Journal of Molecular Liquids, 37 (1988) 59–75
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

NUMERICAL TEST OF THE NONSTATIONARY CHARACTER OF THE CORRELATION FUNCTIONS FOR MICROCANONICAL ENSEMBLES AT SHORT TIMES

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(Received 30 March 1987)

ABSTRACT

Recently Chatzidimitriou-Dreismann has challenged the basic theorem which relates the two stationary correlation functions $\langle B(0)B(t)\rangle$ and $\langle \dot{B}(0)\dot{B}(t)\rangle$ of statistical thermodynamics:

$$\langle \dot{B}(0)\dot{B}(t)\rangle = -\frac{d^2}{dt^2}\langle B(0)B(t)\rangle$$

where the dynamical variable B is, for example, a molecular

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0167-7322/88/$03.50

vector. In this paper the theorem is tested to a precision of one part in a million for the unit vectors along the principal molecular moment of inertia axes of an asymmetric top. The rotational velocity correlation function is fitted with a twenty-five term Chebyshev polynomial and the latter is integrated numerically to give a twenty seven term polynomial expression for the orientational a.c.f. The above relation is tested out rigorously for microcanonical ensembles consisting of 108 molecules each of a) compressed hydrogen selenide gas; b) liquid tritium oxide; c) a nonequilibrium but stationary sample of water subjected to an intense uniaxial z axis electric field. Small Dreismann effects are found in cases b) and c); effects which are about three orders of magnitude greater than the numerical precision of the fitting method used.

INTRODUCTION

It is assumed in the equilibrium and, more generally, stationary nonequilibrium theory of molecular dynamics that for dynamical variables B(t) that depend on the canonical variables of a small number s of particles of a classical N particle ensemble the equalities

$$d^2\langle B(0)B(t)\rangle/dt^2 = -\langle\dot{B}(0)\dot{B}(t)\rangle \qquad (1)$$

are in general true, as can be proved in a straightforward manner from fundamental considerations. Recently, however, Chatzidimitriou-Dreismann has challenged [1] this basic theorem, basing his consideration on the assumption of two body interactions, and building up the hamiltonian on these grounds. For reasons of clarity he also assumed that the liquid is made up of monatomic particles and that the interactions between particles have a finite spatial range. The correlation functions of the time dependent dynamic variables B and $\dot{B}$ can then be written in terms of s particle liouvillians and distribution functions [2,3] which depend on coordinates and momenta of each particle in the system. It is found that the second derivative theorem (1) holds rigorously for N particle dynamical functions ($N \sim 10^{23}$) but for s particle dynamical functions, where s<<N, the equality is no longer always true.

The Dreismann effect can therefore be defined as the <u>difference</u> predicted theoretically in ref. (1), between the r.h.s. and l.h.s. of equ. (1). The analytical prediction can be tested rigorously in a computer simulation, where the dynamics of s particles are considered, so that the correlation functions on the right and left hand sides of equ.(1) can be produced self-consistently. This paper attempts to show that in one such algorithm, there is a non-vanishing Dreismann effect for t>0, in other words the computer simulation shows that for s=108 the simulated correlation function on the left hand side of equ.(1) is not equal to the simulated correlation function on the right hand side for t>0. This is provided as the first numerical evidence for the analytical theory of [1].

In this paper we use the technique of molecular dynamics computer simulation to test the analytical theory [1] with a relatively small ensemble of 108 molecules under equilibrium conditions; a) in a condensed gas; b) in liquid tritium oxide, a T bonded liquid; and finally for a stationary ensemble of H_2O molecules out of equilibrium due to the strong alignment effect of a uniaxial electric field applied in the z axis. The analytical results of [1] hold true also for polyatomic molecules and for cross-correlation functions of time, and can be tested numerically as follows.

