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TRANSLATIONAL ANISOTROPY INDUCED BY A CIRCULARLY POLARISED
LASER FIELD APPLIED TO LIQUID WATER

M. W. Evans,* G. C. Lie, and E. Clementi

IBM Corporation
Data Systems Division
Dept. 48B / MS 428
Neighborhood Road
Kingston, New York 12401

*Permanent Address:
Department of Chemistry, Bourne Laboratory
Royal Holloway and Bedford New College
Egham Hill, Egham
Surrey TW20 0EW, U.K.
and
Honorary Research Fellow
Dept. of Physics
University of Lancaster
Lancaster LA1 4YB, U.K.

Abstract

A computer simulation of 864 water molecules subjected to an intense right circularly polarized laser field is shown to result in anisotropy of the molecular center of mass velocity autocorrelation function in the laboratory frame of reference. The phenomenon is explained qualitatively in terms of the cross correlation between molecular rotational and translational diffusion and is measurable experimentally in nematic liquid crystals.

I. Introduction

Recent computer simulations of the molecular dynamics of liquid water have revealed the phenomenon of electric field induced translational anisotropy.[1] The simulations were carried out with only 108 water molecules interacting with a pair potential devised by Evans[2] and based on the ST2 potential of Rahman and Stillinger.[3] In this paper the investigation has been extended to 864 water molecules interacting via the same five by five site-site pair potential but subjected to a circularly polarized laser field of high intensity, such as that found in a ruby laser pulse train. This paper reports that the well known phenomenon of optical saturation by a laser field applied to a molecular liquid[4] is accompanied by a hitherto unknown effect, laser field induced anisotropy in the molecular center of mass time auto correlation function (a.c.f.). The appearance of this type of anisotropy is accompanied by anisotropy in the far infrared spectrum, the Fourier transform of the rotational velocity auto correlation function.[5] There is also anisotropy in the angular velocity time auto correlation function in the laboratory frame (x,y,z). The laser field exerts no direct body force on the molecular center of mass, and the development of anisotropy in a saturating laser field, especially that in the linear center of mass a.c.f., is taken in this paper to be evidence of the ever present statistical correlation between rotation and translation in molecular diffusion processes. Conversely, the new anisotropy phenomena may be measured experimentally under favorable conditions, and used as information on the fundamental cross correlation properties of diffusing molecules.

II. Computer Simulation Methods

Using a sample of 864 water molecules a laser field of the type

$$E_x = 0 \tag{1}$$

$$E_y = E_0 \cos(\omega t)$$

$$E_z = E_0 \sin(\omega t)$$

where E_0 is the electric field strength and ω is the frequency of the applied field. The field will produce a torque

$$\mathbf{T_q} = -\mu \times \mathbf{E} \tag{2}$$

on each molecule of the ensemble, where μ is the molecular dipole moment, and this results in a net macroscopic effect which is investigated by standard molecular dynamics constant volume simulation as explained elsewhere in more detail.[6-12] It should be noted that at field on equilibrium the sample of 864 water molecules has a total energy considerably above that at field off equilibrium because of the extra potential energy imparted to the liquid molecular ensemble by the applied laser field. In this case the extra potential energy amounts to about 20 kJ per mole. The kinetic energy (i.e., the temperature) of the system at field on and field off equilibrium is about the same, i.e. the sample is effectively "thermostatted".

The intermolecular potential parameters are as follows

$\epsilon/k(H-H) = 21.1K$

$\epsilon/k(O-O) = 58.4K$

$\sigma(H-H) = 2.25A$

$\sigma(O-O) = 2.80A$

$q_H = -q_e = 0.23|e|$

where the usual notation has been used for the Lennard-Jones parameters σ and ϵ/k of the hydrogen and oxygen atoms, and where the partial charges used are the same in magnitude and relative geometry as in the well known ST2 potential of Stillinger and Rahman[3,13-15] This is a potential which has been checked carefully for liquid water under a very broad range of conditions, ranging from splat quenched at liquid helium temperatures to 240 kbar generated by shock waves.[16] The potential has also been compared with far infrared data obtained by submillimeter laser spectroscopy and interferometry.[17]

The input molar volume of the simulation was set at 18.0 cm³ per mole, corresponding to 293 K at one bar. The time step was 0.5 fs and the equations of motion for the 864 water molecules were integrated with the well tried algorithm TETRA which is fully described in the literature.[18] This uses a conventional Verlet method for integrating the translational equations of motion, and integrates the rotational equation from the net torque, computed in turn from the net atomic forces experienced by each molecule. The algorithm uses periodic boundary conditions with cut off potential at half box length. Finally in this work the motion of each diffusing molecule in the applied laser field can be illustrated graphically by video animation as in previous work on a small 108 molecule sample. The animation shows that each molecule spins around its center of torque, but does not undergo net translational diffusion as in a vortex.[20]

