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Long-Range Forces in Molecular Dynamics Calculations on Water

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The possibility is investigated of speeding up molecular dynamics calculations on aqueous systems by calculating force contributions in two parts. Explicit calculations are made every time step within inner shells containing 4 to 20 molecules, corrections being made at longer time intervals for the more slowly varying contribution outside the inner shell cutoff. Results indicate possible time savings of a factor of 2 to 4 with no significant decrease in accuracy or exacerbation of energy-conservation problems. By using a very small inner shell, the approach to equilibrium can be very significantly speeded up. The technique is particularly suited to probing those properties (e.g., dielectric) which require an accurate assessment of long-range forces.

1. INTRODUCTION

In molecular dynamics and Monte Carlo calculations, forces and energies are calculated explicitly out to a specified cutoff distance from each molecule. For simple liquids, where the density is high and the intermolecular pair potential is isotropic, a simple density-dependent correction can be made for the contributions of those centres excluded by the cutoff procedure.

When dealing with water, the relatively low molecular density and the angular dependence of the potential functions raise queries about the effect of this cutoff, and corrections for contributions of centers outside the cutoff range are generally *not* made. Rahman's energy conservation tests suggest that the cutoff distance he uses is adequate for most thermodynamic and transport properties [1, 2], although problems do arise with dielectric and other intrinsically long-range properties (A. Rahman; unpublished). Comparisons with full Ewald summations by Macdonald [3] suggest that errors in force calculations of greater than 5% are rarely caused thereby. The possibility of lining up of dipoles is sometimes thought to be a problem in any attempt to reduce the cutoff radius R_∞; however, no explicit calculations of the effect seem to have been made. R_∞ is often reduced in the early stages of a calculation in order to speed up the approach to equilibrium, but the detailed consequences for the assembly have not been evaluated.

Cutoff distances vary among different workers. In Rahman and Stillinger's work using the ST2 pair potential [4], a cutoff of $R_\infty = 8.46$ Å is used, being slightly less than half the box side (0.5 × 18.626 Å). This gives about 60 to 70 water molecules

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within range, necessitating 60 to 70 intermolecular force and torque calculations for each time step. These calculations consume a large part of the computer time, and any means of reducing them—e.g., by adequately correcting for a reduced cutoff—would be valuable in speeding up molecular dynamics calculations. Thus, some measure of the significance and behavior of long-range forces in an assembly of dipoles would be useful.

2. OUTER SHELL CORRECTION METHOD

We examine here the results of calculating the long-range part of the forces at time intervals considerably greater than the elementary time step Δt. The short-range, most rapidly varying forces are calculated explicitly every Δt, and corrected by the previously calculated long-range contribution.

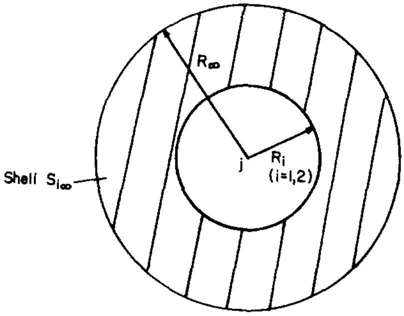

FIG. 1. Schematic showing method used. The forces and torques on molecule j due to molecules within the unshaded sphere radius R are calculated explicitly. These forces and torques are then corrected for the effect of molecules within the shaded volume, a shell radius R_∞.

Assume that a given cutoff R_∞ is adequate, i.e., that pair forces and torques calculated out to this distance are sufficient approximations to the actual forces and torques $\mathbf{F}_\infty$ and $\mathbf{T}_\infty$. Now consider a smaller imaginary sphere drawn with radius R_i from a molecule j (Fig. 1). We need to estimate $\mathbf{F}_\infty$ and $\mathbf{T}_\infty$ sufficiently accurately over a time greater than Δt by explicitly calculating only those forces and torques within R_i, viz., $\mathbf{F}_i$ and $\mathbf{T}_i$, and making a suitable correction to allow for those molecules in the shell $S_{i\infty}$ between R_i and R_∞.

