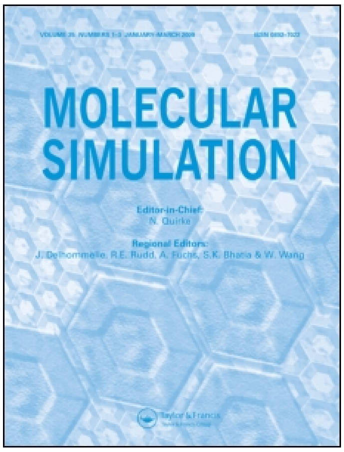

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# Reaction Field Effects on the Simulated Properties of Liquid Water

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# REACTION FIELD EFFECTS ON THE SIMULATED PROPERTIES OF LIQUID WATER

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The effects of including a reaction field contribution on the structure and dynamics of liquid water have been investigated using molecular dynamics simulations. Reaction field effects are determined for two models of water, the simple point charge (SPC) model and the extended simple point charge (SPC/E) model, and at two temperatures (277 K and 300 K). Inclusion of the reaction field leads to a reduced system density, an increase in translational diffusion, which is model dependent, an increase in internal energy, and an increase in rotational diffusion rates, in addition to the large (known) changes in the dielectric properties of liquid water. It is concluded that continued use of the reaction field technique should involve a reparameterization of the water model and not merely a merging with the original model parameters.

KEY WORDS: Reaction field, Water, SPC, SPC/E.

## INTRODUCTION

The development of increasingly more accurate models to describe intermolecular interactions in atomic level detail is a particularly active area of research [1]. It is especially important for the continued development and reliability of molecular dynamics and Monte Carlo simulation results. Current models for most condensed phase simulations are usually restricted to a (small) collection of point charges and Lennard-Jones spheres per molecule. Computer simulations employing these simple representations have helped to broaden our understanding of the structure and dynamics of many condensed phase systems [2].

However, increasing the accuracy of the models is still desirable. More accurate results may be achieved in several ways. Within the classical regime, additional sites may be used to describe atomic charge distributions in more detail [3]. Polarization effects can be modelled using induced dipoles [4,5] or fluctuating charges [6]. Quantum mechanical effects can be included using mixed quantum/classical techniques [7,8], *ab initio* molecular dynamics [9, 10], or path integral techniques [11]. All of these approaches involve a change in the model (or Hamiltonian). Alternatively, the accuracy of a particular model may be increased by examining the assumptions under which it is applied. One such assumption is the use of a cutoff radius for the evaluation of the nonbonded electrostatic interactions in molecular simulations.

A cutoff is usually invoked to reduce the computational expense of a simulation. This assumes that intermolecular interactions are negligible for molecular separations greater than the cutoff distance. Unfortunately, this is not always true for systems containing polar molecules and the cutoff distances commonly used for simulations. Consequently, sizeable errors may occur, depending on the property of interest, which correspondingly reduce the accuracy of the model.

A simple technique to reduce errors generated when using a cutoff is the reaction field technique [12]. In this approach one attempts to include the neglected interactions by assuming that the molecules outside the cutoff behave as a dielectric continuum. The interaction between the charge distribution within the cutoff sphere and the dielectric continuum can be expressed in terms of a reaction from the continuum to the charge distribution, known as the reaction field. This type of method can significantly improve the accuracy of a particular model, especially if dielectric effects are important [13].

Typically, the reaction field contribution is directly combined with the original force field. Although force field parameters are usually determined with the aid of simulations performed with a cutoff, the additional reaction field term is assumed not to adversely affect this parameterization. In this paper we address the validity of this assumption using molecular dynamics simulations of liquid water. Both structural and dynamical properties are investigated. By comparing multiple simulations of two water models (SPC and SPC/E) with and without a reaction field contribution (using a reaction field permittivity of $\varepsilon_{RF} = \infty$ and 1, respectively), the effect of including a reaction field may be determined for this system. In order to gauge how important such effects may be, we also compare the effect of including a reaction field term to that of a change in temperature and to that of a change in the water model.

An early study by van Gunsteren *et al.* investigated the effect of inclusion of a reaction field on the simulation of the ST2 model of water [14]. On addition of the reaction field they observed an increase in the translational diffusion of water by almost a factor of two, and an increase in the rate of rotational diffusion. Here, we expand and generalize their results by investigating more properties and by simulating more than one model at two different temperatures. The increased simulation times should also help to decrease the degree of statistical error.

