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THE DYNAMICS OF LIQUID WATER : ELECTRIC FIELD EFFECTS

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ABSTRACT

The technique of field-effect computer simulation has been used to investigate the decoupling effect; the fall transient acceleration; and related non-linear effects in liquid water at 300 K. Using a pair potential adapted for this purpose from the well known ST2, it is found that fall transient acceleration in water is pronounced and persistent; and accompanies a moderate decoupling at electric field strengths sufficient to saturate the Langevin function. This is interpreted to mean that non-linear effects in water are very strong, and that the system is statistically non-Markovian and non-Gaussian.

INTRODUCTION

The technique of field-effect computer simulation [1] has been used to identify and characterise two general properties of the condensed state of matter. These are the field decoupling effect and fall transient acceleration or deceleration. The first of these was predicted theoretically by Grigolini [2] and confirmed numerically by Oxtoby and co-workers [3] and Evans [1] using independent algorithms and numerical methods. A review article is now available on the work in this area [4] and shows in detail the modifications necessary to conventional diffusion theory in order to begin to take account of the new effects. The field decoupling effect means that only one particular class of equations, recently summarised [5] as Reduced Model Theory, (R.M.T.), seems to be able to provide a rigorous link between the fundamental equations of motion, such as the Liouville equation, and the much simpler-to-solve Langevin equations. If the diffusion equation used to try to explain the decoupling effect analytically falls outside the R.M.T. framework, the effect might not be predicted at all. For example, the diffusion equation used by Praestgaard and van Kampen [6] is a plausible and elegant solution to the problem considered by these authors, but does not reproduce the decoupling effect at all. It is known now that this has to do with the inherently non-Markovian nature of the liquid state of matter. The acceleration or deceleration of fall transients following the instantaneous removal from a molecular ensemble of a strong applied field is much more difficult to describe. It relies for its description [4] on the recognition of the fact that the effective potential between diffusing and interacting molecules is not linear in nature. In order to describe the fall transient acceleration at all it is necessary to supplement Langevin equations with potential terms that are non-linear in the translational or rotational coordinates involved in that equation. Furthermore this must be done for ensembles at equilibrium. In other words the acceleration or deceleration of the fall transient in comparison with the appropriate equilibrium orientational auto-correlation function tells us a lot about the normal, field free, equilibrium behaviour of the molecular ensemble. The effect is not a banal consequence or using strong fields in a numerical simulation. For example, the rotational diffusion theory of Debye - the great "classical" theory of molecular diffusion - will not provide a fall transient acceleration at all, [7] even when the theory is corrected for inertial effects and adapted for arbitrarily strong applied electric fields, [8], either D.C. or A.C. Furthermore, Debye's theory will not provide a decoupling effect for arbitrary external field strength. [7] The reason is that the theory contains no reference to inter - molecular potentials. If the friction coefficient of Debye's diffusion equations is replaced by a memory function, but if no other alteration is made to the equation of rotational diffusion, it becomes possible to describe the field decoupling effect [2,5] but there is still no fall transient acceleration. The fall transient and equilibrium orientational a.c.f. in this case retain an identical dependence upon time. In other words for non-Markovian but linear diffusion equations the first fluctuation - dissipation theorem holds rigorously. The same is true for translational diffusion.

The primary level of sophistication needed for an analytical description of fall transient acceleration is reached [4] when the terms on the left hand side of these diffusion equations are supplemented by a representation of the effective inter-molecular potential which is non-linear in the rotational or translational coordinate, irrespective of whether the friction coefficient has been replaced or not with a memory function. One of the simplest of these is:

$$V = - V_o \cos\theta(t) \qquad (1)$$

which could for example represent the dependence of the potential energy between two molecular dipoles on the angle θ between them at the instant t. This automatically restricts the analytical consideration to two dimensions. In this case the coordinate θ is also the rotational coordinate of the Langevin equation:

$$\ddot{\theta}(t) + \int_0^t \phi(t-\tau)\dot{\theta}(\tau)d\tau + V_0 \sin\theta(t) = \dot{W}(t) \qquad (2)$$

