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SYMMETRY PROPERTIES OF CROSS CORRELATION FUNCTIONS IN MOLECULAR LIQUIDS

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Abstract

The symmetry laws affecting the existence of laboratory frame cross correlation functions are discussed in terms of parity and time reversal.The cross correlation functions are obtained systematically by repeated differentiation in the laboratory and rotating frames of reference. In principle, these c.c.f.'s can all be used to analyse the nature of molecular dynamics in a computer simulation, and are illustrated in this paper in various molecular liquids.

Introduction

The recent introduction[1-7] of the rotating frame of reference has improved our understanding of molecular dynamics by increasing the number of cross correlation functions available for the characterisation of a molecular liquid.Several different types of cross correlation were discovered in the moving frame of reference defined by the principal molecular moments of inertia.However, none of the new cross correlation functions (c.c.f.'s) established by these means exist in the laboratory frame of reference, which is a handicap to their eventual measurement.In this paper systematic use is made of the rotating frame of reference to establish the rules by which the existence of laboratory frame c.c.f.'s may be determined analytically.The rotating frame is defined as in previous work as the frame (1, 2, 3)' which rotates with the angular velocity of the molecule with its origin fixed at that of the lab. frame (x, y, z).A translation to the molecular centre of mass produces the moving frame (1, 2, 3) which both rotates and translates with the molecule- the frame of the principal molecular moments of inertia.

This paper establishes a range of cross correlation functions in the laboratory frame by systematic differentiation with time of dynamical quantities in the frame (1, 2, 3)' and subsequent back transformation

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into (x, y, z).Sets of symmetry rules[8] are constructed to anticipate the existence of c.c.f.'s direct in frame (x, y, z).This shows that the rotation and translation of of a diffusing molecule are linked statistically by sets of cross correlation functions which can be described theoretically by a simple Langevin formalism[9] developed in this paper.The theory describes the c.c.f.'s obtained by computer simulation in terms of two simple parameters, a barrier height and friction coefficient.In this way experimental observations on autocorrelation functions (a.c.f.'s) in the frame (x, y, z) can be used to generate c.c.f.'s for comparison with the computer simulations.In this sense the numerous new c.c.f's shown to exist in this paper can be observed experimentally.[10-15]

The only previous report[16] of c.c.f.'s in frame (x, y, z) described the simple c.c.f. between molecular linear and angular velocity induced by an uniaxial electric field which made the liquid birefringent.The c.c.f.'s reported in this work exist in a field free isotropic molecular liquid for all molecular symmetries, including spherical tops.

Analytical Theory

If the frame (1, 2, 3)′ rotates at the origin of frame (x, y, z) with an angular velocity ω, the time time differential operator D_f in frame (x, y, z) is equivalent to the operator

$$(D_m + \omega \times)_{(1, 2, 3)'} \tag{1}$$

in frame (1, 2, 3)′ by a basic theorem of classical mechanics.(The following analysis has its full quantum mechanical and relativistic equivalent.)If the position of the molecular centre of mass is r then D_f operates on r in (x, y, z) to give the molecular velocity, v. A second operation gives the acceleration and so on as usual.In eqn (1) the operator D_f is implied to act in frame (1, 2, 3)′, the rotating frame, to produce the velocity and acceleration with respect to frame (1, 2, 3)′.With these definitions, we obtain the well known results

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

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

In these equations everything within the parentheses is equivalent on both sides, in the different frames of reference.In molecular diffusion, where rotation is always accompanied by simultaneous translation, terms such as the linear velocity ωxr are important, and cannot be neglected.This may seem elementary in the theory of dynamics, but the accepted approach to molecular diffusion, the theory of rotational diffusion, [17] leaves out of consideration the molecular linear velocity and position vector in frame (x, y, z).With the power of contemporary computer simulation this is no longer a necessary restriction.One way of removing it is to consider sets of c.c.f.'s obtained by repeated application of differential operators in frames (1, 2, 3)′ and (x, y, z).

The accelerations equivalent to the velocities in eqns (2) and (3) are generated by two differential operations

$$D_f(D_f r) = (D_m + \omega \times)((D_m + \omega \times)r) \tag{4}$$

$$D_m(D_m r) = (D_f - \omega \times)((D_f - \omega \times)r) \tag{5}$$

producing the results

$$(\tilde{v})_{x,y,z} = (\dot{v} + 2\omega \times v + \dot{\omega} \times r + \omega \times (\omega \times r))_{1,2,3}' \tag{6}$$

$$(\tilde{v})_{x,y,z} = (\dot{v} - 2\omega \times v - \dot{\omega} \times r + \omega \times (\omega \times r))_{x,y,z} \tag{7}$$

'Eqn (7) reveals the existence in frame (x, y, z) of four molecular linear accelerations, well known in the elementary theory of dynamics, but almost never considered in the theories of molecular diffusion. Two of these are known historically as the Coriolis and centripetal accelerations, and do not appear in the theory of molecular diffusion, due originally to Debye[17]. Apart from the Newtonian acceleration $\dot{v}$ these all involve simultaneously the molecular angular velocity, the linear velocity, and the centre of mass position vector.

Applying the differential operator n times produces

$$(v)^{(n+2)}_{(x,y,z)} = (D_m + \omega \times)_{(1)}(D_m + \omega)_{(2)}\text{......}(D_m + \omega \times)_n$$

$$\times (\dot{v} + 2\omega \times v + \dot{\omega} \times r + \omega \times (\omega \times r))_{(1,2,3)}' \tag{8}$$

$$(v)^{(n+2)}_{(1,2,3)} = (D_f - \omega \times)_{(1)}(D_f - \omega)_{(2)}\text{........}(D_f - \omega \times)_n$$

$$\times (\dot{v} - 2\omega \times v - \dot{\omega} \times r + \omega \times (\omega \times r))_{(x,y,z)} \tag{9}$$

so it becomes clear that the number of terms rapidly increases with the order of differentiation. The structure of eqns (8) and (9) can now be used to provide a set of symmetry rules with which to define the existence of sets of c.c.f.'s in frame (x, y, z), thus providing a far more detailed and complete description of molecular diffusion than allowed for in the traditional approach.

