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MOLECULAR DYNAMICAL SIMULATION OF NEW AUTO AND CROSS CORRELATIONS IN LIQUID WATER

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ABSTRACT

This Letter reports the first simulation of the classical Coriolis, centripetal, and non-uniform auto-correlation functions of the H_2O molecule in liquid water, together with strong single molecule cross correlation functions involving its centre of mass position, linear velocity and angular velocity. These results were obtained with a new empirical, pair potential based on the ST2 of Stillinger and Rahman. [1]

INTRODUCTION

This Letter reports the first detailed numerical investigation of new types of dynamical auto and cross correlations between molecular rotation, translation and position in liquid water. Several original results have been obtained and a brief account is given of each. Using a new empirical atom atom type potential based on the ST2 of Stillinger and Rahman [1] it is found that:

a) autocorrelation functions (a.c.f.'s) of the water molecule's classical Coriolis, centripetal, and non-uniform accelerations exist both in the laboratory (x,y,z) frame and in the moving frame, (1,2,3) of the principal molecular moments of inertia;

b) various types of single molecule cross correlation functions (c.c.f.'s) exist in both frames, showing that it is impossible to consider rotational diffusion in water as being independent of the centre of mass translational motion of the same molecule.

The vast aqueous literature [2] leaves room for detailed studies of the diffusional dynamics of the H_2O molecule, but still within the severe limitations of classical dynamics. A decade of progress in this field may be gauged by choosing two key papers: one by Stillinger and Rahman [1] in 1974 and the other by Clementi et al. [3] in 1985. The essential difference seems to be that the evolution of computer power allows Clementi et al. to introduce ab initio methods of computing the pair potential and to introduce 3 and 4 body terms. The results obtained in the two papers for the centre of mass velocity a.c.f. (in frame (x,y,z) by Stillinger and Rahman and in frame (1,2,3) by Clementi et al.) do not differ markedly. The atom-atom pair distribution functions (p.d.f.'s) of Clementi et al., from a separate Monte Carlo simulation [3], seems to be broadly in agreement with experiment. Empiricism and two body constraints seem to be gradually disappearing therefore from (classical) simulations of liquid water, but the recent paper by Morse and Rice [4] shows clearly that there are many empirical potentials, none of which is entirely satisfactory.

Some new insight has recently been obtained analytically [5,6] by the use of Langevin equations written in rotating and moving frames of reference - the former for the centre of mass molecular translation and the latter for the same molecule's rotational movement. This method removes the need for friction cross terms, [7-9] and provides a natural description of the three dimensional diffusion of an asymmetric top molecule in the liquid state.

Computer Simulation Methods

With the restricted computer power available to me, I chose to modify the well known ST2 potential by including atom-atom terms centred both on the oxygen and hydrogen atoms. The empirical pair potential is then described as follows:

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

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

$$\varepsilon/k(\text{O-H}) = \left(\frac{\varepsilon}{k}(\text{O-O})\,\frac{\varepsilon}{k}(\text{H-H})\right)^{\frac{1}{2}} \quad ; \quad \sigma(\text{O-H}) = \tfrac{1}{2}(\sigma(\text{O-O}) + \sigma(\text{H-H}))$$

where $\frac{\varepsilon}{k}$ and σ are the usual atom-atom Lennard-Jones parameters. In addition, the tetrahedral arrangement of charges in ST2 was used as in the original paper, [1] together with the original ST2 geometry (fig. (I)). One advantage of using separate hydrogen and oxygen atom-atom terms is that the artificial swithing function of Stillinger and Rahman [1] is no longer required. The atom-atom parameters were based closely on independent, experimental, estimates. [10]

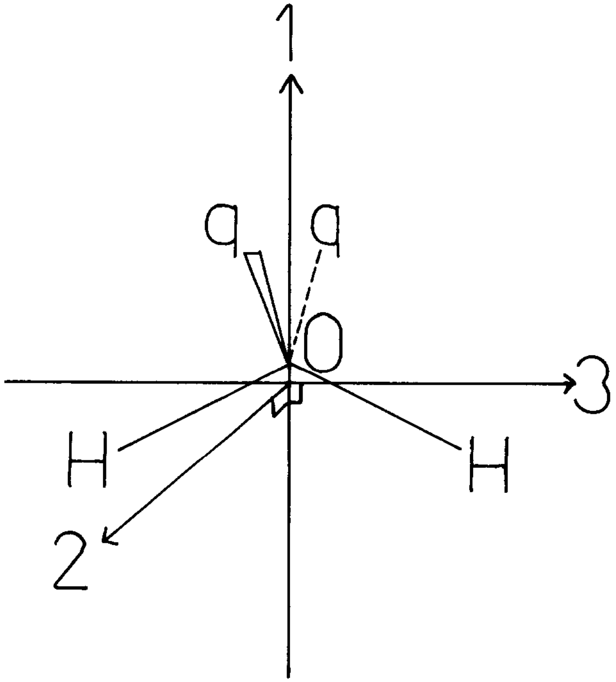

Fig. 1 Illustration of the ST2 geometry, and definition of frame (1,2,3).

