STRUCTURE AND DYNAMICS OF THE “CONFIGURATION INTERACTION” MODEL
OF LIQUID WATER

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Structural and dynamical properties of liquid water have been obtained over a range of temperatures by computer simulation of a 343 molecule system employing the “configuration interaction” potential. Use of an improved molecular dynamics algorithm and a high-speed array processor permitted simulations spanning times an order of magnitude longer than previously feasible.

In the majority of numerical simulations of liquid water two microscopic models have been the focus of attention. These two models are generally referred to by the mnemonics ST2 and CI. The ST2 model [1] is of empirical origin, designed to fit both experimental data and certain preconceived notions as to the structure of liquid water; it has been the subject of considerable study by both molecular dynamics (MD) [1] and Monte Carlo (MC) [2,3] methods, and a great deal is known about its behavior under a variety of physical conditions. The “configuration interaction” (CI) model involves an interaction potential based on a fit to ab initio quantum mechanical calculations for water dimers [4]; while there have been several MC studies of this model [3,5,6], the range of physical conditions under which the studies have been made is more restricted than in the case of the ST2 model, and to the best of our knowledge, no detailed MD study of the CI model has been undertaken to date.

The aim of this letter is to present a selection of structural and dynamical results from an extensive MD study of liquid water, and to demonstrate that currently available, low-priced computer technology is easily capable of simulation studies involving considerably larger systems and spanning time periods an order of magnitude longer than heretofore considered feasible.

Specifically, we have considered a system of 343 water molecules interacting by means of the CI potential [4], with a cut-off radius equal to 9.0 Å. Simulations have been performed for several temperatures, with the experimental water density being used in each case. Periodic boundary conditions were employed to ameliorate the effects of finite system size. The details of the various runs are summarized in table 1, together with some of the measured properties which will be discussed in greater detail below.

These MD simulation runs are approximately an order of magnitude longer than previous MD studies of water [1]. If the relative efficiencies of the MD and MC techniques are taken into account [2] — namely that a single MC pass through the system produces a similar amount of translational and rotational diffusion as the $2 \times 10^{-16}$ s MD time step used in the ST2 simulations [1] — then the degree of configuration space sampling in the present MD work is also considerably greater than in previous MC studies of water [2,3,5,6]. The same also holds true in regard to simulations using the improved “force bias” MC technique [2]. It should also be noted that, with just one exception [5], the earlier MC and MD studies involved systems containing between 64 and 216 molecules, as opposed to the 343 molecule system considered in this study.

The key to the ability to undertake simulations of this magnitude is two-fold: By using a quaternion rep-
Table 1
Summary of the MD runs on liquid water

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Simulated period (ps)</th>
<th>Number of steps</th>
<th>Internal energy (kcal/mole)</th>
<th>$10^5 D$ (cm²/s)</th>
<th>$\tau_1$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>74.7</td>
<td>65260</td>
<td>-8.96</td>
<td>1.5 (0.9) a)</td>
<td>5</td>
</tr>
<tr>
<td>31</td>
<td>58.7</td>
<td>54510</td>
<td>-8.54</td>
<td>2.8 (2.7)</td>
<td>3</td>
</tr>
<tr>
<td>104</td>
<td>43.3</td>
<td>45010</td>
<td>-7.78</td>
<td>6.6 (7.5)</td>
<td>1</td>
</tr>
</tbody>
</table>

a) The experimental values of $D$ are given in parentheses.

The oxygen–oxygen radial distribution functions for the three temperatures studied are shown in fig. 1. Error estimates are typically 3–4%. In order to permit comparison with experiment, the corresponding radial distribution functions obtained from X-ray diffraction measurements [10] are also included in fig. 1. While the agreement of the radial distribution functions of the CI model with the experimental results at room temperature is well known [5], the results near the freezing and boiling points are new, and it is gratifying that the essential similarity with experiment is...
maintained. The results at 31°C are almost identical to the original tabulated MC results for this model at 25°C [5]. The oxygen—hydrogen and hydrogen—hydrogen radial distribution functions at 31°C (not shown) were also found to agree with those of the earlier MC work.

Table 1 includes estimates of the average internal energy. Here the error estimates are ≈2%; the energy values themselves depend of course on the cut-off radius. The value at 31°C agrees with the MC result, viz. –8.51 kcal/mole [5].

An advantage of the MD over the MC approach is that, in addition to providing estimates for the time-averaged structural and thermodynamic properties, it also permits examination of the dynamical behavior of the model. Two of the more readily accessible quantities are the rates of translational and rotational self-diffusion. These and other aspects of the dynamical behavior of the CI model have not been investigated previously; however the translational diffusion of the ST2 model has been studied [1], as has that of its predecessor, the closely related BNS model [11], rotational diffusion has been studied only in the case of the BNS model.

The translational self-diffusion coefficient $D$ is defined as

$$D = \lim_{t \to \infty} \langle \Delta r^2(t) \rangle / 6t, \quad (1)$$

where $\langle \Delta r^2(t) \rangle$ is the mean-square molecular displacement during the time interval $t$, averaged over all molecules. One means of characterizing the rotational self-diffusion is through the autocorrelation function for the molecular dipole moment vector direction

$$\Gamma_1(t) = \langle \cos \theta_i(t) \rangle, \quad (2)$$

where $\theta_i(t)$ measures the angular displacement of the dipole moment vector of a single molecule over an interval $t$, and the average is again taken over all molecules; in this case the time dependence typically involves exponential decay at intermediate and large values of $t$, with a relaxation time constant $\tau_1$. Fig. 2 illustrates the observed translational diffusion for each of the temperatures considered, and the dipole direction autocorrelation functions are shown in fig. 3.

Examination of the translational and rotational diffusion data over much shorter time scales (not shown in these graphs, but typically involving intervals of less than 0.1 ps) reveals the existence of short-term oscillatory and librational molecular motions; the translational self-diffusion curves begin with zero gradient, and the dipole autocorrelation functions exhibit a sharp initial decay.

The estimates of $D$ and $\tau_1$ are included in table 1,
together with the corresponding experimental results for \( D \) [12] (the value at 104°C is obtained by extrapolation [11]). The MD estimates are deduced respectively from the long-time limiting gradients in fig. 2, and from the large \( t \) behavior of the quantity \(-t/\ln \Gamma_1(t)\). Some appreciation of the potential numerical errors involved in estimating dynamical properties from only short MD runs follows from the observation that the estimate of \( D \) at 31°C, based only on diffusion data for time intervals below 1 ps, is 15% larger than the value given in table 1. The results for \( D \) are seen to be in fair agreement with experiment, in particular the value at 31°C, which agrees almost exactly, but the overall temperature dependence of the simulation results is weaker than that observed experimentally. The quantity \( \tau_1 \), while obviously related to the dielectric relaxation rate and showing a similarly strong temperature dependence, is not unambiguously determined by experiment [11]. Neither \( D \) nor \( \tau_1 \) differ significantly from previous MD estimates obtained using the ST2 and BNS models [1,11]: the uncertainties in the estimates tend to obscure the differences.

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References