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Computer Simulation and Group Theoretical Statistical Mechanics of Liquid Water and Methyl Chloride: Part 1, Neumann's Principle.

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Abstract

Neumann's Principle is applied to the molecular dynamics of liquids in the laboratory frame (X, Y, Z) and molecule fixed frame (x, y, z). In the absence of symmetry breaking influences, and in an isotropic medium of diffusing molecules, it states tha the totally symmetric irreducible representation is the key to whether a thermodynamic ensemble average exists in either frame. In liquid water, with molecules of C_{2v} symmetry, and liquid methyl chloride, with molecules of C_{3v} symmetry, the Neumann Principle, evaluated with the help of group theory, is found to be in agreement with computer simulations of components of linear and angular momentum auto correlation functions in both frames.

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Introduction

In a little known work of the nineteenth century, Neumann[1] proposed a potentially very useful principle[2] which can be applied to thermodynamic ensemble (i.e. running time) averages such as time auto and cross correlation functions, the building blocks of spectral analysis according to molecular dynamics[3-7]. On the grounds of symmetry alone, Neumann's Principle is able to isolate those correlation functions that vanish for all t from those that may exist by symmetry. In the laboratory frame (X, Y, Z) it states (in contemporary terms) that the thermodynamic ensemble average over a variable or product of variables exists if the relevant product of irreducible representations contains the totally symmetric representation (t.s.r.) of the $R_h(3)$ rotation-reflection group. If the averaging is carried out in another frame of reference, such as the molecule fixed frame (x, y, z) of the point group character tables, the t.s.r. is that of the molecular point group itself[8]. In the C_{2v} and C_{3v} point groups considered in this paper this is A_1. The number of occurrences of the t.s.r. signifies the number of independent averages which may exist in either frame.

In the presence of symmetry breaking fields, such as a static electric field, or a chiral influence such as that defined by Barron[2] more averages may become visible in either frame according to the field symmetry. For example, in a static electric field, the three dimensional isotropy of the $R_h(3)$ group is broken[9] and averages of the type $D_u^{(1)}$ may exist in frame (X, Y, Z), together with their counterparts in frame (x, y, z). A shearing field of symmetry

$$\frac{\partial v_X}{\partial Z} \; ; \quad \Gamma = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \tag{1}$$

applied in the laboratory frame might make possible the existence of all nine elements of appropriate response auto correlation functions (a.c.f.'s) in this frame according to Neumann's Principle. A typical example is the recent computer simulation proof[10] of the appearance of the cross correlation function (c.c.f.) between orthogonal velocity components

$$C_{XZ}(t) = < v_X(0)v_Z(t) > \quad \neq < v_X(t)v_Z(0) > \tag{2}$$

in the laboratory frame in response to a shearing field of type (1). This is the first observation of a time asymmetric c.c.f., which is a weighted sum of components due to vorticity and deformation which are respectively time antisymmetric and symmetric. This discovery was the result of an extension of Neumann's Principle to involve external field symmetries within the overall context of group theoretical statistical mechanics (g.t.s.m.).

In this paper some predictions of the Neumann Principle as applied to statistical mechanics are tested with computer simulations of liquid water and methyl chloride, respectively of C_{2v} and C_{3v} point group symmetry. Simulations of the velocity and angular momentum a.c.f.'s are carried out in frames (X, Y, Z) and (x, y, z), and the results compared with symmetry predictions in both frames. Predictions are also made concerning the behaviour of time c.c.f.'s in both frames.

Computer Simulation Methods

The simulations were carried out on the Cray 1s computer of the University of London using the algorithm TETRA, described elsewhere in the literature[11]. The intermolecular potentials for water and methyl chloride

were Lennard Jones atom atom terms with partial charge interactions . These potentials are also available in the literature[12]. The liquid water was simulated at a molar volume of 18.0 cm^3 $mole^{-1}$, and the liquid methyl chloride at a molar volume of 55.0 cm^3 $mole^{-1}$. The time step for water was 0.5 fs and for methyl chloride 5.0 fs. The correlation functions were computed by running time averaging during the production run.

