

# Computer simulation of electric-field-induced cross-correlation functions in molecular liquids

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The fundamental time cross-correlation function  $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0) \rangle$  is characterized for the first time using a computer simulation of the effect of an external electric field on 108 interacting dichloromethane molecules in the liquid at 296 K. Here  $\mathbf{v}$  is the molecular center-of-mass linear velocity and  $\boldsymbol{\omega}$  the angular velocity of the same molecule.

## INTRODUCTION

In the 20 years that have passed since the pioneering work of Condiff and Dahler<sup>1</sup> there has been a great deal of theoretical interest in the statistical correlation between molecular rotation and translation. One of the most fundamental cross-correlation functions in this context is  $C_{tr} = \langle \mathbf{v}(t)\boldsymbol{\omega}^T(0) \rangle$ , where  $\mathbf{v}$  is the molecular center-of-mass velocity and  $\boldsymbol{\omega}$  its angular velocity. In the laboratory frame of reference and in the absence of symmetry-breaking fields of force this vanishes for all  $t$  because of parity symmetry. This was first pointed out by Berne and co-workers.<sup>2,3-9</sup> There have been numerous papers since then on the calculation of  $C_{tr}$ . The earliest paper on this subject by Condiff and Dahler<sup>1</sup> remarks that several fluid mechanical phenomena can be generated by the coupling between molecular rotation and mass flow, and may be stimulated by the interaction of molecular electromagnetic multipoles with external fields of force. Conversely, therefore,  $C_{tr}$  ought to be observable directly with the use of external fields, e.g., an electric field.<sup>10,11</sup> Recently, Evans<sup>12</sup> has confirmed analytically that  $C_{tr}$  should be observable experimentally using the conventional well-known technique of electric-field-induced birefringence,<sup>13,14</sup> where the molecular dipole ( $\mu$ ) to field ( $\mathbf{E}$ ) interaction energy ( $\mu E$ ) is at most 1% (or less) of the thermal energy per molecule ( $kT$ ). The equation of interest, derived using linear Mori theory<sup>15</sup> for the column vector  $[\mathbf{v}]$  in the presence of an external z-axis electric field (i.e., a torque per molecule of  $-\mu \times \mathbf{E}$ ) is, in the Markovian limit:<sup>16</sup>

$$C_{tr}^{xy}(p) = \frac{\langle \omega_z^2 \rangle C_{\omega\omega}^{xx}(p)}{\phi_{tr}^{xy} C_{\omega\omega}^{xx}(p)} - \frac{\langle \omega_x^2 \rangle}{\phi_{tr}^{xy}} \quad (1)$$

Here  $\phi_{tr}^{xy}$  is the rototranslational friction coefficient,  $\langle \omega_x^2 \rangle$  and  $\langle \omega_z^2 \rangle$  the mean-square molecular angular velocities  $\perp$  and  $\parallel$  to the electric field, and  $C_{tr}^{xy}(p)$ ,  $C_{\omega\omega}^{xx}(p)$ , and  $C_{\omega\omega}^{zz}(p)$  are the Laplace transforms of  $C_{tr}^{xy}(t)$  and of the angular velocity autocorrelation function (ACF)  $C_{\omega\omega}^{xx}(t)$  and  $C_{\omega\omega}^{zz}(t)$   $\perp$  and  $\parallel$  to the electric field. The difference between  $C_{\omega\omega}^{xx}(t)$  and  $C_{\omega\omega}^{zz}(t)$  is particularly large in aligned, dipolar, nematic liquid crystals,<sup>14,16</sup> because of the pronounced birefringence in this medium. Under

well-defined conditions,<sup>17</sup> the angular velocity ACF may be approximated by the rotational velocity ACF, essentially the Fourier transform of the far-infrared<sup>16</sup> power absorption coefficient so that Eq. (1) provides a method for the measurement of  $C_{tr}^{xy}(t)$ , with molecular dipoles and electric field strengths available experimentally<sup>14</sup> ( $\mu E = 0.01kT$ ). The simple Eq. (1) shows that the appearance of  $C_{tr}^{xy}$  (and  $C_{tr}^{yx}$ ) for a field  $E_z$  is an inevitable consequence of electric-field-induced birefringence. Available techniques can measure small levels of birefringence with reasonable accuracy,<sup>14</sup> and therefore elements of  $C_{tr}$ , however small their amplitude, can always be measured experimentally using these sensitive techniques in the appropriate frequency range, e.g., the far infrared.

