

TIME-ASYMMETRIC CROSS CORRELATION FUNCTIONS IN LIQUID WATER INDUCED BY ELECTRIC FIELD COMBINATIONS: A COMPUTER SIMULATION

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A combination of electric fields, rotating and alternating at the same frequency, and aligned in the same (X) axis of the laboratory frame (X, Y, Z) produces time-asymmetric cross correlation functions of the linear and angular velocities of a diffusing water molecule. This computer simulation result apparently contradicts the Onsager-Casimir relation and is explained as a weighted combination of time-symmetric and -antisymmetric components. This is apparently the first prediction of time asymmetry of this type in molecular liquids.

1. Introduction

Recent computer simulations [1-4] of a Lennard-Jones atomic ensemble subjected to a shear [5-8] of the type $\partial v_x/\partial Z$ have produced the first observation of time-asymmetric cross correlation functions (CCFs) which amount to an apparent counterexample [4] to the Onsager-Casimir reciprocal principle [9]. These non-equilibrium molecular dynamics computer simulation results were explained on the grounds of symmetry, using the recently developed [10-12] principles of group theoretical statistical mechanics (GTSM) as being a weighted combination of time-antisymmetric components due to shear-induced vorticity, of symmetry $D_g^{(1)}$ [13-15], and time-symmetric components due to shear-induced deformation, of symmetry $D_g^{(2)}$. These CCFs, and related CCFs of the pressure tensor, were found to be at the root of the observable Weissenberg effect [7], the pressure generated in a liquid perpendicular to the plane of shear.

In this Letter new time-asymmetric CCFs are reported for the first time in a molecular liquid, water, treated with a combination of electric fields, spinning and alternating at the same frequency about the

same (X) axis of the laboratory frame (X, Y, Z). This result suggests that there is a complete new set of time-asymmetric CCFs, members of which appear in a molecular ensemble subjected to an external field influence of the appropriate symmetry. The latter is discussed in terms of the following three principles of group theoretical statistical mechanics (GTSM). In the light of these considerations, and with the newly available simulation data, it is concluded that time correlation functions in general may have the property of being asymmetric to interchange of orthogonal Cartesian components, or equivalently to the interchange of time argument in the two variables being correlated, i.e.

$$\langle A_Y(t) A_Z(0) \rangle \neq \langle A_Z(t) A_Y(0) \rangle. \quad (1)$$

Principle (1) (Neumann's principle). In an atomic or molecular ensemble at thermodynamic equilibrium, the ensemble average $\langle ABCD... \rangle$ may exist if the product of irreducible representations [13-15] of A, B, C, D, \dots in the rotation-reflection point group $R_h(3)$ contains the totally symmetric representation (TSR) $D_g^{(0)}$.

Principle (2). This ensemble average may exist in the frame (x, y, z) of the molecular point group if the product of irreducible representations of A, B, C, D, \dots in this point group contains that group's TSR at least once [15].

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Principle (3). An ensemble of atoms or molecules in a steady state produced by an applied field of given symmetry may contain new ensemble averages whose symmetry in frame (X, Y, Z) , the laboratory frame, is determined by that of the applied field [1-4,10-12].

Principle (1) shows, for example, that off-diagonal elements of time auto correlation functions (ACFs) do not exist at equilibrium, because their symmetry signatures do not contain the TSR $D_g^{(0)}$. In ACFs the latter is the trace, containing the diagonal elements only, of the generic ACF tensor $\langle A(0)A^T(t) \rangle$. In the presence of applied fields, principle (3) applies, and applied fields with symmetry elements other than $D_g^{(0)}$ may produce off-diagonal elements of time ACFs, which are referred to here as cross correlation functions because they contain different orthogonal elements of the dynamical variable being correlated. Previous work [16-18] has shown that a rotating electric field of symmetry $D_g^{(1)}$ produces time-antisymmetric CCF elements of the type

$$\langle A_Y(0)A_Z(t) \rangle = -\langle A_Z(0)A_Y(t) \rangle \quad (2)$$

in frame (X, Y, Z) . In accordance with principle (3) this is the same symmetry type ($D_g^{(1)}$), which denotes a vector product even to parity reversal (i.e. superscript 1, subscript g)

$$\langle A(0) \times A(t) \rangle \quad (\equiv D_g^{(1)}) \quad (3)$$

In the case of treatment with a rotating electric field whose symmetry is purely $D_g^{(1)}$ there are no time-symmetric components [1-4] of symmetry type $D_g^{(2)}$

$$D_g^{(2)}: \langle A_Y(0)A_Z(t) \rangle = \langle A_Z(0)A_Y(t) \rangle, \quad (4)$$

and in consequence the field-induced CCF is exactly time antisymmetric as observed in computer simulations [16-18].