Non Vanishing C.c.f.'s in Frame (x, y, z)

Type (1)

On elementary grounds the c.c.f. between a vector A and its time derivative $\dot{A}$ exists for t > 0 :

$$< A(t)\dot{A}^T(0) > \tag{10}$$

By combining eqns (9) and (11) the following patterns of non vanishing c.c.f.'s emerge in the lab. frame (x, y, z), almost none of whose members can be described analytically in the theory of rotational diffusion.

The D Pattern

This is simply

$$< D_f B(t) B^T(0) >$$ (11)

where in general the vector quantity B is a linear dynamical variable such as velocity or acceleration.For example, one of the simplest applications of eqn (12) is :

$$< D_f(v(t) - \omega(t) \times r(t))(v(0) - \omega(0) \times r(0))^T >$$ (12)

which can be expanded to produce a total of six c.c.f.'s, all involving the molecule's rotational and translational motion simultaneously.

It is easy to see that repeated application of the differential operators will produce a theoretically infinite number of c.c.f.'s which must be described analytically self consistently with observable a.c.f.'s.Direct observation of the time dependence of such c.c.f.'s can be accomplished, as in this paper, by computer simulation.The same simulation trajectories can be used to match the experimental data from many available sources.The D_f pattern can be extended to cross terms from eqn (9) provided that the general symmetry remains that of eq (12).These terms can be obtained easily by inspection.

Type (2)

By borrowing a well known result in the theory of molecular spectroscopy[18] it follows in the theory of molecular diffusion that the velocity of an atom in a simultaneously rotating and translating molecule is

$$v_a = v + 1/2 \omega \times \mu$$ (13)

where μ is an axis vector through the atom and molecular centre of mass, for example the molecular dipole moment.A simple expansion of the lab frame a.c.f. of the atom's velocity leads to the conclusion that the cross correlation function

$$C_1(t) = < v(t) \dot{\mu}^T(0) >$$ (14)

may exist in the laboratory frame.Recent computer simulations [19-21] have confirmed this result, which, again, is not allowed for in the accepted theory of molecular diffusion.Integrating eqn (14) with respect to time proves the existence of the c.c.f.

$$C_2(t) = < v(t) \mu^T(0) >$$ (15)

By applying the operator theorem (9) to the vector $\dot{\mu}$ we obtain the result

$$(\ddot{\mu})_{(1,2,3)} = (\ddot{\mu} - 2\omega \times \dot{\mu} - \dot{\omega} \times \mu + \omega \times (\omega \times \mu)))_{(x,y,z)}$$ (16)

Constructing the c.c.f. between the four right hand terms of eqn (16) and the equivalent for linear acceleration, eqn (7), :

$$C_3(t) = < \dot{v}(t) \ddot{\mu}^T(0) >_{(1,2,3)} >$$ (17)

we obtain the possible existence in the lab. frame of reference of sixteen further terms with which to characterise molecular dynamics with computer simulation.These terms are also obtainable analytically with the diffusion theory developed later in this paper.Continuing this process also leads to the existence of an infinite number of possible cross correlation functions in the lab. frame of reference. This number is restricted, however, by symmetry rules, two of which are time reversal and parity reversal.

Time Reversal Symmetry

The symmetry arguments of time reversal apply to cross correlation functions in the lab. frame which are themselves symmetric to time reversal, i.e. are even functions of time.Thus time reversal symmetry does not apply at all to c.c.f's such as (10) which are odd functions of time.

Given this restriction the operation of time reversal in the lab. frame is

$$(p, q) \to (q, -p) \tag{18}$$

where q and p are molecular centre of mass position and momentum respectively.

Assuming that the c.c.f.

$$< A(t)B^T(0) >$$

is an even function of time a necessary but not sufficient condition for its existence for t > 0 is that A and B have the same time reversal symmetry in the lab frame (x, y, z).This restriction applies only in isotropic media in which the hamiltonian is invariant to time reversal.Externally applied fields of force may make the hamiltonian negative to time reversal.In this case extra c.c.f's may appear in the lab. frame. In an isotropic medium the symmetries of the fundamental vectors of molecular dynamics are as follows.A plus sign means that the vector is invariant to time reversal. 1) The position vector r is positive to time reversal. 2) The centre of mass linear velocity is negative. 3) The molecular angular velocity is negative. 4) The linear acceleration ω is positive. 5) The angular acceleration is positive. 6) The dipole vector μ is negative. 7) The rotational velocity is positive. 8) The derivative of the rotational velocity is negative.

These rules preclude the existence of any c.c.f. wherein the product of time reversal symmetries is negative, provided that the c.c.f. is not of the type (10) or is not otherwise an odd function of time.Time reversal symmetry thus allows the existence of c.c.f.'s such as

$$< \omega(t) \times \dot{\mu}(t)\dot{v}^T(0) >$$

$$< \dot{\omega}(t) \times \mu(t)\dot{v}^T(0) >$$

which may also be obtained analytically with a theory of linked Langevin equations to be developed in this paper.The overall symmetry therefore guides the theory of molecular diffusion, i.e. it is pointless to construct a theory of lab. frame c.c.f.'s which are forbidden by time reversal symmetry.The results of molecular dynamics computer simulation should also be fully consistent with symmetry, i.e. any c.c.f. forbidden by time reversal or parity reversal in frame (x, y, z) must vanish for all t in the simulation.Symmetry is a necessary but not sufficient condition for the existence of a c.c.f. in frame (x, y, z), i.e. computer simulation may come up with a null result even when the c.c.f. is symmetry allowed.

