

ON THE ABSENCE OF SAMPLE SIZE EFFECTS IN THE COMPUTATION OF CROSS-CORRELATION FUNCTIONS IN LIQUID WATER

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Abstract

A molecular dynamics simulation of liquid water using 864 molecules has confirmed the existence of a range of statistical cross correlation functions observed in earlier simulations with a much smaller sample size of 108 molecules. The amplitude and time dependence of the correlation functions are essentially identical from both simulations, indicating that there are no sample size effects and that the correlation functions themselves are real and characteristic of the molecular liquid state of matter.

Introduction.

In recent work¹⁻⁵ the molecular dynamics of the liquid state have been characterised in terms of a number of new cross-correlation functions (c.c.f.'s). Their existence and time dependence have been established for many molecular symmetries, including water, with a relatively small sample of 108 molecules. In order to eliminate the possibility of artifact due to sample size a computation has been carried out in a sample of liquid water consisting of 864 molecules and the results are reported in this paper for the complete range of c.c.f.'s characterised previously with 108 molecules only. The c.c.f.'s from both samples are identical within the uncertainty, both in time dependence and normalised amplitude, and this result is illustrated with reference to fundamental time cross correlation functions in the laboratory frame (x, y, z) and the frame of the principal molecular moments of inertia (1, 2, 3).

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Computer Simulation Methods.

The potential of interaction between two water molecules was a five by five site-site modification⁶ of the ST2 of Rahman and Stillinger⁷ made up of Lennard Jones terms for atom-atom interactions together with the original ST2 charge configuration. Some more details and results obtained with this potential are in the literature^{8,9}. These were all obtained with only 108 molecules due to lack of computer time. Using the ICAP1 supercomputer at I.B.M. Kingston allows this restriction to be removed and the sample size to be increased to 864, a factor of eight times more molecules in the sample. This is one of the largest simulations of water carried out to date with the relatively complicated Evans potential described already^{8,9}.

One thousand configurations were generated and recorded every two time steps. Each consisted of dynamical data for each of the 864 molecules which were translated with two subsidiary algorithms into a form suitable for running time averaging in both frames of reference (1, 2, 3) and (x, y, z). Data from the main run and two subsidiary runs took approximately sixty hours of ICAP1 time to generate, and storage requirements exceeded 800 cylinders of disk space. After translation the complete range of time correlation functions was computed using a fast running time averaging technique devised by Refson and Evans at I.B.M. Kingston

The simulation was carried out at a density for water of 1.0 gm cm^{-3} , a molar volume of $18.0 \text{ cm}^3 / \text{mole}$ at 296 K.

Simple periodic boundary conditions were retained for direct comparison with the earlier simulations of water with 108 molecules only. The time step was 0.5 fs, identical with that used in the small sample simulation on a CDC 7600.

Results and Discussion.

A detailed comparison of time correlation functions was made with results from the 864 and 108 molecule sample obtained from CDC 7600 and I.B.M. / F.P.S. computer systems. This covered the time dependence of autocorrelation functions, such as those of the molecular orientation, linear centre of mass velocity, angular velocity, rotational velocity, force, and torque, and cross correlation functions recently reported in the literature for 108 molecule samples.

The cross correlation functions exist directly in the laboratory frame, and more indirectly in the moving frame of the principal molecular moments of inertia. Their existence implies a new class of Kubo and Onsager reciprocal relations in both frames of reference. We focus particular attention in this paper on the cross correlation in the laboratory frame between the molecular rotational velocity, $\dot{\Lambda}_i$, and its own centre of mass linear velocity, v_i :

$$C_{-1}^{ij}(t) = \left[\frac{\langle \underline{\mu}_i(t) \underline{v}_j^T(o) \rangle}{\langle \underline{\mu}_i^2 \rangle^{\frac{1}{2}} \langle \underline{v}_j^2 \rangle^{\frac{1}{2}}} \right]_{(x,y,z)}$$

and the equivalent between the molecular orientation vector, (the net dipole moment), and the molecular centre of mass linear velocity:

$$C_{-2}^{ij}(t) = \left[\frac{\langle \underline{\mu}_i(t) \underline{v}_j^T(o) \rangle}{\langle \underline{\mu}_i^2 \rangle^{\frac{1}{2}} \langle \underline{v}_j^2 \rangle^{\frac{1}{2}}} \right]_{(x,y,z)}$$

Both of these were recently quantified for the first time using 108 molecule samples.

