A self-consistent theory of laboratory frame cross correlation functions

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A theory is developed for laboratory frame cross correlation functions detected recently by computer simulation. It is based on the concept of itinerant oscillation as developed by Coffey *et al.*, and for the first time provides a self-consistent analytical description of numerically observed laboratory frame time cross correlation functions in molecular matter.

INTRODUCTION

A number of recent computer simulations[1–5] has revealed the existence and time dependence of cross correlation functions (ccfs) in the laboratory (x,y,z) and moving (1,2,3) frames of reference. These are fundamental to the understanding of classical molecular dynamics.

The first attempt to develop a theory for fundamental laboratory frame ccfs was made by Condiff and Dahler[6] using linked Langevin equations involving the molecular center-of-mass linear velocity and molecular angular velocity in the laboratory frame for statistical cross correlation. This leads, however, to the incorrect result

$$\langle \omega(t)\mathbf{v}(0)^T\rangle > 0.$$

There has been considerable interest, subsequently, in developing the theory of molecular diffusion for the description of ccfs between fundamental dynamical variables.[7–12] Computer simulation has been of key importance in pinpointing the ccfs that are symmetry allowed in the laboratory and moving frame of reference defined by the three principal molecular moments of inertia, and has revealed the shortcomings in the theory of molecular diffusion when this is extended to involve more than one fundamental degree of freedom, i.e., to involve rotation superimposed upon translation. Furthermore, the computer simulation results have in turn promoted further theoretical investigation of the many new types of ccf that have recently come to light in molecular liquids from spherical top to chiral symmetry. During the course of these investigations, several new experimental methods have been devised to measure the effect of statistical cross correlation,[13–15] including a method based on the comparison of far infrared spectra of an enantiomer and its racemic mixture, and another based on the application of an uniaxial electric field. This is especially straightforward in liquid crystal media such as nematogens, where a weak electric or magnetic field easily induces birefringence at room temperature. In field-on equilibrium in these media, the numerous cross correlation functions now known to exist a field-off equilibrium are supplemented by further direct cross correlation[14] in the laboratory frame which vanishes when the aligning external field is removed. In liquid crystals, therefore, the appearance of new cross correlation functions is a fundamental consequence of the aligning effect. The latter cannot be described theoretically without the use of ccfs. Further support for the fundamentally important nature of dynamical ccfs in molecular liquid mixtures has been obtained recently in a computer simulation of water/carbon tetrachloride microemulsions, where the moving frame ccf between molecular linear center-of-mass velocity and angular velocity exists strongly in pure liquid water but vanishes in the microemulsion, thus revealing the link between dynamical ccfs and H bonding. The dynamics of H bonding can be described in terms of the time dependence of statistical cross correlation functions.[4]

The moving frame (1,2,3) is that of the principal molecular moments of inertia, and a vector quantity A defined in the frame (x,y,z) is rotated or projected into (1,2,3) for each molecule of the ensemble. The group theory of cross correlation functions in frame (1,2,3) has recently been developed extensively by Whiffen[16] and provides a method of determining which ccfs exist in frame (1,2,3). The role of parity, time reversal, and reflection symmetry in frame (x,y,z) has been defined by the present author. In neither frame, however, do the symmetry rules define the time dependence of the ccfs explicitly, and in this letter therefore a theory is developed for this purpose. For the first time it provides a simple self-consistent analysis of the time dependence of several auto and cross cfs in terms of two parameters of the itinerant oscillator equations of Coffey *et al.*[17–22]

THEORY

On elementary grounds the ccfs

$$\langle \mathbf{v}(t)\boldsymbol{\mu}^T(0)\rangle$$

and

$$\langle \mathbf{v}(t)\dot{\boldsymbol{\mu}}^T(0)\rangle$$

exist in the laboratory frame of reference. Here $\boldsymbol{\mu}$ is a molecular axis unit vector such as that of the net dipole moment, and v is the molecular center-of-mass linear velocity. This implies that parity, time reversal, and reflection symmetries of the vectors $\mathbf{v}, \boldsymbol{\mu}$, and $\dot{\boldsymbol{\mu}}$ are identical 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 by Coffey *et al.*[18–22] It is resonable to write the equations of motion as the linked Langevin equations of the type used in purely rotational itinerant librator theory[18–21]:

$$\ddot{\mathbf{r}} + \beta\dot{\mathbf{r}} + V'(\mathbf{r}-\boldsymbol{\mu}) = \boldsymbol{\lambda}_1(t)\,, \tag{1}$$

$$\ddot{\boldsymbol{\mu}} + \beta\dot{\boldsymbol{\mu}} - V'(\mathbf{r}-\boldsymbol{\mu}) = \boldsymbol{\lambda}_2(t)\,. \tag{2}$$