Thus, we explicitly calculate $\mathbf{F}_i$ and $\mathbf{T}_i$, $\mathbf{F}_\infty$ and $\mathbf{T}_\infty$ at time $t = 0$ for each molecule j. Provided the force and torque contributions within shell $S_{i\infty}$, defined as

$$\begin{aligned}\mathbf{F}_{i\infty}(0) &= \mathbf{F}_\infty(0) - \mathbf{F}_i(0),\\ \mathbf{T}_{i\infty}(0) &= \mathbf{T}_\infty(0) - \mathbf{T}_i(0)\end{aligned}$$

vary only slowly with time over n time steps, i.e.;

$$\left.\begin{aligned}\mathbf{F}_{i\infty}(t) &\approx \mathbf{F}_{i\infty}(0)\\ \mathbf{T}_{i\infty}(t) &\approx \mathbf{T}_{i\infty}(0)\end{aligned}\right\} \; 0 \leqslant t \leqslant n\,\Delta t \text{ for some } n,$$

we can approximate the total force and torque on molecule j at time t as

$$\begin{aligned} \mathbf{F}_\infty(t) &\doteqdot \mathbf{F}_i(t) + \mathbf{F}_{i\infty}(0) \equiv \mathbf{F}_\infty'(t), \\ \mathbf{T}_\infty(t) &\doteqdot \mathbf{T}_i(t) + \mathbf{T}_{i\infty}(0) \equiv \mathbf{T}_\infty'(t) \end{aligned} \tag{1}$$

over a time inverval $0 \leqslant t \leqslant n\Delta t$. When $t = n\Delta t$, we recalculate the $\mathbf{F}_{i\infty}$ and $\mathbf{T}_{i\infty}$ corrections explicitly and use these new corrections over the next n time steps.

3. PROCEDURE

Five of Rahman's molecular dynamics configurations of 216 water molecules, using the ST2 potential and periodic boundary conditions [4] were used for analysis. The configurations were $10\Delta t$ apart ($\Delta t = 2.1261 \times 10^{-16}$ sec), giving a coverage of $40\Delta t$ in all. The density was 1 g·cm^{-3}, and the nominal temperature 10°C.

The success of the proposed method will depend critically upon the criterion used to fix the inner cutoff. Indeed, the consequent division of the molecules surrounding a given molecule into two groups could be based upon criteria other than distance, for example, effective pair forces or even their rate of change (see below). In the first instance, however, a distance criterion was used, suitable locations for R_i being suggested by the minima in the pair distribution function (PDF) of the actual arrays, at which distances the density of molecules is low. Two different test cutoff spheres were defined at $R_1 = 3.38$ Å, $R_2 = 5.78$ Å, with $R_\infty = 9.31$ Å. The R_∞ value, marginally less than half the box length (18.626 Å), is some 11 % greater than Rahman and Stillinger's 8.46 Å; thus our tests will be more severe than if their cutoff were used. For configuration 1 ($t = 0$), forces and torques were calculated for molecules within spheres R_1, R_2, and R_∞. Neighbor lists were drawn up for each sphere. The same calculations were performed for configurations 2 to 5, using the neighbor lists drawn up for configuration 1 to define sets of interacting molecules for each succeeding configuration.

4. RESULTS

Contribution to Total Forces and Torques From the Two Cutoff Spheres

As expected in an aggregate of dipoles, the relative contributions of the molecules within each sphere R_i to the *total* forces and torques are variable. Figure 2 indicates the force errors that would result by using a premature cutoff R_i for $i = 1, 2$, and making no correction for the contribution from the outer shell $S_{i\infty}$. Histograms of $|\mathbf{F}_i - \mathbf{F}_\infty|/|\mathbf{F}_\infty|$ for all molecules in configuration 1 are plotted. The spreads are wide, and the average errors confirm that both uncorrected cutoffs will give very serious energy conservation problems in a molecular dynamics run, as is known from Rahman and Stillinger's calculations (A. Rahman, personal communication). How-