Other cross correlation functions of interest exist in the moving frame of reference, and are typified by that between the molecular Coriolis acceleration and its own centre of mass linear velocity:

$$C_{-3}^{ij}(t) = \left[\frac{\langle (\underline{v}(t) \times \underline{\omega}(t))_i \underline{v}_j^T(o) \rangle}{\langle (\underline{v} \times \underline{\omega})_i^2 \rangle^{\frac{1}{2}} \langle \underline{v}_j^2 \rangle^{\frac{1}{2}}} \right]_{(1,2,3)}$$

and related correlations such as

$$C_{-4}^{ij}(t) = \left[\frac{\langle (\underline{r}(t) \times \underline{\omega}(t))_i \underline{r}_j^T(o) \rangle}{\langle (\underline{r} \times \underline{\omega})_i^2 \rangle^{\frac{1}{2}} \langle \underline{r}_j^2 \rangle^{\frac{1}{2}}} \right]_{(1,2,3)}$$

and

$$C_{-5}^{ij}(t) = \left[\frac{\langle (\underline{\omega}(t) \times (\underline{\omega}(t) \times \underline{r}(t)))_i (\underline{\omega}(o) \times \underline{r}(o))_j^T \rangle}{\langle (\underline{\omega} \times (\underline{\omega} \times \underline{r}))_i^2 \rangle^{\frac{1}{2}} \langle (\underline{\omega} \times \underline{r})_j^2 \rangle^{\frac{1}{2}}} \right]_{(1,2,3)}$$

which are symmetry allowed in frame (1,2,3) for water.

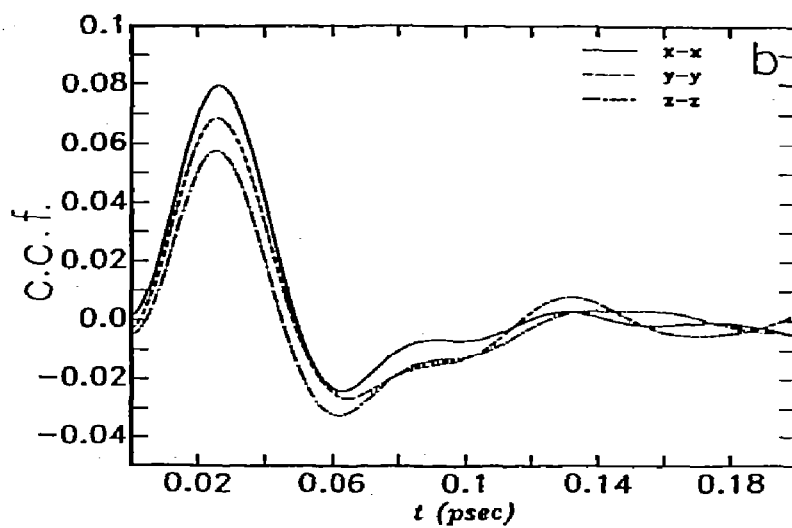
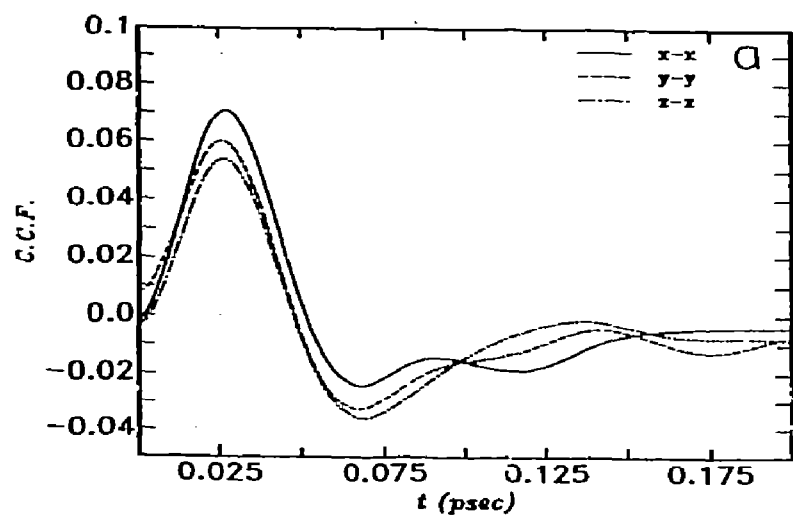


