

NONSTATIONARY CHARACTER OF CROSS-CORRELATION FUNCTIONS IN
STATIONARY NONEQUILIBRIUM ENSEMBLES: A COMPUTER SIMULATION STUDY

M.W. EVANS*

Department of Physics, University College of Wales, Singleton
Park, SWANSEA SA2 8PP (Great Britain)

C.A.CHATZIDIMITRIOU-DREISMANN

I.-N.-Stranski-Institute for Physical and Theoretical Chemistry,
Technical University of Berlin, D-1000 Berlin 12 (Federal Republic
of Germany)

(Received 9 April 1987)

ABSTRACT

Recently it has been proved that equalities like $\langle \dot{a}(t)\dot{b}(0) \rangle = -d^2 \langle a(t)b(0) \rangle / dt^2$ are in general not valid in stationary ensembles; here a and b are dynamical variables of the particles. In this paper we put forward the first evidence of the new effect by investigating the nonstationary behaviour of electric field induced cross-correlation functions in the laboratory frame of reference. It is found that there is a large effect in the subpicosecond time range as predicted in the original analytical paper by Chatzidimitriou-Dreismann.

*Present address: IBM 48B/428, Neighborhood Rd., Kingston, NY
12401 (U.S.A.)

INTRODUCTION

In the theory of correlation functions in classical ensembles [1] at thermal equilibrium (or, more generally, in stationary ensembles) the theorem

$$\langle \dot{a}(t)\dot{b}(0) \rangle = - \frac{d^2}{dt^2} \langle a(t)b(0) \rangle \quad (1)$$

seems to hold true very generally. Here a and b are dynamical variables [2]. A proof of (1) is given by the following derivation:

$$\begin{aligned} d^2 \langle a(t)b(0) \rangle / dt^2 &= d \langle \dot{a}(t)b(0) \rangle / dt = d \langle \dot{a}(0)b(-t) \rangle / dt \\ &= - \langle \dot{a}(0)\dot{b}(-t) \rangle = - \langle \dot{a}(t)\dot{b}(0) \rangle. \end{aligned}$$

However Chatzidimitriou-Dreismann has shown recently [3] that (1) can be violated, if the dynamical variables depend on a small number n of degrees of freedom of a N -particle condensed system ($N \sim 10^{23}$), and if sufficiently short times are considered. It also has been shown that the difference between the two terms appearing in (1) is intimately connected with the BBGKY hierarchy [2]. In more physical terms, the violation of (1) is due to s -particle correlations, where $n < s \ll N$.

The recent study [3] of (1), in the context of classical statistical mechanics, has been motivated by an earlier quantum mechanical consideration [4] of the "autocorrelation case" $a=b$ of (1), in connection with (i) the fundamental criticisms of standard linear response theory [5] made by van Vliet [6] and van Kampen [7] and (ii) the physical context of far-infrared absorption in molecular liquids.

The violation of (1) for the special case $a=b$ was checked very recently by Evans [8] using numerical integration of the rotational velocity autocorrelation function (a.c.f.) resulting from a 108 particle computer simulation under widely varying conditions. In this numerical work [8], the rotational velocity a.c.f. was fitted to one part in a million accuracy for all t

using a twenty five term Chebyshev polynomial expansion. The Chebyshev polynomial was then integrated twice with a numerical routine from the Numerical Algorithms Group Library [9] (N.A.G.) to give the polynomial representation of the orientational a.c.f. The resulting 27 term Chebyshev polynomial differed from the orientational a.c.f. produced by computer simulation to a few parts in a thousand, about three orders of magnitude greater than the estimated numerical accuracy of the integration routine. In this paper we present evidence for a much larger Dreismann effect in laboratory frame cross-correlation functions (c.c.f.) of the type $\langle J(t)v^T(0) \rangle$ where J is the molecular angular momentum and v the center of mass linear velocity of a water molecule. C.c.f.'s such as these only exist [10] in the laboratory frame in the presence of a uniaxial electric field which may be employed to keep the sample out of thermodynamic equilibrium but statistically stationary. Under these conditions, theoretical considerations based on ref. 3 predict that the theorem (1) is least valid, i.e. there is a large predicted Dreismann effect. In this paper it is shown that the numerical technique mentioned above produces under these conditions a Dreismann effect in the angular momentum a.c.f. of a few parts in a thousand, but in the c.c.f. the effect is much larger, a few percent or more at times a few tenths of a picosecond from the time origin. This effect is obtained by fitting the torque/force lab. frame c.c.f. to a few parts in a million, or less, using the twenty five Chebyshev expansion, then integrating numerically [8] twice to give the angular momentum/linear momentum c.c.f. under the same conditions.