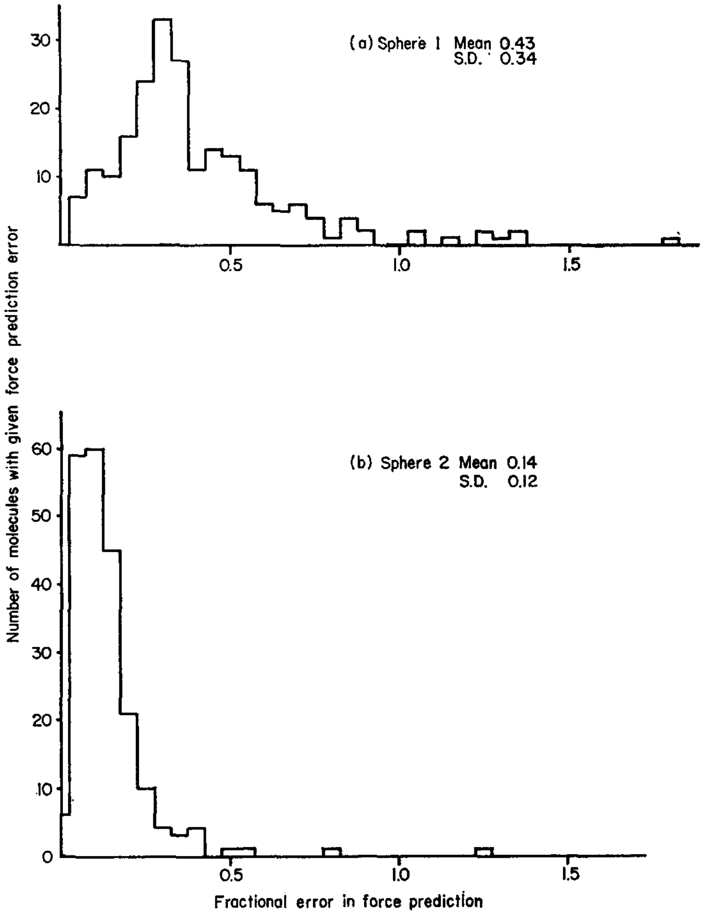

FIG. 2. Normalized fractional errors of forces $|\mathbf{F}_i - \mathbf{F}_\infty|/|\mathbf{F}_\infty|$ calculated using premature cutoffs with no outer shell correction. (a) $R_1 = 3.38$ Å; (b) $R_2 = 5.78$ Å.

ever, for a given center j, the reduced cutoff errors are found to *change* relatively slowly between successive configurations. Thus *correcting* the reduced cutoff forces and torques by some method (e.g., Eq. (1)) should result in much-reduced errors in "predicted" $\mathbf{F}_\infty$ and $\mathbf{T}_\infty$. This postulate is now examined in detail.

"Prediction" of Forces and Torques by Outer Shell Correction to Explicit Calculations Made within a Reduced Cutoff Sphere R_i

$\mathbf{F}'_\infty(t)$, the "predicted" force on molecule j defined by Eq. (1), is calculated in two parts:

(a) explicit pair calculations within sphere R_i at time t ($\mathbf{F}_i(t)$), and

(b) a correction for the shell $S_{i\infty}$ *calculated at* $t = 0$ ($\mathbf{F}_{i\infty}(0)$). Thus, $\mathbf{F}'_\infty(t) = \mathbf{F}_i(t) + \mathbf{F}_{i\infty}(0)$.