In what follows we address the problem of what happens when a rotating electric field of symmetry signature $D_g^{(1)}$ is supplemented by an alternating electric field of symmetry signature $D_u^{(1)}$ aligned along the former's axis of rotation with the same (alternating) frequency.

2. Computer simulation methods

The computer simulation was carried out with the algorithm TETRA, described in the literature, on 108 water molecules interacting with a modified ST2 potential devised and described by the author [19-21]. The model parameters were as follows:

$$\epsilon/k(\text{H-H}) = 21.1 \text{ K}, \quad \epsilon/k(\text{O-O}) = 58.4 \text{ K},$$

$$\sigma(\text{H-H}) = 2.25 \text{ \AA}, \quad \sigma(\text{O-O}) = 2.80 \text{ \AA},$$

$$q_H = -q_O = 0.23 |e|.$$

The time step used was 0.5 fs, and production runs extended over 6000 time steps after equilibration. Running time averages were computed over all 108 molecules using all 6000 time steps for good statistics. The production runs were carried out in the presence of a combination of rotating and alternating electric fields defined as follows:

(1) Rotating electric field

$$E_X = 0,$$

$$E_Y = E_0 \cos \omega_0 t,$$

$$E_Z = E_0 \sin \omega_0 t. \quad (5)$$

(2) Alternating electric field

$$E_X = E_0 \cos \omega_0 t. \quad (6)$$

These were applied simultaneously to produce an overall torque on each molecule of the type [16-18] $-\boldsymbol{\mu} \times \mathbf{E}$. During production runs the sample was thermostatted with a temperature-rescaling routine.

3. Results and discussion

The time-asymmetric CCFs produced by the above field combination are illustrated in fig. 1 (linear velocity, ν) and fig. 2 (angular velocity, ω) for two field frequencies (ω_0), (a) 0.01 and (b) 10.0 THz. In each case the energy imparted by the applied field to the sample was equivalent to 21.2 kJ mol⁻¹. Both types of CCF are asymmetric in the interchange of Y and Z indices, and figs. 3 and 4 show that the trace of each CCF matrix, i.e. of $\langle \nu(t)\nu^T(0) \rangle$ and $\langle \omega(t)\omega^T(0) \rangle$ contains components with three different time dependences, showing that the sample is birefringent. It is especially significant that such

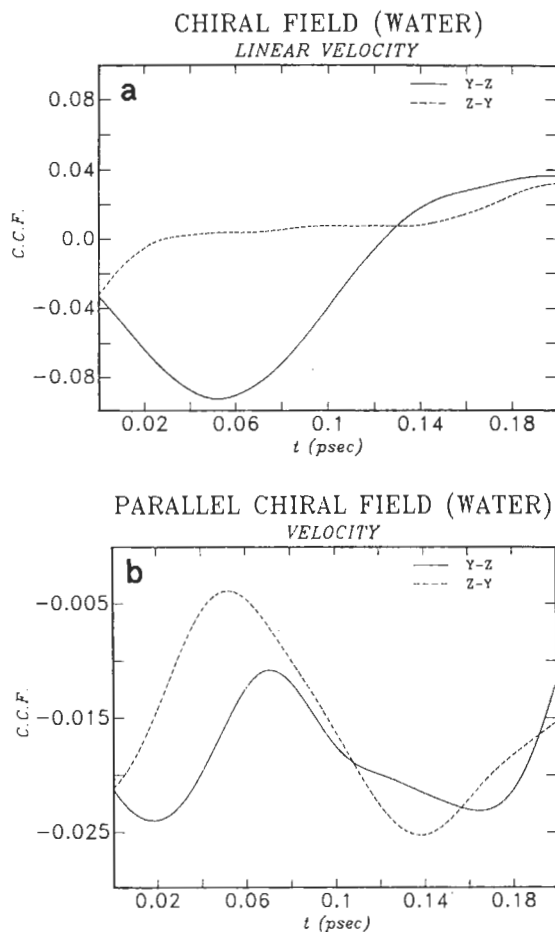


Fig. 1. Time-asymmetric field-induced cross correlation functions of molecular linear velocity, $\langle v_y(t)v_z(0) \rangle$ and $\langle v_z(t)v_y(0) \rangle$ in liquid water at 293 K, computer simulation. (a) Applied field frequency of 0.01 THz; (b) 10.0 THz.

properties are imparted to the linear velocity CCF matrix, because there is no direct body force produced by the field combination, only a torque, $-\mu \times E$.