Fig. 1. The c.c.f. \underline{C}_1 with (a) 864 molecules and (b) 108 molecules

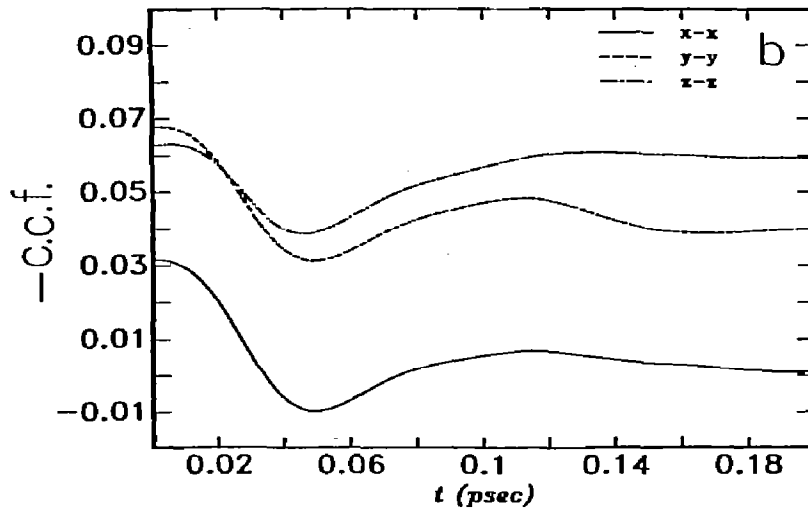
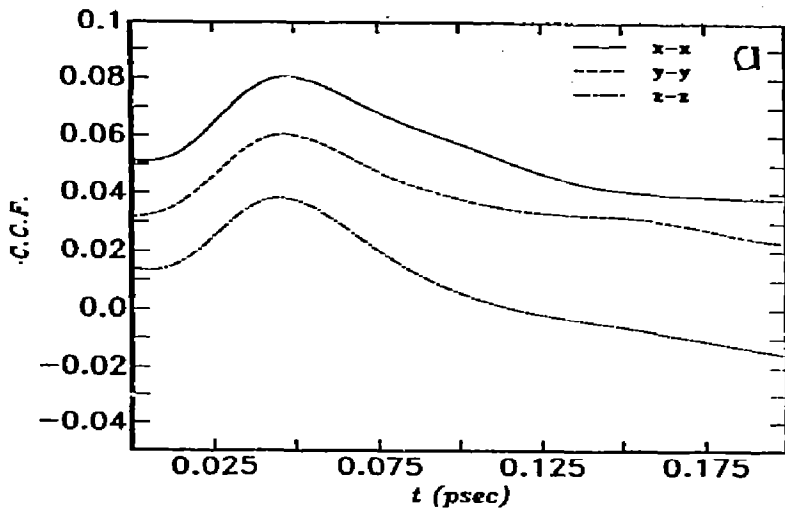


Fig. 2. The c.c.f. C_2 with (a) 864 molecules and (b) 108 molecules.