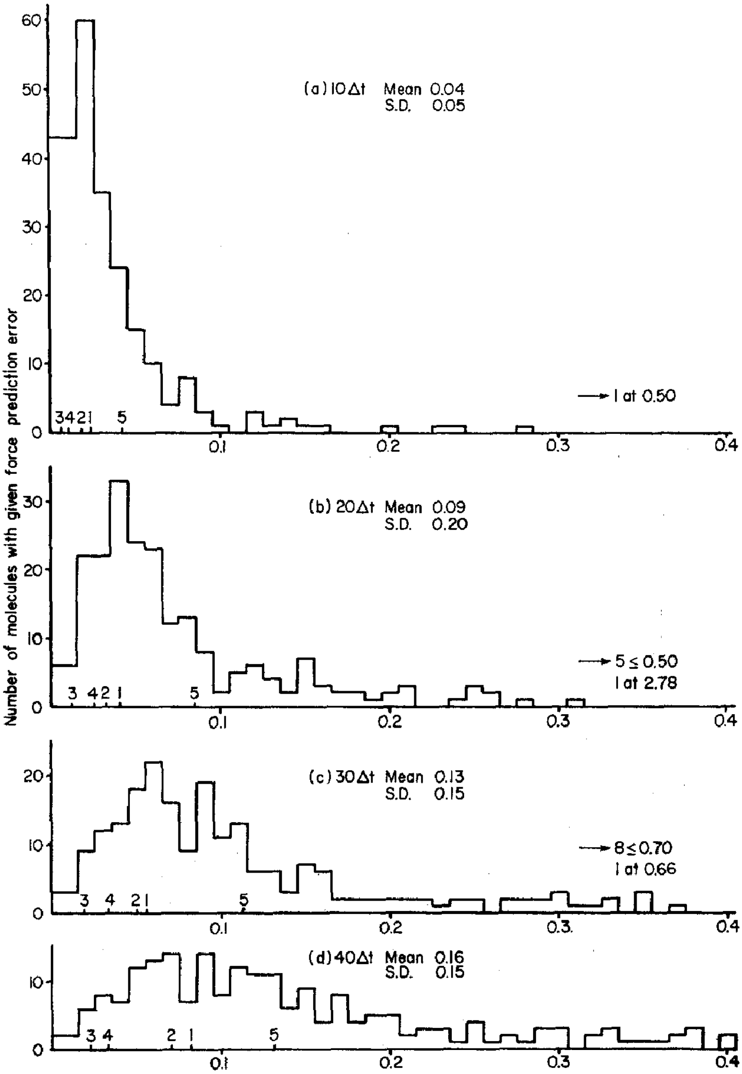

FIG. 3. Normalized fractional errors of predicted forces at four successive times separated by $10\Delta t$ obtained by specific calculations within the smaller cutoff sphere ($R_1 = 3.38$ Å) corrected by the outer shell contribution at $t = 0$. Numbers 1 to 5 refer to errors for five given centers, and show how the error for a given center tends to increase in a predictable way.

Figure 3 shows how the distribution of the normalized errors in the predicted force

$$|\mathbf{F}'_\infty(t) - \mathbf{F}_\infty(t)|/|\mathbf{F}_\infty(t)|$$

spreads with time, using explicit calculations within sphere 1 only. As would be expected, the larger errors occur mainly for molecules where $|\mathbf{F}_\infty(t)|$ is well below $\langle|\mathbf{F}_\infty(t)|\rangle_j$, averaged over all j molecules.

Figure 3 shows also the prediction errors for several specific molecules j chosen at random. They illustrate how the error in a given force prediction in general increases smoothly with time. This memory effect might be used to improve the predictions over longer time periods. However, the marginal increase in speed expected from this second-order correction (see Table II) seems insufficient to justify examining this possibility further.

The comparison between the uncorrected forces of Fig. 2 and the corrected forces in Fig. 3 is interesting. The corrected forces of Fig. 3 are much more reliable, even after $40\Delta t$, than are the uncorrected forces using the same low R_1 cutoff (Fig. 2a). What is more interesting is the comparison between the *uncorrected* forces at the larger $R_2 = 5.78$ Å cutoff (Fig. 2b) and the *corrected* $10\Delta t$ and $20\Delta t$ force predictions using the *much smaller cutoff of* $R_1 = 3.38$ Å (Fig. 3). Even though the R_1 cutoff is at first sight ridiculously small (involving on the average only four explicit pair calculations) the predicted forces are more accurate over at least $10\Delta t$ than are the uncorrected forces using the *larger* R_2 cutoff (~20 molecules). As the prediction using R_1 over $10\Delta t$ is about twice as fast as calculating the uncorrected forces using a cutoff of R_2, the outer shell correction to a very small number of explicit calculations may be used to speed up even more the approach to equilibrium in the early stages of a calculation where a premature cutoff is now used.