Parity Reversal Symmetry

The operation of parity reversal in the lab. frame is defined by,

$$(q, p) \rightarrow (-q, -p)$$

and the c.c.f.

$$< A(t)\overset{T}{B}(0) >$$

may exist if the vectors A and B have the same parity reversal symmetry.Otherwise it vanishes in frame (x, y, z) for all t.The parity reversal symmetry of some fundamental vectors is as follows. 1) The position vector is negative. 2) The centre of mass velocity is negative. 3) The molecular angular velocity is positive. 4) The acceleration is negative. 5) The angular acceleration is positive. 6) The dipole vector is negative. 7) The rotational velocity is negative. 8) The derivative of the rotational velocity is negative.

For any c.c.f. to exist in frame (x, y, z) it must pass the tests of parity and time reversal symmetry simultaneously, and its existence must then be confirmed by computer simulation.Only then is it reasonable to construct an analytical theory for its lab. frame time dependence, a theory that should generate self consistently experimentally observable a.c.f.s.The data from observation (e.g. spectroscopy) and computer simulation should then be interpreted in terms both of a.c.f.'s and c.c.f's.This achieves a much more complete and detailed understanding of the molecular liquid state.

Linked Langevin Equations

It has been shown already that on elementary grounds the c.c.f's $C_1(t)$ and $C_2(t)$ exist in frame (x, y, z).Thus equations of motion involving these vectors may be written in this frame and solved for auto and cross correlation functions with the methods developed recently by Coffey et al.[19-25].It is reasonable to write the equations of motion as the linked Langevin equations of itinerant oscillator theory, i.e. :

$$\ddot{r} + \beta\dot{r} + V'(r - \mu) = \lambda_1(t) \tag{19}$$

$$\ddot{\mu} + \beta\dot{\mu} - V'(r - \mu) = \lambda_2(t) \tag{20}$$

Here β is the Langevin friction coefficient, more generally a memory function.[26] This has been assumed to be the same for the two equations, in general the friction coefficients are different in magnitude, but this leads to mathematical complexity.[23, 24]The potential term V is generated by assuming that the rotational velocity and linear velocity are not statistically independent in frame (x, y, z), a result arrived at by the application of time reversal and parity reversal, together with numerical data from computer simulation. In contrast the parity reversal symmetries of the angular velocity and linear centre of mass velocity are opposite, implying that there is no statistical correlation between these variables.This means that it is basically incorrect to write linked Langevin equations of type (19) and (20) for the angular and linear velocity.In general the dependence of V on its argument is unknown, being the outcome of intermolecular and intramolecular potential energy terms.It is assumed that it can be expanded in a Taylor series.The potential energy will in general have minima and maxima (potential wells and barrier heights) and it is reasonable to approximate these with an even powered Taylor series in the energy, such as a cosine function.In the first approximation only the energy

term in the argument squared is retained.Differentiating this gives

$$V'(\mathbf{r} - \boldsymbol{\mu}) = -2V_0(\mathbf{r} - \boldsymbol{\mu}) \tag{21}$$

The terms on the r.h.s.'s of eqns (19) and (20) are Wiener processes, stochastic accelerations.Dimensionless units are used everywhere to simplify the analytical results.

In the first approximation eqns (19) and (20) have analytical solutions, arrived at with the methods of Coffey et al.[19-25]The results are given in terms of the friction coefficient and the parameter

$$\omega_1 = (4V_0 - \beta^2/4)^{1/2} \tag{22}$$

for a number of a.c.f's, observable experimentally, and c.c.f.'s.

Linear Centre of Mass Velocity A.c.f.

$$< v(t).v(0) > = kT/2(e^{-\beta t} + e^{-1/2\beta t}(\cos(\omega_1 t) - \frac{\beta}{2\omega_1} \sin(\omega_1 t)) \tag{23}$$

Rotational Velocity A.c.f

This is essentially the Fourier transform of the far infra red Poley absorption[18] and is therefore observable by interferometry.It is given analytically by

$$< \dot{\mu}(t).\dot{\mu}(0) > = < v(t).v(0) > \tag{24}$$

Cross Correlation Functions

$$< v(t).\dot{\mu}(0) > = kT/2(e^{-\beta t} - e^{-1/2\beta t}(\cos(\omega_1 t) - \frac{\beta}{2\omega_1} \sin(\omega_1 t))) \tag{25}$$

Other c.f's of interest in the lab. frame can be obtained by differentiation from eqn (25), e.g.

$$< \dot{v}(t).\ddot{\mu}(0) > \tag{26}$$

Angular Velocity A.c.f.

Using the kinematic relation

$$\dot{\mu}(t) = \omega(t) \times \mu(t) \tag{27}$$

and the vector identity

$$(A \times B).(C \times D) = (A.C)(B.D) - (A.D)(B.C) \tag{28}$$

it follows that

$$< \omega(t).\omega(0) > = - < \dot{\mu}(t).\dot{\mu}(0) > / < \mu(t).\mu(0) >$$ (29)

in the lab. frame of reference. The angular velocity a.c.f. is observable experimentally from N.M.R. spin rotation relaxation.

Orientational A.c.f.

This is observable with a number of experiments, including dielectric relaxation, and is obtained analytically by double integration to give

$$< \mu(t).\mu(0) > = \frac{kT}{2}(\frac{e^{-\beta t}}{\beta^2} + \frac{e^{-1/2\beta t}(\frac{\beta}{2}\sin(\omega_1 t) - \omega_1 \cos(\omega_1 t))}{\omega_1(\omega_1^2 + \beta^2/4)})$$ (30)

A.c.f.'s of the Coriolis and Centripetal Accelerations

No experiment has yet been devised to measure these directly, but their time dependence is known by several recent computer simulations. We have the simple analytical results

$$< \omega(t) \times v(t).\omega(0) \times v(0) > = < \omega(t).\omega(0) > < v(t).v(0) >$$ (31)

and

$$< \omega(t) \times (\omega(t) \times r(t)).\omega(0) \times (\omega(0) \times r(0)) > = (< \omega(t).\omega(0) >)^2 < r(t).r(0) >$$ (32)

in terms of the two model parameters. Continuing the analytical process gives higher order c.c.f.'s of the type (10), e.g.