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Here $\mathbf{r}$ is a unit vector in the axis joining the origin of frame (x,y,z) to the center of mass of a diffusing molecule in this frame. Thus, $\mathbf{r}$ is the unit vector of the molecular center of mass linear velocity. In Eqs. (1) and (2), β a Langevin friction coefficient which is assumed equal for the simultaneous rotational velocity and linear velocity of the diffusing molecule. In this limit[20,21] the equations of the two friction itinerant oscillator are soluble analytically. The use of an equal friction model implies that the rotational velocity acf and the linear center-of-mass velocity acf must have the same time dependence when both are normalized to one at the origin. This limits the applicability of the model to molecular diffusion processes in the medium to high friction limit. The present model is not applicable in the free rotation limit because in that case the acf of the center-of-mass linear velocity would be a constant and that of the rotational velocity a hypergeometric Kummer function. The use of a two friction io model with different frictions would produce different time dependencies for the two acf's but at the expense of considerable analytical complexity as fully described in Refs. 20 and 21. For the sake of simplicity the equal friction model is used in this paper. The potential term is generated by assuming that the two types of motion are not statistically independent in frame (x,y,z), i.e., by assuming that the ccf between the rotational and linear molecular velocities exists in frame (x,y,z). In general, the dependence of V on its argument $(\mathbf{r}-\boldsymbol{\mu})$ is intricately nonlinear and is unknown analytically. However, it can be assumed that V can be expanded in a Taylor series in the argument. If it is assumed further that the term V originates from time differentiation of a potential energy generated by the simultaneous rotation and translation of the diffusing molecule, then it follows that the potential energy will be a function of the intermolecular forces and torques, and will have maxima and minima depending on atomic coordinates relative to the molecular center-of-mass. It is reasonable to approximate these potential wells with an even powered Taylor expansion such as a cosine, or in the first approximation by Hooke's law, the harmonic approximation:

$$V'(\mathbf{r}-\boldsymbol{\mu}) = -2V_0(\mathbf{r}-\boldsymbol{\mu}) . \tag{3}$$

The terms on the right-hand sides of Eqs. (1) and (2) are Wiener processes as in the literature.[11]

The use of a nonlinear potential in Eqs. (1) and (2), e.g., a cosine potential, would introduce into consideration barrier crossing processes superimposed on molecular diffusion, and therefore open the door to many interesting nonlinear effects. However, this would again be at the expense of analytical intractability, and considerable numerical difficulty when attempting to solve the cosine potential two friction io equations with differential differencing. This is discussed more fully in Refs. 17 to 22. Note that if the potential energy well is a cosine then the derivative of this with respect to the angular coordinate is a sinusoidal torque which is approximated in this paper by its harmonic limit. This is a physically reasonable assumption when the torsional oscillation of the diffusing molecule is constrained to the bottom of the potential well, with small angle oscillations so that the sine function is adequately approximated by its argument.

In the harmonic approximation, Eqs. (1) and (2) may be solved analytically, adapting straightforwardly the methods developed by Coffey *et al.*[17–22] The results are given here in terms of β and the parameter

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

LINEAR CENTER-OF-MASS VELOCITY ACF

$$\langle \dot{\mathbf{r}}(t)\cdot\dot{\mathbf{r}}(0)\rangle = kT/2\{e^{-\beta t} + e^{-1/2\beta t} \times [\cos(\omega_1 t) - \beta/(2\omega_1)\sin(\omega_1 t)]\} . \tag{5}$$

ROTATIONAL VELOCITY ACF

$$\langle \dot{\boldsymbol{\mu}}(t)\cdot\dot{\boldsymbol{\mu}}(0)\rangle = \langle \dot{\mathbf{r}}(t)\cdot\dot{\mathbf{r}}(0)\rangle . \tag{6}$$

CROSS CORRELATION FUNCTION

$$\langle \dot{\boldsymbol{\mu}}(t)\cdot\dot{\mathbf{r}}(0)\rangle = kT/2\{e^{-\beta t} - e^{-1/2\beta t} \times [\cos(\omega_1 t) - \beta/(2\omega_1)\sin(\omega_1 t)]\} . \tag{7}$$

