THE EFFECT OF ORTHOGONAL ELECTRIC FIELDS ON THE MOLECULAR

DYNAMICS OF LIQUID WATER, PRINCIPLE THREE OF

GROUP THEORETICAL STATISTICAL MECHANICS.

by

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Abstract

Molecular dynamics computer simulation has been used to investigate the effect of orthogonal electric fields on the molecular dynamics of liquid water. It is found that a combination of a static electric field E_X in the X axis and an orthogonal static electric field E_Z in the Z axis results in the appearance of symmetric cross correlation functions of the type $\langle A_X(0) A_Z(t) \rangle = \langle A_Z(0) A_X(t) \rangle$ in the laboratory frame (X, Y, Z). This is in accordance with the third principle of group theoretical statistical mechanics (g.t.s.m.). These cross correlation functions (c.c.f.'s) are observable experimentally at dielectric and far infra red frequencies.

Introduction

It is well known that the basis of the technique of dielectric relaxation (1-4) is polarisation of a sample with a single, polarising, external electric field, which is made frequency *dependent* over as much as fourteen decades. Dielectric relaxation reveals a great deal about the dynamics of molecules in the condensed states of matter (1-4). Utilisation of more than one polarising electric field is much rarer, although first considered theoretically by Born (5) and experimentally by Lertes (6) in the nineteen twenties. Extra experimental information can be gathered in several different ways by using more than one polarising electric field. For example, an arrangement of four

electrodes can be used to produce what is effectively a rotating electric field (5-8). One A.C. field between one pair of electrodes is ninety degrees out of phase with the orthogonal field. The equations describing such a combination of electric fields (7,8) are identical with those of the electric field vector of a circularly polarised laser field, and this combination can physically rotate a sample of molecular liquid. If the latter is suspended from a torsion wire in a thin walled glass container between the four electrodes of a rotating electric field, a torque is produced (5,6) in the wire which can be measured experimentally and described theoretically. This effect was related by Born (5) to the Debye relaxation time (1-4).

In this communication the symmetry of this phenomenon is classified with the third principle of group theoretical statistical mechanics (9-12), which states that the symmetry of extra ensemble averages produced by an external field of force is the same as that of the applied field. In this case the applied field is made up of a combination of orthogonal electric fields. Having found the appropriate D symmetry (9-12) of this combination, ensemble averages of the same symmetry are investigated by molecular dynamics computer simulation in liquid water. The D symmetry of these new ensemble averages are classified for static (zero frequency) orthogonal electric field combinations and also for the rotating (frequency dependent) electric field combination considered by Born (5) and Lertes (6). It is shown that static orthogonal electric fields produce new ensemble averages (cross correlation functions (c.c.f.'s)) with $D_g^{(2)}$ symmetry, which are symmetric to interchange of cartesian indices. The rotating electric field on the other hand produces c.c.f.'s of $D_g^{(1)}$ symmetry which are antisymmetric to interchange of cartesian indices. Both D signatures are components of the complete D symmetry of the tensor product EE of two electric fields in the laboratory frame (X, Y, Z), and both D symmetries are accommodated in the third principle (9-12) of group theoretical statistical mechanics (g.t.s.m.). Both for static and rotating electric fields, the c.c.f.'s can be observed experimentally and may be used to investigate molecular dynamics in the condensed phases of matter.

Considerations of Symmetry

The static electric field E is a polar vector which is odd to parity reversal (9-12), and is described by the irreducible representation $D_u^{(1)}$ of the rotation-reflection point group R_h (3) in the laboratory frame (X, Y, Z). The third principle of g.t.s.m. is used to guide us as to the kind of new averages to expect in an ensemble (13) of molecules in the steady state in the presence of an applied E. It states that we may expect averages with the same symmetry, $D_u^{(1)}$. An example is (9-12)

$$\left\langle v_x(t)\omega_y(o)\right\rangle = -\left\langle v_y(t)\omega_x(o)\right\rangle \qquad -(1)$$

which is observable (14-16) by computer simulation.

The use of simple point group theory allows the extension of these considerations to a combination of two electric fields, which in general is the product EE. The D symmetry of this product is given by the Clebsch-Gordan Theorem (9-12)

$$\Gamma\left(E_i E_j\right) = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \qquad -(2)$$

and is made up of a scalar, vector, and tensor part, each of which is even to parity reversal. The D combination on the right hand side of eqn. (1) is the same as that encountered in a strain rate (17) produced by shear stress. Here $D_g^{(0)}$ is the symmetry of the dot product E.E; $D_g^{(1)}$ is the symmetry of the vector (cross) product ExE; and $D_g^{(2)}$ that of the tensor (dyadic) product excluding the trace. If we use a combination of orthogonal electric fields, for example, E_X and E_Z, the dot product (and trace) disappears. According to the third principle of g.t.s.m., the possible extra ensemble averages produced by this combination can be $D_g^{(1)}$ symmetry, $D_g^{(2)}$ symmetry, or a combination of both. (In response to shear stress, a combination of $D_g^{(1)}$ and $D_g^{(2)}$ averages are observed, producing new, dissymmetric c.c.f's (17) observable with SLLOD and PUT computer simulation.)

The possible extra ensemble averages appear as cross correlation functions (c.c.f.'s) directly in frame (X, Y, Z), and can be observed experimentally, leading to new information on molecular dynamics. This was first demonstrated by Lertes (6), using simple apparatus, although the language of cross correlation functions was not used to describe the results. (The concept of time correlation first appeared in the statistical literature one or two years after Lertes's experiment, and was

first applied to traditional, single field, dielectric relaxation by Cole (18) only in the nineteen sixties, using auto correlation functions of the molecular dipole moment.)

