the translational Langevin equation in frame $(1,2,3)'$, the rotating frame, is

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

where $[\dot{\mathbf{W}}]_{(1,2,3)'}$ is a statistical process generated from the Wiener process $[\dot{\mathbf{W}}]_{(x,y,z)}$ by the frame transformation[16] $(x,y,z) \rightarrow (1,2,3)'$. In Eq. (6), $2\boldsymbol{\omega}\times\boldsymbol{v}$ is the Coriolis acceleration, $\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})$ is the centripetal acceleration, and $\dot{\boldsymbol{\omega}}\times r$ is the nonuniform acceleration of the molecule.

It is well known from the theory of rotational diffusion in an asymmetric top[11-13] that $\boldsymbol{\omega}$ is also governed in the moving frame (1,2,3) by the standard Euler-Langevin equation[14]:

$$\begin{aligned} I_1\dot{\omega}_1 - (I_2 - I_3)\omega_2\omega_3 + I_1\beta_1\omega_1 &= I_1\dot{W}_1, \\ I_2\dot{\omega}_2 - (I_3 - I_1)\omega_3\omega_1 + I_2\beta_2\omega_2 &= I_2\dot{W}_2, \\ I_3\dot{\omega}_3 - (I_1 - I_2)\omega_1\omega_2 + I_3\beta_3\omega_3 &= I_3\dot{W}_3, \end{aligned} \tag{7}$$

when the molecule's rotation is superimposed upon its center-of-mass translation. In Eq. (7), I_1, I_2, and I_3 are the principal molecular moments of inertia; ω_1, ω_2, and ω_3 are the components of $\boldsymbol{\omega}$ in the frame (1,2,3); β_1, β_2, and β_3 are the components in this frame of the (diagonal) rotational friction tensor[17]; and $\dot{W}_1$, $\dot{W}_2$, and $\dot{W}_3$ are the components in frame (1,2,3) of the rotational Wiener process.

Equations (6) and (7) constitute a complete description of the diffusion of an asymmetric top in three dimensions in terms of simple Langevin equations. Their structure suggests the existence of many new cross-correlation functions involving $\boldsymbol{\omega}$, $\mathbf{v}$, and $\mathbf{r}$. They are illustrated in this Letter by means of conventional computer simulation. [The fully *analytical* solution[14] of the fundamental Langevin equations (6) and (7) is a very difficult problem.[18]]

Note carefully that Eqs. (2) and (3) are reversible, because of the relativity of this type of frame transformation,[16] so that

$$[\mathbf{v}]_{(1,2,3)} \equiv [\mathbf{v} + \boldsymbol{\omega} \times \mathbf{r}]_{(x,y,z)}, \tag{8}$$

$$[\dot{\mathbf{v}}]_{(1,2,3)'} \equiv [\dot{\mathbf{v}} + 2\boldsymbol{\omega} \times \mathbf{v} + \dot{\boldsymbol{\omega}} \times \mathbf{r} + \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r})]_{(x,y,z)}. \tag{9}$$

Equations (8) and (9) therefore imply the existence in the laboratory frame itself of new types of accelerations which appear only when the interrelations between $\mathbf{r}$, $\mathbf{v}$, and $\boldsymbol{\omega}$ are considered fully. The laboratory-frame autocorrelation functions of all the right-hand-side molecular accelerations and velocities in Eqs. (8) and (9) exist, and this has been confirmed in this work by computer simulation. Furthermore, any vector $\mathbf{A}$ defined in frame (x,y,z) also exists in frame (1,2,3), and vice versa. The relevant frame transformation relations in this case are available elsewhere.[9-11] This implies that these autocorrelation functions also exist in this frame, and we have also verified this by computer simulation. These results will be reported in full elsewhere.

In this Letter we provide a summary table (Table I) of the properties of some of the new *cross*-correlation functions in both frames, (x,y,z) *and* (1,2,3). Note that *all* the *auto*correlation functions of the vectors in this table exist in *both* frames (1,2,3) and (x,y,z) for $t < \infty$. Although the vector cross-correlation functions of type IV vanish in both frames, some of the off-diagonal elements of the equivalent tensor cross-correlation functions might well exist $0 < t < \infty$. This will be the subject of future computer simulations. Note finally that all these correlation functions refer to the diffusion of one molecule in a bath of others. A great amount of new information is obtainable when the analysis is extended to include correlations between different molecules.

These results were obtained from a molecular-dynamics computer simulation[11] of liquid dicholromethane at 296 K, with use of a molar volume of 5.0×10^{-6} m^3/mole and a segment of 2700 time steps for each computation. The hatched areas in Figs. 2 and 3 illustrate the "computer noise," i.e., the difference in results between two consecutive segments.

It is clear from Fig. 1 that the *auto* correlation functions exist in both frames of reference, whereas Figs. 2

TABLE I. Symmetry classification of cross-correlation functions: Achiral asymmetric top CH_2Cl_2 (C_{2v}). The symbol + indicates the existence for $0 < t < \infty$ of the cross-correlation function above the noise of the simulation. The symbol − means that the cross-correlation function vanishes for all t in the noise.