The technique of molecular dynamics computer simulation was used to generate the original c.c.f.'s in a sample consisting of 108 water molecules held out of equilibrium with an intense z-axis electric field. The computer technique used to generate this stationary nonequilibrium sample is described in detail elsewhere in the literature [11-16], but a brief description of the numerical methods is given here in summary form.

NUMERICAL METHODS

The algorithm used for the computer simulation in this letter is available on request and described fully in the literature [11-14], together with the modifications needed [15,16] for the field on work. The algorithm integrates the equations of motion for 108 water molecules represented by a Lennard-Jones atom/atom potential with partial charges arranged in the ST2 configuration [17]. The model parameters are

$$\epsilon/k(\text{O-O}) = 58.4 \text{ K}; \quad \sigma(\text{O-O}) = 2.8 \text{ \AA};$$

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

$$\epsilon/k(\text{O-H}) = \left[\frac{\epsilon}{k}(\text{O-O}) \cdot \frac{\epsilon}{k}(\text{H-H}) \right]^{1/2};$$

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

together with the original ST2 charge/charge interactions. The ϵ/k and σ parameters above are the usual atom/atom Lennard-Jones parameters. The time step used was 0.5 femtosecond at room temperature (293 K) and one bar input pressure. The energy of the electric field applied was equivalent to 12.5 kT, producing an alignment in the sample equivalent to $\langle \underline{e}_A \rangle = 0.97 \pm 0.005$, where \underline{e}_A is a unit vector in the dipole axis of the water molecule. With no Ewald corrections the mean configurational energy at 300 K, molar volume $18.07 \text{ cm}^3/\text{mole}$, 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 [17] in the absence of Ewald corrections. For two body interactions the inclusion of Ewald sums by Clementi [18], for example, reduces the total configurational energy. After equilibration, rise transients and fall transients to and from a nonequilibrium configuration can be generated using the technique developed by Evans [15,16] and described fully elsewhere. Essentially speaking, the application of a uniaxial static electric field \underline{E} in the lab. frame z-axis produces the torque $-\underline{e}_A \times \underline{E}$ on each molecule in the absence of any polarisability effects. If the unit vector \underline{e}_A is defined in axis A the equilibrium average $\langle \underline{e}_A \rangle$ becomes non zero as a result of this

torque. The field is applied at $t > 0$ and the rise transient brings the sample to a stationary but nonequilibrium condition in the sense that the potential energy is higher than it would be in the absence of the field.

NUMERICAL CURVE FITTING AND INTEGRATION

The methods adopted to test the theorem of ref.3 numerically were as follows. The force/torque lab. frame c.c.f. was first fitted to one part in a million with the N.A.G. routine EO2AGF.

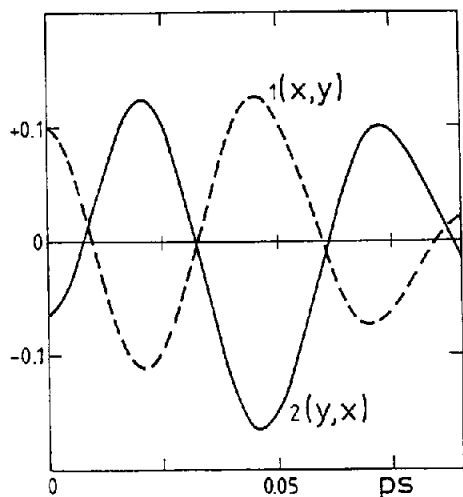


Fig.1: Simulated and fitted torque/force c.c.f.'s in the laboratory frame (x,y,z) for an applied z -axis electric field.