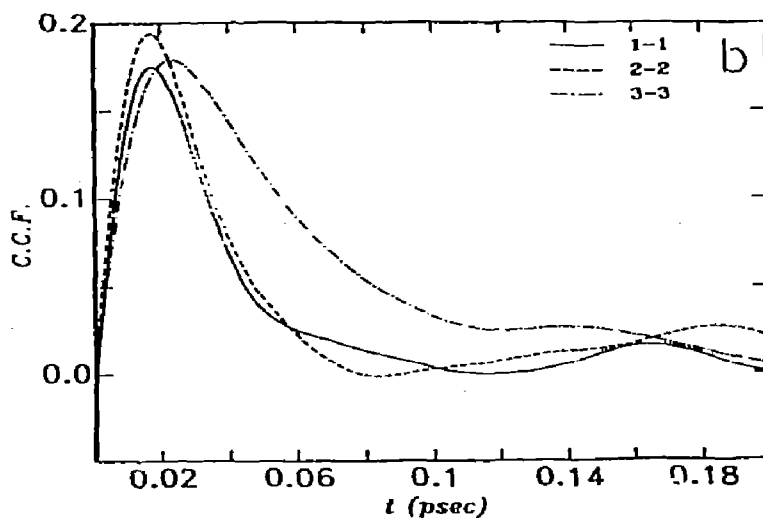
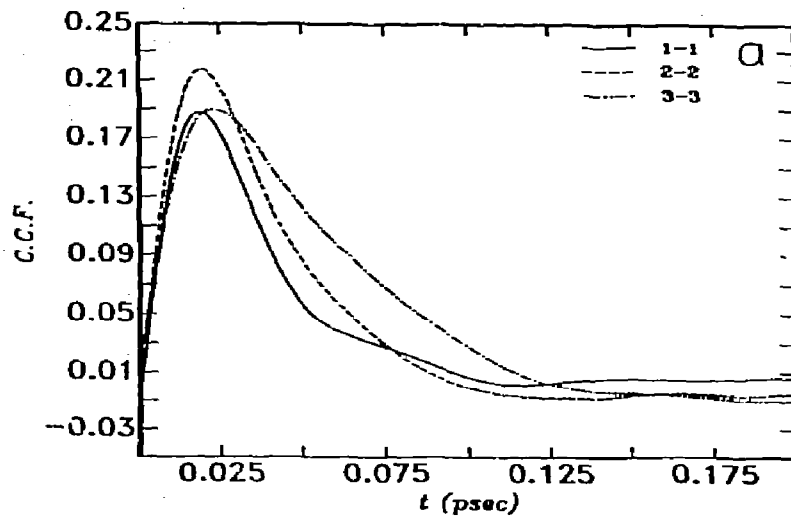


Fig. 3. The c.c.f. C_3 with (a) 864 molecules and (b) 108 molecules

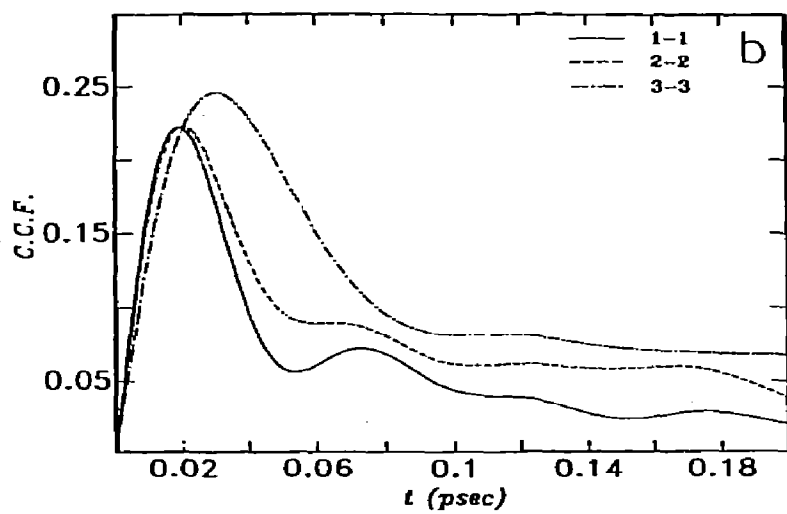
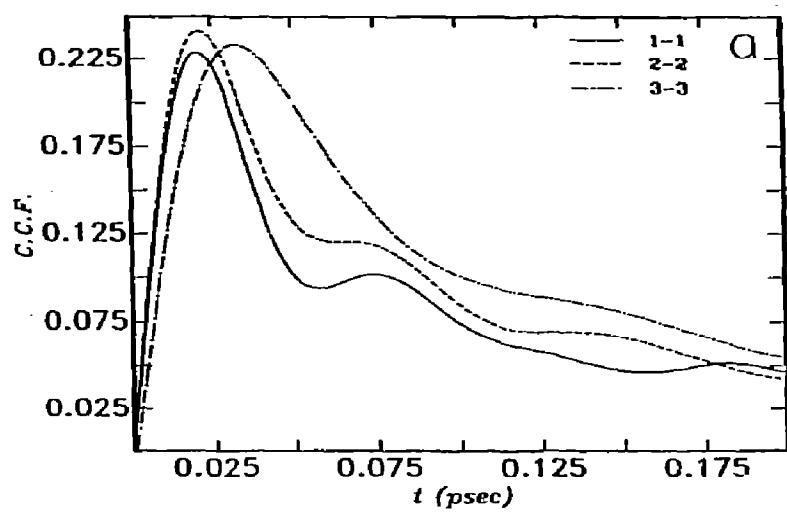