where ϕ is the memory function of the simple type first introduced by Mori, [9],and $\dot{W}(t)$ is a Wiener process representing the random torque of the rotational diffusion equation. An equation of type (2) is capable of providing an elementary description of both the decoupling and fall transient acceleration effects when the external electric field is introduced into the analysis. However, the introduction of the memory function implies the need to use continued fractions, truncation procedures, and moment analysis [10] to solve eqn. (2), so that the problem becomes almost as difficult as solving the original Liouville equation "ab initio". This difficulty can be met, [10] but alternatively, it is possible to go to the next higher level of the R.M.T. framework [5] and to deal with the non-linear itinerant oscillator. This is a version of a model first introduced by Coffey and Calderwood [11] and aimed at describing the diffusion motion of a molecule bound harmonically inside a diffusing cage, treated as a rigid entity, in two dimensions an annulus. It was shown by Evans [12] that this model corresponded mathematically to a particular truncation of the Mori continued fraction expansion [13] of the angular velocity correlation function. Recent work [14] has demonstrated the full equivalence of the two approaches, and also that the linear itinerant oscillator takes on a more plausible and more transparent meaning when the original harmonic binding between cage and encaged molecule is replaced by a non-linear potential of type (1). In this eventuality the so called "non-linear itinerant oscillator model" becomes a relatively simple representation in two dimensions of the rotational diffusion of molecules subjected to an inter-molecular pair potential of type (1).

Grigolini and co-workers have shown [4] that this model can be used successfully to describe fall transient accelerations and decelerations observed numerically using three fully independent molecular dynamics computer simulation algorithms. This has forged an analytical link between the behaviour of fall transients and the effective pair - potential. It follows that real experimental observations of this type are necessary, to test the numerical and analytical predictions in real molecular liquids. Furthermore, the theoretical work of Grigolini and co-workers [4,5,13] and of Coffey and co-workers [11,14] with this model has shown how it may be used to inter-relate apparently disparate phenomena in terms of a few well defined parameters such as V_0 of eqn (1). Among these are the decoupling and fall transient acceleration effects. This implies that the results to be described in this paper, for water at 300 K, could also be described self consistently in terms of the same model, and of the parameters it contains.

Section 1 of this paper describes the computer simulation algorithms and methods used to investigate the molecular dynamics of 108 water molecules subjected to a static electric field in the z axis of the laboratory frame strong enough to saturate [1,15] the Langevin function. This could not be done in practice with electric field, but might be plausible with electromagnetic radiation using contemporary laser technology. However, even with the electric field strengths available in Kerr effect experiments, [16] accurate measurements on the fall transient might be expected to show up deviations from the time dependence of the equivalent orientational auto correlation function at equilibrium. In the continued absence of such investigations, computer simulation remains the only way of looking at fall transient acceleration and it is important to extend the simulation work to liquids such as water that have been investigated exhaustively [17] by other methods. In this respect we have adapted the simple ST2 potential of Stillinger and Rahman [18] to involve atom-atom Lennard Jones terms, and this gets rid of their artificial switching function. The original tetrahedral disposition of partial charges that characterises ST2 has been retained. [19]

In section 11 the results are presented in terms of the fall transients of the water dipole moment, $\underset{\sim}{\mu}$, which happens to coincide with the I axis of the principal molecular moment of inertia frame. The decoupling effect is illustrated using equilibrium a.c.f.'s such as those of the angular velocity, angular momentum, and rotational velocity in axes 1,2 and 3 of the moment of inertia frame. Finally in this section it is shown that the complete set of equilibrium a.c.f.'s investigated is statistically non-Markovian in nature. This implies that the analytical description of the computer simulation will have to rely on a diffusion equation that is non-linear, non Markovian, and also non-Gaussian. These three characteristics can now be inter-related [4] using the model of the non-linear itinerant oscillator.

Finally in section three some suggestions for further work are given, noting in particular the need for experimental data on the fall transient effect.

SECTION 1: COMPUTER SIMULATION ALGORITHM

A complete description of the algorithm and comparison of results with those of Stillinger and Rahman [18] and of Clementi et al., [20] is available in an accompanying paper. [19] Here we restrict the description to the methods employed in treating the sample with very intense external electric fields.