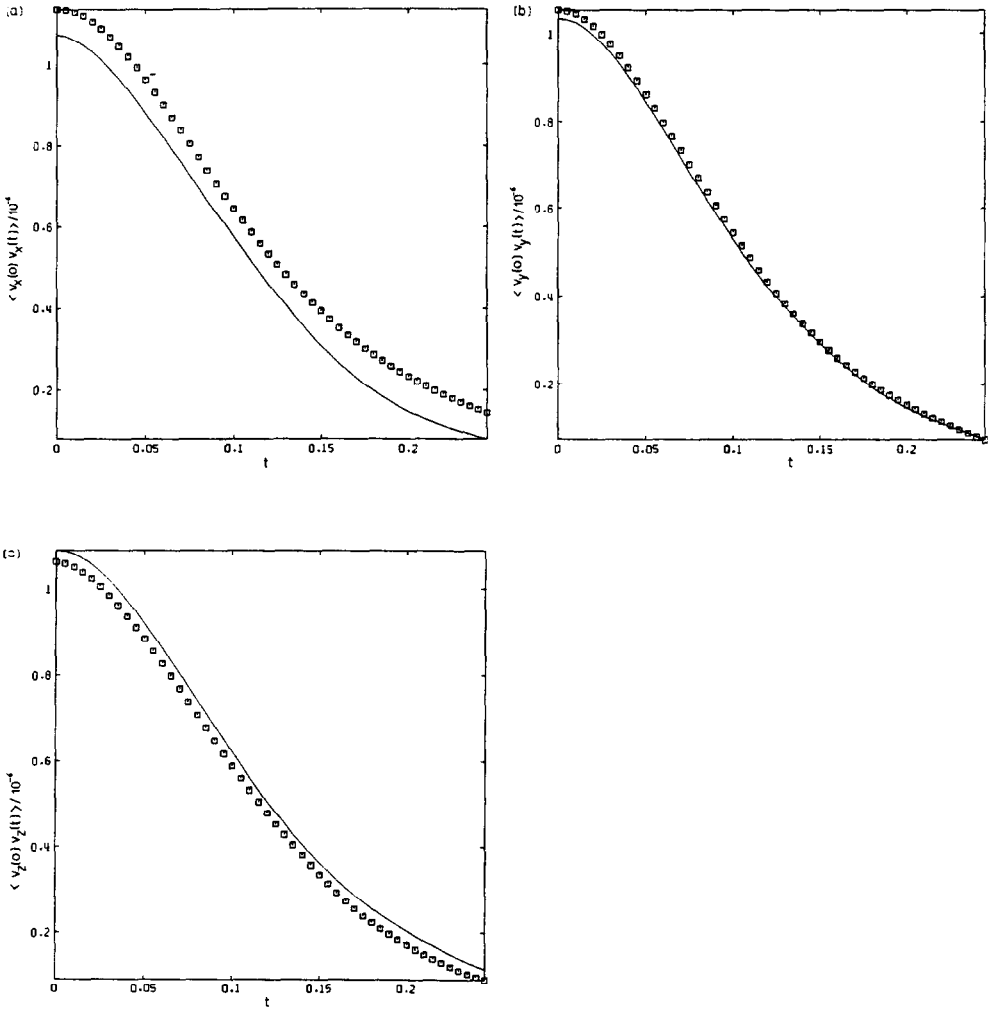

Figure 1

(a) The (X, X) component of the velocity a.c.f. for liquid methyl chloride in the lab. frame from computer simulation, showing two contiguous segments. (b) As for (a), the (Y, Y) component.

(c) As for (a), the (Z, Z) component.

The Application of Neumann's Principle

We consider the linear velocity (v) and angular momentum (J) a.c.f.'s in frame (X, Y, Z). The product of irreducible representations in each case is

$$\Gamma(v)\Gamma(v) = D_u^{(1)}D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$$
$$\Gamma(J)\Gamma(J) = D_g^{(1)}D_g^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \qquad (3)$$

where we have used the Clebsch Gordan Theorem[12] and standard notation for the irreducible (D) representations of the $R_h(3)$ rotation-reflection point group. The subscripts denote even (g) or odd (u) to parity

