Laboratory-frame cross-correlation functions for spherical-top molecules

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Dynamical cross-correlation functions are reported for the diffusion of spherical-top molecules, exemplified by the T_d-symmetry molecule carbon tetrachloride in the liquid state at 296 K. These are novel types of cross-correlation functions which exist directly in the laboratory frame of reference, (x,y,z), and involve rotational and translational motion simultaneously. Contemporary analytical theories for the diffusion of the spherical top are not able to account for these results, which were obtained by computer simulation.

INTRODUCTION

The theory of rotational diffusion was introduced by Debye,[1] who defined the problem without considering explicitly the way in which translation and rotation, the two fundamental modes of motion, are interrelated in a diffusing spherical top. There was good reason for this because otherwise the problem would have become analytically intractable and Debye would not have been able to reduce the problem to its essentials as elegantly as he did. Note, for example, the complexity introduced[2,3] by considerations of molecular inertia, important for the explanation of the far-infrared spectrum. No closed-form solution to the Euler-Langevin system is possible in this case as witnessed by the meticulous work[4] of Lewis, McConnell, and Scaife in the mid seventies, some 60 years after the first papers on the subject by Debye himself. Note that this is true for the spherical top in the case of rotational diffusion, with no considerations at all of center-of-mass translation. A set of Euler-Langevin equations for the three-dimensional (3D) diffusion of the spherical top including center-of-mass translation has been introduced by Evans,[5-8] but these equations are still unsolved because they are intricately nonlinear in nature. There have been many other attempts to write down and solve the diffusion equations for simultaneous molecular rotation and translation, but there are too many parameters ever to be determined in a single, simple, and self-consistent experiment. It seems, therefore, that the methods introduced by Debye and extended in many elegant ways during the century,[9-15] cannot solve the basic problem of molecular diffusion as soon as this is extended to two fundamental modes of motion rather than just one.

The difficulties of the analytical theory are shown up by the relative success of numerical methods in this field of physics, in particular the technique of molecular dynamics computer simulation. This has scored heavily over the analytical methods in this decade—for example, the discovery[16] of the first (simple) CCF (cross-correlation function) $\langle v(t)\omega^T(0)\rangle_{(1,2,3)}$ in 1981 by Ryckaert, Bellemans, and Ciccotti; its confirmation and extension to other molecular symmetries (chiral, for example) by Evans and co-workers;[17-25] the discovery of $\langle v(t)\omega^T(0)\rangle$ direct-

ly in the laboratory frame in 1985 by the use[26] of an external uniaxial electric field; the discovery of the higher-order CCF's;[5-8] and recently the confirmation[27] that these exist in frame (1,2,3), the frame of the molecular principal moments of inertia, in spherical top molecules, the subject of this work. By now many different types of CCF are known, but the time dependence of none of these is obtainable from the analytical theory. Furthermore, the necessary comparison with experimental data is also possible by computer simulation,[24,28] using the self-same trajectories as used to construct the CCF's so that the simulation is providing new information within the framework of natural philosophy. This is, of course, hypothesis followed by measurement followed by modified hypothesis. The stage has now been reached, however, where the analytical theory of molecular diffusion seems incapable of modification without immediately making the new hypothesis so elaborate as to be useless for comparison with observables and the parameters, such as relaxation times, obtained therefrom. This is not true at all of computer simulation, however, because the ability of this method to produce new information—for example, as follows—is paralleled by its ability to produce information of direct experimental interest, such as thermodynamic, structural, and spectral data.

This paper illustrates this by reporting direct laboratory-frame cross-correlation functions in liquid carbon tetrachloride. This is the first time that the fundamental modes of motion have been correlated in frame (x,y,z) for the spherical top. This paper reports CCF's that are positive to time reversal, parity reversal, and reflection in frame (x,y,z) and which also show a distinct and well-defined time dependence from the simulation. This supplements the previous work in frame (1,2,3), and shows clearly and conclusively that the hypothesis of rotational diffusion, considered in both frames (1,2,3) and (x,y,z) by Debye,[1] is a very crude first approximation, even in the case most favorable to that hypothesis, that of the diffusing spherical top. Therefore, it is advisable to use computer simulation to interpret the experimental data available in this field. The CCF's obtained in this paper therefore are no mere exotica, but are fundamental to molecular dynamics in the condensed phases of matter.