$\underline{1}$: (x,y) component, i.e. $\langle T_{qx}(t)F_y(0) \rangle / (\langle T_{qx}^2 \rangle \langle F_y^2 \rangle)^{1/2}$; $\underline{2}$: (y,x) component, i.e. $\langle T_{qy}(t)F_x(0) \rangle / (\langle T_{qy}^2 \rangle \langle F_x^2 \rangle)^{1/2}$.

The simulated and fitted quantities are indistinguishable on the scale of this figure.

The Chebyshev polynomial was then integrated numerically using the routine EO2AJF to provide the angular momentum/momentum c.c.f. The two c.c.f.'s in the computer simulation are not related analytically via a second derivative theorem (1) but the twenty seven term Chebyshev polynomial from the numerical routine EO2AJF is the precise double integral of the original twenty five term polynomial. The precision of the fitting to the (x,y) and (y,x) components of the force/torque c.c.f. is so high that the two curves (the simulated c.c.f. and the fitted Chebyshev polynomial) are indistinguishable on the scale of fig.1. The violation of the basic theorem (1) for cross correlation functions in the lab frame is then measurable by comparing the simulated and numerical c.c.f.'s of momentum/angular momentum, and this is described further as follows.

RESULTS AND DISCUSSION

Fig.2 compares the angular momentum/momentum c.c.f.'s derived as above, and it is clear that the two curves are not the same in time dependence. In Fig.2a is illustrated the (x,y) component of $\langle J(t)v^T(0) \rangle / (\langle J^2 \rangle \langle v^2 \rangle)^{1/2}$, both from the simulation (solid curve) and the numerical integration (dashed curve). The divergence begins at about 0.05 ps and becomes progressively greater as time increases. At about 0.08 ps the size of the effect under consideration reaches about 50 percent, and is therefore two orders of magnitude greater at this point than the equivalent in a.c.f.'s discussed already.

Because the applied field is in the lab. frame z-axis the (y,x) component of the considered c.c.f. also exists and is the mirror image of the (x,y) component, see fig. 2b. The Dreismann effect is also seen clearly in this component of the field induced lab. frame c.c.f.

Therefore this paper and its results are presented as the first evidence for the existence of the nonstationary effect between c.c.f.'s of the type predicted analytically [3]. We note that only one segment of the simulation run has been used but that

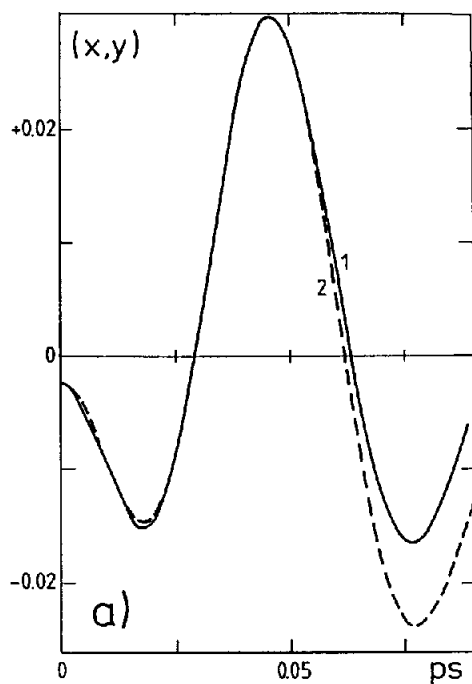


Fig. 2a.

1: Simulated angular momentum/momentum c.c.f., (x,y) component.
2: Calculated angular momentum/momentum c.c.f. as following from double integration of the fitted torque/force c.c.f., (x,y) component.