The key to such methods [1] is that the kinetic energy of the ensemble is always kept constant, both during the rise transient process, which takes place in the picoseconds after the field is applied, and also during the fall transient process after the instantaneous removal of the electric field. This is achieved numerically with standard temperature rescaling routines. It is easy to control the temperature (i.e. the rotational and translational kinetic energy) during the fall transient process of interest here, and the procedure is, in actuality, no different from the control of temperature at field free equilibrium in a standard molecular dynamics simulation. In energetic terms the fall transient process does not affect the kinetic part of the Hamiltonian, but the potential energy, in strong contrast, is reduced considerably by the release of the external torque $-\underset{\sim}{\mu}\mathrm{x}\underset{\sim}{E}$ on each molecule in the ensemble. With strong enough external fields $\underset{\sim}{E}$ the regression to equilibrium after its release cannot be described at all by the first fluctuation dissipation-theorem, which was derived for statistical ensembles infinitesimally removed from thermodynamic equilibrium. [21] This theorem actually implies that the fall transient and the equivalent equilibrium a.c.f. must be identical in their

Table 1

Mean Energies, Field Off and Field On.

Kinetic (kJ / mole)		Potential (kJ / mole)	μE(kJ / mole)
Translation	Rotational		
3.78	3.88	-35.77	0.00
3.85	3.76	-35.27	0.50
3.85	3.81	-25.12	10.65
3.85	3.74	-17.34	18.43
3.90	3.73	-15.58	20.19

time dependence. Note that this is assumed implicitly in all the experimental investigations of molecular dynamics based on spectroscopy [22,23] i.e. the perturbation of the ensemble with external radiation.

The application, therefore, of a z axis electric field $\underset{\sim}{E}_2$ produces the torque $-\underset{\sim}{\mu}x\underset{\sim}{E}_z$ on each H_2O molecule. If the unit vector $\underset{\sim}{e}_1$ is defined in the dipole moment axis $\underset{\sim}{\mu}$ the equilibrium average $<e_{12}(t)>$ becomes non-zero as a result of this torque. Here the average $<e_{12}(t)>$ is just a simple average over the 108 molecules at each instant t after field application. The dependence of this average on time is the rise transient. This eventually saturates, [1] i.e. reaches a plateau level, after which the external field can be removed instantaneously to generate the fall transient. The potential energy in the simulation was continuously monitored and is summarised in table 1, together with the rotational and translational kinetic energies.

RESULTS AND DISCUSSION

With the use of computer simulation it is possible to saturate the Langevin function for water (fig. (1)). This function was constructed from the saturation level of each rise transient plotted against $\mu E/kT$. The curve in this figure is the theoretical Langevin function and the points are obtained

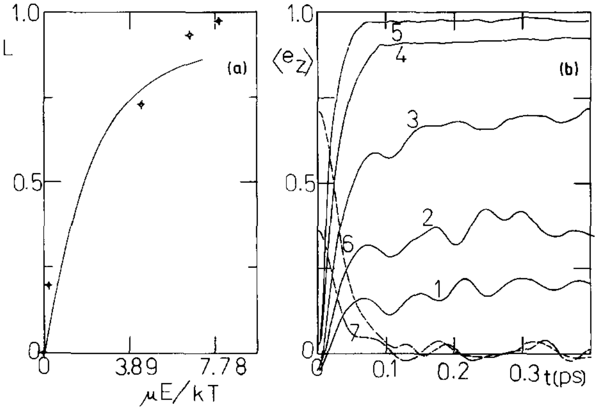

Fig. 1. a)________ The Langevin function L ($\mu E/kT$). Saturation levels of rise transients from the computer simulation see fig. (1b).
b) Rise transients $<e_z>$ plotted vs. time in picoseconds.
(1) - (5) Increasing field strength; (6) - (7) fall transients corresponding respectively to (3) and (2).

from the simulation (fig. (1b)). The rise transients are field dependent - the stronger the field the shorter the rise time.