In this paper the time dependence and amplitude of  $C_{tr}$  are characterized for the first time using computer simulation<sup>18</sup> of liquid dichloromethane at 296 K. The interaction energy  $\mu E$  is varied from 0.28kT to 28.0kT, and the response of the cross-correlation function (CCF) measured computationally as a function of time and field strength. The limited amount of computer time and power available for this work meant that electric field strength equivalent to  $\mu E = 0.01kT$  could not be reached because the "signal" ( $C_{tr}$ ) is buried in the "noise" generated by the computer runs. In principle, there should be no great difficulty in extending these computations to the "experimentally interesting" case of  $\mu E \ll kT$ , using linked-cell and difference-method algorithms to boost the power of the simulation and cut down the noise. It is possible, given the linked-cell method<sup>12</sup> and the requisite computer power, to use up to about 7000 molecules compared with the 108 available for this paper. An important consequence of  $C_{tr} \neq 0$  ( $\mathbf{E} \neq 0$ ) is that methods such as dielectric relaxation must be seeing  $C_{tr}$  indirectly via the orientational autocorrelation function, because the probe electric fields, however weak, must always generate polarization, and thereby must always violate the "parity theorem"  $C_{tr} = 0$ .

## ALGORITHM AND METHOD

The equations of motion for 108 interacting dichloromethane molecules are integrated with a routine developed by Ferrario and Evans and described elsewhere.<sup>18</sup> The potential energy is pairwise additive and the intermolecular potential is a  $3 \times 3$  site-site potential made

up of Lennard-Jones and partial-charge terms. The effect of the  $z$ -axis electric field is simulated with a technique developed by Evans.<sup>18</sup> This produces rise and fall transients and correlation functions at field-on equilibrium. Orientational averages such as  $\langle e_{AZ}^n \rangle$ , where  $e_A = \mu / |\mu|$ , are  $n$ th-order Langevin functions of  $\mu E / kT$  at field-on equilibrium, i.e.,  $\langle e_{AZ}^n \rangle_{t \rightarrow \infty}$  of the rise transient. Each element of the CCF matrix  $C_{tr}$  is normalized, e.g.,

$$C_{tr}^{xy} = \langle v_x(t) \omega_y(0) \rangle / (\langle v_x^2 \rangle^{1/2} \langle \omega_y^2 \rangle^{1/2}).$$

The result  $C_{tr} = 0$  ( $E=0$ ) may be used to test the noise level in the computer simulations [the difference between two or more separate (e.g., consecutive) runs on the same CCF]. In most of the results illustrated in Fig. 1 the noise