COMPUTER SIMULATION METHOD

A standard constant-volume algorithm, developed by the author,[15–28] was used to solve approximately the rotational and translational equations of motion for 108 CCl_4 molecules. The approximations used in the simulation were also standard,[29] e.g., cubic periodic boundary conditions, the pair interaction approximation, cutoff criteria, and virial corrections. The pair interaction potential between two carbon tetrachloride molecules was modeled with a five-by-five Lennard-Jones atom-atom potential with the Lorentz-Berthelot combining rules for cross terms, as usual. The Lennard-Jones parameters were as follows:

$$\epsilon(Cl—Cl)/k = 175.0 \text{ K}, \quad \sigma(Cl—Cl) = 3.35 \text{ Å} ,$$

$$\epsilon(C—C)/k = 51.0 \text{ K}, \quad \sigma(C—C) = 3.20 \text{ Å} ,$$

$$q_{Cl} = q_C = 0 .$$

The novel (x,y,z) frame CCF's of this work were computed over a time span of 2000 time steps of 5.0 fs each. The CCF's are well behaved statistically with this amount of information for the running time averaging of the subsidiary algorithms coded in this work. The new CCF's are naturally a little more difficult and time consuming to compute than autocorrelation functions (ACF's), but are otherwise straightforwardly obtainable once their existence has been inferred. The following section deals with the way in which this inference was obtained.

GENERAL THEORY OF "NONINERTIAL" MOLECULAR DYNAMICS

Newton's three laws of motion are derived in what is sometimes termed an "inertial" frame of reference.[30] They refer to uniform translational motion and acceleration in this frame. When rotational motion is superimposed on the translation of the center of mass, then the frame (x,y,z) becomes[30] "noninertial" with respect to the rotation of the molecule, which is in effect the rotation of frame (1,2,3) with respect to frame (x,y,z). The frame (1,2,3), whose origin is at the molecular center of mass, also translates with respect to (x,y,z) with the molecular center-of-mass velocity $\mathbf{v}$. This relative translation is filtered out by use of the rotating frame (1,2,3)' whose origin is fixed at the (x,y,z) origin and whose angular velocity with respect to (x,y,z) is conveniently defined as the molecular angular velocity ω.

A basic theorem of dynamics is available[31] to relate a vector, such as the molecular center-of-mass linear velocity, defined with respect to (x,y,z) to its equivalent defined in frame (1,2,3)'. For linear center-of-mass velocity the relation is

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

In this equation $[\mathbf{v}]_{(x,y,z)}$ is the linear center-of-mass velocity in frame (x,y,z), which is equivalent in the rotating frame (1,2,3)' to the sum on the right-hand side. The latter is made up of the Newtonian linear center-of-mass velocity $\mathbf{v}$ plus the noninertial linear velocity $\omega \times \mathbf{r}$, which evidently appears only for finite ω, i.e., when there is rotation superimposed on translation.

The corollary of theorem (1) is

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

which shows that the noninertial linear velocity exists in frame (x,y,z) and is a real velocity in the laboratory frame. This basic theorem of dynamics is at the root of the new CCF's discovered in this work. The equivalent of theorems (1) and (2) for acceleration are, respectively,

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

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

Equation (4) shows that there are three noninertial accelerations in the laboratory frame. These are real linear accelerations, but confusion is often caused in the literature by calling them the "pseudo" accelerations. This misleading reference is due to the fact that they do not appear in Newton's second law. In previous work[5–8,27] we have computed the ACF's of each type of noninertial acceleration and have obtained their time dependence in frames (1,2,3) and (x,y,z) for different molecular symmetries, including[27] that of the spherical top.

The key to the novel results obtained in this paper, and the kernel of this work, is the extra insight obtained into the cross correlations in frame (x,y,z) by the fact that noninertial CCF's of the type

$$\langle [\dot{\mathbf{v}}(t)]_{(1,2,3)'} \cdot [\mathbf{v}(0)]_{(1,2,3)'} \rangle \tag{5}$$

exist in frame (x,y,z). This result comes directly from the general theorem on cross-correlation functions[2]

$$\langle \dot{\mathbf{A}}(t) \cdot \mathbf{A}(0) \rangle_{(x,y,z)} , \tag{6}$$

where $\mathbf{A}$ is a classical dynamical time-dependent stochastic variable. A combination of results (5) and (6) then produces a variety of possible CCF's in the laboratory frame directly. If any member of the set of possible laboratory-frame CCF's obtained in this way is positive to time reversal, parity reversal, and reflection in frame (x,y,z), then it may exist[32] for $t > 0$ in an isotropic medium such as CCl_4 liquid. The reflection operations are necessary[32] but not sufficient conditions for the existence of the laboratory-frame CCF's, and in previous work in liquid water[33] it has been shown that some CCF's which are symmetry allowed do not actually exist for $t > 0$ in the simulation.