$$\frac{d}{dt}(< \omega(t).\omega(0) > < v(t).v(0) >) = < \dot{\omega}(t) \times v(t).\omega(0) \times v(0) > + < \omega(t) \times \dot{v}(t).\omega(0) \times v(0) >$$ (33)

Computer Simulation Methods

Examples of some of the laboratory frame c.c.f.'s established already in this paper by symmetry and analysis have been obtained by constant volume computer simulation. The equations of motion for 108 molecules were integrated with the algorithm TETRA details of which are given elsewhere in the literature.[1-7] Examples of the lab frame c.c.f. between the molecular dipole moment and the molecular linear centre of mass velocity were obtained for water[27], over a broad range of conditions, and for spherical, [28] rod-like[29] and plate-like[30] molecules in the liquid state at room temperature. The c.c.f.'s were computed with running time averages with up to 6000 time steps. Details of the inter molecular pair potentials are as follows.

Water

This is a five by five site site potential made up of Lennard Jones and partial charge terms as follows

$\epsilon/k(H) = 13.4K; \sigma(H) = 2.75A$

$\epsilon/k(O) = 21.1K; \sigma(O) = 2.40A$

$q_H = 0.23|e|; q_e = -0.23|e|$

and has been successfully tested in the literature against thermodynamic and spectral data for liquid water up to 250 kbar and 1043 K. It is based on a modified ST2 potential with added Lennard Jones terms.

Spherical Molecules, Liquid Phosphorus

Liquid phosphorus is composed of spherical top molecules with P atoms arranged tetrahedrally in each molecule. The potential was a four b four site site type made up of the Lennard Jones terms

$\epsilon/k(P) = 119.8K; \sigma(P) = 3.41A$

Rod Like Molecules

The power of the IBM ICAP1 supercomputer at Kingston was used to integrate the equations of motion for 108 rod like methyl hexa-tri-yne molecules with an eleven by eleven site site potential made up of the Lennard Jones terms

$\epsilon/k(C) = 51.0K; \sigma(C) = 3.2A$

The molecule is a highly elongated symmetric top which spins rapidly about the C_{3v} axis and tumbles more slowly about the other two mutually perpendicular axes of the principal molecular moment of inertia frame.

Plate Like Molecule - Benzene

The molecular dynamics of liquid benzene were simulated with a twelve by twelve Lennard Jones atom atom potential with carbon and hydrogen terms as defined already with 108 molecules and 6000 time steps on the ICAP1 supercomputer. A typical run lasted about 36 hours of CPU time.

PLate Like Molecule - Iodobenzene.

Liquid iodobenzene was simulated with 108 molecules over 6000 steps with a 144 term site site potential for pair interactions made up of Lennard Jones parameters as already defined with the additional iodine parameters

