A MOLECULAR DYNAMICS SIMULATION OF ROTATIONAL FLOW INDUCED BY A LEFT CIRCULARLY POLARIZED HIGH-ENERGY INFRARED LASER FIELD

M.W. EVANS [1,2], G.C. LIE and E. CLEMENTI

Data Systems Division, Department 48B/MS 428, IBM Corporation, Neighborhood Road, Kingston, NY 12401, USA

Received 3 January 1987; in final form 1 May 1987

In a preliminary small-scale simulation, a high-energy, infrared frequency, left circularly polarized laser field has been used to induce rotational motion in liquid water at 293 K. The effect on the molecular dynamics has been analyzed subsequently using a range of molecular autocorrelation and cross correlation functions. The field symmetry is such as to make possible the existence in the laboratory and moving frames of reference of new cross correlation functions. The simulation shows laboratory-frame birefringence in the orientational and rotational velocity autocorrelation functions. The appearance of birefringence is coincident with that of cross correlations in the laboratory frame, and could be used experimentally for their determination, with computer simulation as an interpretative method.

1. Introduction

The present work is designed as a preliminary small-scale simulation [1–3] of rotational flow in a molecular environment in three dimensions. We consider liquid water in a left circularly polarized laser field, which is applied to a small sample of 108 water molecules. The electric component of the electromagnetic field is used to produce a torque on the water molecule through the vector product of the molecular dipole moment and the field. This produces an effect on the water molecule which is transmitted throughout the sample. In order to produce a measurable effect on the scale of the simulation the laser energy is made comparable with the thermal energy of the water sample at room temperature and pressure. The frequency of the field is adjusted to 1.6×10^{13} Hz in order to complement the time scale of the simulation (femto/picosecond range). Gigawatt power levels are routinely available with Nd:YAG lasers and the simulation could be matched experimentally in the laboratory. Note that rotating electric fields have been used for over sixty years to study vortex effects in molecular liquids, and the work in this area was summarized by Dahler [4], using hydrodynamics. The theory was first formulated by Born [5]. The present left circularly polarized laser field is a variation on the rotating electric field method, known theoretically to produce a vortex flow and a rotational torque on the walls of the container to which the field is applied.

This work is motivated by the potential ability of the computer simulation method to produce the classical phenomena of three-dimensional hydrodynamics from the dynamics of interacting molecules. Water is of supreme importance in practical flow engineering, and it is reasonable and important to work towards a full understanding of simple rotational flow in water in terms of time correlation functions. Our ultimate goal is the detailed and direct inter-relation of molecular dynamics with classical flow hydrodynamics. In this Letter we attempt to analyze the effect of induced rotational motion in terms of the symmetry of time correlation functions. An understanding of the various symmetry changes induced by the field will be useful in larger-scale simulations involving the natural phenomena of classical hydrodynamics, such as vortices and eddies. Our objective is the detailed understanding of flow effects in three dimensions in terms of the symmetry of fun-

[1] Permanent address: Department of Physics, University College of Swansea, Singleton Park, Swansea SA2 8PP, UK.

[2] Visiting Academic, Department of Microelectronics & Electrical Engineering, Trinity College, Dublin 2, Republic of Ireland.

0 009-2614/87/$ 03.50

damental molecular time correlation functions. This will unite two major branches of contemporary theoretical physics. Much bigger samples would be needed to verify whether the effects actually being observed through time correlation functions are visible macroscopic flows, and this will be the subject of future work in this laboratory.

2. Molecular dynamics simulation methods

The basic simulation algorithm is for 108 water molecules and is based on the well tried code TETRA, used many times for different molecular symmetries and fully described in the literature [6–9] [#1]. The water pair potential [11] is a three-site Lennard-Jones empirical representation with partial charges for the lone pair. The methods of generating flow in this work are equally applicable with the ab initio potentials for water [12,13].

The algorithm is coded to produce the thermodynamic properties of the sample, such as pressure, mean rotational and translational temperature, configurational energy, and site–site pair distribution functions. Time correlation functions were evaluated with running time averages over time segments of 6000 time steps of 0.5 fs each, recorded every two time steps.