NUMERICAL METHODS

The numerical problem is to check against the results of molecular dynamics computer simulation [4-11] whether or not the rotational velocity autocorrelation function (r.v.c.f), for example, is the precise second time derivative of the orientational a.c.f. for a limited number (s) of pairwise interacting molecules, e.g. the 108 used in the simulation. This would check whether there is a difference between the r.h.s. and the l.h.s. of equ.(1). The method adopted was to fit the former very precisely with a Chebyshev polynomial and then to integrate the polynomial numerically, while defining carefully the constant of integration. Using this method it was found possible to fit the r.v.c.f. to one part in a million for all t. Furthermore, precision is gained and not lost by numerical integration, so that the test provided by this method is <u>precise to at least one part in a million</u> for both the rotational velocity and the orientational a.c.f.'s. Up to twenty five terms of the Chebyshev polynomial expansion were used to fit the rotational velocity a.c.f. and after two numerical integrations a twenty seven term expansion becomes available to fit the orientational a.c.f.

This was achieved for input molecular dynamics simulation data using the N.A.G. routines EO2AGF and EO2AKF.

The Chebyshev polynomial was integrated using the N.A.G. routine EO2AJF, and the orientational a.c.f. obtained in this way from the rotational velocity a.c.f. compared with the equivalent from computer simulation, obtained entirely self consistently with the same set of simulation trajectories, using the basic [12] kinematic relation:

$$\dot{\underline{\mu}} = \underline{\omega} \times \underline{\mu} \, . \tag{2}$$

In the computer simulation it is not assumed that the one correlation function is the second time derivative of the other. In equ.(2) $\underline{\mu}$ is the molecular dipole moment and $\underline{\omega}$ the molecular angular velocity. The two correlation functions are, however, obtained using the same number of time steps and under precisely similar thermodynamic conditions using the same algorithm to compute the running time averages. Therefore they are obtained entirely self consistently and there is no reason to suppose that one is any less precisely computer simulated than the other.

CHECKS ON THE NUMERICAL INTEGRATION METHOD

A check to machine precision on the UMRCC CDC 7600 was carried out on the accuracy of the numerical integration algorithm. The first step consisted of the simple integration

$$\iint \cos(t)\ dt\ dt = -\cos(t) \tag{3}$$

The initial machine generated cosine function was fitted accurately with a twenty five term Chebyshev polynomial so that the fitted cosine was indistinguishable from the original cosine to machine single precision (about fifteen decimal places). The Chebyshev polynomial expansion of the cosine was then integrated numerically twice to produce the coefficients of a twenty seven term Chebyshev sum. This was then evaluated for all t and it was checked that this gave the original machine generated cosine with all signs reversed, as implied in equ. (3), to machine single precision.

The Constant of Integration

Having carried out this check for the elementary double integration of the cosine there remains the need to determine the role of the constant of integration and to incorporate into the algorithm a method of evaluating this under exactly self consistent conditions with the computer simulation of each correlation function. The proper constant of integration for the results from the computer simulation can be found by a Taylor series expansion [2] of the (classical) orientational a.c.f.:

$$\langle\underline{\mu}(t)\cdot\underline{\mu}(0)\rangle = 1 - \langle\dot{\underline{\mu}}(0)\cdot\dot{\underline{\mu}}(0)\rangle\frac{t^2}{2!} + \langle\ddot{\underline{\mu}}(0)\cdot\ddot{\underline{\mu}}(0)\rangle\frac{t^4}{4!} - \ldots \tag{4}$$

Double differentiation of the Taylor series leaves at t=0 the constant $-\langle\dot{\underline{\mu}}^2(0)\rangle$. If the numerical integration exercise is carried through by fitting a rotational velocity a.c.f. initially normalised to unity at the time origin, as in the computer simulation then the proper constant of integration is:

$$-\langle\underline{\mu}^2(0)\rangle/\langle\dot{\underline{\mu}}^2(0)\rangle.$$

This was incorporated into the numerical integration algorithm and after evaluation from exactly the same set of molecular dynamics data as used in the computation of the individual rotational velocity and orientational autocorrelation functions. If the data being considered are for an asymmetric top molecule then the three individual ratios:

$$\langle \underline{e}_1^2 \rangle / \langle \dot{\underline{e}}_1^2 \rangle; \quad \langle \underline{e}_2^2 \rangle / \langle \dot{\underline{e}}_2^2 \rangle; \quad \langle \underline{e}_3^2 \rangle / \langle \dot{\underline{e}}_3^2 \rangle$$

were evaluated from the same segment of simulation data, where $\underline{e}_1$, $\underline{e}_2$ and $\underline{e}_3$ are unit vectors in the three principal molecular moments of inertia. The rotational velocity and orientational a.c.f.'s of each of these vectors can be obtained from the simulation and the second derivative theorem (1) explored for each ratio.

