

# Molecular dynamics simulation of direct laboratory frame cross correlations in spherical, plate-like, and rod-like molecules

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(Received 10 September 1987; accepted 5 November 1987)

Direct laboratory frame cross correlation functions (ccfs) are reported for the spherical top sulfur hexafluoride, and the symmetric tops, methyl hexa-tri-yne, hexafluorobenzene, and benzene. The direct correlations appear between the molecular dipole moment and the molecular center-of-mass velocity. The simulation provides the time dependence of the correlation functions for all four molecules. A simple theory for the computer simulation results is given, based on linked Langevin equations.

## I. INTRODUCTION

Direct laboratory frame cross correlations control the molecular dynamics of complicated molecular liquids in a way which is incompletely understood by the contemporary theory of molecular diffusion.<sup>1-3</sup> It is important, therefore, to gather numerical information on such correlations in order to measure their likely experimental importance. Despite its great elegance, the theory of molecular diffusion runs into difficulties of overparametrization and too much empiricism when it is applied to the patterns of cross correlations now becoming visible from various computer simulations.<sup>4-10</sup> It is failing to provide an understanding of molecular diffusion based on its own simple axioms and basic equations. An example of this difficulty is met when attempting to describe self-consistently the various forms of cross correlation now known to exist from a self-consistent combination of computer simulation and group theory. These cross correlations involve, e.g., molecular center-of-mass linear velocity and molecular angular velocity, two fundamental modes of classical dynamics. The Langevin equation needed to describe such a cross correlation function<sup>8</sup> is at once cumbersome and highly nonlinear. It can be written down, but so far remains unsolved. Even if solved, e.g., by analog circuit simulation,<sup>11</sup> the solution would contain various friction coefficients for rotation, translation, and their superposition which could not be determined experimentally and uniquely. The recent simulations have shown that this is true even for an  $O_h$  symmetry spherical top, a seemingly "ideal" case of rotational diffusion which turns out to be far from ideal due to the presence of many cross correlations not predicted or predictable from the analytical theory and not suspected to exist prior to the computer simulations. This is why the simulations are fundamentally important at this stage. They uncover details not known in analytical theory and promote new analytical activity in the field of molecular diffusion, such as the recent development of group theory by Whiff-

fer<sup>12,13</sup> and the development of analog circuit simulation for Kramers equations.<sup>11</sup> The simulation is a data gathering exercise, but made in the expectation of theoretical developments to explain the numerical data with new axioms and concepts.

In this paper the direct cross correlation between the center-of-mass linear velocity and dipole moment vector is computed directly in the laboratory frame of reference, the frame of the experimental observer. The existence of this cross correlation function can be inferred<sup>14</sup> from first principles, by considering the motion of an atom with respect to its center of mass, but its time dependence cannot be described by theories of diffusion based on the simple Langevin equation (or equivalent Fokker-Planck equation) unless these representations are made accountable for more than one mode of motion taking place simultaneously. An attempt is made in this work to develop simultaneous Langevin equations for translational diffusion and rotational velocity, but even this simple approach contains two parameters which must be determined independently given the necessary breadth of experimental data. When it is recalled that Langevin's friction coefficients are first order approximations<sup>15</sup> in the hierarchy of memory functions, then it becomes clear that the complexity of this approach to molecular diffusion must be controlled so that there are not too many parameters for unequivocal determination from experimental data. If the number becomes excessive, then the time dependence of fundamental cross correlation functions cannot be determined unequivocally by the classical method of comparing data with the results of Langevin equation theory, however elegant mathematically. This leaves computer simulation as a numerical intermediary between the experimental data and the analytical theory. In this paper the simulation is used to produce cross correlation functions in the laboratory frame direct between the molecular dipole moment time derivative and the molecular center-of-mass linear velocity. Langevin equations are then constructed for the cross correlations in terms of a friction coefficient and a barrier height for harmonic oscillation in a potential well. The analytical theory manages to reproduce the bare bones of the computer simulations and can be used self-consistently to interpret a

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variety of correlation functions from the two parameters of the analytical theory.

