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, 3ωx = iωz = jωy = kωt = 0, here 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 v.

INTRODUCTION

This Rapid Communication presents firm evidence that the historically popular theory of rotational diffusion is fundamentally incomplete when applied to the 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-correlation functions involving the angular velocity ω̇ of the diffusing dipole molecule, and its own linear velocity 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 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 hindered unknown cross-correlation functions involving the diffusion molecule's position vector r, v (−ṙ), and 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. This frame has its origin fixed at that of the laboratory frame (x,y,z), but rotates at an angular velocity ω̇ of that of the diffusing asymmetric top. In this frame, the translational Langevin equation becomes

\[ \dot{\vec{v}} + 2\alpha \times \vec{v} + \alpha \times (\alpha \times \vec{v}) - \vec{W}(\vec{x},\lambda) = \beta \vec{v} + \vec{u}(\vec{x},\lambda) \]

where β denotes the scalar translational friction coefficient which is the same in any frame of reference, and \[ \vec{W}(\vec{x},\lambda) \] is a stochastic process generated from the laboratory-frame Wiener process \[ \vec{W}(\vec{x},\lambda) \] by the frame transformation \[ (x,y,z) \rightarrow (1,2,3) \].

The angular velocity ω̇ 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

\[ \dot{I}_{11} = -I_{12}I_{23} + I_{12}I_{33} - I_{13}I_{22} \]
\[ \dot{I}_{22} = -I_{12}I_{23} + I_{13}I_{22} - I_{12}I_{33} \]
\[ \dot{I}_{33} = -I_{13}I_{22} + I_{12}I_{33} - I_{12}I_{23} \]

(2)

Essentially speaking, the original Debye theory of rotational diffusion does only use Eq. (2) in describing the dynamical evolution of \[ \vec{w} \] 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, \[ I_{11}, I_{22}, \text{and } I_{33} \] are the three principal molecular moments of inertia, and \[ \beta_1, \beta_2, \text{and } \beta_3 \] are the rotational friction coefficients diagonalized in frame (1,2,3) with the rotational Wiener processes \[ \vec{W}_{11}, \vec{W}_{22}, \text{and } \vec{W}_{33} \]. The theory is therefore incomplete because Eq. (1) is missing, and consequently v, x, and z are undefined.

With contemporary analytical methods\(^2\) 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\(^2\) to be (i) the Coriolis acceleration, \[ 2\omega \times v \], (ii) the centripetal acceleration, \[ \alpha \times \vec{v} \], and (iii) the "nonuniform" acceleration, \[ \alpha \times \vec{a} \], and (iv) the linear velocity \[ \alpha \times \vec{r} \].

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

\[ \begin{pmatrix} 1,2,3 \\ x,y,z \end{pmatrix} \]

(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 CH₃CH₂ molecules were simulated\(^3\) at 296 K, rotor volume of 5.0 × 10⁻⁴ m³/mol for E = 0, where 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

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

$$C_{xy}(t) = \frac{\langle u(t)x(t), w(t) \rangle}{\langle w(t)^2 \rangle}.$$

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 $(x,y)$ and $(y,z)$ and $(z,x)$ and $(x,z)$ pairs seem to be similar images.

trouds, each separated by three time steps of $5 \times 10^{-11}$ sec each. The computation was repeated at fixed-on equilibrium, where the molecules are aligned by the field to so that the Langevin function is effectively saturated. In this condition, the overall Hamiltonian is no longer invariant to parity reversal, 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

$$C_I(t) = \langle 2w(t)x(t), \psi(t) \rangle,$$

and

$$C_I(t) = \langle 2w(t)x(t), \mu(t) \rangle.$$ 

The equivalent tensor cross-correlation functions $^{14,17}$ are, therefore,

$$C_I(t) = \langle 2w(t)x(t), \psi(T) \rangle,$$

and

$$C_I(t) = \langle 2w(t)x(t), \mu(T) \rangle,$$

where $T$ denotes vector transposition.

The results of this Rapid Communication is that the off-diagonal elements of the $C_I(t)$ are shown to exist

FIG. 2. As for Fig. 1 with a strong electric field $B$ applied in the $x$-axis of the $(x,y,z)$ frame. The overall symmetry of $C_I(t)$ is changed. $(x,y)$ and $(x,z)$ are still mirror images, but two symmetas $(y,z)$ and $(x,z)$, have disappeared in the noise. In contrast $(x,y)$ and $(x,z)$ have increased in amplitude compared with Fig. 1.
TABLE I. Symmetry patterns for single molecule tensor cross-correlation functions.

<table>
<thead>
<tr>
<th>Correlation matrix</th>
<th>Frame of reference</th>
<th>((x,y,z)+E)</th>
<th>((x,y,z)+E)</th>
<th>((1,2,3)+E)</th>
<th>((1,2,3)+E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\mathbf{v}(i) \cdot \mathbf{v}(j)) \mathbf{v}(0))</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
</tr>
<tr>
<td>((\mathbf{w}(i) \cdot \mathbf{v}(j)) \mathbf{v}(0))</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
<td>([0,0,0])</td>
</tr>
</tbody>
</table>

directly in the laboratory frame \((x,y,z)\) (see Fig. 1). This means that there always exists in confined molecular matter direct statistical correlation between a diffusing molecule's Coriolis acceleration \(2\omega \times \mathbf{v}\) and its own angular velocity \(\omega\) 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 \(v\) is left undefined.\(^{4,5}\) and, therefore, the molecule's Coriolis acceleration is also undefined. Equations (1) and (2) have been used in the Rapid Communication to suggest this result by inspection, and therefore seem to be useful as a basis for extending the rotation-

at 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.\(^{6}\) A comparison can then be made with the computer simulation results, exemplified in Fig. 1.

The symmetry characteristics of \(C_{ij}(t)\) are completely different in the laboratory frame \((x,y,z)\). No elements of \(C_{ij}(t)\) could be detected above the noise of two segments of the simulation. Therefore, as with statistical correlation was found between the molecular Coriolis acceleration and the linear velocity \(v\) of the same molecule's center of mass. In the moving frame \((1,2,3)\) the symmetry characteristics of \(C_{ij}(t)\) and \(C_{ij}(t)\) are again different. In this case the diagonal elements of \(C_{ij}(t)\) exist above the noise, but all the off-diagonal elements vanish. All the nine elements of \(C_{ij}(t)\) vanish in frame \((1,2,3)\).

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

These symmetry characteristics are summarized in Table 1, where the symbol \(\pm\) means that no "signal" (i.e., cross-correlation function) could be detected above the noise for \(0 < t < \infty\). The symbol \(\times\) 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,\(^{6}\) and also involve memory functions\(^{7}\) in an attempt to link them with basic equations of motion such as the Liouville equation.

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