MOLECULAR DYNAMICS SIMULATION METHODS

A sample of 108 molecules was chosen to represent the stationary ensemble. The conditions chosen to test the considered theoretical prediction [1] ranged from a compressed gaseous sample of hydrogen selenide to a T bonded sample of liquid tritium oxide at room temperature. A stationary, non equilibrium sample of liquid water subjected to an intense uniaxial electric field was also investigated using the same number (108) of water molecules. The following sections deal in turn with the conditions under which the simulations were carried out, the nature of the potential, the time step, number of time steps per segment, and so on. Common to each computer simulation is the use of periodic boundary conditions, the pairwise interaction approximation; and centre of mass to centre of mass cut off of the interaction potential.

Compressed Hydrogen Selenide Gas

This is a C_{2v} triatomic asymmetric top with one very heavy central (Se) atom attached to two very light hydrogen atoms. It was simulated in the gaseous state at 300K at a molar volume of 404.1 cm^3. A literature bond length of 1.47 Å was used with the known [13] included angle of 91°. The pair potential was mimicked with a three by three Lennard Jones potential with atom-atom parameters as follows:

σ(H-H) = 2.40 Å; ϵ/k(H-H) = 21.1 K;

σ(Se-Se) = 3.90 Å; ϵ/k(Se-Se) = 218.0 K.

It is known that hydrogen bonding in liquid hydrogen selenide, unlike liquid water, is negligible, and in consequence it was not considered necessary to mimick H bonding with for example an ST2 type of potential [14]. The mass distribution in hydrogen selenide is such that the Se atom is about 79 time heavier than each H atom. This makes the principal moment of inertia distribution very anisotropic, and in this paper we attempt to explore the consequencies for the three orientational and three rotational velocity autocorrelation functions. The Lennard-Jones parameters used in this simulation produced a pressure satisfactorily constant at about six bar of compressed gas, with a much smaller uncertainty of about 0.5 bar either side of the computed mean.

For each simulation segment the rotational equation of motion for the 108 molecules were integrated by computing the torque from the resultant forces on each atom. The torque is evaluated at four points in time before being integrated numerically for the angular momentum. This integration proceeds in four stages, is relatively time consuming, but accurate. The translational equation of motion in TETRA, the simulation algorithm, is valid for the polyatomic asymmetric top provided that this is rigid. It uses periodic boundary conditions and centre of mass to centre of mass cut off criteria. It uses periodic boundary conditions in an entirely conventional cubic array, the melt run being carried out from a face centred lattice. The number of atoms in each molecule and the number of molecules can be increased indefinitely provided the computer time is available. It incorporates corrections for long range forces and has facilities for using pair potentials of the site-site type. For input temperature and molar volume the mean pressure is computed, together with the relevant thermodynamic parameters such as the mean internal energy, potential energy, and translational and rotational kinetic energy. The run can be stopped and restarted at will, and therefore an indefinite number of steps can be used. The restrictions on time steps and number of molecules reported in this paper are purely economic.

Liquid Tritium Oxide

This is a modified ST2 potential which includes atom-atom terms centred both on the oxygen and tritium atoms. This method eliminates automatically the need to use the switching function devised by Stillinger and Rahman [15]. The empirical pair potential is then described as follows:

$$\varepsilon/k(O-O) = 58.4K;\ \sigma(O-O) = 2.8\ \text{Å};$$

$$\varepsilon/k(^3H-^3H) = 21.1\ K;\ \sigma(^3H-^3H) = 2.25\ \text{Å};$$

$$\varepsilon/k(O-H) = [\frac{\varepsilon}{k}(O-O)\cdot\frac{\varepsilon}{k}(^3H-^3H)]^{1/2};$$