## II. ANALYTICAL THEORY

A simple consideration of the motion of an atom in the laboratory frame  $(x, y, z)$  leads to a proof of the existence in this frame of the cross-correlation function

$$C_1^{\bar{r}}(t) = \frac{\langle \dot{\mu}_x(t) \dot{\mu}_x(0) \rangle}{\langle \dot{\mu}_x^2 \rangle^{1/2} \langle \dot{v}_y^2 \rangle^{1/2}}$$

between the center-of-mass velocity and the rotational velocity  $\dot{\mu}$ , defined by the time derivative of the dipole moment. It follows that this is a direct measure of rotation-translation coupling in the laboratory frame of reference. The existence of this cross correlation function also implies that the symmetry properties of the rotational velocity and linear center-of-mass velocity are the same. These vectors have the same time reversal, parity reversal, and reflection-operation symmetry in the laboratory frame of reference.<sup>16,17</sup> It follows that Langevin equations linking rotational velocity and linear center-of-mass velocity are meaningful in the laboratory frame because they can be solved, as in this work, for the laboratory frame cross correlation function  $C_1(t)$ . However, because the parity reversal symmetry of angular velocity and linear velocity are opposite in the laboratory frame, linked Langevin equations between these two variables are not meaningful if they would produce a finite cross correlation at  $t > 0$  between angular velocity and linear velocity direct in the laboratory frame itself. This is incorrect because of the parity rule just cited, which indicates that the laboratory frame cross correlation function between linear and angular velocity must vanish for all  $t$ . This fundamental restriction leads us to write the linked Langevin equations as follows:

$$\bar{r} + \beta \dot{r} + V(r, \mu) = \lambda_1(t), \quad (1)$$

$$\bar{\mu} + \beta \dot{\mu} - V(r, \mu) = \lambda_2(t). \quad (2)$$

Here  $\bar{\mu}$  is the molecular rotational velocity (the time derivative of the molecular dipole moment unit vector),  $\lambda_i$  the random fluctuating noises.

The Langevin friction is  $\beta$ , and  $V$  is a potential energy generated by the mutual constraints in the laboratory frame between rotational velocity and linear velocity. It is assumed that this potential energy can be expanded in an even powered Taylor series.

If we restrict the series to the first term  $V_0$ , the set of equations (1) and (2) are linked pendulum equations with the extra presence of noise and friction as in standard Langevin theory. The stochastic terms on the right-hand sides of Eqs. (1) and (2) are Wiener processes, and in the harmonic approximation, they are soluble analytically following the methods of Coffey *et al.*<sup>18-20</sup> They can be solved for the time dependence of a number of auto- and cross correlation functions self-consistently in terms of the friction coefficient and the potential parameter  $V$ , the barrier height to translation caused by the simultaneous rotational velocity of the diffusing molecule. The potential barrier  $V$  is thus an intermolecular potential energy of the type first used in this context by Budo<sup>21</sup> and developed by Coffey.<sup>22</sup> These correlation func-

tions are also available numerically and self-consistently from various computer simulations.<sup>23,24</sup> The normalized rotational velocity, linear velocity, and their cross correlation function in the laboratory frame are obtained from Eqs. (1) and (2) as follows:

$$\langle \dot{r}(t) \cdot \dot{r}(0) \rangle = \frac{kT}{2} \left[ e^{-\beta t} + e^{-1/2\beta t} \left( \cos \omega_1 t - \frac{\beta}{2\omega_1} \sin \omega_1 t \right) \right], \quad (3)$$

$$\langle \dot{\mu}(t) \cdot \dot{\mu}(0) \rangle = \langle \dot{r}(t) \cdot \dot{r}(0) \rangle, \quad (4)$$

$$\langle \dot{r}(t) \cdot \dot{r}(0) \rangle = \frac{kT}{2} \left[ e^{-\beta t} - e^{-1/2\beta t} \left( \cos \omega_1 t - \frac{\beta}{2\omega_1} \sin \omega_1 t \right) \right], \quad (5)$$

$$\omega_1 = (4V_0 - \beta^2/4)^{1/2}. \quad (6)$$

In the so-called "equal friction" limit, where there is only one friction coefficient, the rotational velocity and linear velocity autocorrelation functions have the same time dependence. It can therefore be seen immediately that Eqs. (1) and (2) are first order approximations which do not properly reduce to the limit of free rotation and translation. This is because in this limit the linear velocity autocorrelation function is a constant and the rotational velocity correlation function is a hypergeometric Kummer function. This can be cured by using an unequal friction model, but with greatly increased mathematical complexity. A complete cure is not easy to achieve because the class of Langevin equations in general does not give the correct rotational behavior in the free rotor limit from any tractable approximation.