Type	Examples	Frames (x,y,z)	Frames (1,2,3)
I	$\dfrac{\langle \mathbf{r}(t) \times \boldsymbol{\omega}(t) \cdot \dot{\boldsymbol{\omega}}(0) \times \mathbf{r}(0) \rangle}{\langle r^2 \rangle \langle \omega^2 \rangle^{1/2} \langle \dot{\omega}^2 \rangle^{1/2}}$	+	+
	$\dfrac{\langle \boldsymbol{\omega}(t) \times \dot{\boldsymbol{\omega}}(t) \cdot \dot{\boldsymbol{\omega}}(0) \rangle}{\langle \omega^2 \rangle^{1/2} \langle \dot{\omega}^2 \rangle}$	+	+
II	$\dfrac{\langle \mathbf{A}(t) \times \boldsymbol{\omega}(t) \cdot \mathbf{A}(0) \rangle}{\langle A^2 \rangle \langle \omega^2 \rangle^{1/2}}$	−	+
	$(\mathbf{A} \equiv \mathbf{v}; \boldsymbol{\omega} \times \mathbf{r}; \mathbf{r})$		
	$\dfrac{\langle \dot{\boldsymbol{\omega}}(t) \times \mathbf{r}(t) \cdot \boldsymbol{\omega}(0) \times [\boldsymbol{\omega}(0) \times \mathbf{r}(0)] \rangle}{\langle \dot{\omega}^2 \rangle^{1/2} \langle \omega^2 \rangle \langle r^2 \rangle}$	−	+
	$\langle \mathbf{v}(t) \boldsymbol{\omega}^T(0) \rangle$ [a]		
	$\langle [\mathbf{v}(t) \times \boldsymbol{\omega}(t)] \mathbf{v}^T(0) \rangle$	−	+
III	$\langle [\boldsymbol{\omega}(t) \times \mathbf{v}(t)] \boldsymbol{\omega}^T(0) \rangle$	+	−
IV	$\dfrac{\langle \boldsymbol{\omega}(t) \times \mathbf{v}(0) \cdot \boldsymbol{\omega}(0) \rangle}{\langle \omega^2 \rangle \langle v^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \mathbf{v}(t) \times \boldsymbol{\omega}(t) \cdot \mathbf{r}(0) \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2} \langle r^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \dot{\boldsymbol{\omega}}(t) \times \mathbf{r}(t) \cdot \mathbf{v}(0) \rangle}{\langle \dot{\omega}^2 \rangle^{1/2} \langle r^2 \rangle^{1/2} \langle v^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \boldsymbol{\omega}(t) \times \mathbf{r}(t) \cdot \mathbf{v}(0) \rangle}{\langle \omega^2 \rangle^{1/2} \langle r^2 \rangle^{1/2} \langle v^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \mathbf{v}(t) \times \boldsymbol{\omega}(t) \cdot \dot{\boldsymbol{\omega}}(0) \times \mathbf{r}(0) \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2} \langle \dot{\omega}^2 \rangle^{1/2} \langle r^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \mathbf{v}(t) \times \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0) \times \mathbf{r}(0) \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle \langle r^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \boldsymbol{\omega}(t) \times [\boldsymbol{\omega}(t) \times \mathbf{r}(t)] \cdot \mathbf{v}(0) \rangle}{\langle \omega^2 \rangle \langle r^2 \rangle^{1/2} \langle v^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \mathbf{v}(t) \times \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0) \times [\boldsymbol{\omega}(0) \times \mathbf{r}(0)] \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2} \langle \omega^2 \rangle \langle r^2 \rangle^{1/2}}$	−	−
	$\dfrac{\langle \mathbf{v}(t) \cdot \boldsymbol{\omega}(0) \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2}}$	−	−

[a] Reference 19.

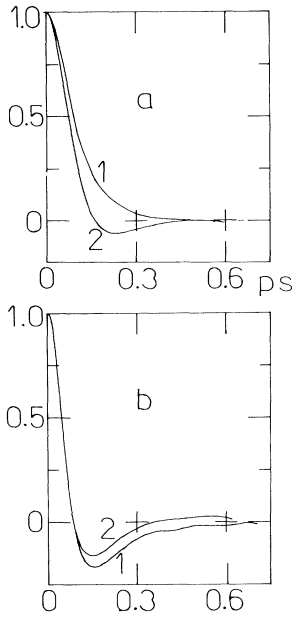

FIG. 1. (a) The autocorrelation function of the Coriolis acceleration, normalized to unity at the origin: A computer simulation treating 108 CH_2Cl_2 molecules (see text). Curve 1, laboratory frame (x,y,z); curve 2, moving frame [(1,2,3)], *with origin at the molecular center of mass* (Refs. 9 and 10). (b) Autocorrelation function of the acceleration $\dot{\boldsymbol{\omega}}(t)\times\mathbf{r}(t)$, as in (a). These autocorrelation functions illustrate the existence of the acceleration terms in Eqs. (2) and (9).