The electric component of the left (or right) circularly polarized laser field is

$$\epsilon_x = 0, \quad \epsilon_y = \epsilon_0 \cos \omega t, \quad \epsilon_z = \pm \epsilon_0 \sin \omega t, \qquad (1)$$

where (x, y, z) is the coordinate frame of the laboratory, ω the field frequency, and ϵ the field strength. The + component is left circularly polarized, and the − component right circularly polarized. The axis of the field is therefore the x axis of the laboratory frame. This electric component of the complete electromagnetic field is assumed to take effect on the H_2O molecule through the torque

$$(\boldsymbol{\mu} \times \boldsymbol{\epsilon})_R = \epsilon_0 \sin \omega t \, (\mu_y \boldsymbol{i} - \mu_x \boldsymbol{j}) + \epsilon_0 \cos \omega t \, (\mu_x \boldsymbol{k} - \mu_z \boldsymbol{i}), \qquad (2)$$

where $\boldsymbol{\mu}$ is the molecular dipole moment, and $\boldsymbol{i}, \boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in the x, y, and z axes respectively.

[#1] For a review of field effect computer simulations, see ref. [10].

This torque was coded into the forces loop of the algorithm TETRA and was applied either to all the molecules in the sample or to the inner cube molecules as the case may be.

3. Results and discussion

The circularly polarized laser field has the effect of promoting the existence in the laboratory frame (x, y, z) of time cross correlation functions (CCFs) which vanish at field off equilibrium. This is in response to an applied field equivalent to 18.7 kJ/mole in the total energy of the system. This is clearly a rotational effect of the left circularly polarized laser field. Both the rotational and translational temperatures increase upon application of the external field because of the energy imparted to the system by the laser. The temperature increase is countered by the temperature rescaling of the constant volume algorithm, which is used as a thermostat. This is programmed to keep the temperature at the input temperature of 293 K.

The appearance of the laboratory frame CCFs is accompanied by the development of birefringence, and one effect may therefore be consequent upon the other. If so, then the birefringence could be used experimentally to obtain actual practical information on the new laboratory frame CCFs. The birefringence phenomenon seems to be akin to rotational-flow-induced birefringence, and is evidence of the ability of the computer simulation method to predict new phenomena [14]. The birefringence is illustrated in fig. 1 through the different time dependences of the x, y, and z components in the laboratory frame of reference. Simultaneously, the (y, z) and (z, y) components of the orientational time correlation tensor appear in the laboratory frame and are illustrated in fig. 2. The overall effect of the circularly polarized field is therefore to induce the symmetry change

$$\begin{bmatrix} + & 0 & 0 \\ 0 & + & 0 \\ 0 & 0 & + \end{bmatrix}_{(x,y,z)} \rightarrow \begin{bmatrix} + & \delta & \delta \\ \delta & + & + \\ \delta & - & + \end{bmatrix}_{(x,y,z)}$$

in the orientational ACF tensor. The notation used above means that the existence of a time dependence

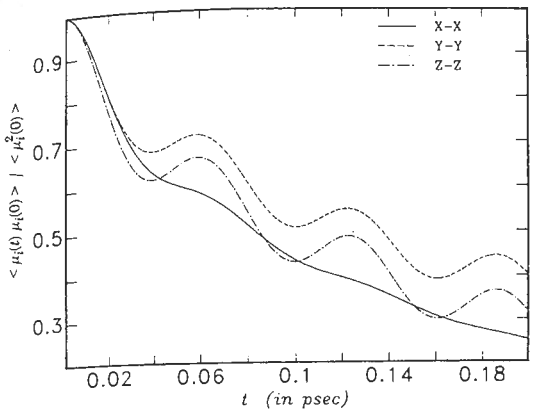

Fig. 1. Illustration of birefringence in the orientational ACF induced in the laboratory frame by the left circularly polarized field whose axis is the x axis of the laboratory frame (x, y, z). $i=x, y$, or z.

in the diagonal elements is unaffected by the application of a field. In contrast, the left polarized field promotes the existence of off-diagonal elements yz and zy which vanish in the absence of the field. The first peak of yz is positive and the first peak of zy is negative. We have observed similar effects in this work on a range of other autocorrelation and cross correlation tensors, which will be reported in full elsewhere. Here we restrict our discussion to two well known lab frame ACFs which are fundamental to the theory of dielectric relaxation and far-infrared spectroscopy respectively: the orientational (or dipole ACF), considered in the early classical work of Born,