The simple equations (1) and (2) have the advantages, however, of being soluble and of having a simple physical meaning. This can be seen by adding Eqs. (1) and (2) to give the Langevin equation

$$\bar{r} + \bar{\mu} + \beta(\dot{r} + \dot{\mu}) = \lambda_1(t) + \lambda_2(t). \quad (7)$$

Equation (7) is a Langevin equation written for the position of a point in the diffusing particle at the end of the dipole axis. In a dipolar molecule this could well be an atom at one end of the dipole axis. The Langevin equation (7) would then be the diffusion equation of the atom. It is easy to see, furthermore, that the atom's "random walk" is constrained by forces coming from the rest of the molecule to which it is attached, this constraint being described by the potential  $V$ . The atom's diffusion is determined in other words by the molecular center-of-mass velocity and rotational velocity simultaneously in the laboratory frame of reference. By writing the equations directly in the laboratory frame, instead of the principal moment of inertia frame of the Euler-Langevin equations for angular velocity, we remove the inherent nonlinearities of the Euler equations, which appear in the theory<sup>25-28</sup> of three-dimensional diffusion. These nonlinearities are implicitly present in the molecular motion, but do not appear explicitly in Eqs. (1) and (2). They are accounted for in the potential  $V$ . This leads to a great simplification of the kinematics of the rotational part of the diffusional motion of the particle. Note that the nonlinear terms of the Euler equations complicate greatly the solution of the Langevin equation even for the diffusion of spherical top molecules.<sup>27</sup>

The angular velocity autocorrelation function (acf) can

be obtained from the kinematic relation

$$\dot{\mu} = \omega \times \mu$$

which leads to the following expansion of the rotational velocity acf:

$$\begin{aligned} \langle \dot{\mu}(t) \cdot \dot{\mu}(0) \rangle &= \langle \omega(t) \times \mu(t) \cdot \omega(0) \times \mu(0) \rangle \\ &= \langle \omega(t) \cdot \omega(0) \rangle \langle \mu(t) \cdot \mu(0) \rangle \\ &\quad - \langle \omega(t) \cdot \mu(0) \rangle \langle \mu(t) \cdot \omega(0) \rangle \end{aligned} \quad (8)$$

using the vector identity

$$(A \times B) \cdot (C \times D) = (A \cdot C)(B \cdot D) - (A \cdot D)(B \cdot C). \quad (9)$$

Now the existence of

$$\langle \mu(0) \cdot v(t) \rangle$$

and

$$\langle \dot{\mu}(0) \cdot v(t) \rangle$$

in the laboratory frame implies that the parity symmetry of  $\mu$  and  $\dot{\mu}$  are both the same as that of  $v$ . However, the parity reversal symmetry of  $\omega$  is opposite to that of  $v$ , so it follows that the parity reversal symmetry of  $\omega$  is also opposite to that of both  $\mu$  and  $\dot{\mu}$ . Thus,

$$\langle \omega(t) \cdot \omega(0) \rangle = \frac{\langle \dot{\mu}(t) \cdot \dot{\mu}(0) \rangle}{\langle \mu(t) \cdot \mu(0) \rangle}. \quad (10)$$

The denominator of Eq. (10) is the double integral over time of the numerator, and can be found from Eq. (4), *viz.*,

$$\begin{aligned} \langle \mu(t) \cdot \mu(0) \rangle &= \frac{kT}{2} \left[ e^{-\beta t} / \beta^2 + \frac{e^{-(1/2)\beta t}}{\omega_1(\omega_1^2 + \beta^2/4)} \right. \\ &\quad \left. \times \left( \frac{\beta}{2} \sin \omega_1 t - \omega_1 \cos \omega_1 t \right) \right]. \end{aligned} \quad (11)$$

Therefore, from the Langevin equations (1) and (2) we self-consistently obtain a broad range of correlation functions to match the numerous results available from computer simulation.

It is also possible to obtain the laboratory frame Coriolis acceleration by

$$\begin{aligned} \langle \omega(t) \times v(t) \cdot \omega(0) \times v(0) \rangle \\ = \langle \omega(t) \cdot \omega(0) \rangle \langle v(t) \cdot v(0) \rangle, \end{aligned} \quad (12)$$

so that the acf of the Coriolis acceleration is simply a product of Eqs. (3) and (10). Similarly, it is also possible to obtain the laboratory frame acf:

$$\langle r(t) \times \omega(t) \cdot r(0) \times \omega(0) \rangle,$$

and therefore the acf of the centripetal acceleration

$$\omega(t) \times [\omega(t) \times r(t)].$$

These time correlation functions are all obtained in terms of the friction coefficient  $\beta$  and the potential barrier height  $V_0$ . Additionally, by differentiating the acf of the Coriolis acceleration, it is possible to obtain the higher order laboratory frame acfs recently obtained in the literature for the spherical top molecule carbon tetrachloride in the liquid phase.<sup>29</sup> Continued time differentiation will lead to the complete set of higher order cross correlation functions in the laboratory frame of reference allowed by restrictions on parity reversal and reflections through planes  $xy$ ,  $xz$ , and  $yz$ .

Equations (1) and (2), therefore, have the major advantage of being soluble analytically and self-consistently for a range of time auto- and cross correlations known from computer simulation. In this paper the solution for the velocity and rotational velocity acfs, and for the cross correlation between these two vectors in the laboratory frame of reference are given for various values of friction and the potential barrier  $V_0$  and compared with the computer simulation data for spherical, rod-like, and plate-like molecules in the liquid state.