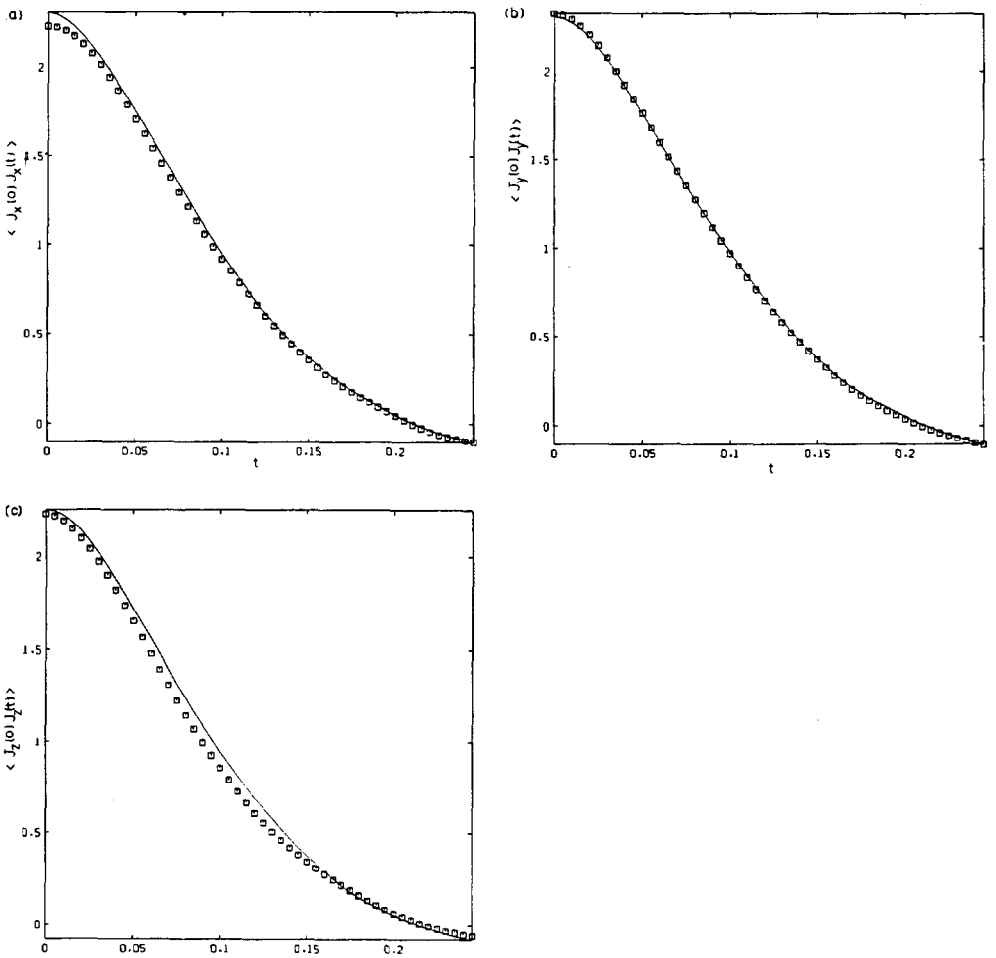

Figure 2

As for Fig. (1), the angular momentum a.c.f.

reversal, and the superscripts the order of the spherical harmonics. In both cases, and indeed for all time a.c.f.'s, the product contains the t.s.r. $D_g^{(0)}$. This signifies the existence of one independent element of the a.c.f., which in isotropic media is:

$$\begin{aligned} &< v_X(0)v_X(0) > = < v_Y(0)v_Y(t) > = < v_Z(0)v_Z(t) > \\ &< J_X(0)J_X(t) > = < J_Y(0)J_Y(t) > = < J_Z(0)J_Z(t) > \end{aligned} \tag{4}$$

This prediction is corroborated for the linear velocity a.c.f. of liquid methyl chloride in Fig. (1), showing the time dependence of each diagonal element to be tha same within the noise for two contiguous segments. The same is true in Fig. (2) for the angular momentum a.c.f. in frame (X, Y, Z). These reults are in agreement therefore with Neumann's Principle.

Fig. (3) shows how a Z axis electric field of symmetry $D_u^{(1)}$ breaks the isotropy of the trace of the tensor $< J(0)J^T(t) >$. The independent element $D_g^{(0)}$ now represents

$$\frac{1}{3}(< J_X(0)J_X(t) > + < J_Y(0)J_Y(t) > + < J_Z(0)J_Z(t) >)$$

The full symmetry is that of eqn. (3), but the $D_u^{(1)}$ electric field has no effect on the off diagonal elements. This has again been confirmed by computer simulation in this work.