## METHOD

A total of eight molecular dynamics simulations were performed. The SPC [15] and SPC/E [16] models of water were simulated at both 277 K and 300 K using a reaction field permittivity of $\varepsilon_{RF} = 1$ and $\infty$. All simulations involved a system of 512 waters in a cubic periodic box. The systems were initially equilibrated at constant pressure and temperature ($N, P, T$) for 50 ps. The average box lengths from these simulations were then used as the box dimensions for a series of constant volume ($N, V, T$) simulations. After a further 50 ps equilibration, each system was simulated for a further 1000 ps and configurations were saved every 0.1 ps for analysis. All simulations were performed with the GROMOS programme [17], with a cutoff distance of $R_C = 0.9$ nm. Temperature and pressure (if applicable) regulation was achieved with the weak coupling method [18] and coupling constants of $\tau_T = 0.1$ ps and $\tau_P = 0.5$ ps, respectively. Bond lengths and angles were constrained using SHAKE [19] and a relative tolerance of $10^{-5}$. The time step was 2 fs.

## RESULTS AND DISCUSSION

The molecular dynamics results are presented in Table 1. During the ($N, P, T$) runs the addition of a reaction field resulted in an increase in the box length, and a corresponding decrease in the density of the system of 2–3%. From the nanosecond ($N, V, T$) runs, an increase in the total potential energy per molecule of about 1 kJ/mol was observed. The effect of a reaction field on the self diffusion constant of water was to increase the mobility of the water by as much as 35%. This trend essentially mirrors the decrease in density for all but the SPC/E model at 277 K. This is in agreement with the results of van Gunsteren *et al.* for the ST2 model of water [14], although the percentage increase is substantially less since we use a larger cutoff of $R_C = 0.9$ nm (to be compared with $R_C = 0.578$ nm in reference 14). The zero frequency shear viscosity has been determined previously for each system [20]. However, although the viscosity and diffusion constant are intimately related [21], the viscosity is unaffected by the different treatments of the long range electrostatic interactions.

Changes in the structure of liquid water are presented in Table 1 and also in Figure 1, where we display the water oxygen-oxygen radial distribution function for SPC/E water at 300 K without a reaction field. As the same trends appear for different models and temperatures, all simulations results are presented as deviations from the simulation of SPC/E water at 300 K without a reaction field contribution. The position of the first maximum ($g_{OO}^{\max}$) was the same for all simulations. However, the height of this peak (Fig. 1), and the distance to the first minimum ($g_{OO}^{\min}$), varied between the different

**Table 1** Molecular dynamics simulation results[a]

| *Model* | *SPC* | *SPC* | *SPC* | *SPC* | *SPC/E* | *SPC/E* | *SPC/E* | *SPC/E* |
|---|---|---|---|---|---|---|---|---|
| $T$(K) | 277 | 277 | 300 | 300 | 277 | 277 | 300 | 300 |
| $\varepsilon_{RF}$ | 1 | $\infty$ | 1 | $\infty$ | 1 | $\infty$ | 1 | $\infty$ |
| $L$(nm) | 2.4902 | 2.5076 | 2.4998 | 2.5229 | 2.4721 | 2.4911 | 2.4813 | 2.5026 |
| $\rho$(g/cm$^3$) | 0.991 | 0.971 | 0.980 | 0.953 | 1.013 | 0.990 | 1.002 | 0.976 |
| $P$(atm) | −54 | 14 | 28 | 2 | −27 | −5 | −5 | −37 |
| $U/N$(kJ/mol) | −43.2 | −42.2 | −41.9 | −40.8 | −49.5 | −47.3 | −47.0 | −45.9 |
| $D(\times 10^{-9}\,\mathrm{m^2/s})$ | 2.8 | 3.6 | 3.9 | 5.3 | 1.6 | 1.8 | 2.7 | 3.2 |
| $\eta$(cp)[b] | 0.8 | 0.8 | 0.5 | 0.6 | 1.4 | 1.4 | 0.8 | 0.8 |
| $g_{OO}^{\max}$(nm) | 0.276 | 0.279 | 0.279 | 0.278 | 0.276 | 0.276 | 0.276 | 0.276 |
| $g_{OO}^{\min}$(nm) | 0.338 | 0.338 | 0.350 | 0.350 | 0.330 | 0.330 | 0.330 | 0.330 |
| $n_{OO}$ | 4.7 | 4.6 | 5.3 | 5.1 | 4.5 | 4.4 | 4.4 | 4.3 |
| $G_K$ | 0.15 | 3.26 | 0.16 | 3.38 | 0.14 | 3.23 | 0.15 | 3.46 |
| $\tau_M$(ps) | 0.5 | 7.8 | 0.3 | 6.0 | 0.6 | 13.6 | 0.4 | 8.1 |
| $\varepsilon$[c] |  | 56 |  | 54 |  | 69 |  | 62 |
| $\tau_1$(ps) | 4.3 | 3.4 | 3.0 | 2.3 | 7.6 | 6.2 | 4.6 | 3.8 |
| $\tau_2$(ps) | 1.4 | 1.2 | 0.9 | 0.8 | 2.5 | 2.1 | 1.5 | 1.3 |
| $\tau_3$(ps) | 0.7 | 0.6 | 0.5 | 0.4 | 1.2 | 1.1 | 0.7 | 0.6 |