### III. COMPUTER SIMULATION METHODS

#### A. Sulfur hexafluoride

The diffusion of the  $O_h$  spherical top molecule  $SF_6$  was followed using the molecular dynamics simulation algorithm TETRA, fully described elsewhere.<sup>30</sup>

The effective pair potential was a Lennard-Jones 7 by 7 atom-atom potential with no charges. The Lorentz-Berthelot combining rules were implemented for cross terms with the following parameters:

$$\begin{aligned} \epsilon/k(S-S) &= 190.0 \text{ K}; & \sigma(S-S) &= 3.80 \text{ \AA}; \\ \epsilon/k(F-F) &= 54.9 \text{ K}; & \sigma(F-F) &= 3.10 \text{ \AA}. \end{aligned}$$

The translational and rotational equations of motion were integrated, respectively, with a Verlet algorithm and through the forces on each individual atom, as fully described elsewhere. Time correlation functions were then calculated by running time averages as usual, and normalized according to

$$C^j(t) = \frac{\langle A_i(t) B_j(0) \rangle}{\langle A_i \rangle^{1/2} \langle B_j \rangle^{1/2}}.$$

In this paper interest is focused especially on the linear and rotational velocity acf, together with the cross correlation in the laboratory frame between these vectors. This was computed over 6000 time steps of 0.005 ps each. A range of other cross correlation functions for sulfur hexafluoride has been reported in full elsewhere.<sup>24</sup>

#### B. Benzene and hexafluorobenzene

The intermolecular pair potential in these molecules was a 12 by 12 site-site potential consisting of Lennard-Jones and partial charge terms as follows:

$$\begin{aligned} q(F \text{ in } C_6F_6) &= -0.2e; & q(C \text{ in } C_6F_6) &= +0.2e; \\ \epsilon/k(C-C) &= 51.0 \text{ K}; & \sigma(C-C) &= 3.20 \text{ \AA}; \\ \epsilon/k(F-F) &= 54.9 \text{ K}; & \sigma(F-F) &= 3.10 \text{ \AA}; \\ \epsilon/k(H-H) &= 13.4 \text{ K}; & \sigma(H-H) &= 2.75 \text{ \AA}. \end{aligned}$$

The dynamics and time correlation functions were evaluated with a time step of 0.01 ps over a total of 6000 time steps in three time segments. Site-site pair distribution functions were evaluated over 2000 configurations for the various site-site interactions in benzene and hexafluorobenzene. The results for benzene are illustrated in Fig. 1 and compared with the equivalent from the flexible benzene model of Anderson *et al.*<sup>31</sup>

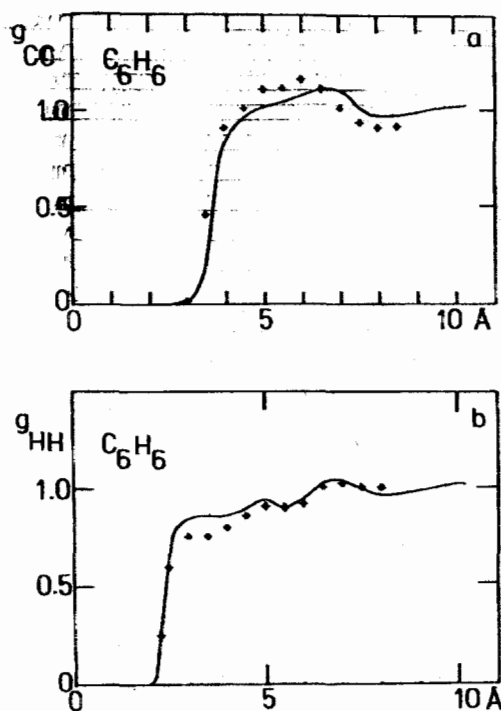


FIG. 1. Carbon-carbon (a) and hydrogen-hydrogen (b) pair distribution functions for liquid benzene at 296 K. — present simulation;  $\odot$  results of Anderson *et al.* (Ref. 31).

### C. Methyl hexatriyne

This molecule is an elongated symmetric top and a good approximation to a rod-like molecule whose dynamics approximate, if long enough and under appropriate thermodynamic conditions, those of liquid crystals. It contains three triple bonds and the pair interaction was approximated by an 11 by 11 site-site model made up of carbon and hydrogen terms with Lorentz-Berthelot combining rules. The carbon and hydrogen Lennard-Jones parameters were as above. Input molar volume and temperature are  $400 \text{ cm}^3/\text{mol}$  and 296 K, respectively. The dynamics and time correlation functions were evaluated over 6000 time steps of 0.01 ps each.