$\epsilon/k(I - I) = 350K; \sigma(I - I) = 4.0A$
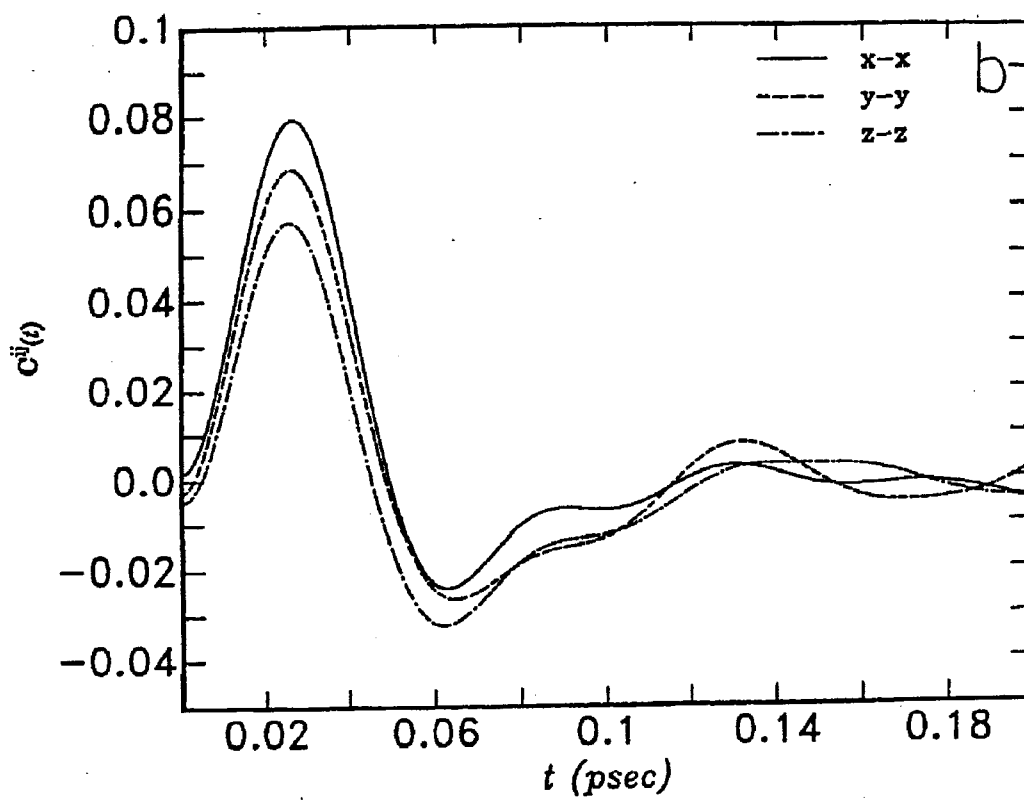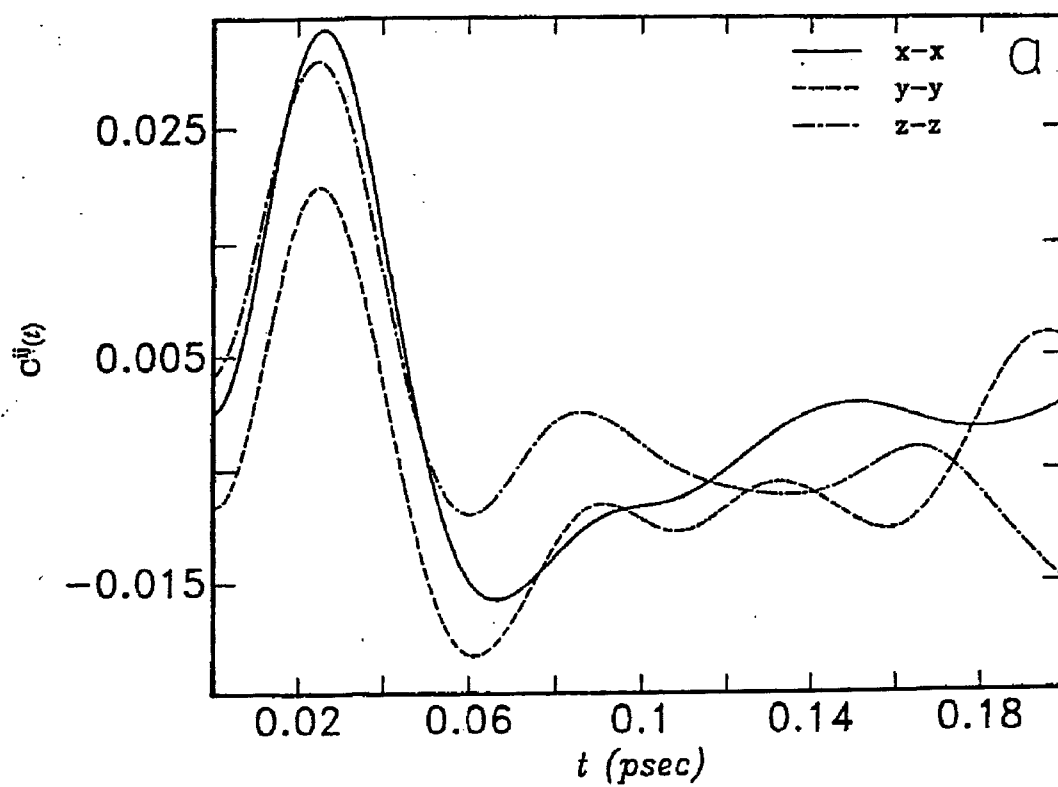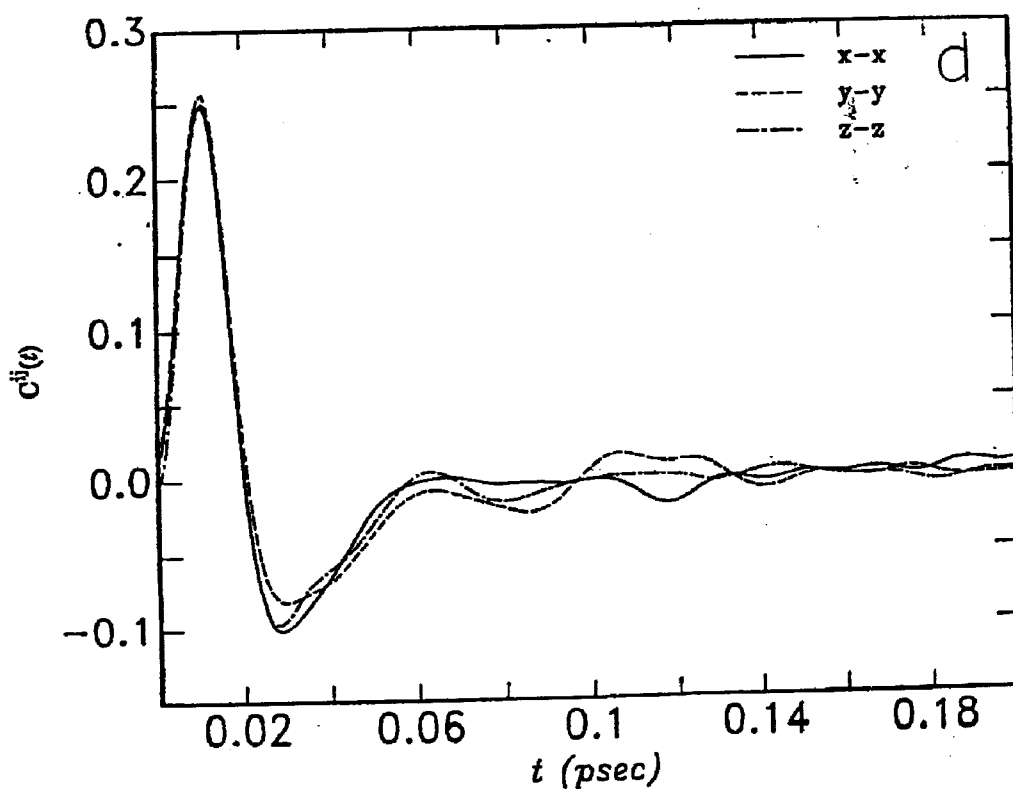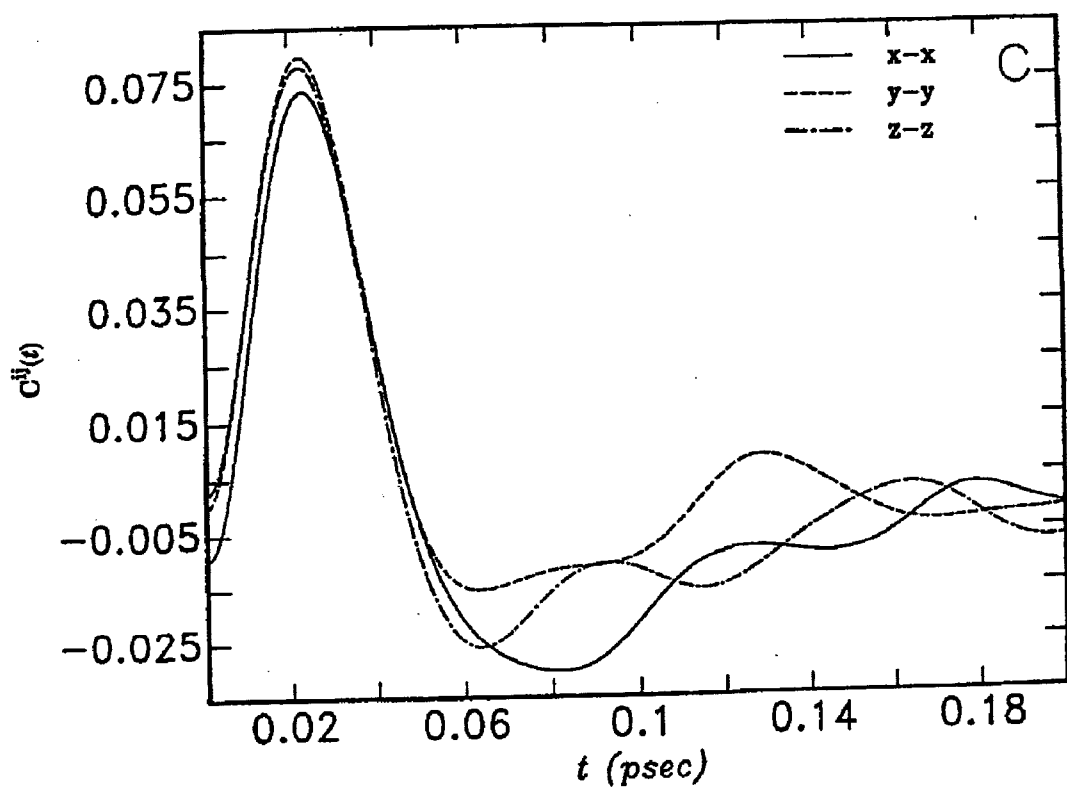
1. Figure (1)