Results and Discussion

The main results of this investigation are illustrated in Fig. 1 which shows the field induced anisotropy in the center of mass velocity autocorrelation function. Note that all correlation func

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tions between dynamical variables a and b shown in Fig. 1 and subsequent figures are all normalized by $<a^2>^{1/2} <b^2>^{1/2}$. It can be seen clearly from this figure that the time dependence of the x component is composed of slower oscillation than in the y and z directions. The axis of the applied laser field is the x axis, and it is therefore clear that the laser has the effect of making the dynamics anisotropic in the laboratory frame (x,y,z). The explanation of this new effect is not a simple one, because the applied laser field exerts only a torque, (Eq. 2), and not a direct body force. Anisotropy in the rotational and reorientational dynamics must therefore be transmitted during the molecular diffusion process to direct anisotropy in the translational molecular motion in the picosecond time range. It is reasonable to assume that the intermediate mechanism for transmission of laser induced rotational anisotropy to translational anisotropy must involve direct and indirect statistical cross correlation between rotation and translation which does not appear in conventional theories of molecular diffusion.[21-25]
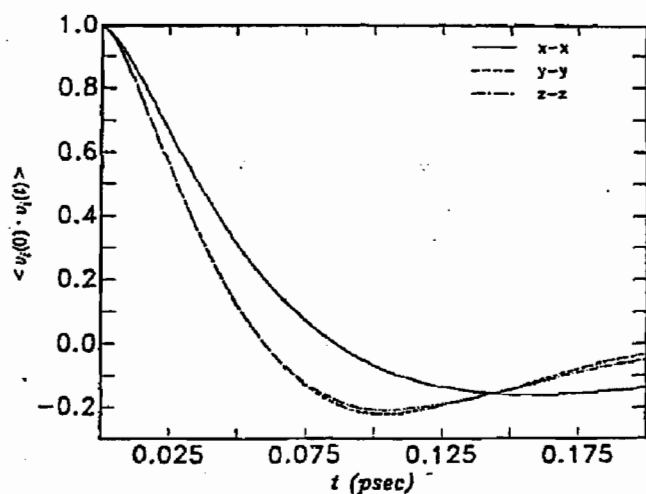

Fig. 1: Illustration of laboratory frame anisotropy in the linear center of mass velocity autocorrelation function under the influence of a right circularly polarized laser field.
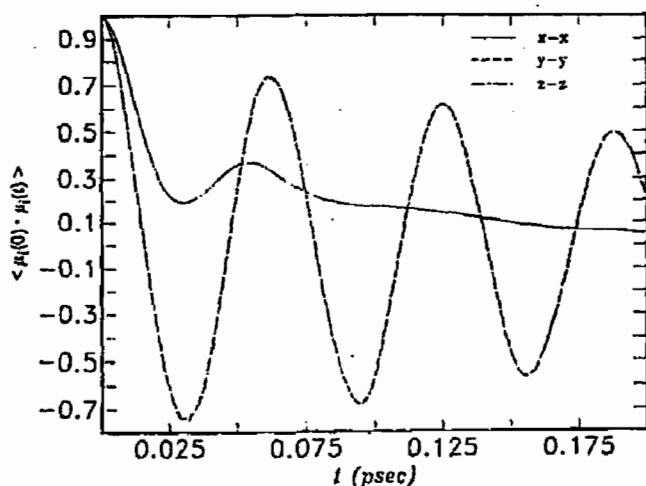

Fig. 2: As for Fig. 1, anisotropy in the orientational autocorrelation function.
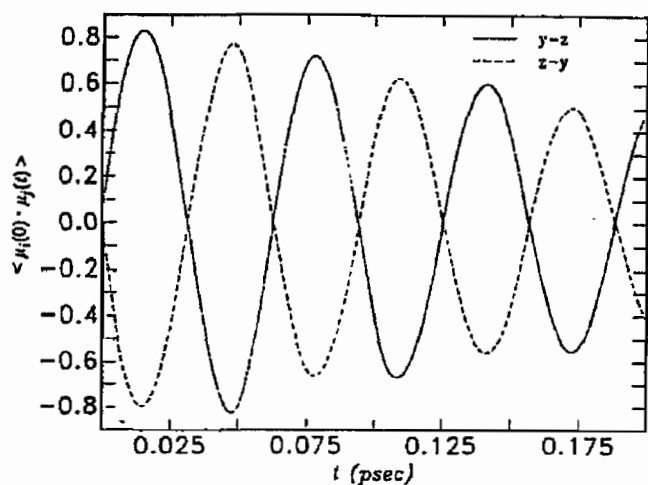
Fig. 3: Cross correlation between the y and z elements of the laboratory frame autocorrelation function.