In this work on carbon tetrachloride liquid three laboratory-frame CCF's are illustrated which are symmetry allowed and actually have a real time dependence for $t > 0$. These are oscillatory in the femtosecond and/or picosecond range and, when conveniently normalized, reach a maximum value of the order of 20% of the denominator. For example, the maximum value reached by the laboratory-frame CCF

$$\mathbf{C}_1(t) = \left[\frac{\langle \mathbf{v}(t) \times \omega(t) [\mathbf{r}(0) \times \omega(0)]^T \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle \langle r^2 \rangle^{1/2}} \right]_{(x,y,z)}$$

is, for the (2,2) diagonal element, 0.132. If there is no cross correlation, this value would be zero for all t. The value of 0.132 therefore shows considerable statistical cross correlation in the spherical-top CCl_4 in the liquid state at 293 K.

DISCUSSION

Curves 1 to 3 of Fig. 1 show the time dependence of elements of the three (x,y,z) frame CCF's:

$$\mathbf{C}_1(t) = \left[\frac{\langle \mathbf{v}(t) \times \boldsymbol{\omega}(t)[\mathbf{r}(0) \times \boldsymbol{\omega}(0)]^T \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle \langle r^2 \rangle^{1/2}} \right]_{(x,y,z)},$$

$$\mathbf{C}_2(t) = \left[\frac{\langle \dot{\boldsymbol{\omega}}(t) \times \mathbf{v}(t)[\boldsymbol{\omega}(0) \times \mathbf{v}(0)]^T \rangle}{\langle \dot{\omega}^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2} \langle v^2 \rangle} \right]_{(x,y,z)},$$

$$\mathbf{C}_3(t) = \left[\frac{\langle \dot{\mathbf{v}}(t) \times \boldsymbol{\omega}(t)[\mathbf{v}(0) \times \boldsymbol{\omega}(0)]^T \rangle}{\langle \dot{v}^2 \rangle^{1/2} \langle v^2 \rangle^{1/2} \langle \omega^2 \rangle} \right]_{(x,y,z)},$$

normalized as shown in the denominators. The curves illustrate a well-defined time dependence in each CCF. These three are samples of cross correlations between noninertial linear velocities and noninertial linear accelerations. Many more such CCF's exist among higher time derivatives of the noninertial velocities and accelerations. All these laboratory-frame CCF's are composed of vectors such as $\mathbf{r}$, $\mathbf{v}$, and $\boldsymbol{\omega}$ which, naturally, characterize both translational and rotational modes of motion. The normalized amplitudes of the CCF's are such as to invalidate any theory of spherical-top diffusion which attempts to "decorrelate" the angular and linear variables. For example, the theories of rotational diffusion, such as the original Debye theory,[1] the Ornstein-Uhlenbeck theory,[9] the Chandrasekhar theory,[11] and Kramers theory,[12,34] the various Kubo-Mori-Zwanzig rotational theories,[34] and the many variations thereof, will not produce the results of curves 1 to 3. Furthermore, none of the attempts, from 1965 to the present,[35-45] to extend the theories of rotational diffusion to involve center-of-mass translation will produce curves 1 to 3 because the CCF's illustrated there are double vector products. Any attempt to produce the CCF's analytically, even for the spherical top, will run immediately into fundamental difficulties of nonlinearity in the Euler-Langevin system of equations,[4] coupled with
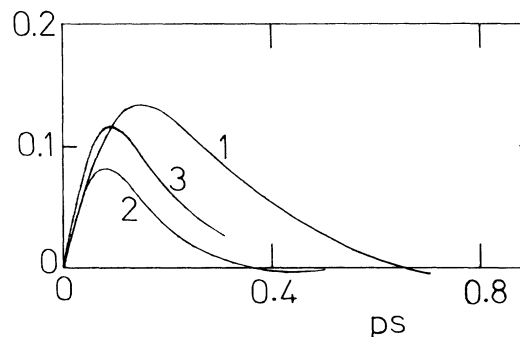

FIG. 1. The (2,2) elements of the three laboratory-frame cross-correlation functions are (1) $\mathbf{C}_1(t)$, (2) $\mathbf{C}_2(t)$, (3) $\mathbf{C}_3(t)$.

the intrinsic nonlinearities[5-8] of the translational Langevin equation when this includes the three noninertial linear accelerations. The complete set of equations in this case has been derived by Evans,[5-8] but this has not yet been solved analytically. This is hardly surprising in view of the intricacies of the Euler-Langevin equations for the rotational diffusion in three dimensions of the spherical top, as demonstrated by the work of Lewis, McConnell, and Scaife[4] in 1976. Add to this a highly nonlinear translational Langevin equation[5-8] and the mathematical difficulties become obvious. This shows conclusively that the techniques of computer simulation are now capable of providing fundamental information available in no other way.

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