$$\sigma(O-H) = \frac{1}{2}\cdot(\sigma(O-O) + \sigma(^3H-^3H));$$

where ε/k and σ are the usual atom-atom Lennard Jones parameters. In addition the original tetrahedral arrangement of charges in the ST2 potential was used unchanged together with the original ST2 geometry. The time step used was 0.5 femtosecond, with no Ewald corrections and simple cubic periodic boundary conditions. The total mean configurational energy at 300K, molar volume = 18.07 cm^3/mole, was for a typical segment of about 1000 time steps -35.2 kJ/mole. Long range corrections were applied to the virial sum and to the total configurational energy for Lennard Jones terms only, because they diverge for charge-charge terms. The range of a.c.f.'s illustrated in Section III were evaluated with running time averages over two or more segments of 1000 time steps each.

Liquid Water Subjected to an Intense Uniaxial Electric Field

These results were obtained using a sample of 108 water molecules as described in detail elsewhere [15]. The H_2O pair interaction potential was the same as that used above for liquid tritium oxide, although the mass distribution among the atoms was of course different.

With a time step of 0.5 femtosecond and no Ewald corrections the mean configurational energy at 300K, molar volume 18.07 cm^3/mole, for a typical segment of about 1000 time steps was -35.5 kJ/mole. This compares with -34.3 kJ/mole at 314 K obtained by Stillinger and Rahman [16] also in the absence of Ewald corrections. For two body interactions the inclusion of Ewald sums by Clementi et al. [17] reduced the internal energy from their Monte Carlo simulation to -38.6 kJ/mole, and their consideration of three and four body terms brought this closer to the experimental result of -41.0 kJ/mole. After equilibration, rise transients and fall transients to and from a nonequilibrium configuration can be generated using the technique developed by Evans and described fully elsewhere [18]. Essentially speaking, the application of a uniaxial, static, electric field $\underline{E}$ in the lab. frame z axis produces the torque $-\underline{\mu}x\underline{E}$ on each molecule in the absence of any polarisability effects. If the unit vector $\underline{e}_1$, is defined in axis $\underline{1}$ the equilibrium average $\langle e_{1z}\rangle$ becomes nonzero as a result of this torque. The field is applied at t=0 and the rise transient brings the sample to a stationary but non equilibrium condition in the sense that the potential energy is higher than it would be in the absence of the field [19].

RESULTS AND DISCUSSION

Liquid Tritium Oxide

The rotational velocity and orientational a.c.f.'s and the constants of integration were simulated self consistently from a segment of 886 time steps of 0.5 fsec recorded every two time steps. This provided 443 records from which the relevant averaging was carried out using the same algorithm for both correlation functions. The ratios of relevance were averaged for each record over the 108 molecules of the sample. For liquid tritium oxide this gave the results

$$\langle e_1^2\rangle/\langle \dot{e}_1^2\rangle = 1/136.998 \times 10^{-24}s^2;$$

$$\langle e_2^2\rangle/\langle \dot{e}_2^2\rangle = 1/147.644 \times 10^{-24}s^2;$$

$$\langle e_3^2\rangle/\langle \dot{e}_3^2\rangle = 1/61.913 \times 10^{-24}s^2;$$

which were then used in the numerical integration algorithm. The simulated rotational velocity a.c.f. was fitted with a twenty five term Chebyshev polynomial to a precision of one part in a million as described already, and the numerical integration then carried out to give the twenty seven term Chebyshev polynomial as described above. For tritium oxide the results of this fitting are illustrated in fig. (1). The vector $\underline{e}$ coincides in direction with the dipole moment vector $\underline{\mu}$. In fig. (1a) the comparison is made between the two correlation functions $\langle \underline{e}_1(t)\cdot\underline{e}_1(0)\rangle$ and $\langle \dot{\underline{e}}_1(t)\cdot\dot{\underline{e}}_1(0)\rangle/\langle \dot{e}^2\rangle$ from the simulation and numerical integration. The simulated and fitted a.c.f.'s are indistinguishable on this scale but there is a small difference of about one part in a thousand between the simulated and numerically integrated results for the orientational a.c.f. This difference is given in detail in table (1). The difference is small relative to the value of unity taken by the a.c.f. at the time origin, but is estimated to be at least <u>three orders of magnitude larger</u> than the precision with which the rotatinal velocity a.c.f. was fitted. Bearing in mind that the technique used of integration with the NAG routine E02AJF increases numerical precision rather than decreasing it as in numerical differentation then fig. (1) and table (1) are presented as the first evidence for the effect predicted analytically.