The Molecule Fixed Frame, (x, y, z)

Liquid Methyl Chloride

In the C_{3v} point group the frame (x, y, z) is defined with reference to the literature point group character table. The $D_u^{(1)}$ symmetry of v maps on to $A_1 + E$ in this point group and the $D_g^{(1)}$ symmetry of J on to $A_2 + E$. In the isotropic liquid the relevant product of representations for the a.c.f.'s of v and J in frame (x, y, z) are respectively

$$\begin{aligned} &\Gamma(v)\Gamma(v) = (A_1 + E)(A_2 + E) = 2A_1 + A_2 + 3E \\ &\Gamma(J)\Gamma(J) = (A_2 + E)(A_2 + E) = 2A_1 + A_2 + 3E \end{aligned} \tag{5}$$

showing in each case the existence of two independent elements of the a.c.f. With reference to the point group character tables these are

$$\begin{aligned} &< v_x(0)v_x(t) > = < v_y(0)v_y(t) > \neq < v_z(0)v_z(t) > \\ &< J_x(0)J_x(t) > = < J_y(0)J_y(t) > \neq < J_z(0)J_z(t) > \end{aligned} \tag{6}$$

Thus, Neumann's Principle shows that the time dependence of two diagonal elements are the same , and the third is different. Figs (4) and (5) show that this is exactly what is found by computer simulation for two contiguous elements, each of about 4,000 time steps. Neumann's Principle is applicable both in the familiar lab. frame (X, Y, Z) and in the molecule fixed frame (x, y, z) of the standard point group character tables.

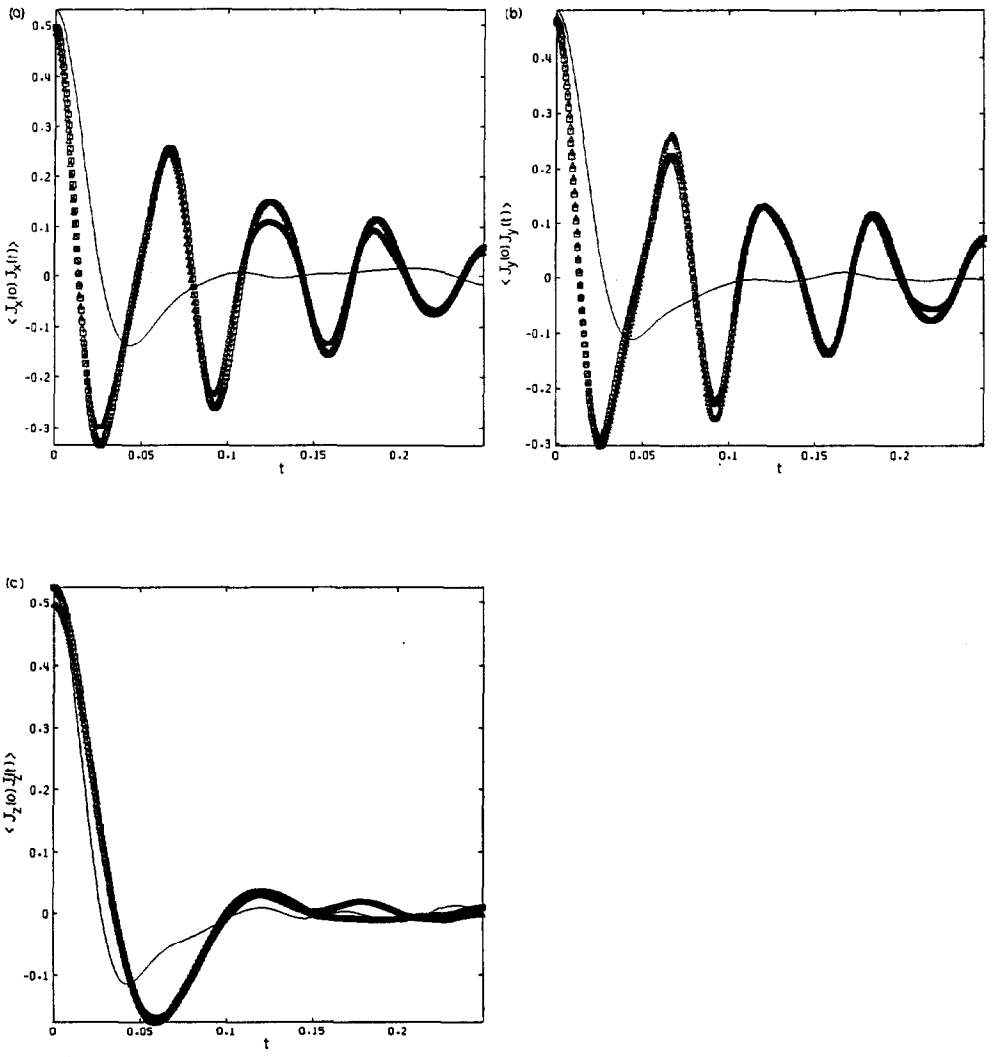

Figure 3

The angular momentum a.c.f., diagonal elements, simulated for liquid water in the laboratory frame (X, Y, Z). (a) Field on (points); field-off (line); (X, X) element. The points denote two contiguous runs. (b) As for (a), the (Y, Y) component. (c) As for (a), the (Z, Z) component.