Fig. (2) plots three fall transients against the appropriate equilibrium dipole a.c.f. $\langle \boldsymbol{\mu}(t).\boldsymbol{\mu}(o)\rangle/\langle \mu^2\rangle$ computed, of course, at field free equilibrium. It can be seen that the fall transients decay much more rapidly to zero than the a.c.f. and are therefore accelerated considerably with respect to it for all $\mu E/kT$ shown in the figure. The fall transient acceleration effect is very large and is also persistent. It is reasonable to assume that this is characteristic of real water, and that these accelerations can be detected with available electric field Kerr effect apparatus. [16]

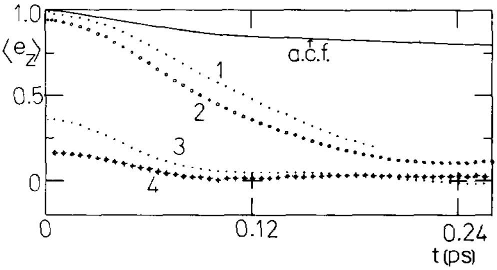

Fig. 2. ________ Field-off equilibrium dipole auto-correlation function for water $\langle \boldsymbol{\mu}(t).\boldsymbol{\mu}(o)\rangle/\langle \mu^2\rangle$. . . . . Fall transients $\langle e_z\rangle$, (see text). (1)-(4): Decreasing field strength.

Table 1 shows that the rotational and translational kinetic energy in water is approximately constant in this simulation for all $\boldsymbol{E}$, but the mean potential energy is more than halved by the strongest applied field. This point is emphasised by the atom-atom pair distribution functions of fig. (3). These show that the difference in equilibrium structure between the field free case (potential energy = - 35.77 kJ/mole) and equilibrium in the presence of the strongest applied field (-15.58 kJ/mole) is small. The sample is clearly still a liquid in the presence of the strongest field and the fall - transient acceleration of fig. (2) is therefore a property of liquid water.

Although the atom-atom p.d.f.'s are little affected even by the strongest field, the dynamical properties of the H_2O molecule are changed significantly. One of the clearest ways of seeing this is through the appearance of electric field induced time cross-correlation functions [24-27] (c.c.f.'s). The simplest of these is:

$$\boldsymbol{C}_{tr} = \langle \boldsymbol{\omega}(t)\boldsymbol{v}^T(o)\rangle/(\langle \omega^2(o)\rangle^{\frac{1}{2}}\langle v^2(o)\rangle^{\frac{1}{2}})$$

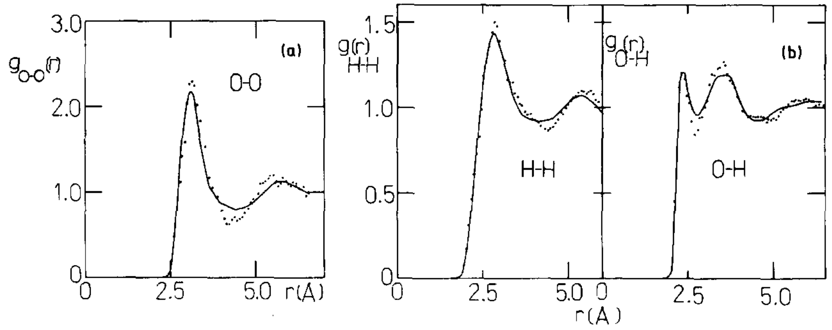

Fig. 3. ———Atom atom pair distribution functions.

——— Field-off equilibrium (potential energy = −35.77 kJ/mole)

. . . . Field-on equilibrium (potential energy = −15.58 kJ/mole).

where the subscript T denotes vector transposition. Ryckaert et al. [28] have shown analytically that $\underset{\sim}{C}_{tr}$ vanishes for all t when $\underset{\sim}{E} = \underset{\sim}{0}$ using general symmetry arguments. However fig. (4) shows clearly that the (x,y) and (y,x) elements of $\underset{\sim}{C}_{tr}$ appear directly in the laboratory frame (x,y,z) for $\underset{\sim}{E} > \underset{\sim}{0}$ in liquid water. This result confirms others in the literature [24] obtained using two independent numerical computer simulation algorithms. Strictly speaking therefore, cross correlation functions such as these appear in condensed molecular matter whenever the sample is subjected to a symmetry