Other cfs of interest in the laboratory frame can be obtained from Eqs. (5)–(7), e.g.,

$$\langle \boldsymbol{\mu}(t)\cdot\dot{\mathbf{r}}(0)\rangle = -kT/2[e^{-\beta t}/\beta + e^{-1/2\beta t}/\omega_1 \sin(\omega_1 t)] . \tag{8}$$

ANGULAR VELOCITY ACF

Using the vector identity

$$(\mathbf{A}\times\mathbf{B})\cdot(\mathbf{C}\times\mathbf{D}) = (\mathbf{A}\cdot\mathbf{C})(\mathbf{B}\cdot\mathbf{D}) - (\mathbf{A}\cdot\mathbf{D})(\mathbf{B}\cdot\mathbf{C}) \tag{9}$$

then

$$\begin{aligned}\langle \dot{\boldsymbol{\mu}}(t)\cdot\dot{\boldsymbol{\mu}}(0)\rangle &= \langle \boldsymbol{\omega}(t)\times\boldsymbol{\mu}(t)\cdot\boldsymbol{\omega}(0)\times\boldsymbol{\mu}(0)\rangle \\ &= \langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle\langle \boldsymbol{\mu}(\mathbf{t})\cdot\boldsymbol{\mu}(0)\rangle \\ &\quad - \langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\mu}(0)\rangle\langle \boldsymbol{\mu}(t)\cdot\boldsymbol{\omega}(0)\rangle .\end{aligned} \tag{10}$$

The existence on elementary grounds[23] of

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

and

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

implies that the parity, time reversal, and reflection symmetry of $\boldsymbol{\mu}$ and $\dot{\boldsymbol{\mu}}$ are both the same as that of v. However, the parity symmetry of ω is opposite to that of v so it follows that it is also opposite to that of both $\boldsymbol{\mu}$ and $\dot{\boldsymbol{\mu}}$ so that

$$\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\mu}(0)\rangle = \langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\mu}(0)\rangle = 0 \tag{11}$$

and

$$\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle = \frac{\langle \dot{\boldsymbol{\mu}}(t)\cdot\dot{\boldsymbol{\mu}}(0)\rangle}{\langle \boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\rangle} . \tag{12}$$

ORIENTATIONAL ACF

Double integration of Eq. (6) produces the result

$$\langle \boldsymbol{\mu}(t)\cdot\boldsymbol{\mu}(0)\rangle = kT/2\,\frac{\{e^{-\beta t}/\beta^2 + e^{-1/2\beta t}[\beta/2\sin(\omega_1 t) - \omega_1\cos(\omega_1 t)]\}}{\omega_1(\omega_1^2 + \beta^2/4)} . \tag{13}$$

ACFS OF THE CORIOLIS AND CENTRIPETAL ACCELERATIONS

The molecular Coriolis, centripetal, and nonuniform accelerations appear in frame (x,y,z) for all molecular ensembles and have recently been simulated.[1-5] The vector identity (9) provides the simple result

$$\langle \boldsymbol{\omega}(t)\times\mathbf{v}(t)\cdot\boldsymbol{\omega}(0)\times\mathbf{v}(0)\rangle$$
$$=\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle \tag{14}$$

so that the acf of the Coriolis acceleration is obtainable from Eqs. (5) and (11). Similarly, the acf of the lab frame centripetal acceleration

$$\langle \boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{r}(t)]\cdot\boldsymbol{\omega}(0)\times[\boldsymbol{\omega}(0)\times\mathbf{r}(0)]\rangle$$
$$=[\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle]^2\langle \mathbf{r}(t)\cdot\mathbf{r}(0)\rangle \tag{15}$$

and is obtainable analytically in terms of two parameters.

Finally, by differentiating the analytical expression (14) for the Coriolis acf it is possible to obtain analytical expressions for laboratory frame ccfs such as shown[5] to exist recently in all molecular symmetries, including spherical top symmetry, i.e.,

$$\frac{d}{dt}\,[\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle]$$
$$=\langle \dot{\boldsymbol{\omega}}(t)\times\mathbf{v}(t)\cdot\boldsymbol{\omega}(0)\times\mathbf{v}(0)\rangle$$
$$+\langle \boldsymbol{\omega}(t)\times\dot{\mathbf{v}}(t)\cdot\boldsymbol{\omega}(0)\times\mathbf{v}(0)\rangle\,, \tag{16}$$

which is also obtainable analytically.