### D. Video animations

The dynamics of each of these systems have been animated on video at IBM Kingston, Dept 48B, and the results show clearly a number of features of which time correlation functions and pair distribution functions are numerical averages. These videos are available at IBM Kingston and are normally distributed free of charge.

## IV. RESULTS AND DISCUSSION

### A. Spherical top molecules

The spherical top symmetry is represented in this paper by sulfur hexafluoride (point group  $O_h$ ). Although noisy, the results of Fig. 2 indicate a cross correlation between linear center-of-mass velocity and rotational velocity in the laboratory frame of reference, and Fig. 3 the equivalent cross correlation between linear center-of-mass velocity and orientation. These results are consistent with the fact that the

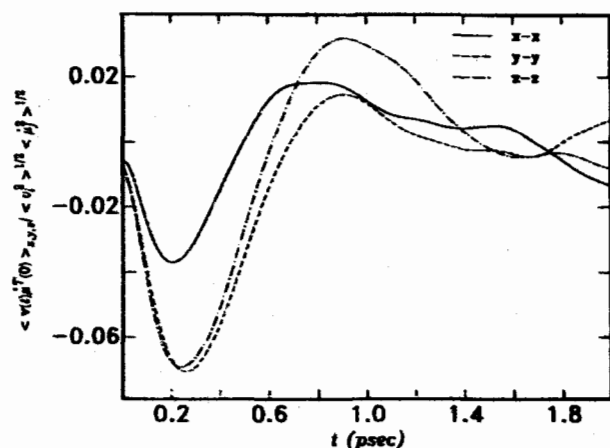


FIG. 2. Cross correlation between linear velocity and rotational velocity for liquid sulfur hexafluoride. Direction of  $\mu$  is defined along one of the principal axes.

response of orientation and rotational velocity to parity reversal and reflection operations in the laboratory frame are the same. The results can be understood in terms of the motion of an atom of the spherical top molecule whose laboratory frame coordinates are displaced from the center of mass. In the theory of rotational diffusion the translational motion of the center of mass itself is not accounted for explicitly, so that cross correlations such as that between the rotational velocity and the linear velocity are also left undescribed. The theory of the preceding section is an attempt to remedy the situation using simple Langevin equations.

Figures 4 to 7 illustrate some of the different types of behavior obtained from the analytical theory for the rotational velocity, orientation, and linear velocity acfs. It is seen that for a given friction coefficient, the behavior of the correlation functions becomes more oscillatory and the cross correlation function increases in amplitude for increasing  $V_0$ . The strength of the cross correlation in this theory is therefore directly dependent on the potential well depth  $V_0$ , which is in turn dependent on the intermolecular forces and torques. No attempt has been made in this work to force fit

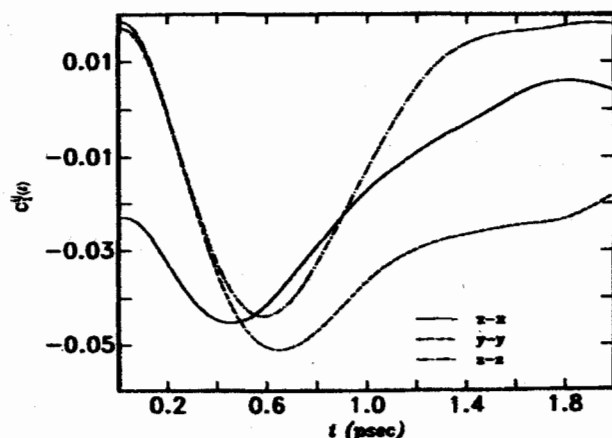


FIG. 3. As for Fig. 2, cross correlation between center-of-mass velocity and orientation.

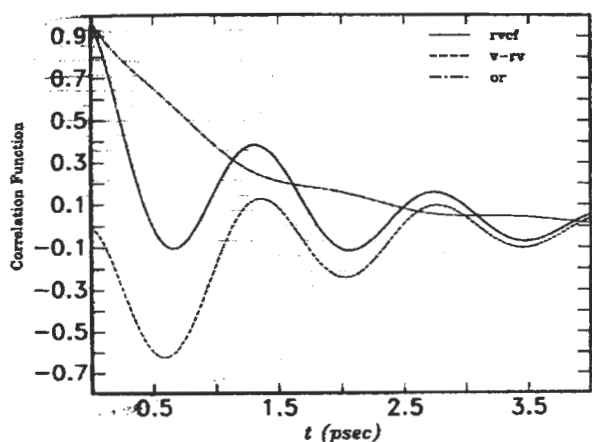


FIG. 4. Some theoretical results of rotational velocity acf (rvcf), velocity-rotational acf (v-rv), and orientational acf (or) obtained from Eqs. (3)–(6) with  $V_0 = 500$  and  $\beta = 10$ .

the theory and simulation, but the parameters of the theory provide an acceptable match to the results of the simulation for sulfur hexafluoride.