[a] $L$ = box length, $\rho$ = density, $P$ = pressure, $U/N$ = potential energy per molecule (no polarization correction), $D$ = diffusion constant, $\eta$ = shear viscosity, $g_{OO}^{\max}$ = position of the first maximum in the oxygen-oxygen radial distribution function, $g_{OO}^{\min}$ = position of the first minimum $n_{OO}$ = coordination number to $g_{OO}^{\min}$, $G_K$ = finite system Kirkwood $g$ factor, $\tau_M$ = total dipole moment correlation time, $\varepsilon$ = dielectric constant, $\tau_i$ = single molecule rotational correlation times.

[b] Reference 20

[c] Reference 26

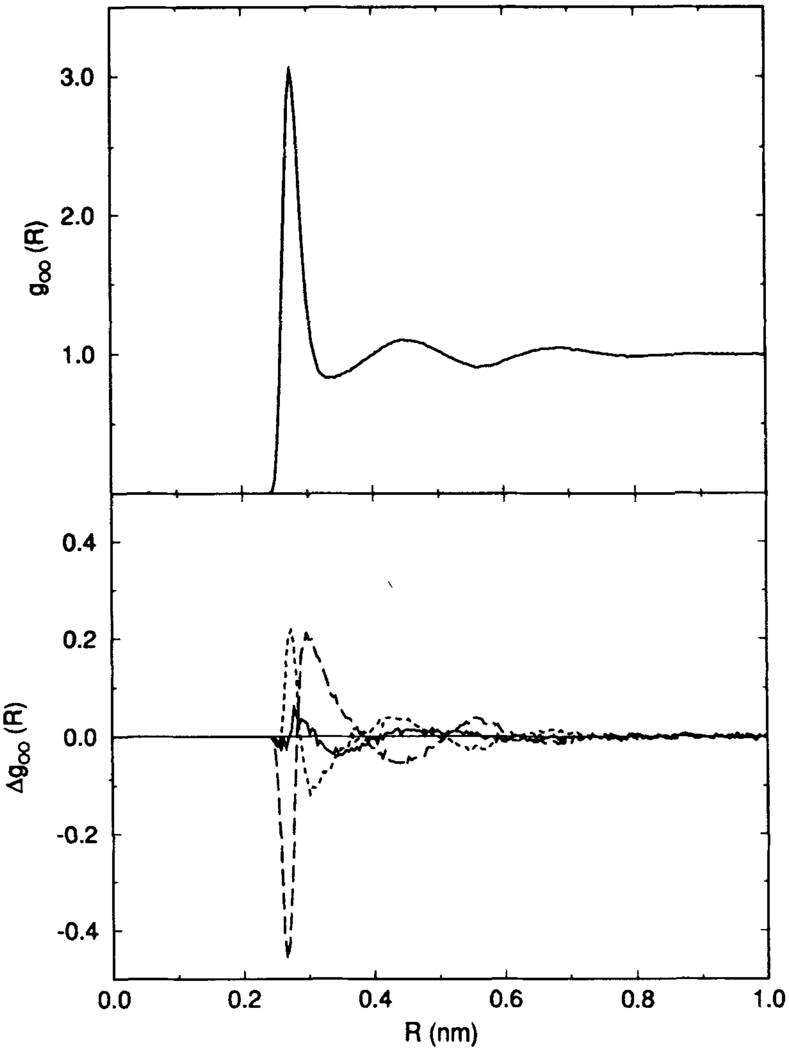

**Figure 1** The oxygen-oxygen radial distribution function for the SPC/E water model at 300 K without a reaction field (top). The bottom figure displays the change in the radial distribution function upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

temperatures and models. The effect of adding a reaction field contribution was small and corresponded to a slight increase in the structure of water, although not as significant as that observed upon a decrease in temperature. Coordination numbers ($n_{OO}$), obtained by integrating the respective radial distribution functions to the first minimum, displayed no variation between the different reaction field treatments.