Fig. 4. The c.c.f. C_4 with (a) 864 molecules and (b) 108 molecules.

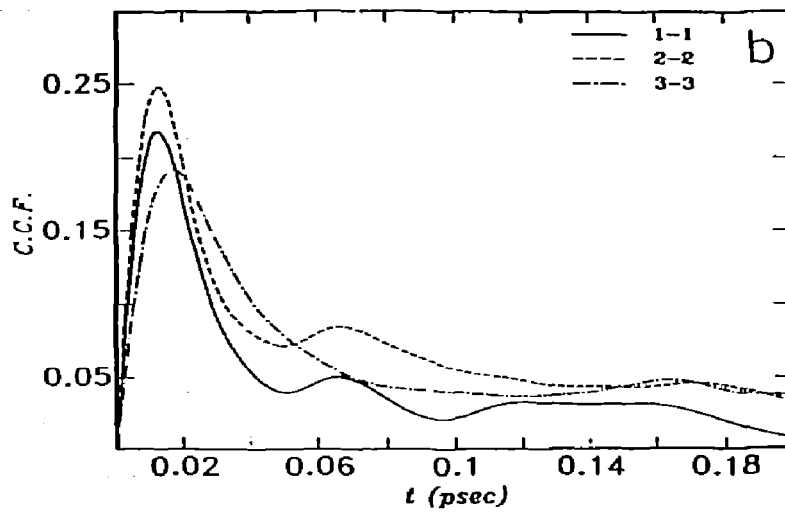
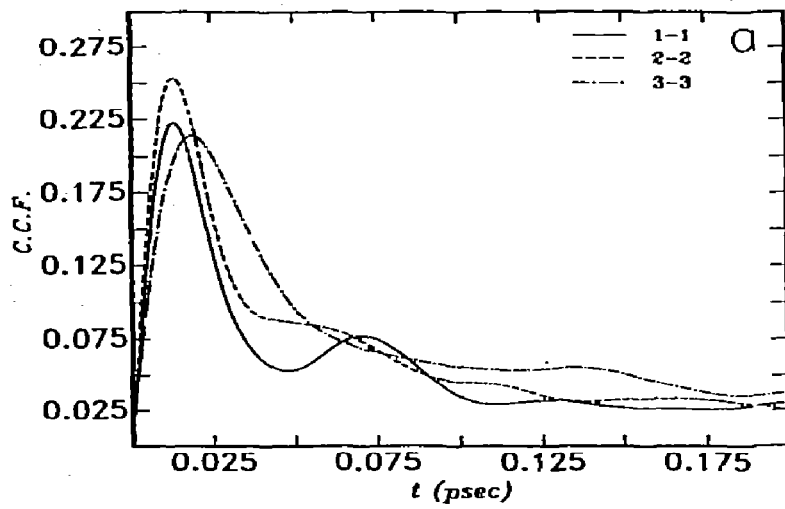