COMPUTER SIMULATION

In order to match the analytical results against independently obtained numerical results, a computer simulation of liquid water was carried out under conditions designed to maximise the cross correlation between rotational velocity and linear center-of-mass velocity. This was achieved by simulating liquid water under shock wave treatment[24] at 250 kbar, 1043 K. The interaction between two water molecules was modeled by a potential devised elsewhere in the literature[25] consisting of Lennard-Jones terms between the oxygen and hydrogen atoms superimposed on an ST2 charge distribution. The simulation was carried out using standard constant volume methods and provided the results illustrated in Fig. 1 for the normalized linear center-of-mass velocity acf, the rotational velocity acf and the cross correlation between the two dynamical variable, which under shock wave conditions is very intense.

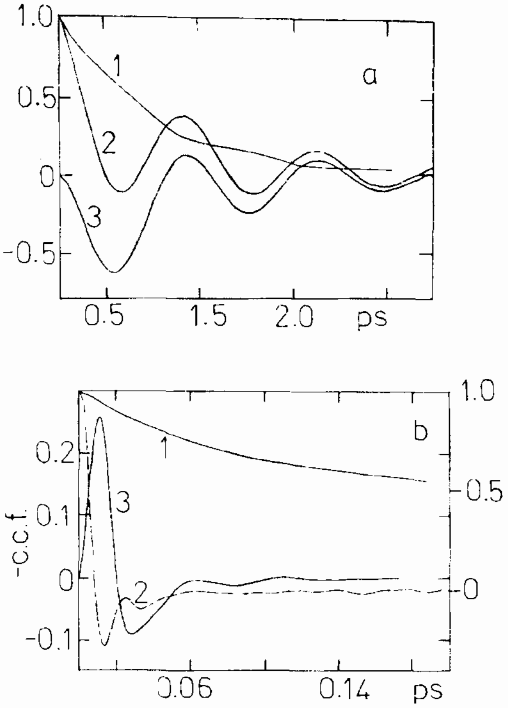

FIG. 1. Comparison of theoretical correlation functions (a) with computer simulated equivalents for liquid water, computed using a site–site model of water described in Refs. 4–6. (a) (1) Orientational correlation function for $\beta=10$: $v_0=1000$. (2) Rotational velocity acf. (3) The cross correlation function (Ref. 8). (b) As for (a) from the simulation, carried out at 250 kbar, 1043 K. Note that the sign of the cross correlation function from the computer simulation has been reversed, for the sake of illustration. The simulated ccf is normalized according to $\mathbf{c}^{ij}(t)=\langle \dot{\boldsymbol{\mu}}(t)\mathbf{v}^T(0)\rangle/[\langle \dot{\mu}_i^2\rangle^{1/2}\langle v_j^2\rangle^{1/2}]$. (a) and (b) are not intended as "best fit" comparisons but as illustrations of the theoretical results for a given set of parameters.

RESULTS AND DISCUSSION

The overall behavior of the system of Eqs. (1) and (2) is similar to that of cfs from computer simulation. A comparison is given in Fig. 1. For a given value of the friction coefficient the rotational velocity and velocity acfs become more oscillatory with increasing V, and the cross correlation function between the rotational and linear velocities becomes stronger and more oscillatory. The barrier height V is therefore directly responsible in this theory for the strength of the laboratory 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 is the simplest possible representation of these complicated dynamics. There are mathematical and physical limitations on the theory as follows: (1) The friction coefficient β is assumed to be the same in both Eqs. (1) and (2). More generally (and more intractably[17-22]), different friction coefficients can be generated by linear and rotational velocity. (2) The nonlinearities of the Euler equations[20] 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 Eqs. (1) and (2), giving

$$\frac{d^2}{dt^2}(\mathbf{r}+\boldsymbol{\mu})+\beta\frac{d}{dt}(\mathbf{r}+\boldsymbol{\mu})=\boldsymbol{\lambda}_1(t)+\boldsymbol{\lambda}_2(t), \tag{17}$$

which is a simple Langevin equation in the linear velocity of a point in the molecule at one end of the axis μ. The rotational motion of the molecule affects this linear velocity through the potential V and there are no explicit Euler terms[11] in Eqs. (1), (2), or (3). (3) Equations (1) and (2) are subject to the general limitations on all Langevin equations, recently discussed in detail in the literature.[22] Given these limitations, systems (1) and (2) appear to be a new approach to theoretical molecular dynamics which has the advantage of being analytically tractable, giving results which can be compared with computer simulations and data.

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