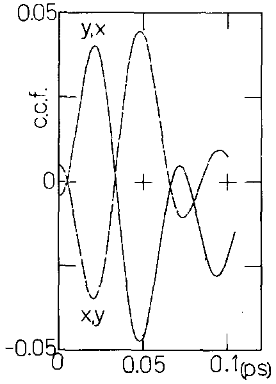

Fig. 4. (x,y) and (y,z) elements of the cross-correlation function $\underset{\sim}{C}_{tr}$

$$(x,y) \equiv \frac{\langle \omega_x(t)v_y(o)\rangle}{\langle \omega_x^2(o)\rangle^{\frac{1}{2}}\langle v_y^2(o)\rangle^{\frac{1}{2}}} \quad ; \quad (y,x) \equiv \frac{\langle \omega_y(t)v_x(o)\rangle}{\langle \omega_y^2(o)\rangle^{\frac{1}{2}}\langle v_x^2(o)\rangle^{\frac{1}{2}}}$$

at field on equilibrium, energy as for fig. (3).

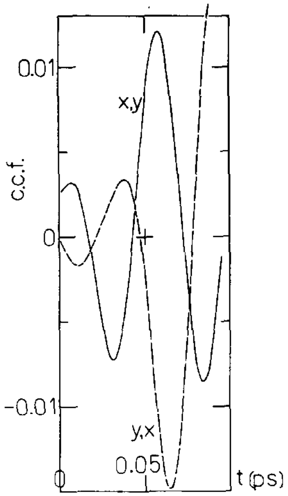

Fig. 5. (x,y) and (y,x) elements of the cross-correlation $\underset{\sim}{C}_2$

$$(x,y) \equiv \frac{\langle(\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t))_x \omega_y(o)\rangle}{\langle\omega^2(o)\rangle\langle v^2(o)\rangle^{\frac{1}{2}}} \quad ; \quad \text{etc.} \; ;$$

at field-on equilibrium.

breaking external field, as, for example, in dielectric and Kerr effect spectroscopy. The simple theory of rotational diffusion takes no account whatsoever of these effects. Recent work has shown furthermore [25-27], that $\underset{\sim}{C}_{tr}$ is only one out of very many possible c.c.f.'s that may exist in molecular liquids in frame (1,2,3) of the principal molecular moments of inertia, or for $\underset{\sim}{E} > \underset{\sim}{0}$, directly in frame (x,y,z). Another example is shown in fig. (5) in the shape of two elements of the second order c.c.f.

$$C_2(t) = \frac{\langle\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle}{\langle\omega^2(o)\rangle \; \langle v^2(o)\rangle^{\frac{1}{2}}}$$

between the molecular Coriolis acceleration and its own angular velocity in frame (x,y,z). In fig. (5) the two elements again seem to be mirror images, but are much more difficult to pick up from the noise than the mirror-image elements of fig. (4).

THE DECOUPLING EFFECTS

These show up in laboratory frame a.c.f.'s, and some of these are illustrated in this section. The decoupling effect can be identified by looking at the envelope of the oscillations induced by the external field. It is present when the time dependence of this envelope begins to be slower *than that of the equivalent field-free a.c.f. It is known now that some* analytical models [6] fail to produce this effect because the former are inherently Markovian in statistical nature. The effect has received many independent analytical and numerical confirmations, [4,5] but there has been virtually no attempt to look for it experimentally. Its experimental investigation could be achieved, however, by the use of induced birefringence at far infra-red frequencies, using a giga watt laser to induce birefringence in a liquid and monitoring with a submillimeter laser or an interferometer with suitably fast detector systems. The present situation, where the phenomenon is well-defined theoretically and numerically, and un-investigated experimentally, is out of balance and unsatisfactory.

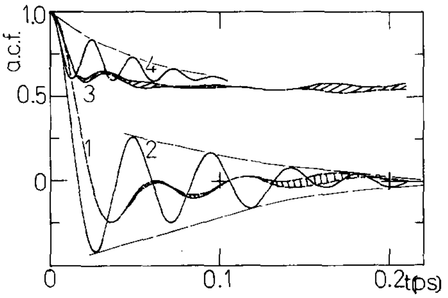

Fig. 6. Illustration of the decoupling effect with the angular velocity autocorrelation functions.

1. Angular velocity a.c.f. at field off equilibrium.
2. Angular velocity a.c.f. at field on equilibrium.

. . . . . . Envelope of the field oscillations in 2).