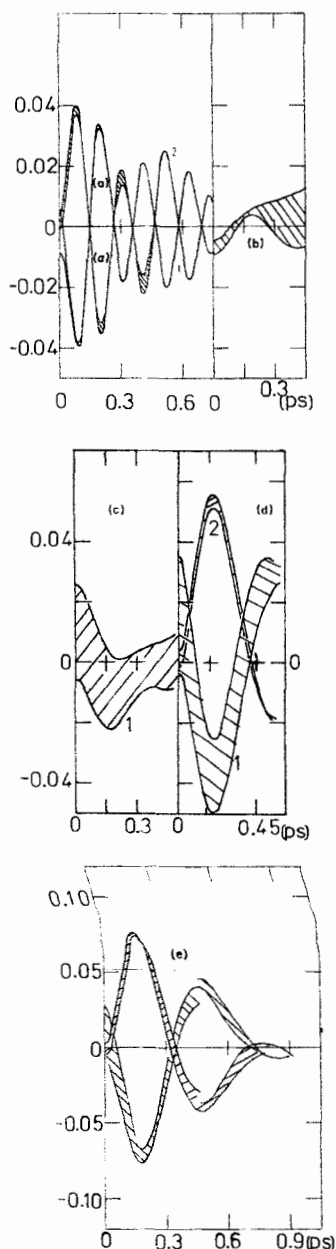


FIG. 1. Development of (1)  $C_{tr}^{xy}$  and (2)  $C_{tr}^{yz}$  with interaction energy  $\mu E / kT$ . (a) 28.0; (b)  $\mu E / kT = 0.0$  (noise only); (c) 0.28 (curve 1 only); (d) 1.4; (e) 2.8.

level of two consecutive runs straddles the zero mark at  $t=0$ . The CCF for  $E=0$  [Fig. 1(a)] is "all noise" and happens to miss the origin for the two consecutive runs illustrated. By taking a series of runs and averaging, the result should be the background noise level, distributed evenly about the zero axis in Fig. 1(a).

Finally in this section we emphasize that an  $N$  dependence of these results is expected, where  $N$  is the number of molecules used in the simulation. The dependence will show up as a decrease in noise (the hatched areas in Fig. 1, for example), allowing us to measure the amplitude of the CCF's more accurately.

#### SOME DETAILS OF THE SIMULATION METHOD

The method is based on the application of an external electric field to 108 interacting dichloromethane molecules at equilibrium. A detailed description of the field-off method can be found in the last two papers of Ref. 18. The intermolecular potential is a  $3 \times 3$  Lennard-Jones atom-atom potential with point charges representing the electrostatic part of the complete potential. The  $\text{CH}_2$  group is thereby represented by a moiety of mass 14, with Lennard-Jones and partial charge parameters, respectively:

$$\epsilon(\text{CH}_2\text{-CH}_2) / k = 70.5 \text{ K},$$

$$\sigma(\text{CH}_2\text{-CH}_2) = 3.96 \text{ \AA},$$

$$q_{\text{CH}_2} = 0.302 |e|.$$

The C1 group is represented by a mass of 35.5 and Lennard-Jones and partial-charge parameters

$$\epsilon(\text{C1-C1}) / k = 173.5 \text{ K},$$

$$\sigma(\text{C1-C1}) = 3.35 \text{ \AA},$$

$$q = -0.151 |e|.$$

The molar volume used was  $8.0 \times 10^{-5} \text{ m}^3$ .

The  $C_{tr}$  functions should vanish at the origin. The fact that they do not do so in the figures of this paper is due to insufficient sampling in the computer simulation runs (the use of only two time origins). This can be rectified by repeated averaging, or by using many more time steps in the simulation runs. Probably, about ten runs would be needed, each of about 3000 time steps, to ensure the convergence of the  $C_{tr}$  function to zero at the origin to within about  $\pm 1\%$  of its maximum or minimum value at  $t > 0$ .

#### HEATING EFFECTS

The  $C_{tr}$  functions computed for this paper were obtained at thermodynamic equilibrium. The heating effects, if any, introduced by the presence of a constant electric field are dissipated using the standard methods of molecular dynamics simulation. In this work the standard temperature rescaling routine was utilized with the temperature allowed to fluctuate by 25 K either side of the mean input temperature of 296 K. Therefore, there are no extraneous heating effects, other than those normally encountered in the standard simulation method. In

this context, the only effect of the electric field is to increase the potential energy, i.e., to make it less negative. The kinetic energy remains the same in the field-off and field-on cases because the sample is thermostated by the temperature rescaling routine.

The influence of temperature rescaling on the cross-correlation function  $C_{tr}$  can therefore be gauged bearing this in mind. It follows that if the kinetic energy is the same in the field-on and field-off cases, the temperature rescaling process should have the same effect in both cases. There is no sign of spurious oscillation due to temperature rescaling in the field-off case of the figure, and there seems to be no reason to suppose that there should be any spurious influence in the equilibrium condition, field-on, if the kinetic energy is the same. To be sure of the absence of spurious oscillation, more work is needed with different temperature rescaling algorithms and rescaling rates.