The time dependence of both the rotational velocity and the center-of-mass velocity autocorrelation functions from the theory is identical, because the friction coefficients operative in both the linked Langevin equations have been assumed to be the same. This means that agreement with the computer simulation is necessarily restricted. More generally, the time dependence of the theoretical acfs can be made independent by choosing different friction coefficients, but this leads to far greater mathematical complexity and to the introduction of another adjustable variable. However, the theory and simulation both point towards correlation between orientation and center-of-mass velocity, which ought to be directly observable in a video animation of the motion of the molecules of the sample. Observation of the video animation shows the effect of collisions in three dimensions in interrelating the two fundamental types of motion.

## B. Plate-like molecules

In this case the cross correlation in the laboratory frame of reference is weaker in amplitude than that for the spheri-

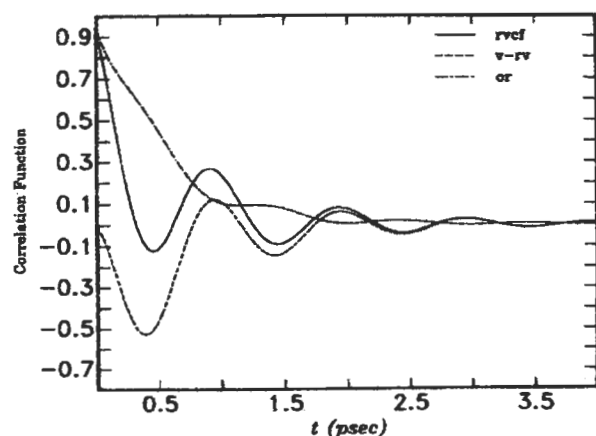


FIG. 5. As Fig. 4, but for  $V_0 = 1000$  and  $\beta = 20$ .

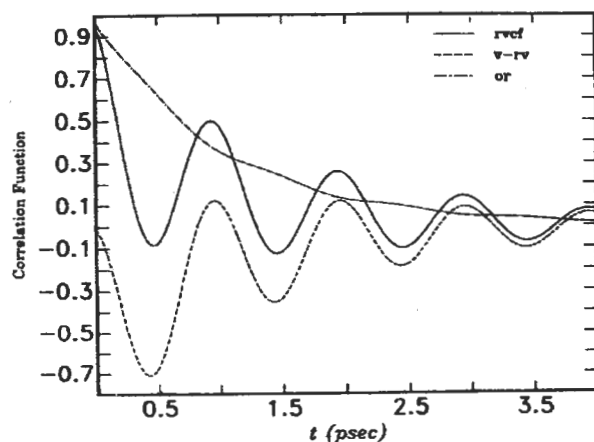


FIG. 6. As Fig. 4, but for  $V_0 = 1000$  and  $\beta = 10$ .

cal top, and the explanation for this is given clearly by the video animation. The latter reveals that the molecular motion in a liquid of plate-like molecules is much more cooperative in nature than that in a liquid made up of spherical tops. The end over end diffusion of a plate-like molecule in the animation is seen to be a much slower process than the itinerant (subpicosecond, far infrared) libration. The itinerant torsional oscillation is localized about an equilibrium point in the sample and diffusion of this point takes place much more slowly. For both hexafluorobenzene and benzene, the two molecules under consideration, the packing is seen clearly from the animation to be T-shaped, and not parallel. This confirms the indications of other simulations of liquid benzene, including a recent study by Anderson *et al.*<sup>31</sup> using a flexible *ab initio* pair potential. The C–C and H–H pair distribution functions (pdfs) from the two simulations are compared in Fig. 1. This shows that the flexible and rigid potentials produce very much the same results (as also found in simulations of liquid water using *ab initio* potentials<sup>32,33</sup>), a flattened pair distribution function caused by multiple site averaging in both cases. The equivalent pdfs for hexafluorobenzene from this work are similar. However, the animation shows much more clearly than the pdfs the nature of the packing in both hexafluorobenzene and benzene.

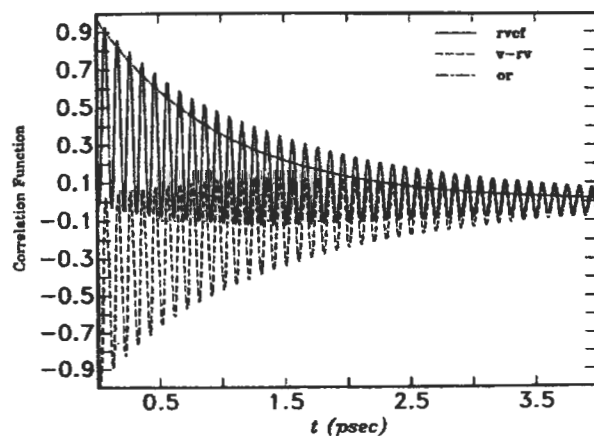


FIG. 7. As Fig. 4, but for  $V_0 = 100\,000$  and  $\beta = 10$ .