A histogram of water-water pair interaction energies is presented in Figure 2. The familiar maximum associated with directly hydrogen bonded water pairs was observed

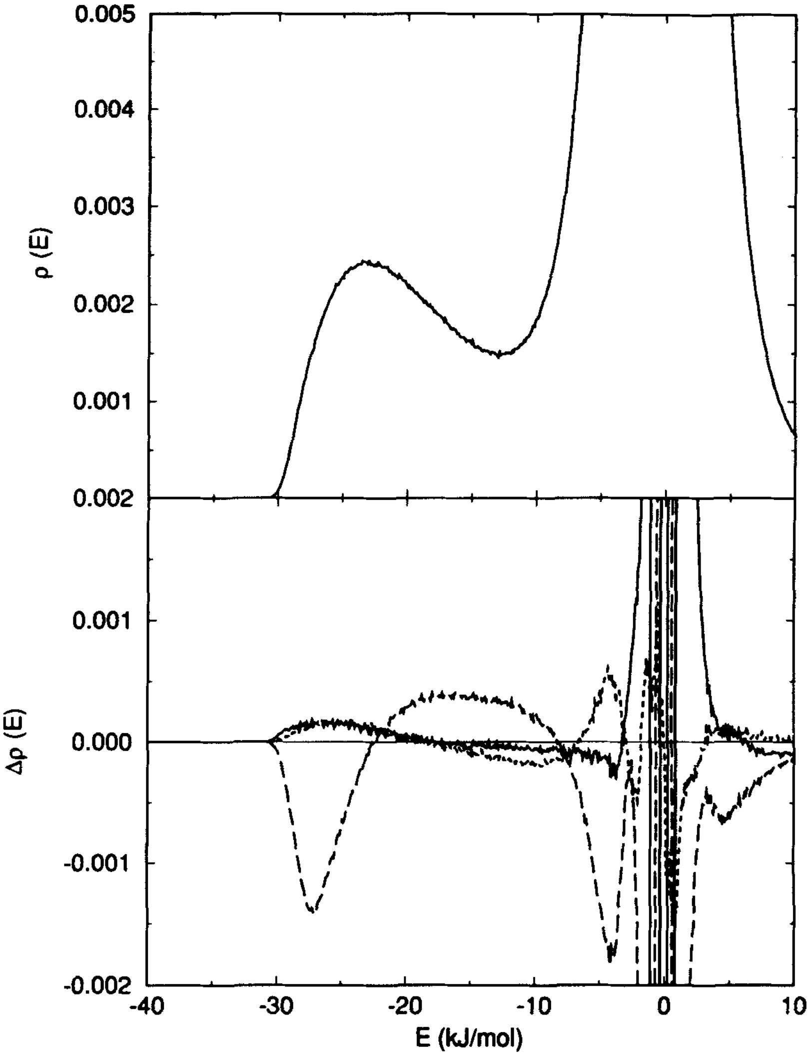

**Figure 2** The water molecule energy pair distribution function for the SPC/E water model at 300 K without a reaction field (top) normalized to unit area. The bottom figure displays the change in the energy distribution function upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

at about $-25$ kJ/mol. On addition of the reaction field, the probability of occurrence of interaction energies lower than this maximum appear to have increased, and are comparable with the effect of decreasing the temperature to 277 K. Not surprisingly, changing to the SPC model produced the largest differences. Here, the pair energy probability decreased for energies less than $-25$ kJ/mol, and increased for intermediate values between $-20$ and $-10$ kJ/mol.

Dielectric properties are known to be sensitive to the method of truncation of electrostatic interactions [22–24] and accordingly they represent the largest differences between simulations performed with and without a reaction field term. Figure 3 displays the average orientation $C_{\mu\mu}$ between water dipoles as a function of the water separation defined as,

$$C_{\mu\mu}(R) = \left\langle \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\boldsymbol{\mu}_i||\boldsymbol{\mu}_j|} \right\rangle, \quad r_{ij} = R \tag{1}$$