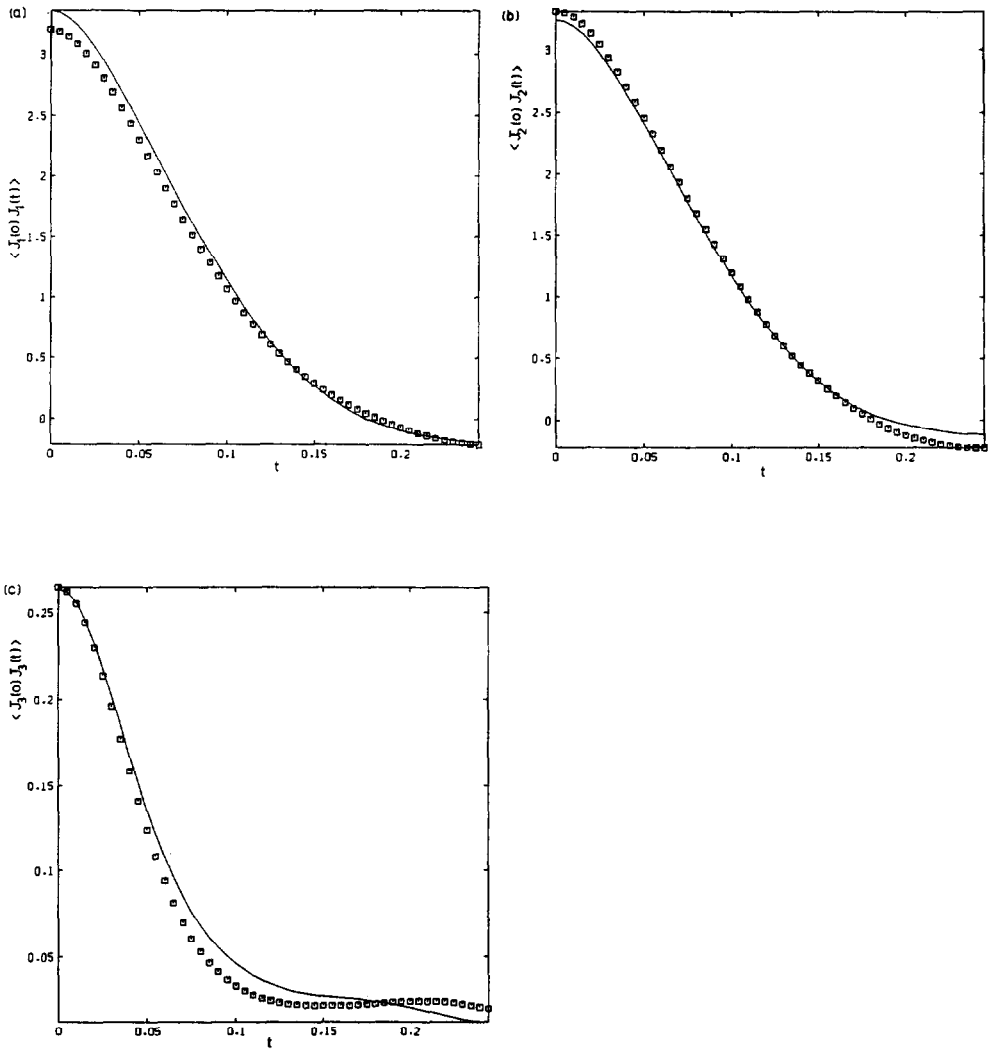

Figure 4

As for Fig. 2, moving frame (x, y, z) of the point group character table. Note that the time dependence of one element is different as predicted by group theory and Neumann's Principle. No applied electric field.