Similar results were obtained for the tritium oxide r.v.c.f.'s and orientational a.c.f.'s pertaining to the vectors $\underline{e}_2$

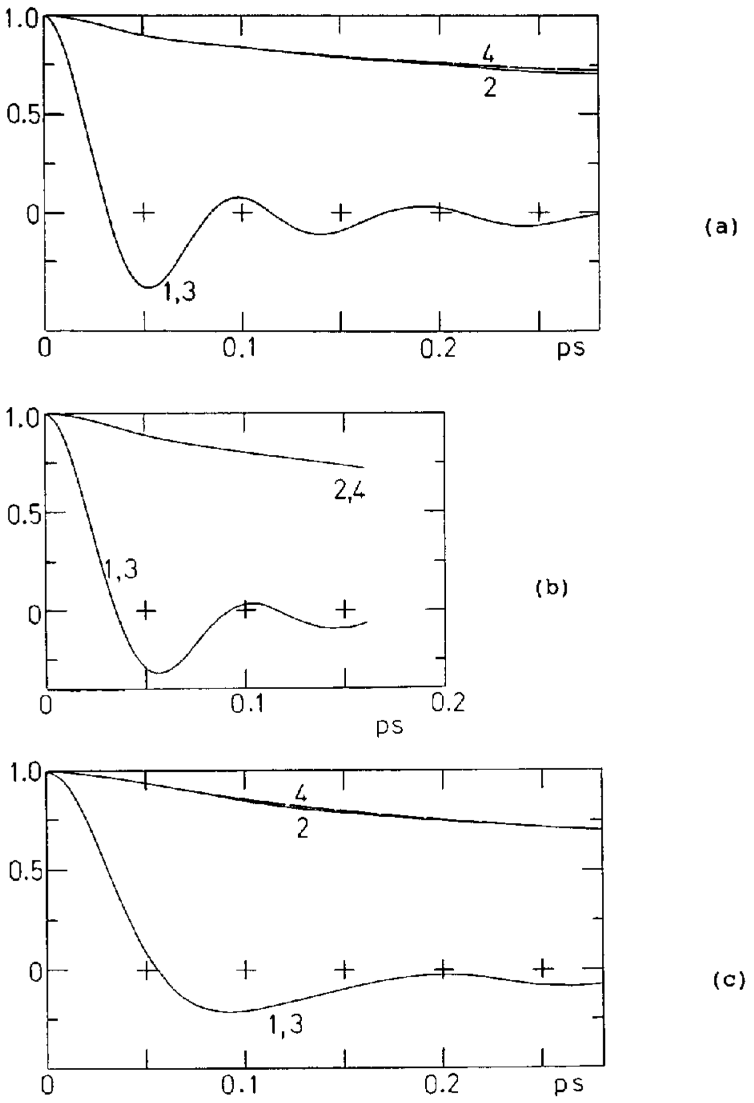

Fig.1. Curve 1: Rotational velocity a.c.f. of liquid tritium oxide obtained from the computer simulation. Curve 3: Fit to curve 1 using a 25 term Chebyshev polynomial. Curve 2: Orientational a.c.f. obtained from the computer simulatin. Curve 4: Fit to curve 2 using a 27 term Chebyshev polynomial integrated from 3.
Figure (a): Results for the orientational unit vector $\underline{e}_1$.
Figure (b): Results for $\underline{e}_2$. Figure (c): Results for $\underline{e}_3$.