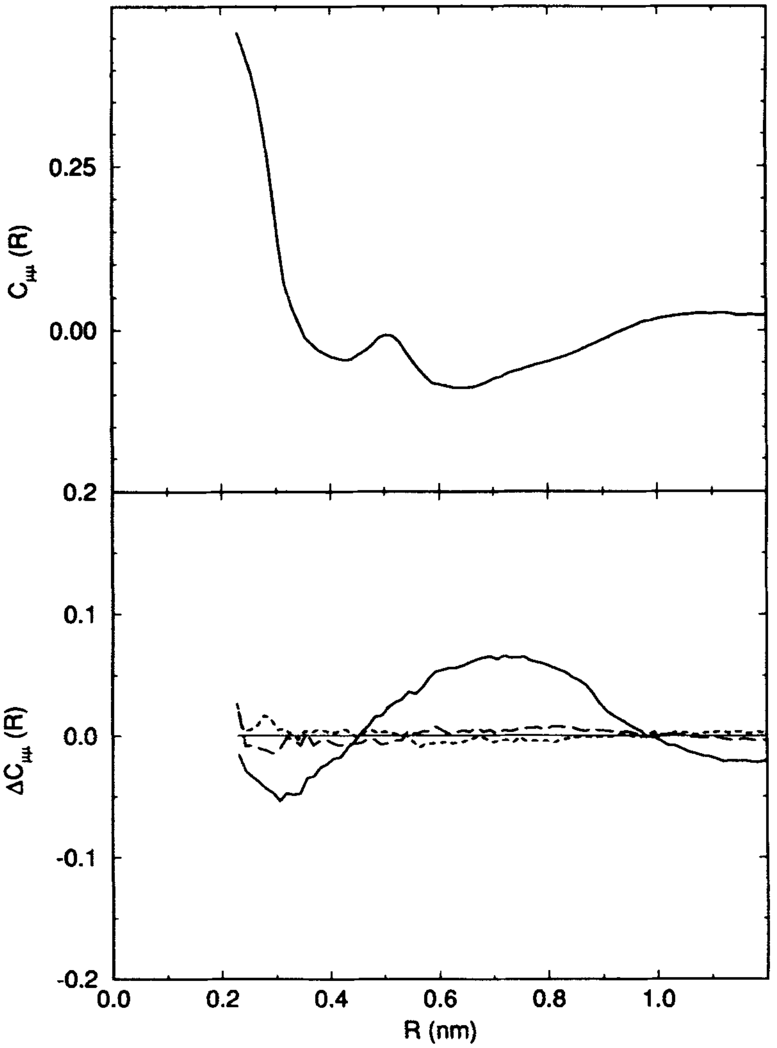

**Figure 3** The water dipol-dipole correlation as a function of separation for the SPC/E water model at 300 K without a reaction field (top). The bottom figure displays the change in the spatial correlation function upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

where $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ are the dipole moments of molecules $i$ and $j$, respectively. On addition of the reaction field the spatial correlations changed considerably, displaying far less anti correlation in the region between 0.5 and 0.9 nm, just within the cutoff. A consequence of this was the occurrence of larger finite system Kirkwood $g$ factors $G_K$ (Table 1) [25], defined as,

$$G_K = \frac{\langle |\mathbf{M}|^2 \rangle - \langle |\mathbf{M}| \rangle^2}{N \langle |\boldsymbol{\mu}|^2 \rangle} \tag{2}$$

where $\mathbf{M}$ is the total dipole moment of the whole system, $N$ is the number of molecules and $\boldsymbol{\mu}$ is the dipole moment of a single water molecule. The differences between simulations performed with and without a reaction field indicated a severe damping of the total dipole moment fluctuations for the traditional cutoff techniques [26].

The dielectric relaxation time of the system is related to the decay of the total dipole moment time autocorrelation function [25],

$$\boldsymbol{\Phi}(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle} \tag{3}$$

which may be described by a relaxation time $\tau_M$ given by,

$$\tau_M = \int_0^\infty \boldsymbol{\Phi}(t)\,dt \tag{4}$$

Here, $\mathbf{M}(t)$ is the total dipole moment of the system at time $t$. Values of $\tau_M$ obtained from the simulations are presented in Table 1. Simulations performed without a reaction field resulted in substantially increased dielectric relaxation rates.

Figures 4 and 5 show the centre of mass and atomic velocity autocorrelation functions, respectively. The effect of the addition of a reaction field on these functions was fairly negligible, even though the integral of the differences curve is proportional to the difference in diffusion constants, which was found to be significant. The atomic velocity autocorrelation functions appear to display quite pronounced periodically oscillating differences between the simulations. The corresponding velocity frequency spectra are shown in Figures 6 and 7. Significant differences were only observed at zero frequency, corresponding to the difference in observed diffusion constants.

Single molecule rotational diffusion constants were obtained by monitoring the angle of rotation of the molecular dipole moment vector as a function of time,

$$\cos\theta(t) = \left\langle \frac{\boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0)}{|\boldsymbol{\mu}|^2} \right\rangle \tag{5}$$

where the angular brackets denote an average over water molecules and time origins. The corresponding correlation times $\tau_l$ were obtained from a fit using the following