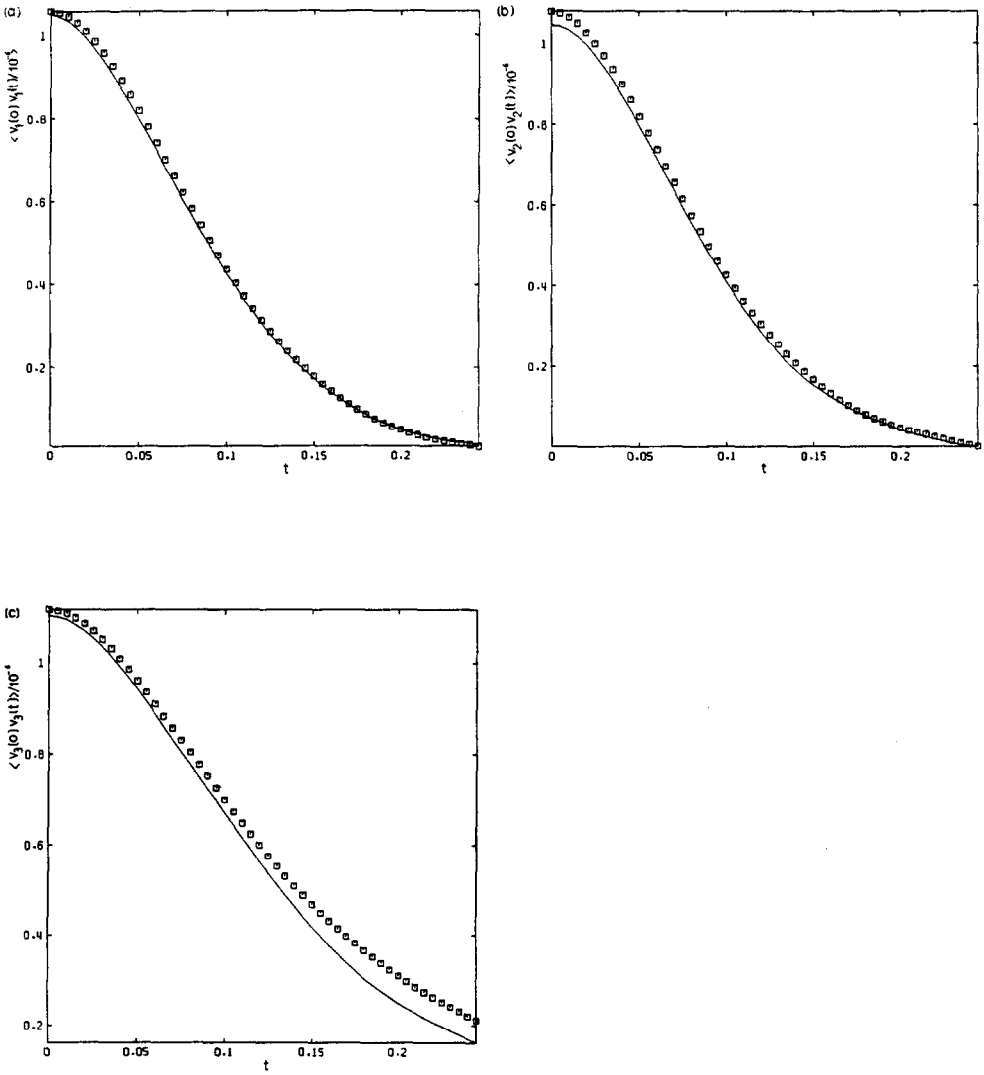

Figure 5

As for Figure (1), frame (x, y, z).

Liquid Water (The C_{2v} Point Group)

The product of representations of the velocity and angular momentum a.c.f.'s in this case are

$$\Gamma(v)\Gamma(v) = (A_1 + B_1 + B_2)(A_1 + B_1 + B_2) = 3A_1 + 2A_2 + 2B_1 + 2B_2 \tag{9}$$

which is the same for the angular momentum a.c.f. In either case there are three independent elements, which