The application of GTSM to these results must proceed on the basis that the field-induced CCFs have an overall even parity reversal symmetry, because they are off-diagonal components of the same vector (v or ω , respectively). Therefore, the computer simulation results show that they are not generated by a simple product

$$D_g^{(1)}D_u^{(1)} = D_u^{(0)} + D_u^{(1)} + D_u^{(2)} \quad (7)$$

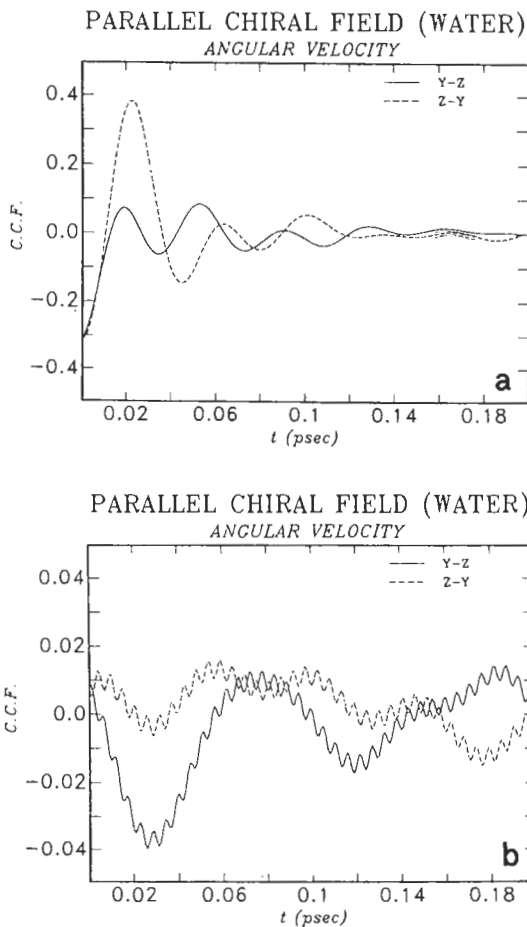


Fig. 2. As for fig. 1, molecular angular velocity.

of the $D_g^{(1)}$ symmetry of the axial vector of the rotating electric field and the $D_u^{(1)}$ symmetry of the polar vector of the alternating electric field. Evidently, the three electric field components can combine to give different symmetry signatures, for example eq. (7) above and also D products such as

$$D_u^{(1)}D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \quad (8)$$

generated between field-component pairs. The overall symmetry in eq. (8) is gerade, even to parity reversal, consisting of three symmetry components with superscripts 0, 1 and 2. By principle (3) these make possible respectively the scalar product (trace), vector product (time antisymmetric) and tensor product (time symmetric) in the generic ACF tensor