With a time step of 5.0×10^{-16} sec., a sample of only 108 molecules, no Ewald corrections, and simple cubic periodic boundary conditions, the total mean configurational energy at 300 K; $\rho = 0.997$ gm/cm, molar volume = 18.08 cm/mole; was, for a typical segment of about 1000 time steps, - 35.5 kJ/mole; the mean pressure - 137 ± $(1.15 \times 10^6)^{\frac{1}{2}}$ bar. The configurational energy can be compared with a value of -34.3 kJ/mole at 314K obtained by Stillinger and Rahman [1], also in the absence of Ewald corrections. For two body interactions the use of Ewald sums by Clementi et al. [3] reduced this internal energy to -38.6 kJ/mole, which compares with an experimental estimate [3] of -41.0 kJ/mole.

These results were obtained by integrating the classical rotational equations of motion numerically in two stages; [11,12] the total torque on each molecule was first computed from the atom-atom and charge-charge forces, and the angular momentum in frame (1,2,3) then by a numerical cubic interpolation over the four previous values in time sequence. The translational equation of motion - Newton's equation - was integrated numerically with the Verlet algorithm, and the cut off criterion applied with respect to the intermolecular centre of mass separation. The total energy was observed to be constant within a few parts in a thousand. Long range corrections were applied to the virial sum and to the total configurational energy for Lennard Jones terms only.

NUMERICAL RESULTS

Atom-Atom P.D.F.'s

Atom atom p.d.f.'s were averaged over about four consecutive segments (4000 time steps). The oxygen to oxygen (O-O)p.d.f. is compared in Table 1 with equivalent results from Stillinger and Rahman [1] and from Clementi et al. [3]. (The notation is that of the former paper.)

TABLE 1

Oxygen - oxygen p.d.f.'s

T/K	Potential	R_1(Å)	R_2(Å)	R_3(Å)	$r(M_1)$/Å	M_1	$r(M_2)$/Å	M_2
314	ST2[1]	2.63	3.21	4.31	2.86	3.02	4.74	1.08
300	Clementi[3] et al.				∿2.8	2.45	∿4.0	∿1.1
300	This work	2.72	3.70	5.25	3.10	2.18	5.66	1.11
323	Exptl.[1,3]	2.64	3.31	4.21	2.85	2.28	4.75	1.11

As usual [4], the empirical potential for this letter has its strengths and weaknesses. In table 1, for example, the first peak of the experimental O-O p.d.f. (at 323 K) is reproduced much better in intensity than ST2; the maximum intensity of the second peak is also close to the experimental value, but the position of the second peak is too far out. In this respect Clementi et al. [3] seems to be too far in, by about the same amount, with their two body potential and Monte Carlo simulation. The H-H p.d.f.'s of this work are broadly similar in detail [1] to ST2, and will be illustrated in full elsewhere.

Time Correlation Functions for the H_2O Molecule

The more original results of this Letter are given in this section on dynamical properties [9] - a.c.f.'s and c.c.f.'s of the H_2O molecule.

1) Coriolis, centripetal and non-uniform accelerations [13] of the H_2O molecule exist in liquid water at 300 K in both frames of reference, and can

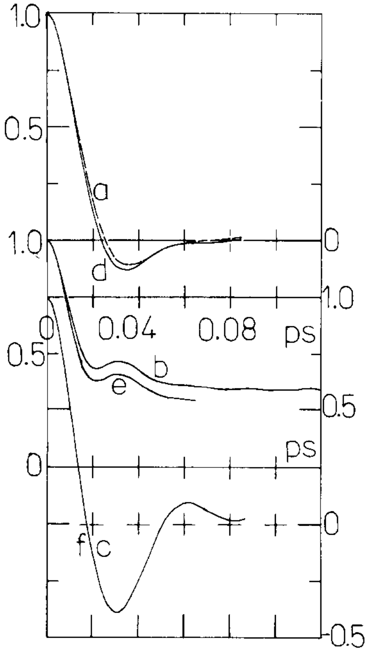

Fig. 2

a) The a.c.f. of the H_2O Coriolis acceleration, frame (x,y,z).

b) A.c.f. of the centripetal acceleration, frame (x,y,z).

c) A.c.f. of the non-uniform acceleration, frame (x,y,z).