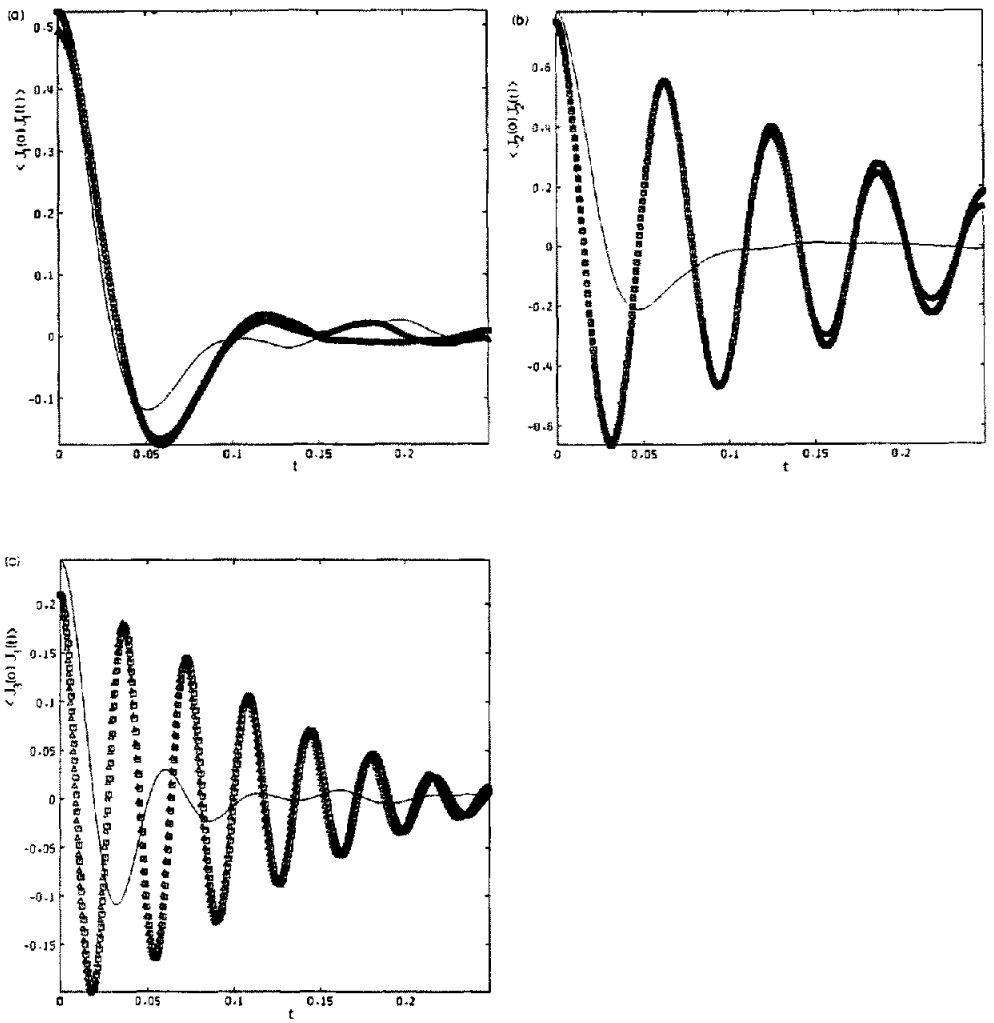

Figure 6

As for Figure 3, frame (x, y, z).

signify three independent diagonal elements. Again these symmetry predictions are confirmed by computer simulation as in Figs. (6) and (7). In these figures are illustrated the effect of a static electric field applied to the Z axis of the frame (X, Y, Z). The $D_u^{(1)}$ symmetry of the static electric field maps on to A_1 B_1 + B_2 of the frame (x, y, z) in the C_{2v} point group. We have seen the effect of the electric field in not being able to promote new off-diagonal elements of the a.c.f. of velocity or angular momentum in frame (X, Y, Z). What is the equivalent effect in frame (x, y, z)?