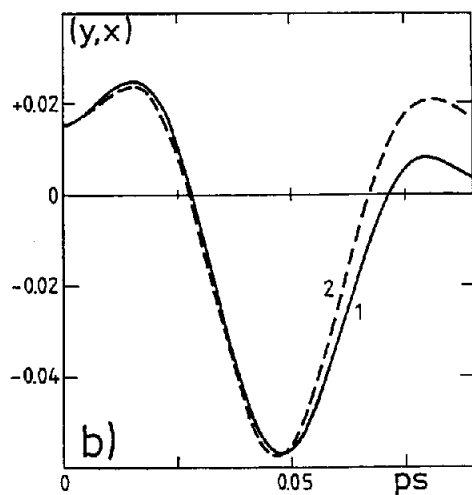


Fig. 2b.

As for figure 2a;
 (y,x) component.

is a sufficient and also necessary condition for the test of the theorem of ref.3 as carried out with the numerical integration method developed here. Indeed it would be inconsistent to use anything for this test except one segment (of 466 records each of two time steps) because the simulated force/torque and momentum/angular momentum c.c.f.'s must necessarily have been computed by running time averaging over precisely the same set of trajectories. Also taking into account that the double integrated (27 term) Chebyshev polynomial must be the precise numerical double integral of the 25 term polynomial then there is no alternative but to conclude from the divergence of fig.2 that the simulated c.c.f.'s do not obey theorem (1), thus according with the theoretical result of ref.3.

ACKNOWLEDGEMENTS

IBM is thanked for the award of a Visiting Professorship for MWE. CAC-D is indebted to the Churchill College (Cambridge, U.K.) and the Fonds der Chemischen Industrie (Frankfurt am Main) for the award of the "German Fellowship 1985/86".

REFERENCES

- 1 M.W. Evans, G.J. Evans, W.T. Coffey, and P. Grigolini, "Molecular Dynamics and the Theory of Broad Band Spectroscopy", Wiley Interscience, New York, 1982.
- 2 R. Balescu, "Equilibrium and Nonequilibrium Statistical Mechanics", Wiley, New York, 1975.
- 3 C.A. Chatzidimitriou-Dreismann, J. Math. Phys., 27 (1986) 2770.
- 4 E. Lippert, C.A. Chatzidimitriou-Dreismann, and K.-H. Naumann, Adv. Chem. Phys., 57 (1984) 311.
- 5 R. Kubo, J. Phys. Soc. Jpn., 12 (1957) 570.
- 6 K.M. van Vliet, J. Math. Phys., 19 (1978) 1345.
- 7 N.G. van Kampen, Phys. Norv., 5 (1971) 279.
- 8 M.W. Evans and C.A. Chatzidimitriou-Dreismann, J. Molec. Liq., submitted.

- 9 Numerical Algorithms Group Library, Vol.11.
- 10 M.W. Evans, *Physica B*, 131 (1985) 273; *Phys. Scripta*, 30 (1984) 94.
- 11 M.W. Evans, *J. Chem. Soc. Faraday Trans. II*, in press.
- 12 M.W. Evans, *Adv. Chem. Phys.*, 62 (1985) 183; M.W. Evans and G.J. Evans, *ibid.*, 63 (1985) 377.
- 13 M.W. Evans and G.J. Evans, *J. Chem. Soc. Faraday Trans. II*, 79 (1983) 767.
- 14 M.W. Evans, *Phys. Rev. Lett.*, 50 (1983) 371.
- 15 M.W. Evans, *J. Chem. Phys.*, 76 (1982) 5473.
- 16 M.W. Evans, *J. Chem. Phys.*, 76 (1982) 5480.
- 17 F.H. Stillinger and A. Rahman, *J. Chem. Phys.*, 60 (1974) 1545.
- 18 E. Clementi, *Analytical Potentials from Ab Initio Computations*, Chaire Francqui Lecture Series, Part 4, IBM Internal Report (Kingston, New York State).