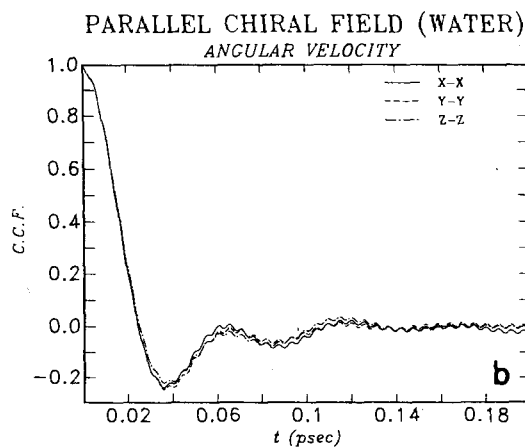
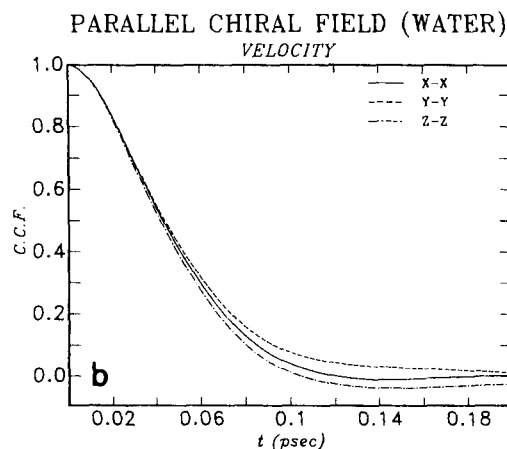
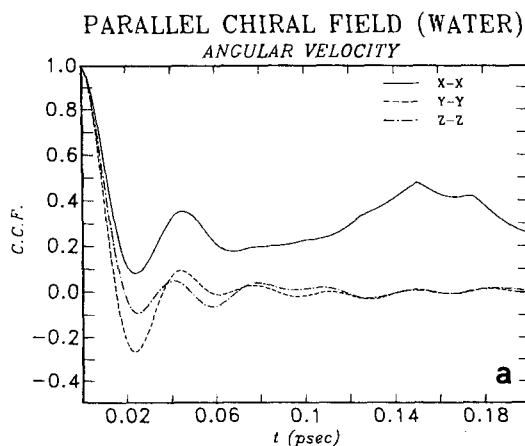
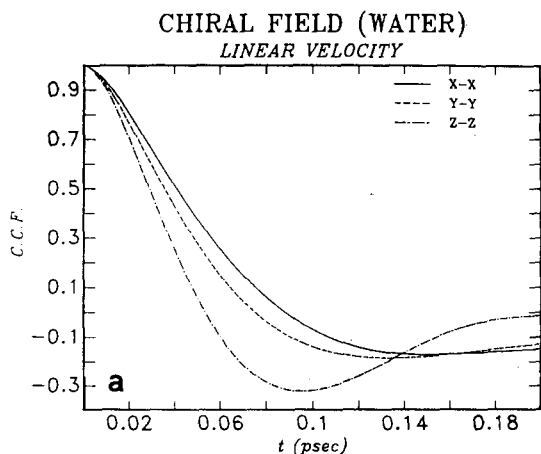


Fig. 3. As for fig. 1, diagonal components of the molecular linear centre of mass-velocity time correlation induced by the electric field combination.

$\langle A(t)A^T(0) \rangle$ in the steady state under the influence of the applied field. The evident time asymmetry in figs. 1 and 2 therefore emerges from a weighted combination of $D_g^{(1)}$ and $D_g^{(2)}$ components in eq. (8). In physical terms, there is an apparent competition between the symmetry signatures (7) and (8), each of which could by principle (3) be generated by different combinations of electric field components. The signature (8) is dominant when the frequency of the rotating and alternating electric fields is the same, as in this simulation. Under other circumstances it is conceivable that the symmetry (7) dominates, generating ungerade quantities in the field-on steady state. We note that (7) represents a

Fig. 4. As for fig. 3, molecular angular velocity.

chiral influence according to Barron's definition [22], i.e. an odd parity field combination, but even to time reversal symmetry.

4. Equivalence to elliptical polarisation

We note finally that the field combination used in eqs. (5) and (6) is equivalent to an elliptically polarised electric field component of an electromagnetic field. This can be shown by tilting the coordinate system used in eqs. (5) and (6) by 45° to give a new coordinate system (X_i, Y_i, Z_i) . In this coordinate system we have

$$E_{X_i} = 2^{1/2} E_0 \cos \omega t,$$

$$E_{Zt} = E_0 \sin \omega t,$$

$$E_{Yt} = 0. \quad (9)$$

It follows that the symmetry analysis and results presented in this Letter also describe the effect of a strong elliptically polarised electromagnetic field on the molecular dynamics of liquid water. The elliptically polarised laser field introduces an asymmetry in the time correlation functions which is similar to that observed in a shearing field.

The symmetry signature of the elliptically polarised laser field is that of eq. (7), because eq. (9) is the same as eqs. (5) and (6) except for tilting the coordinate system. All the results presented here are therefore also valid for an elliptically polarised laser applied with a coordinate system tilted at 45° to the plane of the applied field, or in other words for a laser beam whose plane is tilted at 45° to the coordinate system (X, Y, Z).

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