    Elements of the function $C_i(t)$ for steam and liquid water. (a) Steam at 20.0 bar, 293 K. (b) Liquid water at 1.0 bar, 293 K. (c) Liquid water at 15.0 kbar, 1273 K. (d) Liquid water at 250.0 kbar, 1043 K.

Results and Discussion

The lab. frame c.c.f. between the rotational velocity and the molecular centre of mass linear velocity varies greatly in magnitude with the conditions under which it is observed and for different types of molecular liquid.This is illustrated in fig (1) for liquid water from 293 K , 1 bar to 250 kbar, 1043 K through the critical point.The normalised amplitude of the c.c.f. is greatest at 250 kbar, but the c.c.f. is persistent throughout the whole range of existence of liquid water.The same is true for other lab. frame c.c.f.'s such as the one between the molecular dipole moment and the linear centre of mass velocity, and for the various derivative c.c.f.'s described in the analytical section.The theory of rotational diffusion cannot be used to explain this set of results, but a comparison between the theory of this paper and the simulation is given later.

For liquid phosphorus the c.c.f. $C_1(t)$ is smaller in amplitude (Fig. (2)) than that for liquid water, but nevertheless exists directly in the lab frame for the spherical top, a direct contradiction of the accepted theory of rotational diffusion.This is a good illustration of how the technique of computer simulation leads to a more profound analytical appreciation of liquid state molecular dynamics.
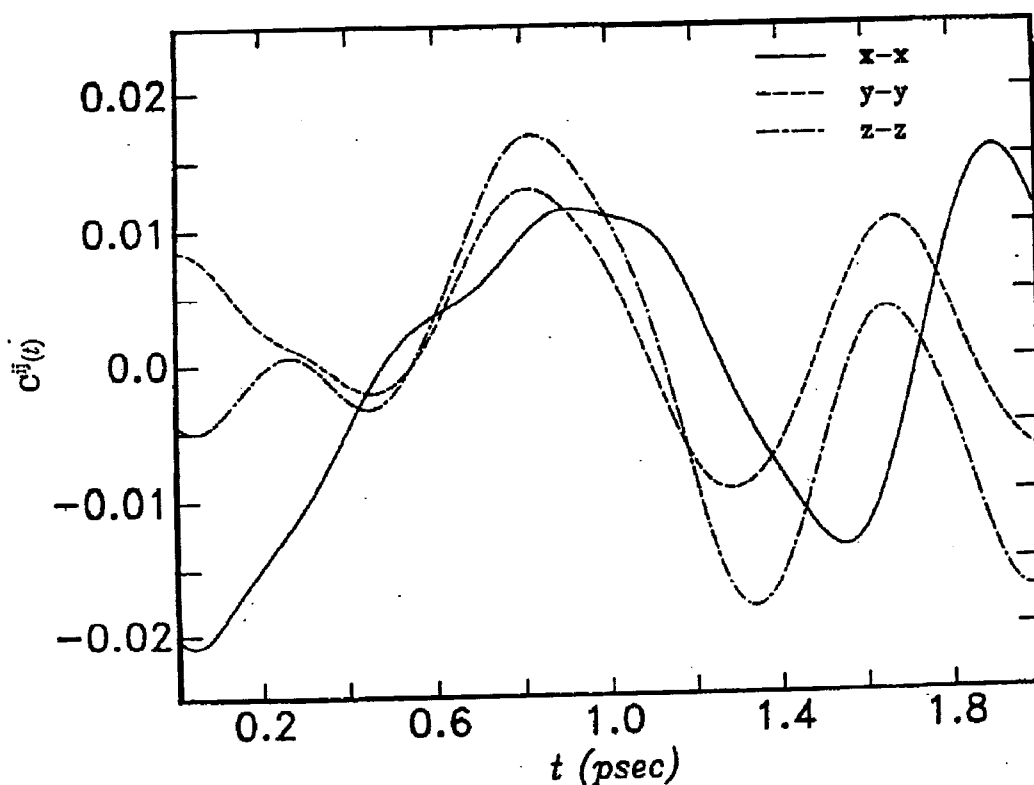

Figure (2)
As for Fig. (1), liquid phosphorus at 1.0 bar, 293 K.