d) As for a), frame (1,2,3).

e) As for b), frame (1,2,3).

f) As for c), frame (1,2,3).

be observed through their respective a.c.f.'s. This is true, essentially speaking, because frame (1,2,3) is a non-inertial frame of reference with respect to frame (x,y,z) and vice-versa. [5,6] As far as I am aware, fig. 2 is the first illustration of these a.c.f.'s - that of the H_2O molecule's Coriolis acceleration, $2\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t)$; centripetal acceleration, $\underset{\sim}{\omega}(t) \times (\underset{\sim}{\omega}(t) \times \underset{\sim}{r}(t))$; and non-uniform acceleration $\dot{\underset{\sim}{\omega}}(t) \times \underset{\sim}{r}(t)$. Here $\underset{\sim}{v}$ is the linear centre of mass velocity, $\underset{\sim}{r}$ is the position vector of the molecular centre of mass, and $\underset{\sim}{\omega}$ is the resultant molecular angular velocity. These results show clearly the basic inapplicability of theories of purely rotational or translational diffusion in liquid water.

2) Ryckaert et al. [14] were the first to observe the simple c.c.f. $<\underset{\sim}{\omega}(t)\underset{\sim}{v}^T(o)>$ in frame (1,2,3), and fig. 3 confirms the existence of two of its off-diagonal elements [11,12] for liquid water. The hatched area denotes the difference between two different segments, each of about 1000 time steps, and is a measure of my computer "noise". The intensity of these elements shows

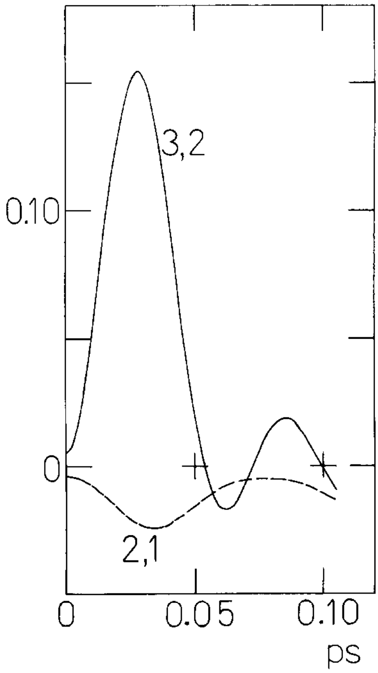

Fig. 3 Non-vanishing elements of $<\underset{\sim}{\omega}(t)\underset{\sim}{v}^T(o)>$ in frame (1,2,3).
$(i,j) \equiv <\omega_i(t)v_j(o)> / (<\omega_i^2>^{\frac{1}{2}} <v_j^2>^{\frac{1}{2}})$.

the strength of cross-correlation and indicates the dominant role of H-bonding in this dynamical context. [2]

3) The development of rotating frame Langevin equations has been used recently [5,6] to reveal the existence of numerous new types of moving frame c.c.f.'s, typified by the diagonal elements of $<\underset{\sim}{A}(t) \times \underset{\sim}{\omega}(t)\ \underset{\sim}{A}^T(o)>$ where $\underset{\sim}{A} \equiv \underset{\sim}{v}, \underset{\sim}{\omega} \times \underset{\sim}{r}$ or $\underset{\sim}{r}$. I have checked that these all exist for liquid water confirming, inter alia, the validity of the new Langevin equations [6] and the existence of strong dynamical cross-correlation. The c.c.f. for $\underset{\sim}{A} \equiv \underset{\sim}{v}$ is shown in Fig. 4.

