

Shear induced asymmetric cross-correlation functions in liquid water: a computer simulation

M.W. Evans

Theory Center, Cornell University, Ithaca, NY 14850, USA

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A computer simulation of liquid water under an applied shearing force has been used to show the presence of asymmetric cross-correlation functions (ccf's) of molecular orientation, implying that the frequency dependence of dielectric complex permittivity depends on shear, even though there is no net shear induced polarisation. These results confirm earlier simulations in atomic ensembles.

1. Introduction

The first time-asymmetric cross-correlation function (ccf) appeared in response to applied shear in a simple atomic ensemble in two and three dimensions [1–5]. It was observed numerically that ccf's in response to shear are neither symmetric nor antisymmetric to index reversal. The center of mass velocity ccf, for example, in response to a strain rate $\partial v_x / \partial Z$ has the property [1–5]

$$\langle v_x(t)v_z(0) \rangle \neq \langle v_z(t)v_x(0) \rangle, \quad (1)$$

which can be explained with group theory applied to statistical mechanics (the three principles of group theoretical statistical mechanics [6–8]). These same principles predict the appearance of asymmetric cross-correlation functions (ccf's) of the general type

$$A_x(t)A_z(0) \neq A_z(t)A_x(0) \quad (2)$$

in response to shear. Here A is a molecular dynamical variable such as orientation (μ), rotational velocity ($\dot{\mu}$), angular velocity (ω), or linear molecular center of mass velocity (v).

In this Letter shear induced asymmetric ccf's of the permanent molecular electric dipole moment are computed in liquid water with a modified "molecular dynamics" algorithm which introduces a systematic laboratory frame shearing force in the Z axis. This is the first time that shearing force has been ap-

plied in a molecular dynamics simulation of molecular as opposed to atomic ensembles. The results confirm the prediction of group theoretical statistical mechanics (g.t.s.m.) of asymmetric orientational ccf's which are the fundamental signatures of dielectric response to shear in molecular ensembles.

2. Simulation algorithm

The algorithm is a modification of one fully described in the literature [8–12] for the "molecular dynamics" simulation of ensembles in the presence of external fields. To account for shear, a force is introduced in the Z axis of the laboratory frame (X, Y, Z), whose magnitude is linearly proportional to X , taking the origin at the mid point of a cube of 108 water molecules. The equations of motion are integrated in the presence of this shearing force using a site-site potential described in the literature [8–12]. This applied shearing force increased the steady state energy of the system by 23 kJ per mole from an initial 296 K, 1.0 bar, and was applied with sufficient magnitude to show the presence of asymmetric ccf's of the various molecular dynamics variables present in the system. The system was re-equilibrated in the shear applied steady state. Using this technique with periodic boundary conditions and simple temperature rescaling, the following results were obtained for

a sample of 108 water molecules, using a time step of 5.0 fs, and independent segments of 2000 time steps each in double precision on the IBM 3090-6S of the Cornell National Supercomputer Facility.

The water-water interaction potential was modelled with a Lennard-Jones/charge-charge system which was designed to include the lone pair electronic charges. This has been described in the literature, but is given here for reference:

$$\phi_{ij}(r_i, r_j) = 4\epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6],$$

$$\phi_{ij} = \sum \sum \phi_{ij}(\text{atom}),$$

$$\epsilon/k (\text{H-H}) = 21.1 \text{ K}, \quad \sigma(\text{H-H}) = 2.25 \text{ \AA},$$

$$\epsilon/k (\text{O-O}) = 58.4 \text{ K}, \quad \sigma(\text{O-O}) = 2.80 \text{ \AA},$$

$$q_{\text{H}} = 0.23|e|, \quad q(\text{lone pair}) = -0.23|e|,$$

$$q_{\text{O}} = 0.00|e|, \quad \sigma(\text{O-H}) = \frac{1}{2}[\sigma(\text{O-O}) + \sigma(\text{H-H})],$$

$$\epsilon/k (\text{O-H}) = [\epsilon/k (\text{O-O})\epsilon/k (\text{H-H})]^{1/2}.$$

3. Results and discussion

Asymmetric ccf's of the type (2) were observed for the off-diagonal (X, Z) and (Z, X) elements of the ccf of the molecular permanent dipole moment, defined by

$$C_1(t) \equiv \frac{\langle \mu_i(t) \mu_j(0) \rangle}{\langle (\mu_i^2 \mu_j^2)^{1/2} \rangle}. \quad (3)$$

These are illustrated in fig. 1, using two contiguous segments. The hatching is a measure of the uncertainty in the ccf's, which cut the $t=0$ axis (in picoseconds (ps)) at the same finite negative value within the noise. (Results from individual contiguous segments cut the axis at exactly the same negative value.) This is a measure of the symmetric ($D_g^{(2)}$) part of the complete D symmetry of shear [6-8]. The antisymmetric part ($D_g^{(1)}$) takes effect at $t>0$, and the overall symmetry is the asymmetric sum of these parts. These results echo closely those obtained with atomic ensembles [1-5], where the finite $t=0$ value is observed for the velocity ccf. In atomic ensembles the ccf's of orientation and rotational velocity are undefined. For water ensembles the orientation is fixed with the axis of the perma-

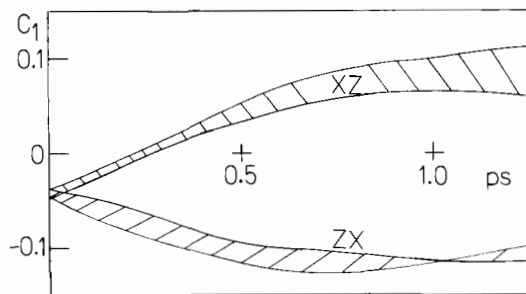


Fig. 1. The (X, Z) and (Z, X) elements [1-5] of the orientational time correlation matrix $C_1(t) = \langle \mu_i(t) \mu_j(0) \rangle$ for liquid water under a shearing force applied in the Z axis of the laboratory frame (X, Y, Z). Note that the elements are asymmetric and show the presence of shear induced dielectric relaxation.

nent molecular electric dipole moment, and the rotational velocity is defined as its time derivative. The Fourier transform of the auto correlation function of the dipole moment is essentially the spectrum of complex dielectric permittivity [13-15], and the Fourier transform of its second time derivative, the acf of rotational velocity, is essentially the power absorption coefficient and frequency dependent refractive index in the far infrared [16-19].

The simulations briefly reported here show that the shearing force changes the time dependence of both types of acf, (we also observed off-diagonal (X, Z) and (Z, X) elements of the rotational velocity acf) and we arrive at the important conclusions that shearing a molecular liquid affects both the dielectric and far infrared spectra of that liquid. This is despite the fact that no net orientation was observable, the spectral effect of shear is dynamical in nature, and is always accompanied by the emergence of asymmetric orientational ccf's as in fig. 1. Shear induced dielectric relaxation is a potentially useful method of investigating non-Newtonian response [1-5], because the experimentally accessible shear rates overlap with dielectric loss peak frequencies in samples of relatively high viscosity [13-15]. Our first results indicate that the orientational acf decays more quickly under shear, so that the peak frequency of the dielectric loss would be shifted to higher frequencies. The negative overshoot of the rotational velocity acf becomes much smaller under shear, and the overall decay rate is faster, indicating that the far

infrared spectrum is shifted to higher frequencies.

There are many possibilities opened up by these results, and systematic exploration of the new asymmetric ccf's as a function of effective strain rate will reveal the fundamental non-Newtonian molecular dynamics of a sheared ensemble.

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