Computer Simulation Methods

In our search for new c.c.f.'s of the symmetry anticipated by g.t.s.m. the molecular dynamics of water were computer simulated in the steady state under the simultaneous influence of the orthogonal electric fields E_x and E_z . Each field was assumed to interact with the water molecule's dipole moment through the torque $-\underset{\sim}{\mu} \times \underset{\sim}{E}$ as described elsewhere (19-21).

A sample of 108 water molecules was used at a fixed molar volume of 18.0 cm per mole. The input temperature was 293 K, which was maintained in the field applied steady state with temperature rescaling (19-21). The integration algorithm was TETRA, as described in the literature (19-21). The field-applied steady state was characterised by a steady, negative, total energy, and translational and rotational temperatures which fluctuated about the input temperature. Dynamical trajectories in the field-on steady state were used to compute correlation functions by running time averaging over 6,000 time steps and 108 molecules. The time step was 0.5 fs throughout.
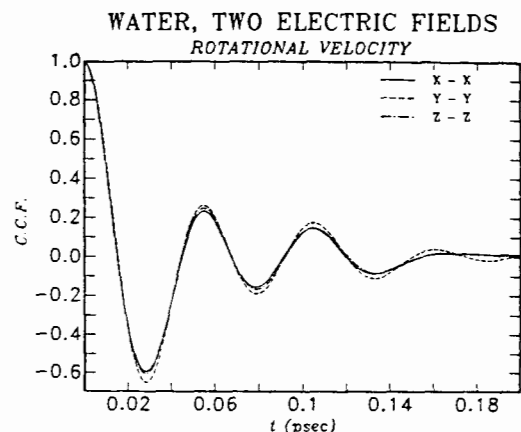

WATER, TWO ELECTRIC FIELDS
ROTATIONAL VELOCITY

Figure (1)

Rotational velocity correlation function, $D_9^{(o)}$ symmetry elements (rotational velocity), field free equilibrium.

WATER, TWO ELECTRIC FIELDS
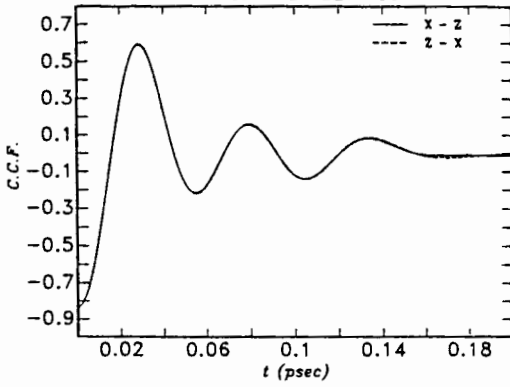### *ROTATIONAL VELOCITY*

Figure (2)

Field applied $D_g^{(2)}$ elements of the rotational

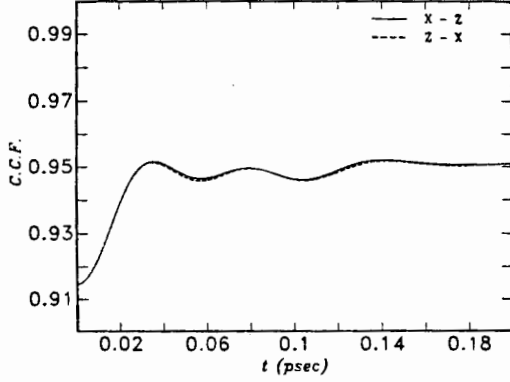velocity.

WATER, TWO ELECTRIC FIELDS
ORIENTATION

Figure (3)

Field applied $D_g^{(2)}$ elements of orientation.

Results and Discussion

Figs. (1) to (3) illustrate the appearance of c.c.f.'s of $D_g^{(2)}$ symmetry of the type

$$C_1(t) = \langle \mu_i(t)\mu_j(o) \rangle \qquad - (3)$$

and

$$C_2(t) = \langle \dot{\mu}_i(t)\dot{\mu}_j(o) \rangle \qquad - (4)$$

where $\dot{\underset{\sim}{\mu}}$ is the water molecule's rotational velocity and $\underset{\sim}{\omega}$ its angular velocity. The figures show that as the strength of one of the electric fields is gradually reduced the c.c.f. gradually disappears. The $D_g^{(2)}$ symmetry c.c.f. can be supported only with two electric fields, which combine to generate this symmetry. Interestingly, c.c.f's of this type are also generated for the centre of mass linear velocity, $\underset{\sim}{v}$, and this is the result of indirect rotation / translation coupling, because the electric field can have no direct effect on the centre of mass diffusion of the molecules in the sample.

These are static electric field combinations, but if the electric fields are made frequency dependent, as in the rotating fields considered elsewhere (22-24) by computer simulation, the symmetry of the induced c.c.f.'s switches from the symmetric $D_g^{(2)}$ of this paper to the asymmetric $D_g^{(1)}$. In general the induced c.c.f.'s are expected to be dissymmetric, as in shear induced atomic dynamic phenomena reported elsewhere.

Conclusions

The third principle of group theoretical statistical mechanics has been tested with the application of two orthogonal static electric fields to a sample of 108 water molecules in a computer simulation. The $D_g^{(2)}$ part of the overall symmetry expected from the third principle is observed with static electric fields, and the $D_g^{(1)}$ with rotating electric fields. In general the full D symmetry can be generated, and this produces dissymmetric c.c.f.'s in the laboratory frame (X, Y, Z).

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