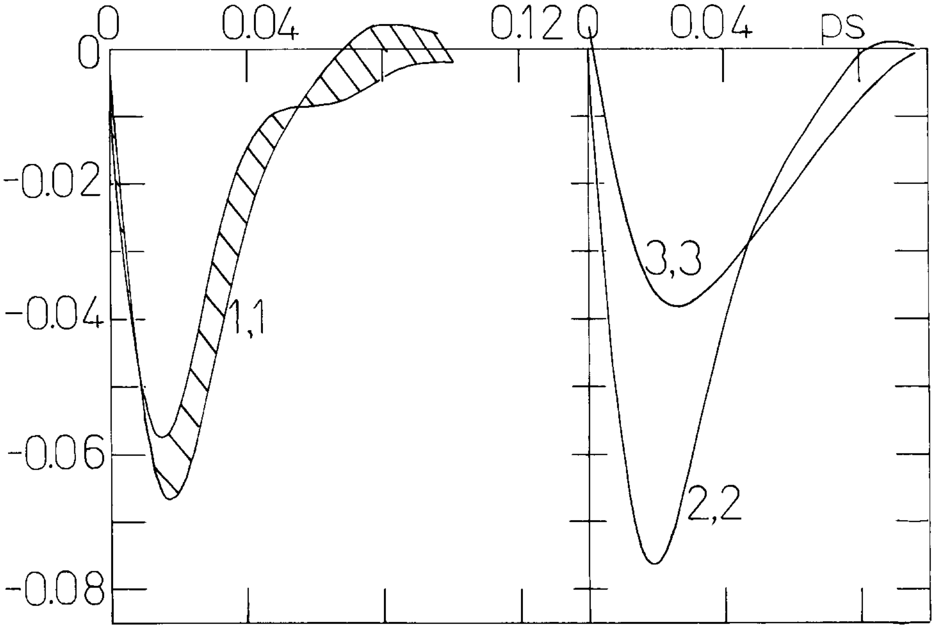

Fig. 4. The non-vanishing (diagonal) elements of $<\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t)\underset{\sim}{v}^T(o)>$ in frame (1,2,3); $(i,i) = <(\underset{\sim}{v}(t) \times \underset{\sim}{\omega}(t))_i v_i(o)> /<(v^2>\omega^2>^{\frac{1}{2}})$

4) C.c.f.'s of types (2) and (3) above all vanish [6] in the frame (x,y,z) but of off-diagonal elements of the type $<\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)>$ exist [15] in frame (x,y,z) for the C_{2v} symmetry asymmetric top CH_2Cl_2. This simulation result is confirmed in this Letter for the H_2O molecule in liquid water (also C_{2v}) in Fig. 5.

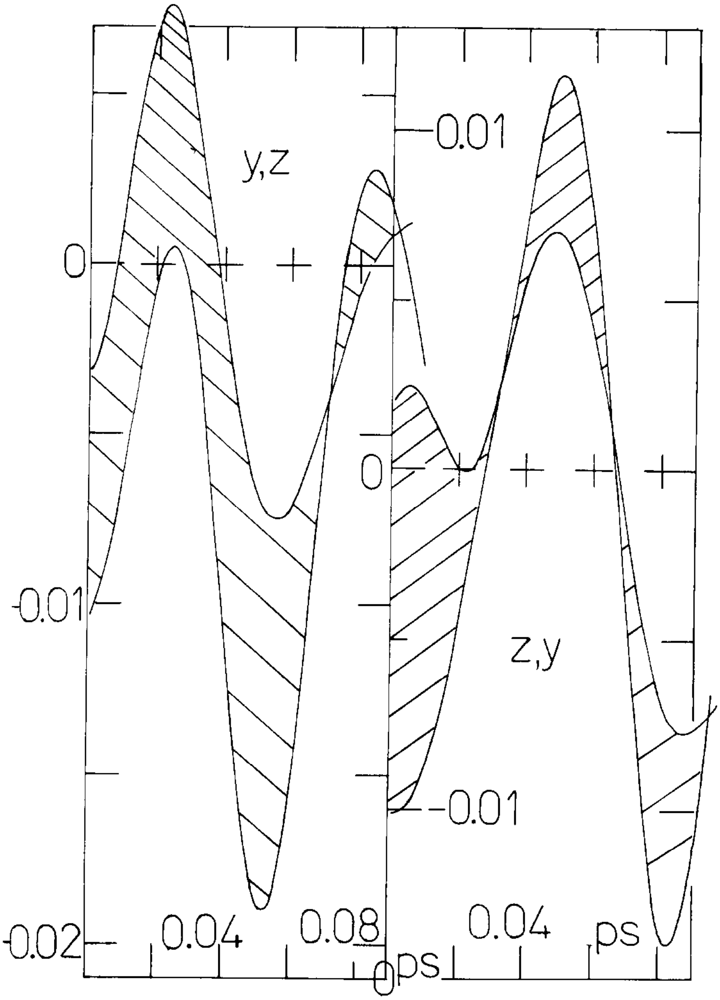

Fig. 5. The non-vanishing (off-diagonal) elements of $\langle \underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t)\underset{\sim}{\omega}^{T}(o)\rangle$ in frame (x,y,z);

$$(i,i) = \frac{\langle(\underset{\sim}{\omega}(t) \times \underset{\sim}{v}(t))_i \omega_i(o)\rangle}{\langle v^2\rangle^{\frac{1}{2}} \langle\omega^2\rangle}$$

CONCLUSIONS

The existence of the classical Coriolis, centripetal, and non-uniform accelerations of the H_2O molecule in liquid water is demonstrated explicitly for the first time, together with strong dynamical cross-correlation on the single molecule level. These results were obtained with a new empirical pair potential, based on the well-known ST2 of Stillinger and Rahman. [1]

ACKNOWLEDGEMENTS

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