It is significant in this context that the laser field also induces pronounced anisotropy in the orientational autocorrelation function of the molecular dipole moment, as illustrated in Fig. 2. It is again clear from this figure that the component of the autocorrelation function in the x axis of the laboratory frame of reference has a time dependence considerably slower than those in the other two axes, which are oscillatory. Fig. 3 shows that the y and z elements of the orientational autocorrelation function are correlated with each other in a symmetrical pattern, the correlation vanishes at t = 0.

These results are similar to those expected in the well known phenomenon of electric field induced birefringence[26] and in the Kerr effect, but the contemporary theory of electric field induced birefringence[27-28] has no explanation for the new effect reported in Fig. 1, and which is clearly related to orientational anisotropy induced by a laser field.[27] Previous work on the computer simulation of anisotropy induced by a simple electric field in a small sample of 108 water molecules has resulted in the same observation of first order birefringence both in the orientational and rotational velocity autocorrelation function accompanied by the new type of anisotropy in the linear center of mass velocity autocorrelation function.[29,30]

Therefore, both a laser field and a simple electric field promote anisotropy in linear molecular diffusion which can only be explained through statistical cross correlation.

There are several clues available to the nature of these cross correlations, which have been studied extensively over the past five years by computer simulation.[31-35] One of these is the promotion by a simple electric field of direct laboratory frame correlation[36,37] between the molecular center of mass velocity and the same molecule's angular velocity a time t later. Another, Fig. 4, is the cross correlation in the laboratory frame between the z and y components of the linear velocity autocorrelation function. This means that the laser field forces the molecule to move on a circular track as well as to correlate its angular motion, i.e., to spin about the x axis. The combined motion of each diffusing
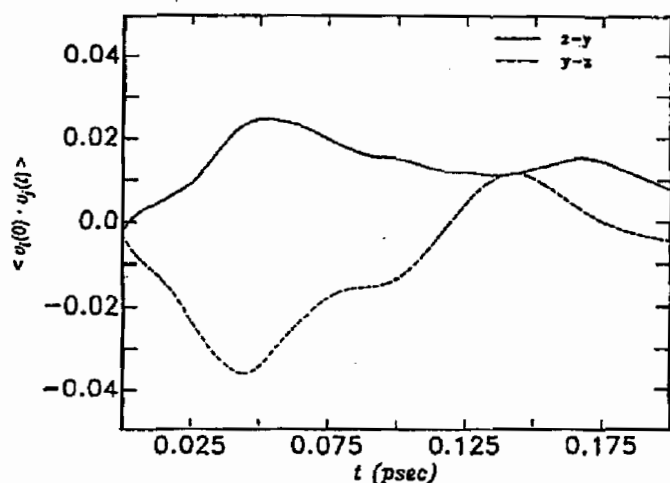
Fig. 4: As for Fig. 3, linear center of mass velocity autocorrelation functions.

molecule in response to the laser field is therefore spin superimposed on orbital motion about the axis of the imposed laser field, the x axis. The orbital and spin motions are statistically correlated in the laboratory frame of reference, and this should be observable with probes such as the dynamical Kerr effect spectroscopy,[38] N.M.R. spin lattice relaxation,[39] and far infrared spectroscopy.[40]. The medium most responsive to the imposed circularly polarized laser field should be an aligned nematic liquid crystal at room temperature.[41] To avoid heating effects, techniques are available for the implementation of pulses of laser radiation of very great power from a Nd-YaG laser, or a giant ruby laser.

In order to investigate in more depth the nature of statistical cross correlation generated by the applied laser field we have computed in this work some time cross correlation functions in the laboratory frame (x,y,z) and also in the frame (1,2,3) of the principal molecular moments of inertia of water, i.e,. the frame defined by the dipole axis 1, and the mutually perpendicular axes 2 and 3. Fig. 5 typifies the results in frame (1,2,3) by illustration of the cross correlation function between the molecular Coriolis acceleration, $v(t) \times \omega(t)$, and the molecular linear velocity, v. In comparison with the field off elements available elsewhere in the literature,[42] these moving frame cross correlation functions are more oscillatory, and show a strong interdependence between rotational and translational variables. In other words the two motions are always linked, and the cross correlation becomes stronger in the presence of the laser field. There is direct cross correlation between linear and angular velocity as illustrated in Fig. 6, which shows the oscillatory time dependence of the (2,3) element.