Methyl Hexa Tri yne.

Although rotation / translation coupling in the moving frame of reference is strong in this case, the direct c.c.f. vanishes almost completely. In contrast, other c.c.f.'s such as those defined on the right hand side of eqn (33) exist for this rod like molecule direct in the lab. frame.This is perhaps counter intuitive, but irrefutable evidence for the limited applicability of the traditional theory of rotational diffusion.

Liquid Benzene

Animations of the molecular dynamics of liquid benzene, carried out on video in this laboratory, show very clearly that the motion of the plate like benzene molecules is cooperative.The torsional and linear oscillation of one molecule is correlated to those of its first and second shell of neighbours.However, this does not imply a strong correlation between the centre of mass velocity and molecular rotational velocity, which again vanishes for liquid benzene.As for the rod-like molecules the result is counter intuitive but uequivocal.Again various other types of cross correlation exist for the plate-like molecule, recorded elsewhere in the literature.

Liquid Iodobenzene

For liquid iodobenzene the c.c.f. between the linear and rotational velocity in the lab. frame is one of the strongest observed to date, (Fig. (3)).This leads to the conclusion that the c.c.f. is generated by the details of molecular symmetry.In a molecule such as benzene,with inversion symmetry in the lab. frame,the rotational velocity about the centre of mass is not correlated statistically to the centre of mass linear velocity.In an offset rotor such as iodobenzene,the centre of mass is close to the massive iodine atom on the dipole axis and the rotational velocity of this axis inevitably generates translation in the lab. frame of the centre of mass itself.This results in strong statistical cross correlation in the lab. frame. The consequencies of this cross correlation are seen clearly in animations of the molecular dynamics of liquid iodobenzene made in this laboratory,and available on video.

Theorem

The general conclusion from this series of simulations/animations is that the rotational velocity of a diffusing molecule is statistically correlated to its own centre of mass linear velocity in the lab. frame when that molecule's center of mass is far removed on average from the centre of the volume of rotation.

Thus, in iodobenzene, the approximate centre of rotation coincides on average with the centre of the molecule, inside the benzene ring and far removed on average from the centre of mass.The molecule is therefore an offset rotor,with centre of mass translation strongly dependent on rotation.In liquid water, the centre of mass, in analogous fashion, is near the relatively massive oxygen atom.In a
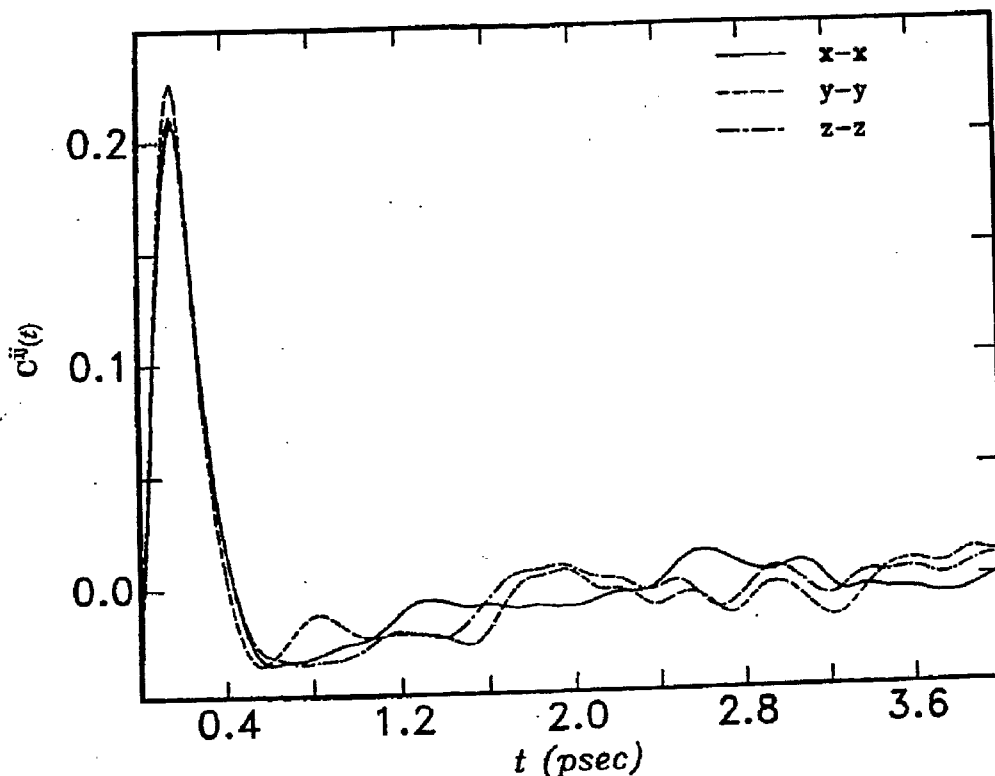
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Figure (3)
As for Fig. (1), liquid iodobenzene at 1.0 bar, 293 K.

diffusing benzene molecule, in contrast, the centre of mass and centre of volume of rotation coincide on average, because the mass distribution in the molecule is exactly symmetric.In the diffusing methyl hexa tri yne molecule the mass distribution is almost exactly symmetric (rod like) the rsidual asymmetry being due to the three very light hydrogen atoms of the methyl group.In consequence the c.c.f. between the rotational velocity of the dipole axis and the molecular centre of mass linear velocity vanishes in the statistical uncertainty of the computer simulation segment of 6000 time steps.

In other words, if the molecular mass distribution about the molecular centre of mass and in the dipole axis is exactly symmetric the c.c.f. will vanish for all t. This is the case in benzene because on any axis drawn throgh the centre of mass and two carbon atoms in the plane of the molecule the distance of the carbon (and hydrogen) atoms from the centre of mass is the same on either side.This is not true in liquid tetrahedral phosphorus, so that there is a small residual c.c.f. observable in Fig (2).

These findings invalidate the theory of "rotational" diffusion.