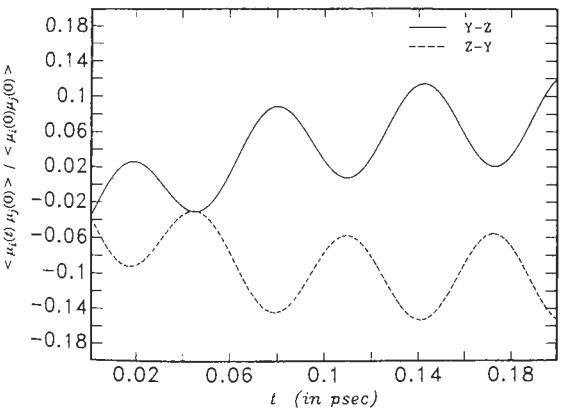

Fig. 2. Off-diagonal elements of the orientational time correlation tensor in the laboratory frame of reference induced by the same field as for fig. 1. Note the mirror image symmetry. $i, j=x, y$, or z.

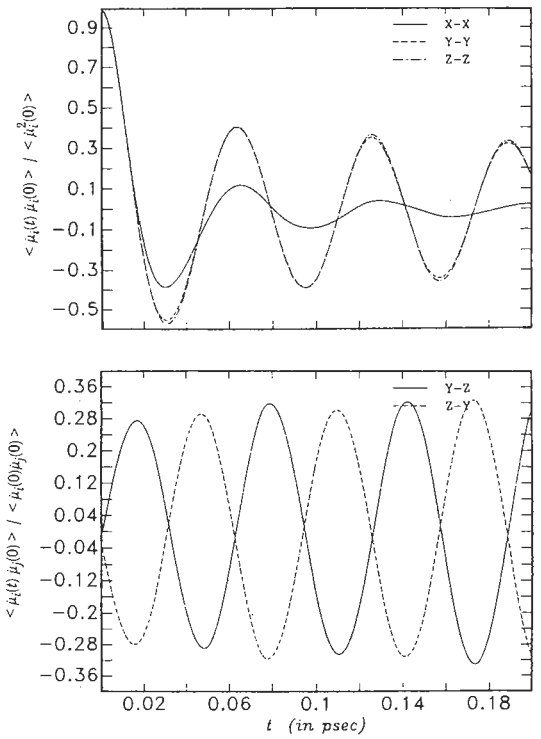

Fig. 3. (a, top) Birefringence in the rotational velocity ACF induced by the circularly polarized laser field as in fig. 1. The results of the figure imply birefringence in the far-infrared. (b, bottom) The off-diagonal elements (y, z) and (z, y) of the rotational velocity ACF induced by the same field as for (a). The appearance of the cross correlation functions is linked to that of measurable birefringence.

and the rotational velocity ACF. The latter is the time ACF of the derivative of the dipole unit vector, and its Fourier transform is essentially speaking the far-infrared spectrum. The overall effect of the laser-induced rotational motion on the rotational velocity time correlation tensor is to promote anisotropy in the diagonal elements (fig. 3) and to make possible the existence of four new off-diagonal elements, so that the symmetry of the tensor is affected as follows

$$\begin{bmatrix} + & 0 & 0 \\ 0 & + & 0 \\ 0 & 0 & + \end{bmatrix}_{(x,y,z)} \rightarrow \begin{bmatrix} + & \delta & - \\ \delta & + & + \\ + & - & + \end{bmatrix}_{(x,y,z)} .$$

Figs. 1 to 3 therefore show that both the dielectric and far-infrared spectra will be birefringent in the presence of the left polarized field. This results from

the different orientations along the x axis and the y and z axes. The relevance of this to hydrodynamics may be seen most clearly by reference to the theoretical work of Born and the experimental work of Lertes in the early 1920s [16] later greatly elaborated by Grossetti [17] and Dahler [4]. These authors show experimentally and theoretically that a circular electric field of the form

$$\epsilon = \epsilon_0 \, \mathrm{Re}[(\boldsymbol{i} + \mathrm{i}\boldsymbol{j}) \, \mathrm{e}^{-\mathrm{i}\omega t} \sin\psi + \boldsymbol{k} \cos\psi]$$

applied to a molecular liquid suspended in a thin walled glass sphere by a torsion wire results in a macroscopic torque on the walls of the sphere caused by cooperative flow. The effect is accompanied by a shift in the Debye relaxation time [4] and therefore in the far-infrared spectrum, the high-frequency adjunct of the dielectric spectrum.