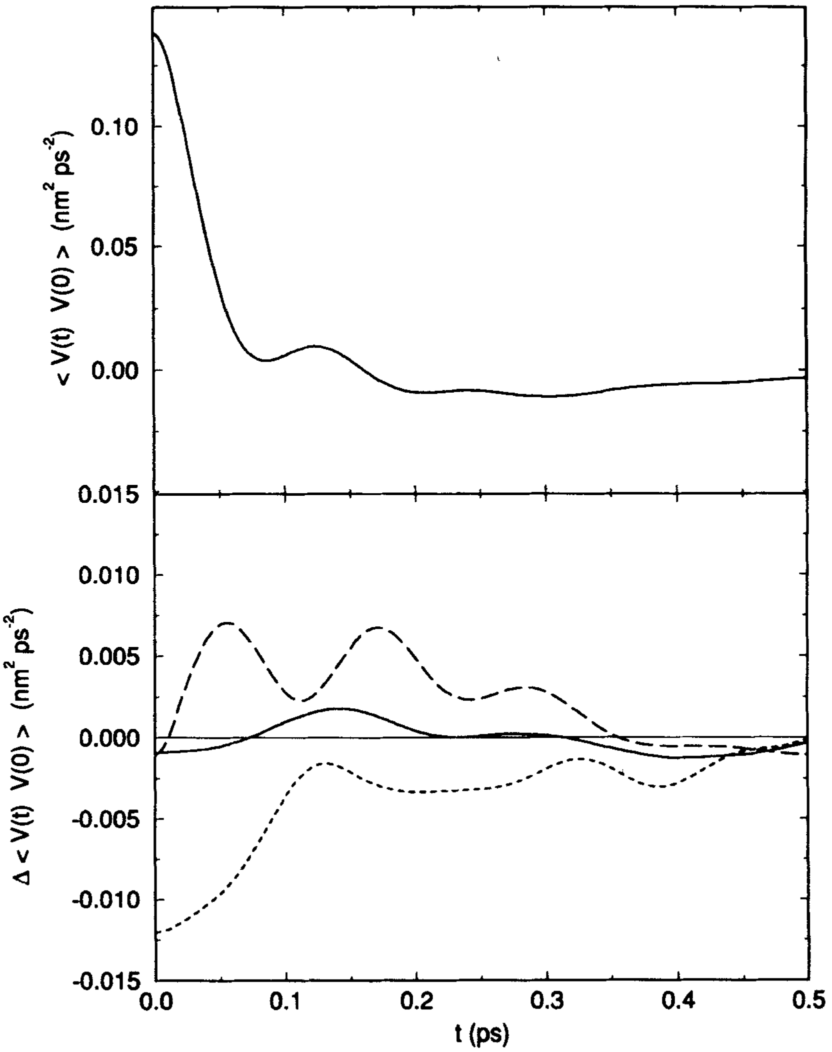

**Figure 4** The centre of mass velocity autocorrelation function for the SPC/E water model at 300 K without a reaction field (top). The bottom figure displays the change in the correlation function upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

relationship [2],

$$\langle P_l[\cos\theta(t)]\rangle = e^{-t/\tau_l} \tag{6}$$

where $P_l$ denotes the $l$th rank Legendre polynomial. Examination of the resulting correlation times in Table 1 suggests a sizeable increase in rotation rate on inclusion of