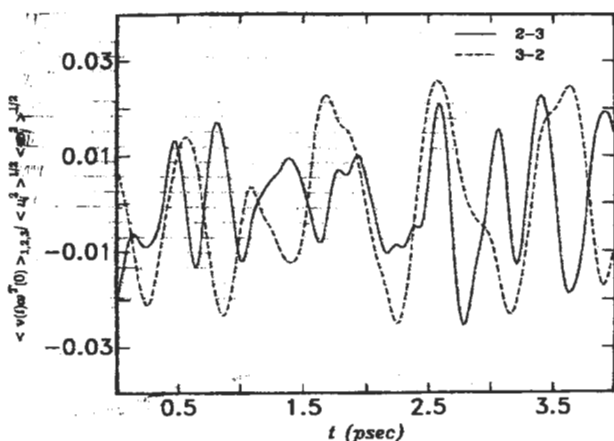


FIG. 8. (2,3) and (3,2) elements of the normalized moving frame cross correlation function between linear and angular velocity for liquid benzene. The coupling is weak and the elements are buried in statistical noise (in contrast with Fig. 10).

The nature of rotation/translation coupling in the plate-like molecules is distinctly different from that in the spherical top sulfur hexafluoride. The direct laboratory frame cross correlation between the rotational velocity, or orientation, and the linear center-of-mass velocity is much smaller than in the spherical top. Both types of ccf vanish in the background noise of the simulation. This is caused by the relative lack of translational and rotational freedoms in the plate-like molecules compared with the spherical tops. Thus we arrive at a conclusion which is directly opposite to the theory of rotational diffusion: direct laboratory frame cross correlation can actually be stronger in spherical tops than in plates, or as we shall see, rods. This runs directly contrary to the intuition behind the theory of rotational diffusion, and shows how unreliable this theory can be. This conclusion is further supported by the fact that in the moving frame (1,2,3) of the principal molecular moments of inertia there exists strong rotation-translation coupling in the plate-like molecules between the linear velocity and the angular velocity

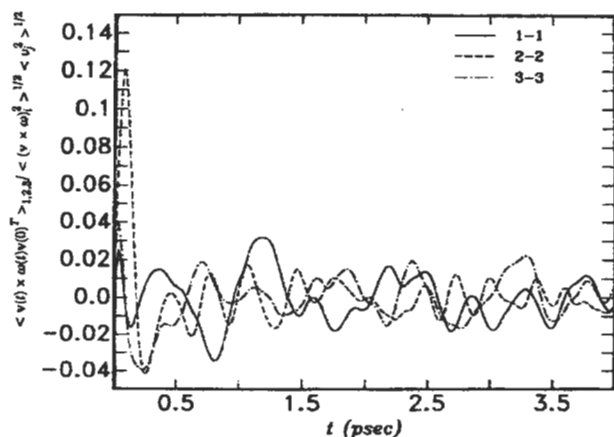


FIG. 9. Diagonal elements of the normalized moving frame cross correlation function between the molecular Coriolis acceleration and the same molecule's linear center-of-mass velocity for liquid benzene.

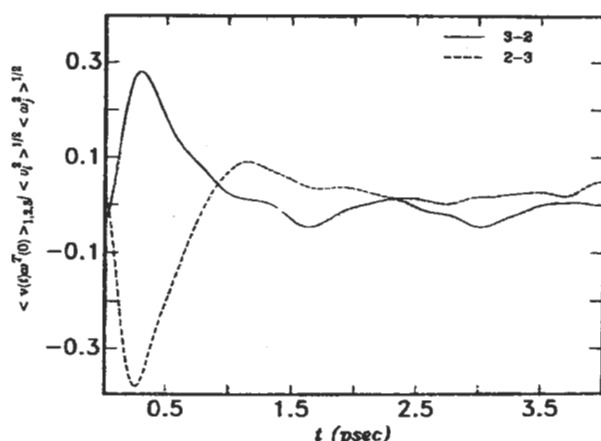


FIG. 10. As Fig. 8, but for liquid hexafluorobenzene. Note that the signal is more than ten times stronger than that for liquid benzene shown in Fig. 8.

ity and between such variables as the Coriolis acceleration and the linear velocity. These are illustrated for both benzene and hexafluorobenzene in Figs. 8 to 11.