TABLE 1. Dreismann Effect in $\langle \underline{e}_2(t)\cdot\underline{e}_2(0)\rangle$ for Liquid Tritium Oxide

t/ps	Autocorrelation Function	
	Simulated	Integrated
0.00	1.00000	1.00000
0.05	0.99589	0.99789
0.10	0.99052	0.99251
0.15	0.98203	0.98400
0.20	0.97101	0.97296
0.25	0.95817	0.96010
0.30	0.94425	0.94614
0.35	0.92997	0.93183
0.40	0.91593	0.91777
0.45	0.90261	0.90442
0.50	0.89034	0.89212
0.55	0.87928	0.88104
0.60	0.86945	0.87119
0.65	0.86073	0.86245
0.70	0.85295	0.85466
0.75	0.84583	0.84753
0.80	0.83912	0.84080

and $\underline{e}_3$. Here again the precision of the fitting of the r.v.c.f.'s was better than one part in a million for all t (i.e. for nearly one hundred input points along the time evolution of the a.c.f.). Again there was a difference of some one part in a thousand between the simulated and numerically integrated a.c.f.'s. Therefore this is presented as evidence for the Dreismann effect for the other orientational vectors of tritium oxide. The effect is therefore present for the three orientational vectors along the principal moment of inertia axes.

Compressed Gaseous Hydrogen Selenide

In this case the orientational a.c.f.'s are different in appearance to those for tritium oxide because of the anisotropy in the moment of inertia distribution of the hydrogen selenide molecule and the absence of hydrogen bonding in the compressed hydrogen selenide gas. The rotatinal velocity a.c.f.'s are highly oscillatory in appearance and generate in consequence oscillatory orientational a.c.f.'s.

The procedure described above for tritium oxide was adopted for hydrogen selenide with a self consistent set of simulation data from a segment consisting of 910 records, over which the a.c.f were computed by running time averages and the integration constants found to be

$$\langle e_1^2(0)\rangle/\langle \dot{e}_1^2(0)\rangle = 1/103.380 \times 10^{-24} s^2;$$

$$\langle e_2^2(0)\rangle/\langle \dot{e}_2^2(0)\rangle = 1/135.828 \times 10^{-24} s^2;$$

$$\langle e_3^2(0)\rangle/\langle \dot{e}_3^2(0)\rangle = 1/99.331 \times 10^{-24} s^2.$$

The effect under consideration for compressed gaseous hydrogen selenide was found to be very small, less than one part in ten thousand. This result indicates that the dynamics of correlations, which cause the effect under consideration, are more pronounced in a liquid than in a gas. This is in line with the general ideas of nonequilibrium statistical mechanics; cf. ref.(1).

Liquid Water in a Nonequilibrium Condition.

In this case the r.v.c.f.'s of the three orientational vectors are highly oscillatory in appearance and generate in consequence oscillatory orientational a.c.f.'s, as for hydrogen selenide. The origins of the oscillations are, however, different, they are induced by the electric field which holds the molecules