The birefringence induced by the laser field is accompanied by the appearance of cross correlation functions (fig. 3), but there is at present no direct way of relating the one to the other with an analytical theory of molecular diffusion. The left circularly polarized field used in this simulation is precisely the same as the rotating field considered theoretically by Dahler in his hydrodynamic calculations [4]. Dahler succeeded in explaining the shift in the Debye relaxation time induced by the rotating electric field using the hydrodynamics of "structured" media. The small scale simulation used here has succeeded in finding an analogous effect of birefringence, which is accompanied by the appearance of laboratory frame cross correlation functions. In a larger scale simulation, using, say, 100000 water molecules over a million time steps, and mimicking water suspended in a thin glass walled container, it might reasonably be expected that the phenomenon described theoretically by Born [5] and experimentally by Lertes [16] would be reproduced by computer simulation. In this eventuality, we would have achieved our aim of linking the two branches of contemporary theoretical physics involved in the description of an essentially simple observation first made some sixty five years ago. In the language of molecular dynamics the phenomenon would be understood in the language of time cross correlation functions; in the language of hydrodynamics we would understand in great detail why a simple rotating electric field produces a macroscopic torque on a molecular liquid to which it is applied. We would understand all this furthermore in terms of the Newton equations themselves. We regard the results of this paper as a small step towards this end.

Acknowledgement

MWE would like to thank IBM, Kingston for a visiting professorship. Discussions with Drs. E.L. Hannon and S. Kandadai are also acknowledged.

References

[1] L. Hannon, E. Kestemont, G.C. Lie, M. Mareschal, D.C. Rapaport, S. Chin and E. Clementi, IBM Tech. Rept. "Chaire Francqui" Lecture Series, Part 7 (Feb. 1986).
[2] D.C. Rapaport and E. Clementi, Phys. Rev. Letters 57 (1986) 695.
[3] E.L. Hannon, G.C. Lie and E. Clementi, Phys. Letters A119 (1986) 174.
[4] J.S. Dahler, in: Research frontiers in fluid dynamics, eds. R.J. Seeger and G. Temple (Interscience, New York, 1965).
[5] M. Born, Z. Physik 1 (1920)22.
[6] M.W. Evans, Physica 131B&C (1985) 273.
[7] M.W. Evans, Phys. Rev. A31 (1985) 3947.
[8] M.W. Evans, Phys. Rev. A30 (1984) 2062.
[9] M.W. Evans, Physica Scripta 30 (1984) 91.
[10] M.W. Evans, P. Grigolini and G. Pastori Parravicini, eds., Memory function approaches to dynamical processes in condensed matter (Wiley–Interscience, New York, 1985).
[11] M.W. Evans, J. Mol. Liquids 32 (1986) 173.
[12] G.C. Lie and E. Clementi, Phys. Rev. A33 (1986) 2679.
[13] O. Matsuoka, E. Clementi and M. Yoshimine, J. Chem. Phys. 64 (1976) 1351.
[14] G.J. Evans, M.W. Evans, P. Minguzzi, C.J. Reid, P. Salvetti and J.K. Vij, J. Mol. Liquids, to be published.
[15] M.W. Evans, Phys. Rev. Letters 55 (1985) 1551; M.W. Evans and G.J. Evans, Phys. Rev. Letters 55 (1985) 818; Phys. Rev. A34 (1986) 468.
[16] P. Lertes, Z. Physik 4 (1921) 315; 6 (1921) 56; 22 (1921) 621.
[17] E. Grossetti, Nuovo Cimento 10 (1958) 193; 13 (1959) 621.