This work differs from similar work in the field of non-linear shear viscosity<sup>12</sup> because it deals with equilibrium, not transient, effects of the external force field. There are, however, many interesting similarities between the two areas of investigation which could reveal many new cross correlations made visible by a parity-breaking force field.

## RESULTS AND DISCUSSION

The original result of this paper is shown in Fig. 1 in terms of  $C_{tr}$  at different  $\mu E/kT$ . The  $(x,z)$  element of the matrix  $\langle v(t)e_A^T(0) \rangle$  has also been observed in this work, showing that in the presence of  $E$ , and therefore of birefringence,  $v$  is correlated *directly* both with  $\omega$  and  $e_A$  in the laboratory frame  $(x,y,z)$ .

For  $C_{tr}$ , the  $(x,y)$  and  $(y,x)$  elements are mirror images and are oscillatory. They attain a maximum normalized amplitude (measured through that of the first peak) for intermediate field strengths. The other elements of  $C_{tr}$  lie below the noise of the runs used for this work, but may exist for  $t > 0$ . As the field strength is increased the Grigolini decoupling effect<sup>15</sup> is observed in  $C_{tr}^{xy}$  and  $C_{tr}^{yx}$ . This means that the strong field competes with the thermal forces in the molecular ensemble, whose influence on the correlation function decreases as the field strength increases. In consequence, the CCF becomes longer lived, as measured through the envelope of its oscillations. The frequency of these oscillations also increases because this is given approximately<sup>15</sup> by  $\omega_1 = (\mu E/I)^{1/2}$  where  $I$  is the mean (effective) molecular moment of inertia.

At  $\mu E/kT = 0.28$  the CCF  $C_{tr}$  is still just visible as a systematic time dependence above the noise of the simulation [Fig. 1] and it is clear that the computer-simulation technique could be used to pick it up for  $\mu E/kT \ll 1$ , where the natural oscillation of the CCF would be relatively fast compared with the frequency  $\omega_1$ . The "difference method" of molecular dynamics simulation, currently used for the computation of transport coefficients could be adapted for  $C_{tr}$  at  $\mu E \ll kT$ . This technique works by picking up the signal from the noise by comparing two simulation runs, one unperturbed and the other slightly perturbed, and illustrates perfectly how  $C_{tr}$  would be measured in a birefringence experiment, where the sample is slightly perturbed (or polarized) by the probe (an electric field). The interpretation of such spectra must therefore be extended<sup>8,11</sup> to include  $C_{tr}$ . Finally the existence of CCF's such as  $\langle v(t)e_A^T(0) \rangle$  in birefringent media has an important bearing on the theory of relaxation of aligned, dipolar, liquid crystals in the presence of an electric field. It is well known that the dielectric loss and dispersion of an aligned nematogen differs significantly from their counterparts in the unaligned condition. A secondary loss process appears, where frequency depends on whether the probe and aligning fields are  $\parallel$  or  $\perp$  to each other. In the aligned nematic condition, the orientational order parameter corresponding to  $\langle e_{Az} \rangle$  is, typically, in the region of 0.5 at intermediate densities, and increases to 1.0 at high densities. Such values were confirmed in the unaligned "nematic" condition, in a recent computer simulation by Kushick and Berne<sup>19</sup> using ellipsoidal pair potentials and no external field.

We have shown elsewhere<sup>12,20,21</sup> that the existence of laboratory-frame CCF's between orientational vectors such as  $e_A$  and the same molecule's center-of-mass linear velocity has a big effect on, for example, dielectric spectra, causing the loss to be split into two separate peaks. This is exactly what is observable in the *aligned* dipolar nematic mesophase. It would be interesting in this context to simulate CCF's such as  $C_{tr}$  or  $\langle v(t)e_A^T(0) \rangle$  in liquid crystals, where a weak electric or magnetic field causes substantial alignment.

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