Comparison of Theory and Computer Simulation

The overall behaviour of the system of eqns (19) and (20) is similar to that of c.f.'s from computer simulation. A comparison is given in Fig.(4).For a given value of the friction coefficient the rotational velocity and velocity a.c.f.'s become more oscillatory with increasing V, and the c.c.f. between the rotational and linear velocities becomes stronger and more oscillatory.The barrier height
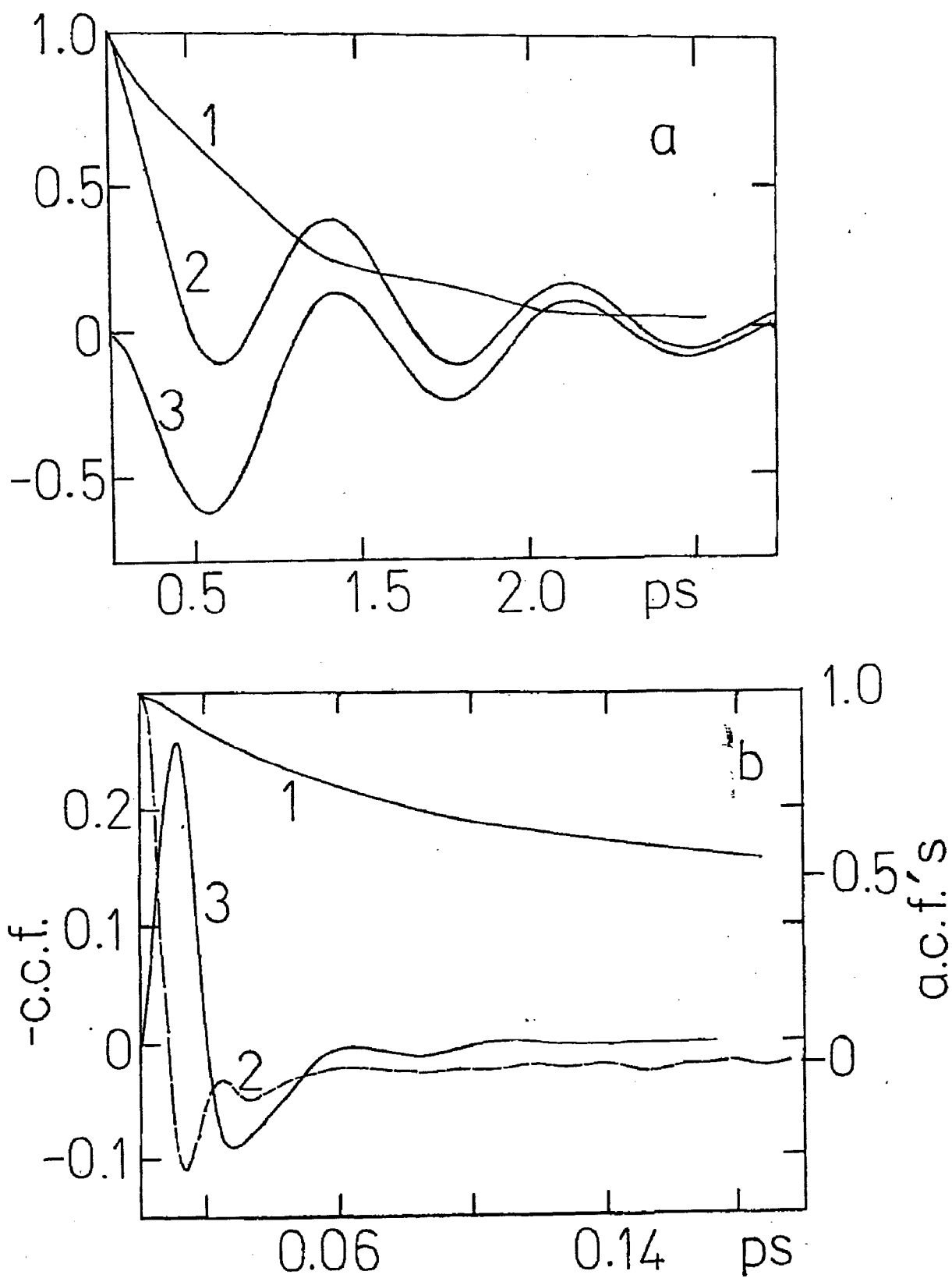
Figure (4) (a) Comparison of theoretical correlation functions with computer simulated equivalents for liquid water. (1) Orientational a.c.f. for $\beta = 10$, $V_0 = 1000$. (2) Rotational velocity a.c.f. (3) The cross correlation function $C_l(t)$. (b) As for (a) from the simulation of Fig. (1d).

V is therefore directly responsible in this theory for the strength of the lab. frame cross correlation.It follows therefore that V is dependent on intermolecular forces and torques as well as the molecular point group symmetry.The harmonic approximation used in eqns (19) and (20) is a first approximation to potential energy responsible for the statistical correlation between rotational and linear velocity. There are mathematical and physical limitations on the theory as follows 1) The friction coefficient is assumed to be the same in both eqns. (19) and (20).More generally, but also more intractably, different friction coefficients can be generated by linear and rotational velocity.2) The non linearities of the Euler equations are assumed to be operative through V and do not appear explicitly in the linked Langevin equations.The assumptions underlying this statement can be seen more clearly by adding eqns (19) and (20) giving

$$\frac{d^2}{dt^2}(\mathbf{r} + \mu) + \beta\frac{d}{dt}(\mathbf{r} + \mu) = \lambda_1(t) + \lambda_2(t)$$

which is a simple Langevin equation in the linear velocity of a point in the molecule at one end of the axis.The rotational motion of the molecule affects this linear velocity through the potential V and there are no explicit Euler terms, although these are of course implicit in the motion.

Given these limitations, the system (19) and (20) appears to be a new fundamental approach to molecular dynamics, subject to the general limitations on all Langevin equations now known in detail. Given these limitations this approach appears to have the advantage of being analytically tractable, providing a wide range of correlation functions in terms of two parameters.

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