Computations in the absence of the field, (i.e. at field-off equilibrium are available in the literature both for 108 and 864 molecule samples,[43,44] and comparison between the field-off and field-on results shows that the latter are much more oscillatory and lower in intensity.

Directly in the laboratory frame of reference the cross correlation function between the molecular rotational velocity and the molecular center of mass linear velocity exists for finite t from funda-
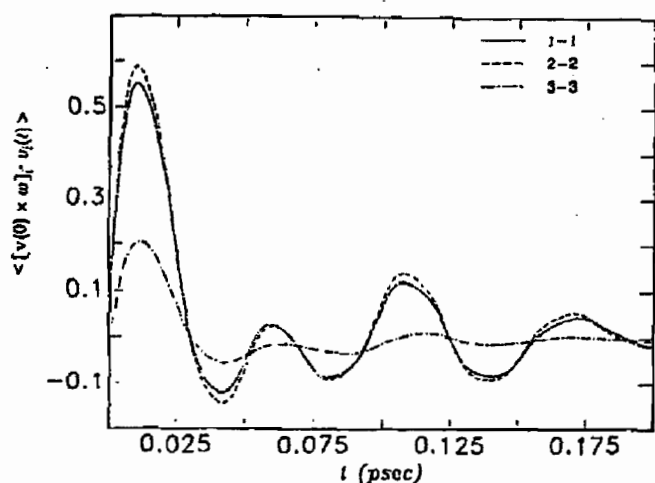
Fig. 5: Moving frame cross correlation function between the molecular Coriolis acceleration and the molecular linear velocity.
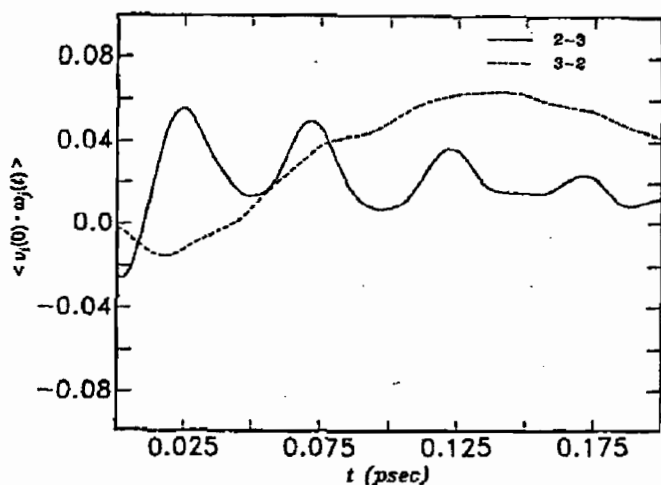

Fig. 6: Two elements of the moving frame cross correlation function between the molecular linear and angular velocity.

mental considerations and has been characterized recently in several computer simulations.[45] The rotational velocity vector is defined as the time derivative of the molecular dipole moment, μ, and its Fourier transform is well known to be the far infrared power absorption coefficient.[5]