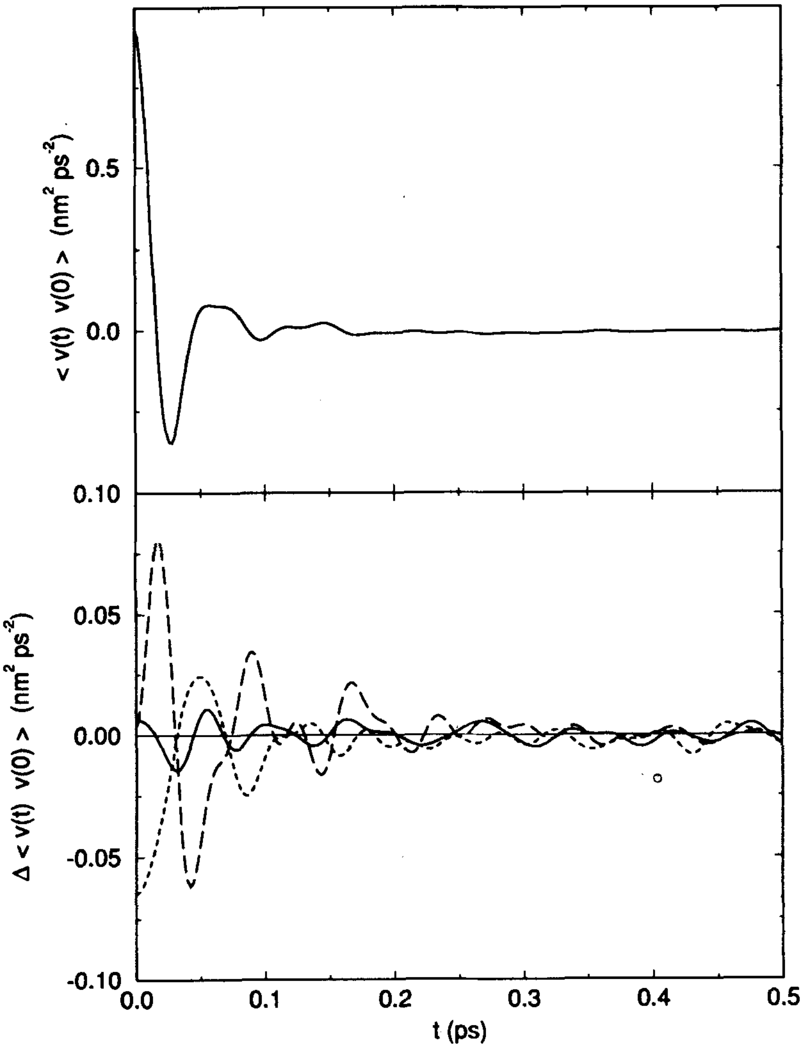

**Figure 5** The atomic velocity autocorrelation function for the SPC/E water model at 300 K without a reaction field (top). The bottom figure displays the change in the correlation function upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

the reaction field contribution. This increase of about 25% was also observed for the ST2 model of water [14]. The increase in rate was comparable with that observed on increasing the temperature from 277 K to 300 K. We note that inclusion of a reaction field contribution results in increased translational and rotational diffusion, and yet the total dipole moment correlation function, which is a collective property, decays an order of magnitude slower.

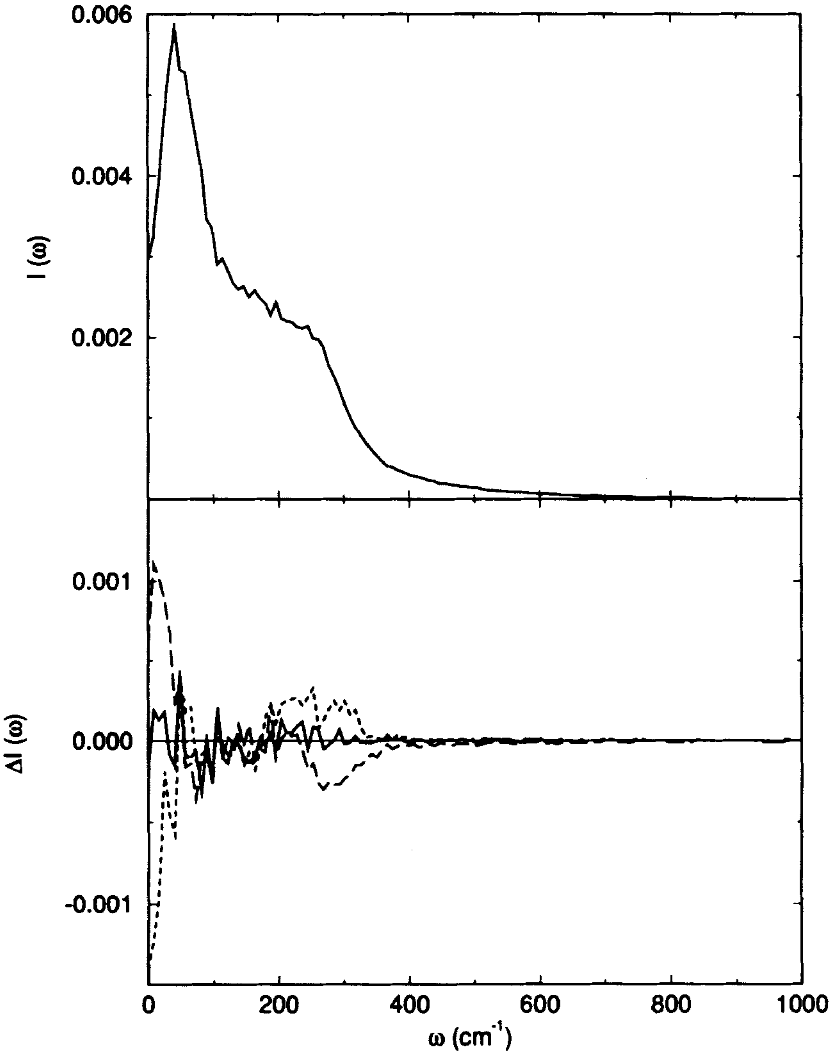

**Figure 6** The centre of mass velocity frequency spectrum for the SPC/E water model at 300 K without a reaction field (top) normalized to unit area. The bottom figure displays the change in the spectrum upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