3. Rotational kinetic energy a.c.f. at field off equilibrium.
4. Rotational kinetic energy a.c.f. at field on equilibrium.

- - - - - Envelope of the field oscillations in 4).

For water the extension of the oscillation envelope with respect to the field free time dependence of the a.c.f. is visible in the angular velocity a.c.f. $\langle \underset{\sim}{\omega}(o).\underset{\sim}{\omega}(t)\rangle \; \langle\omega^2\rangle$ (fig. (6)) and in the second order rotational kinetic energy a.c.f.

$$\langle \underset{\sim}{\omega}(t).\underset{\sim}{\omega}(t)\underset{\sim}{\omega}(o).\underset{\sim}{\omega}(o)\rangle/\langle\omega^4\rangle$$

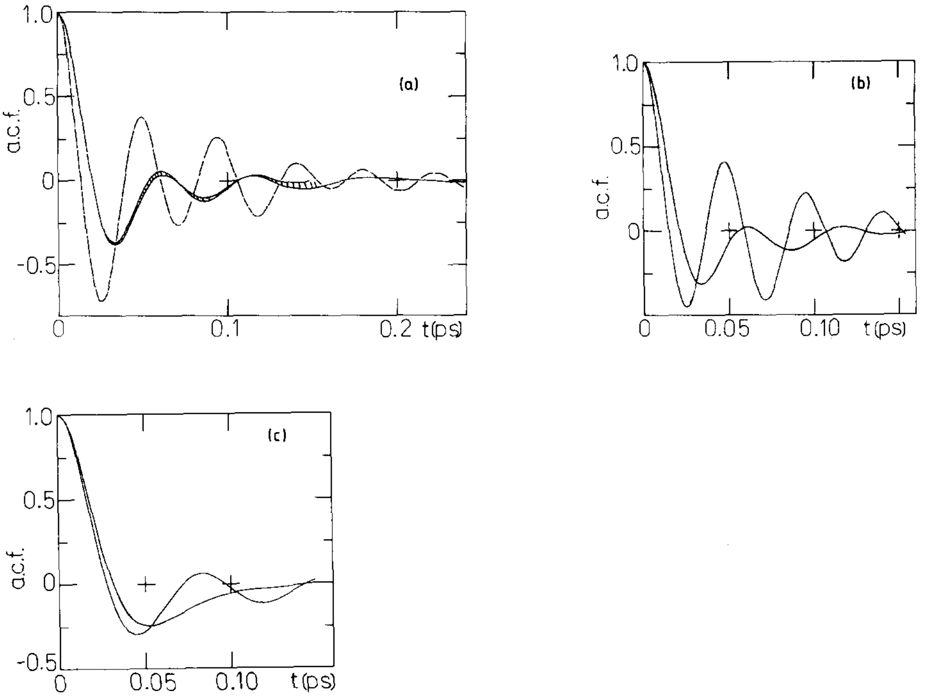

Fig. 7.

a) Field decoupling effect in $\langle \underset{\sim}{\dot{e}}_1(t) \cdot \underset{\sim}{\dot{e}}_1(o)\rangle / \langle \dot{e}_1^2 \rangle$;

b) Field decoupling effect in $\langle \underset{\sim}{\dot{e}}_2(t) \cdot \underset{\sim}{\dot{e}}_2(o)\rangle / \langle \dot{e}_2^2 \rangle$;

c) Field decoupling effect in $\langle \underset{\sim}{\dot{e}}_3(t) \cdot \underset{\sim}{\dot{e}}_3(o)\rangle / \langle \dot{e}_3^2 \rangle$.

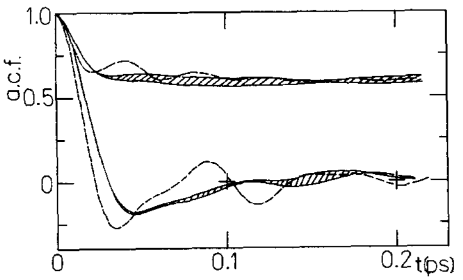

Fig. 8. Field decoupling effect in the angular moment a.c.f.