### C. Rod-like molecule: Methyl hexatriyne

The dynamics of a rod-like molecule are of considerable interest in liquid crystals, and theories of rod-like diffusion are available in the literature.<sup>34,35</sup> Methyl hexa-tri-yne has three triple bonds and is a symmetric top with one moment of inertia very much smaller than the other two. In consequence, the diffusion as simulated and animated in this work is composed of rapid rotation about the symmetry axis and much slower end over end tumbling. The molecular geometry thus has a clear effect on the molecular diffusion, which consists of spinning and simultaneous tumbling interrupted by collisions which slow, completely stop, or reverse the direction of the rapid spin. This is very clear from the animation sequence prepared on video in this laboratory. The same animation shows as clearly that the molecules are not long enough to be ordered in parallel, the thermal motion is too strong and the intermolecular interactions too isotropic for the formation of a discernible director axis. Nevertheless, it

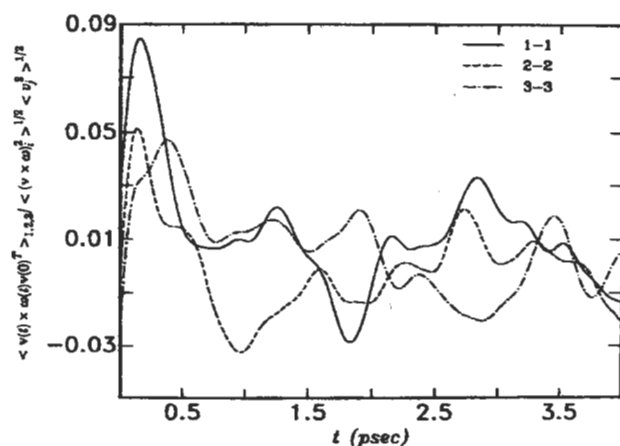


FIG. 11. As Fig. 9, but for liquid hexafluorobenzene.



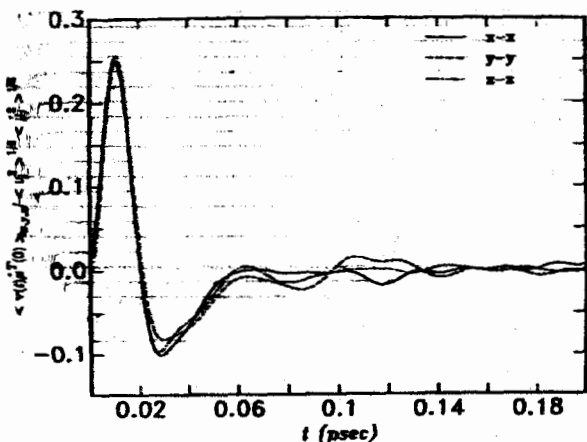


FIG. 12. Illustration of strong laboratory frame cross correlation between molecular center-of-mass velocity and rotational velocity in liquid water pressurized to 1043 K and 250 kbar by a shock wave. This strong cross correlation persists in liquid water at room temperature and pressure, but with a different time dependence.

is clear that the technique of animation can be used to display the onset of liquid crystal behavior given the right conditions and big enough samples.

Again in the laboratory frame the direct cross correlation between rotational velocity and velocity or between orientation and velocity is much weaker than that for the spherical top, but in the moving frame (1,2,3) of the three principal moments of inertia there is copious evidence for strong and very anisotropic cross correlation between such dynamical variables as center-of-mass velocity, angular velocity, and Coriolis acceleration (the acceleration that keeps a spinning top from falling over). The theories in the literature for rod-like diffusion, such as the Doi-Edwards<sup>31</sup> and Frenkel-Maguire<sup>34</sup> theories, are not yet in sufficient state of development to match these simulations and animations.

#### D. An example of very strong laboratory frame coupling

It happens that the direct coupling, with which the theory of this paper is concerned, between the rotational and linear molecular velocities, is weak in the plate-like and rod-like molecules simulated in this work. In order to show by simulation that this coupling can be very strong under the right conditions we reproduce an example in Fig. 12 for liquid water simulated<sup>36</sup> at 250 kbar and 1043 K. The coupling exemplified in Fig. 12 persists in liquid water to more usual conditions at room temperature and pressure, the various video animations made in this laboratory showing that the motion of the water molecules is considerably freer than those of the the plates, despite the hydrogen bonding. For liquid water there is strong cross correlation in both frames  $(x,y,z)$  and  $(1,2,3)$ . A simple theory such as that of this

paper succeeds in explaining the laboratory frame results self-consistently, but there is a need to extend the theory further, to envelope both laboratory frame and moving frame cross correlation in terms of the two parameters.

#### ACKNOWLEDGMENT

One of us (M. W. E.) acknowledges the financial support of IBM, Kingston.

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