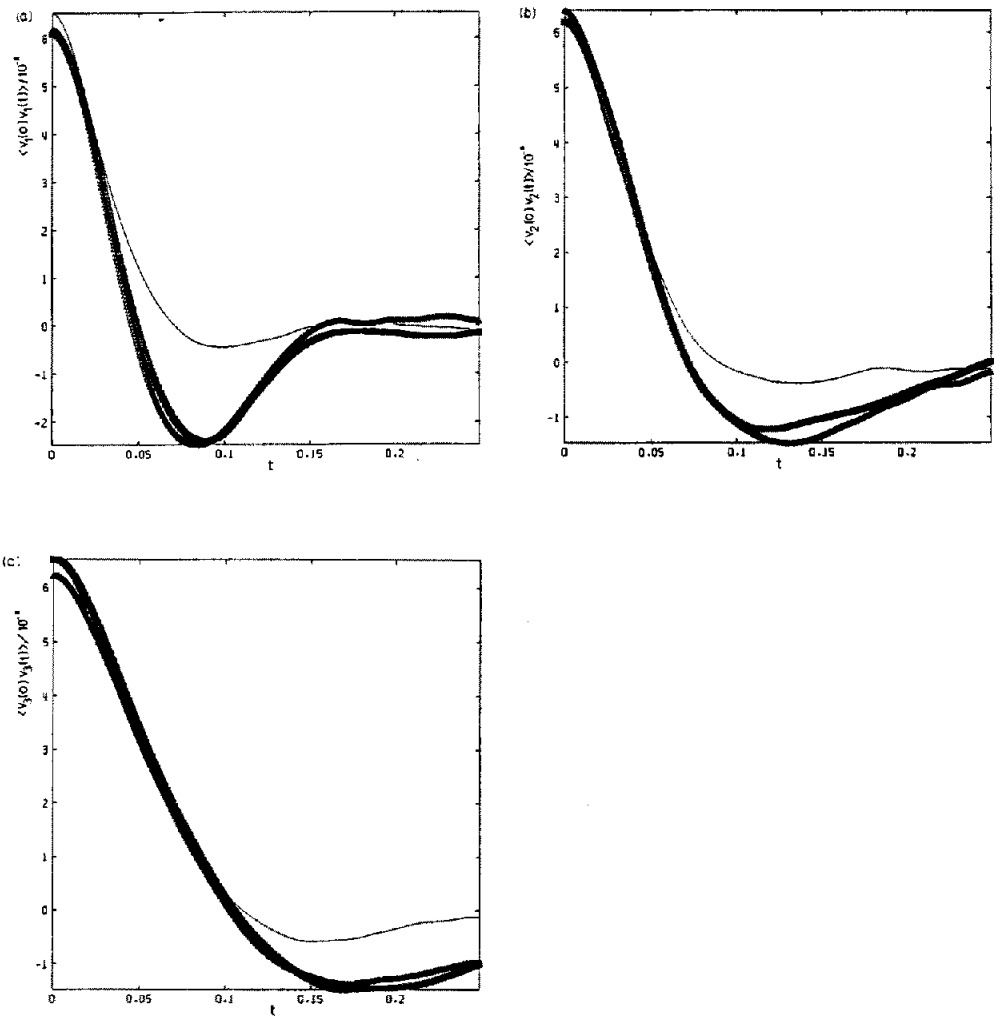

Figure 7

As for Figure 6, velocity a.c.f.

In group theoretical terms the symmetry of the electric field maps on to (x, y, z) as described, allowing the possible existence of thermodynamic averages corresponding to A_1, B_1, and B_2. In the absence of the field only the A_1 type averages survive. These are illustrated in the field-off and field-on cases in Figs. (6) and (7). The possible extra off diagonal elements in frame (x, y, z) are those of B_1 and B_2 symmetry, i.e.

$$< v_z(t)v_x(0) > ; \quad < v_z(t)v_y(0) > ; \quad < v_x(t)v_z(0) > ; \quad < v_y(t)v_z(0) >$$

and these may be discernible by computer simulation, of foe example, aligned liquid crystals.

Conclusions

Computer simulation of water and methyl chloride have confirmed the validity of Neumann's Principle in the laboratory frame of reference, (X, Y, Z), and in the molecule fixed frame (x, y, z) of the standard point group character tables.

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REFERENCES

1. F. E. Neumann, "Vorlesungen uber die Theorie Elastizitat der Festen Korper und des Lichtathers." (Teubner, Leipzig, 1885).
2. L. D. Barron, Chem. Soc. Rev., 15 (1986) 192.
3. M. W. Evans, G. J. Evans, W. T. Coffey and P. Grigolini, "Molecular Dynamics", (Wiley / Interscience, New York, 1982).
4. M. W. Evans, W. T. Coffey, and P. Grigolini, "Molecular Diffusion", (Wiley Interscience, New York, 1984).
5. M. W. Evans, P. Grigolini, and G. Pastori-Parravicini (eds.), "Memory Function Approaches to Stochastic Problems in Condensed Matter", vol. 63 of "Advances in Chemical Physics", (ser. eds. I. Prigogine and S. A. Rice, (Wiley / Interscience, New York, 1985).
6. ibid., vol. 63, "Dynamical Processes in Condensed Matter", ed. M. W. Evans.
7. M. W. Evans, "Supercomputer Simulation of Molecular Dynamics", (Oxford University Press, 1990).
8. D. H. Whiffen, Mol. Phys., 53 (1988) 1063.
9. M. W. Evans, Chem. Phys. 128 (1988) 413.
10. M. W. Evans and D. M. Heyes, Mol. Phys., in press; ibid., Phys. Rev. Letters, in press.
11. M. W. Evans, J. Chem. Soc., Faraday Trans. 2, 82 (1986) 1967.
12. M. W. Evans and D. M. Heyes, J. Mol. Liq., in press (1989).