It is confirmed in the three rotational velocity a.c.f.'s

$$\langle \dot{\underset{\sim}{e}}_1(t) \cdot \dot{\underset{\sim}{e}}_1(o)\rangle / \langle \dot{e}_1^2 \rangle \;;$$

$$\langle \dot{e}_2(t) \cdot \dot{\underset{\sim}{e}}_2(o)\rangle / \langle \dot{e}_2^2 \rangle \;;$$

$$\langle \dot{\underset{\sim}{e}}_3(t) \cdot \dot{\underset{\sim}{e}}_3(o)\rangle / \langle \dot{e}^2 \rangle \;;$$

(fig. (7)); in the angular momentum a.c.f. (fig. (8)) and in the first and second order a.c.f.'s of the Coriolis acceleration, [25-27] which automatically considers the centre of mass linear velocity, $\underset{\sim}{v}$, and the resultant molecular angular velocity, $\underset{\sim}{\omega}$ simultaneously (fig. (9)). Therefore decoupling occurs in all aspects of the molecular motion and is clearly a fundamental property of water, needing experimental investigation. Our future analytical investigation of these results will use the non-linear itinerant oscillator to express these numerical results in terms of the parameters of that model [4,14] *and to provide a self consistent interpretation of the results of this* paper.

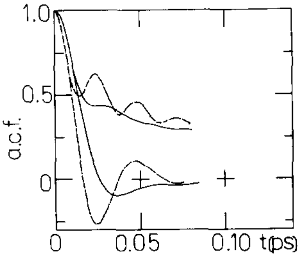

Fig. 9. Field decoupling in the first and second order a.c.f.'s of the Coriolis acceleration (see text).

NON-MARKOVIAN AND NON-GAUSSIAN PROPERTIES OF LIQUID WATER

This section deals finally with these properties, which are characterised and defined in the literature. [4,12,14,22,23] The non-Markovian dynamical properties of liquid water have been known since the first simulations by Stillinger and Rahman. [18] It is well known, for example, that the linear velocity a.c.f. in frames (x,y,z) and (1,2,3) has a negative overshoot [18,19,20] and is not a simple exponential. The simple Langevin equation would produce an exponential decay, characteristic of the Markov process through Doob's theorem. [22,23] These and other results for liquid water show that the whole range of correlation functions is similarly non-Markovian in nature.

The non-Gaussian nature of molecular liquids was first detected by Berne and Harpe [29] using computer simulation for carbon monoxide liquid. This property can be detected by investigating second order a.c.f.'s such as that of the translational kinetic energy:

$$\langle \underset{\sim}{v}(t) \cdot \underset{\sim}{v}(t)\underset{\sim}{v}(o) \cdot \underset{\sim}{v}(o)\rangle / \langle v^4 \rangle ,$$

and comparing the result with that calculated analytically from the first order linear velocity a.c.f. $\langle \underset{\sim}{v}(t) . \underset{\sim}{v}(o)\rangle / \langle v^2 \rangle$ assuming rigorously Gaussian statistics. [4] We have carried out this exercise for this work and the result confirms that the dynamics of water in the liquid state at 300 K are not Gaussian, in the well-defined sense that Gaussian statistics do not succeed in describing the evolution of these two a.c.f.'s self-consistently. At thermodynamic equilibrium (i.e. $t \rightarrow \infty$) their behaviour becomes Gaussian once more, because computer simulation builds this assumption into the algorithm. [30]

Clearly the range of numerical data reported here must be interpreted using a model capable of describing the complete range of new phenomena self consistently. Future work aims to show that the non-linear itinerant oscillator is qualitatively capable [4,14] of this.

For an isotropic liquid sample in the absence of an electric field group theory can be used to predict the existence of cross correlation functions in the moving frame (1,2,3). For example, the triple product is reducible in frame (1,2,3) as nine elements, of which A_1 is the only property which survives after averaging in the absence of anisotropy. This implies that the diagonal elements exist in frame (1,2,3) and these are illustrated elsewhere. [19] The group theory implies that all other elements of this tensor must vanish in frame (1,2,3) (the off diagonal elements) and all elements in frame (x,y,z). This is indeed what is found in the simulation. At the time origin the triple product must vanish for all the molecules in the ensemble because two out of the three vectors in the product are equal. The application of group theory therefore shows that the computer simulation provides the elements which exist theoretically on the grounds of molecular symmetry in the absence of the external electric field.

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