In Fig. 7 we illustrate the auto correlation function of the molecular rotational velocity for liquid water in an applied right circularly polarized laser field. The anisotropy in the components of the autocorrelation function is clear from this figure. The components in the z and y axes are considerably more oscillatory than that in the x axis, which is also the axis of the applied field. This result means that a right circularly polarized electromagnetic field causes the far infrared spectrum of a molecular liquid to become birefringent. Consequently, the power absorption coefficient in the far
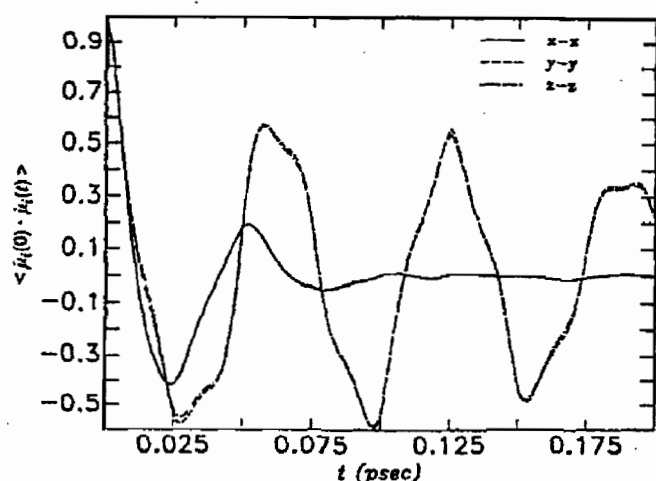
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Fig. 7: Anisotropy in the rotational velocity autocorrelation function.
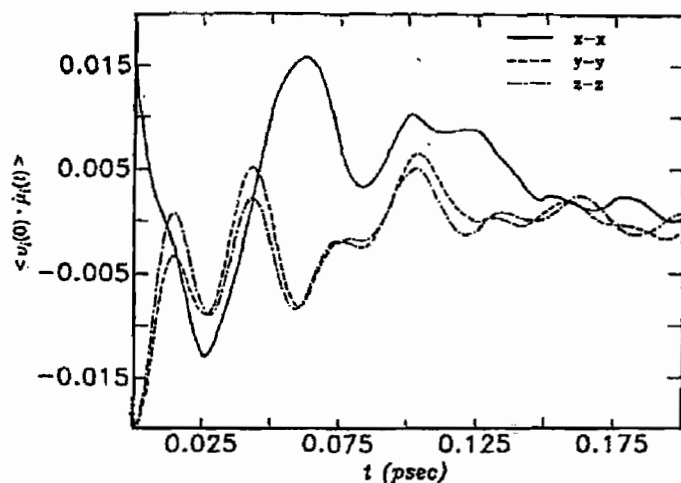

Fig. 8: Laboratory frame cross correlation between the rotational and linear molecular velocity.

infrared becomes different in intensity when viewed along the x axis and y axis of the laboratory frame, i.e., parallel and perpendicular respectively to the applied laser field. This effect is interesting in itself, and does not seem to have been reported in the literature, but of additional and fundamental interest is the cross correlation function of Fig. 8 between the molecular rotational velocity and the same molecule's linear center of mass velocity in the laboratory frame (x,y,z). Fig. 8 clearly shows a small but real correlation in the laser field between these two classical variables. The cross correlation in the x axis is again different from those in the two mutually perpendicular axes, and the cross correlation is, furthermore, finite at the time origin. These results therefore confirm that the molecular diffusion processes are statistically interdependent, and that the development of anisotropy in the components of the various auto-correlation functions illustrated in this paper is accompanied by changes in cross correlation between fundamental dynamical variables.

The optimum condition for the observation of effects induced by the applied laser field seems to be the nematic phase of liquid crystals at room temperature. It is known that nematics are sensitive to the application of electric and magnetic fields which are relatively weak in energy per unit time in comparison with the power available in pulses of laser radiation such as that from a giant ruby laser. In principle, therefore, the application of pulses of laser radiation in nematics should, according to the numerical results reported in this paper, produce measurable birefringence in interesting regions of the electromagnetic spectrum such as the far infrared, and also measurable anisotropy in the power absorption spectrum. Furthermore, trains of laser pulses applied to a nematogen should allow sufficient time for the far infrared measurements to be made with sufficient accuracy, while avoiding the heating effects which would be the inevitable accompaniment to prolonged treatment with an intense laser beam. Within each laser pulse the frequency of the applied circularly polarized laser field could be adjusted to that used in the simulation of this paper. i.e., 10^{14} Hz. By using the frequency of the applied electromagnetic field as a variable, interesting experimental information could be obtained about the cross correlation between various dynamical variables using computer simulation as a numerically intensive interpretative method. In other words the measured birefringence could be reproduced by computer simulation and the cross correlations of interest computed. Additionally a diffusion theory could be developed to explain the experimental and numerical results self-consistently. Some steps in this direction have been taken by the present authors, but a complete theory of three dimensional asymmetric top diffusion is still lacking.[49,50]

It is likely that significant effects of an applied electromagnetic field could be generated in probes of relaxational dynamics such as N.M.R. spin lattice relaxation[51] and inelastic, incoherent, neutron scattering.[52]

An applied field of the type (1) has the same symmetry as that of a rotating electric field, and will produce time correlation functions even to parity reversal as illustrated in this paper. The simulation of anisotropy in the linear velocity time autocorrelation function is consistent with these symmetry expectations. It has been assumed effectively that only the rotating electric field component of the circularly polarized field is effective at the frequencies considered. The k dependent part, operative at higher frequencies, would tend to destroy the birefringence effects observed here.

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