## CONCLUSIONS

In this paper we have investigated the effects of including the reaction field technique to compensate for the neglect of interactions beyond the traditional cutoff employed in many condensed phase simulations. Examination of these effects for two different water models, and at two different temperatures, allows for a generalization of the observed trends. By examining both structural and dynamical properties of liquid water we conclude that inclusion of a reaction field leads to the following effects;

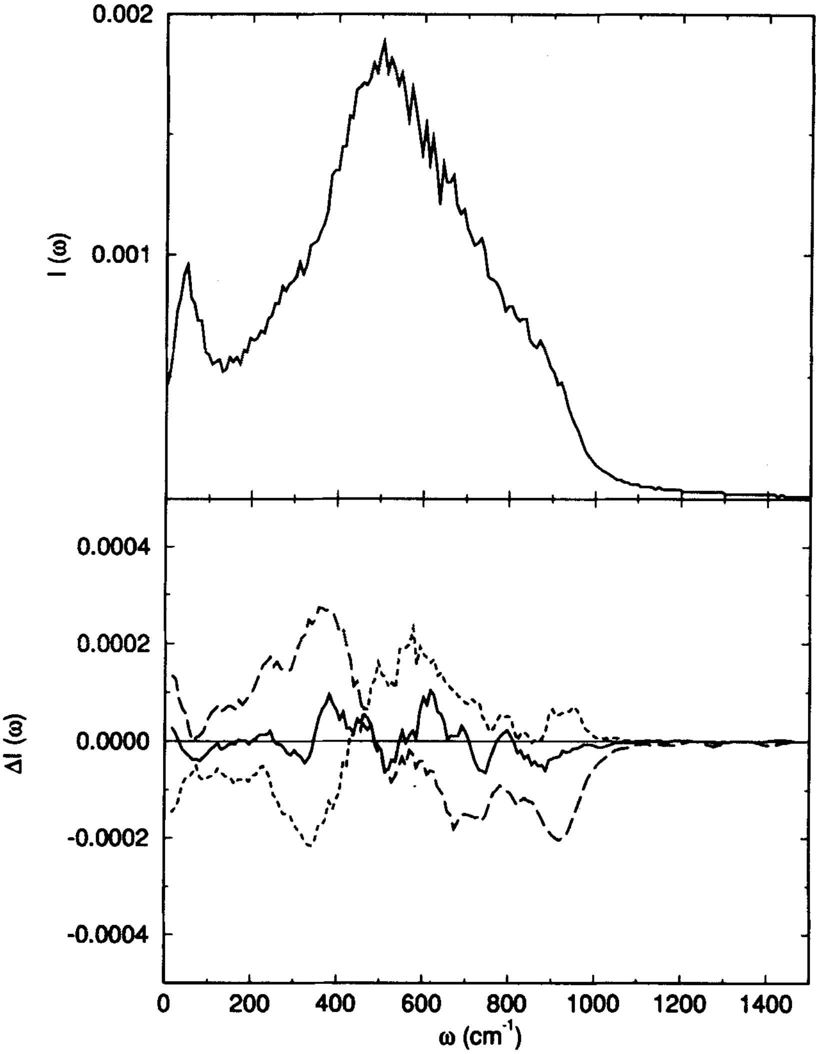

**Figure 7** The atomic velocity frequency spectrum for the SPC/E water model at 300 K without a reaction field (top) normalized to unit area. The bottom figure displays the change in the spectrum upon inclusion of the reaction field (solid line), decreasing the temperature to 277 K (dotted line), or using the SPC model (dashed line).

1) An increase in pressure within the system leading to lower densities under standard state conditions ($\approx 2\%$ change).
2) An increase in the internal energy of the system ($\approx 2\%$ change).
3) An increase in translational diffusion rates, the size of which is dependent on the exact model (30% for SPC, and 15% for SPC/E).
4) Significantly different dielectric properties, including a decrease in the water-water dipole anti correlations at larger distances, just within the cutoff, and an

increase in the total dipole moment correlation time of more than an order of magnitude.

5) Shorter single molecule rotation correlation times ($\approx$ 10–20%).

These results are generally consistent with the previous study of van Gunsteren *et al.* [14], although the degree of change for many of the properties is different due to the use of a different cutoff and water model. They are significant. Hence, the method of treatment of long range interactions (if any) should be considered an integral part of the force field. The above changes suggest that the inclusion of a reaction field for the simulation of condensed systems will lead to an imbalance in the parameterization which should be readdressed if the full advantages (increased accuracy) of the reaction field technique are to be exploited.

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