Fig. 5. The c.c.f. C_5 with (a) 864 molecules and (b) 108 molecules

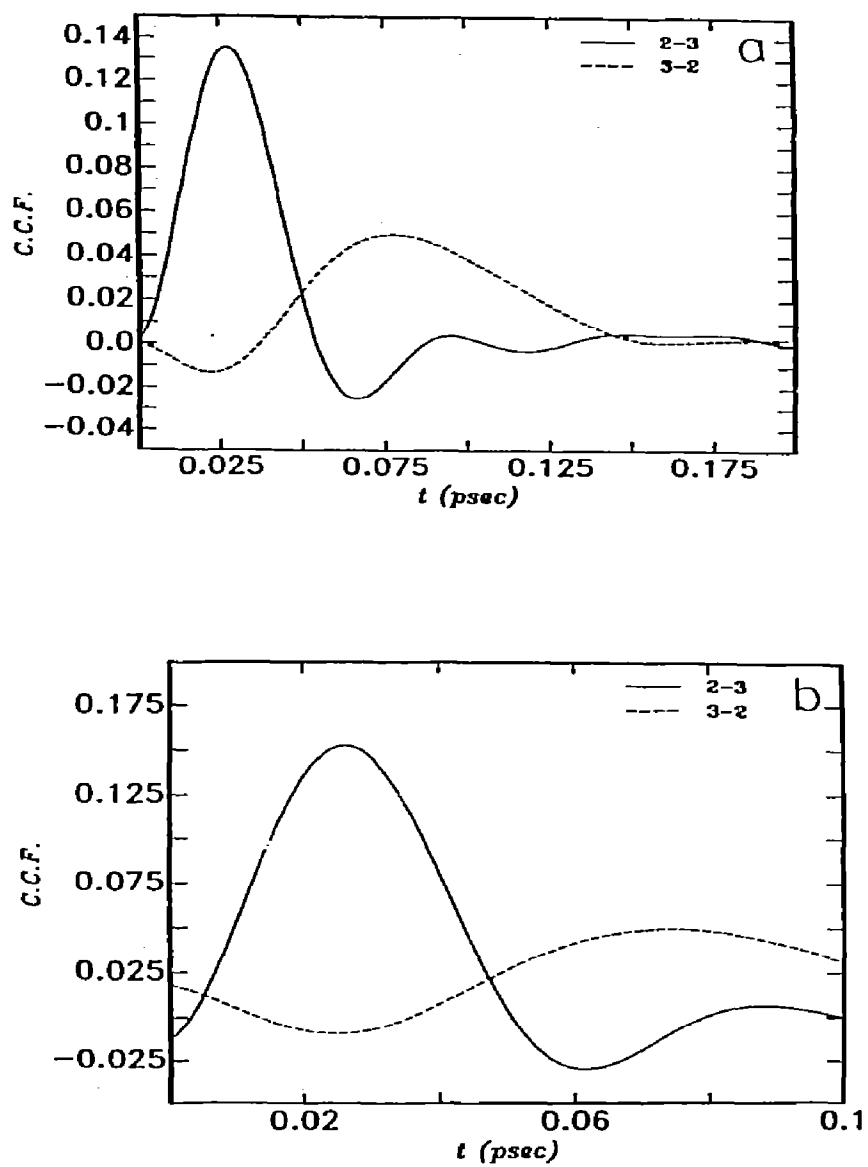


Fig. 6. The c.c.f. C_6 with (a) 864 molecules and (b) 108 molecules.

The results for these cross correlation functions from the 108 and 864 molecule simulations are illustrated in Figs. (1) to (5), where a direct comparison is made for each case. In Fig. (6) a similar comparison is made for the direct cross correlation between the molecular centre of mass velocity, v , and the same molecule's angular velocity in frame (1,2,3):

$$C_{-6}^{ij}(t) = \left[\frac{\langle v_{-i}(t) \omega_{-j}^T(0) \rangle}{\langle v_{-i}^2 \rangle^{1/2} \langle \omega_{-j}^2 \rangle^{1/2}} \right]_{(1,2,3)}$$

In general the cross correlation functions that exist for a sample of 108 water molecules also exist for 864 water molecules, with similar time dependence. Time auto correlation functions are much less "noisy" in a computer simulation, and there are no significant sample size effects for autocorrelation in this work.

Conclusions.

It is concluded that the new cross correlation functions recently characterised with 108 molecule samples in water also exist when the sample size is increased by a factor of eight. There is little effect of increasing sample size on time auto-correlation functions.

It is probably safe to infer that the cross correlation functions are not artifacts introduced, for example, by periodic boundary conditions in small samples, and are real and interesting statistical properties of the molecular liquid and related states of matter.

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