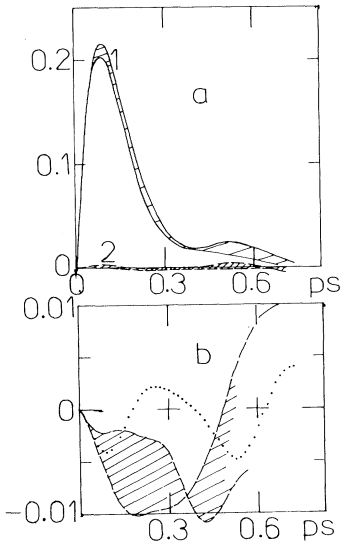

FIG. 2. (a) Cross-correlation function between the Coriolis acceleration $\boldsymbol{\omega}(t)\times\boldsymbol{v}(t)$ and the center-of-mass velocity $\boldsymbol{v}$,

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

Curve 1, moving frame (1,2,3); curve 2, laboratory frame (x,y,z). The hatching denotes the noise level in the computer simulation. (b) Cross-correlation function

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

dashed curve, in the moving frame (1,2,3); dotted curve, in the laboratory frame (x,y,z). In contrast to (a) the cross-correlation function does not exist in either frame, and (b) illustrates the noise level.

and 3 show that the cross correlations can, for example, exist in the moving frame but vanish in the laboratory frame.

For the spherical top, we have $I_1=I_2=I_3$, so that the three equations (7) become independent, but the components of (6) *do not* because, for this group, $r_1\neq r_2\neq r_3$; $\omega_1\neq\omega_2\neq\omega_3$. Therefore, cross-correlation functions of the type $\langle\dot{r}_1(t)\omega_2(0)\rangle$, etc., may exist even for the spherical top, when this diffuses in three dimensions.

$$[\ddot{\psi}+\beta_3\psi=\dot{W}_3]_{(1,2,3)},$$

$$\begin{bmatrix}\ddot{r}_1-2\psi\dot{r}_2-\ddot{\psi}r_2-r_1\psi^2+\beta_v(\dot{r}_1-\psi r_2)=\dot{W}_{1v}\\ \ddot{r}_2+2\psi\dot{r}_1+\ddot{\psi}r_1-r_2\psi^2+\beta_v(\dot{r}_2+\psi r_1)=\dot{W}_{2v}\\ \ddot{r}_3+\beta_v\dot{r}_3=\dot{W}_{3v}\end{bmatrix}_{(1,2,3)'}.$$

In this case, therefore, the components ω_3 and $\dot{r}_3$ [i.e., ω_3 and v_3 of frame $(1,2,3)'$] are independent, so that $\langle v_3(t)\omega_3(0)\rangle=0$ for all t, but other cross correlations may exist.

However, if we also restrict the translational motion so that $v_1=v_2=0$, then Eqs. (7) and (6) become

$$[\dot{\omega}_3+\beta_3\omega_3=\dot{W}_3]_{(1,2,3)},\quad [\dot{v}_3+\beta_v v_3=\dot{W}_{3v}]_{(1,2,3)'}.$$

This is the Brownian motion of a body that is rotating perpendicularly to the 3 axis of frame (1,2,3) and translating parallel to the 3 axis of frame $(1,2,3)'$. In this case there is no statistical correlation between the rotational and translational motion.

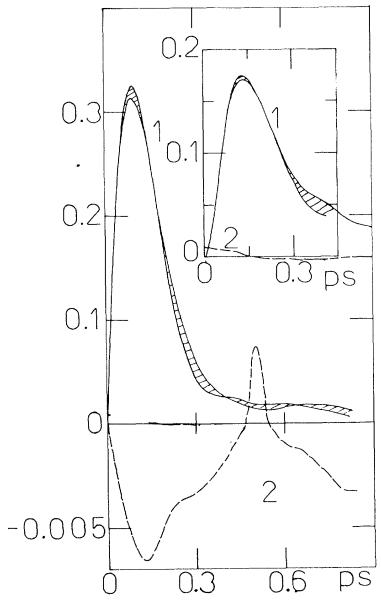

FIG. 3. Curves 1 (solid), two segments of the moving-frame [(1,2,3)] cross-correlation function between $\mathbf{r}(t)\times\boldsymbol{\omega}(t)$ and $\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]$,

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

Curve 2 (dashed), one laboratory frame segment, which is *noise* only, i.e., vanishes for all t, when averaged over a sufficient number of segments. Inset: Cross-correlation function between $\dot{\boldsymbol{\omega}}(t)\times\mathbf{r}(t)$ and $\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]$,

$$\frac{\langle \dot{\boldsymbol{\omega}}(t)\times\mathbf{r}(t)\cdot\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]\rangle}{\langle\dot{\omega}^2\rangle^{1/2}\langle r^2\rangle\langle\omega^2\rangle}.$$

Curves 1, moving frame [(1,2,3)]; curve 2, laboratory frame.

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