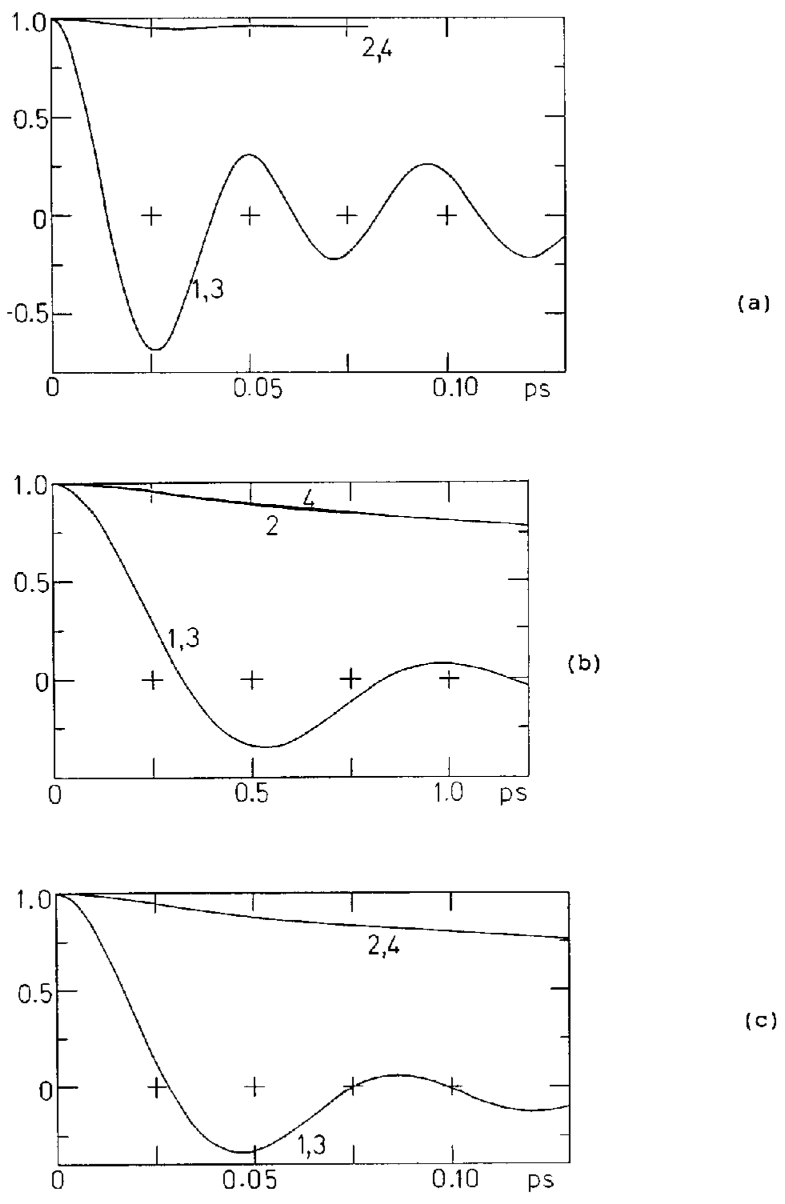

Fig.2. As for figure 1; liquid water in an external electric field.

TABLE 2. Nonequilibrium Water $\langle \underline{e}_1(t)\cdot\underline{e}_1(0)\rangle$ Correlation Function

t/ps	Autocorrelation Function	
	Simulated	Integrated
0.000	1.0000	1.0000
0.005	0.9940	0.9962
0.010	0.9839	0.9860
0.015	0.9706	0.9728
0.020	0.9582	0.9604
0.025	0.9496	0.9518
0.030	0.9462	0.9485
0.035	0.9474	0.9498
0.040	0.9515	0.9538
0.045	0.9558	0.9581
0.050	0.9584	0.9607
0.055	0.9588	0.9611
0.060	0.9575	0.9598
0.065	0.9554	0.9580
0.070	0.9547	0.9572
0.075	0.9553	0.9579
0.080	0.9574	0.9601

in a nonequilibrium state due to an externally imposed torque.

As for the other two microcanonical ensembles considered in this paper, the rotational velocity a.c.f. was fitted with the twenty five term Chebyshev expansion to one part in a million or better for all input data and the orientational a.c.f was generated from this fitting using the twenty seven term integrated Chebyshev polynomial. The difference between the orientational a.c.f. obtained in this way from the numerical integration and the simulated a.c.f. is shown in table (2) for the motion of the unit vector in the dipole axis of the principal moment of inertia frame. The difference is also just discernible on the scale of fig.(2) and is about one part in a thousand.

CONCLUSIONS

The existence of the effect predicted analytically in [1] is evidenced in this paper for a microcanonical ensemble of 108 molecules whose dynamical properties have been investigated using computer simulation. The equality in equ.(1) is not obeyed by the results from the simulation. The effect is about one part in a thousand in the picosecond interval of the evolution of the orientational a.c.f. as compared with its numerically exact second derivative. This effect is about three orders of magnitude greater than the precision of the determination of the correlation functions involved. Therefore it seems that a microcanonical ensemble of 108 molecules behaves dynamically in much the same way as the complete equilibrium ensemble, despite the fact that periodic boundary conditions were imposed in the usual way in the computer simulation. This is a good test therefore of the reliability of our algorithm, TETRA, whose results are reported in many papers and articles in the literature. Further work on cross-correlation functions showing the effect under consideration is in preparation.

ACKNOWLEDGEMENTS

The University of Wales is thanked for the Pilcher Senior Fellowship to MWE and IBM for a Visiting Professorship. CA C-D is indebted to Churchill College, Cambridge and the Fonds der Chemischen Industrie (Frankfurt am Main) for the award of the "German Fellowship, 1985/1986".

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