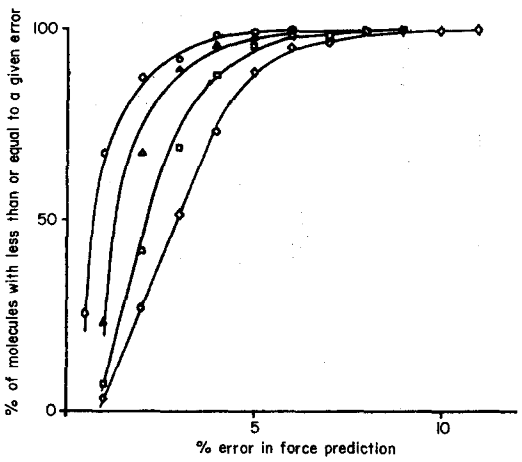

FIG. 4. Force predictions using larger cutoff ($R_1 = 5.78$ Å). ○, After $10\Delta t$; △, after $20\Delta t$; □, after $30\Delta t$; ◇, after $40\Delta t$.

In Table I and Fig. 4, we compare predicted $\mathbf{F}'_\infty(t)$ with actual $\mathbf{F}_\infty(t)$ at intervals of $10\Delta t$ through $\Delta\mathbf{F}(t) \equiv \mathbf{F}'_\infty(t) - \mathbf{F}_\infty(t)$ for all centers j. A fractional error

$$|\Delta\mathbf{F}(t)|/\langle|\mathbf{F}_\infty(t)|\rangle_j$$

is defined, where $\langle|\mathbf{F}_\infty(t)|\rangle$ is averaged over all molecules j. This procedure avoids missing changes in direction unaccompanied by significant changes in force magnitude,

TABLE I

Estimation of Forces and Torques on the Basis of Outer Shell Correction for Long-Range Contributions

Confidence limit (within the given % of average)	Percentage of predictions within the given confidence limits after various times														Uncorrected forces from $R_2 = 5.7$ 8Å truncation
	Forces							Torques							
	Sphere 1			Sphere 2				Sphere 1			Sphere 2				
	$10\Delta t$	$20\Delta t$	$30\Delta t$	$10\Delta t$	$20\Delta t$	$30\Delta t$	$40\Delta t$	$10\Delta t$	$20\Delta t$	$30\Delta t$	$10\Delta t$	$20\Delta t$	$30\Delta t$	$40\Delta t$	
±2	32	5	2	87	67	42	27	6	1	0	51	14	5	2	2
±5	91	49	22	100	99	96	89	49	11	5	91	63	39	27	8
±10	97	87	70	100	100	100	100	94	46	22	98	93	81	72	50
±25	99	96	94	100	100	100	100	98	93	82	100	100	100	100	100
±50	100	100	100	100	100	100	100	100	97	94	100	100	100	100	100

and also prevents overemphasis of differences in direction and/or magnitude when the magnitudes are too small for them to be significant (e.g., see the one large "error" in Fig. 3b.) Similar procedures are followed for the torques.

The following points are of interest:

(1) The force prediction data using sphere 2 ($R_2 = 5.78$ Å) for explicit calculations is very good, giving predictions within 5% with 100% confidence after 10 time steps, 99% confidence after $20\Delta t$, and 96% after $30\Delta t$.

(2) Force predictions using sphere 1 ($R_1 = 3.38$ Å) are surprisingly good within ±5% at 10 time steps, even though the apparently ridiculously low cutoff leaves only four molecules on the average for explicit calculations.

(3) The uncorrected forces using the larger cutoff sphere R_2 are much worse than the corresponding corrected sphere 2 data even after $40\Delta t$. Also, as mentioned previously, even predictions based on the very small sphere 1 ($R_1 = 3.38$ Å) are more reliable up to at least $20\Delta t$ than are the uncorrected forces using the much larger sphere R_2.

(4) The torque figures are significantly worse in all cases. For example, to obtain torque predictions of quality similar to that of the sphere 1 force predictions, we have to use the sphere 2 data, entailing about five times as much calculation. The average torque is only about a quarter of the average force in numerical terms, with in general greater variations in both magnitude and direction with time. This is to be expected from the mass M and moment of inertia I of the water molecule: Taking a typical internal coordinate as 10^{-8} cm, the ratio $I^{1/2}/10^{-8}$: $M^{1/2}$ is about 1:3.5. This is also familiar from water simulation calculations where the rotational motion implies a shorter time step than does the translational motion (see below).

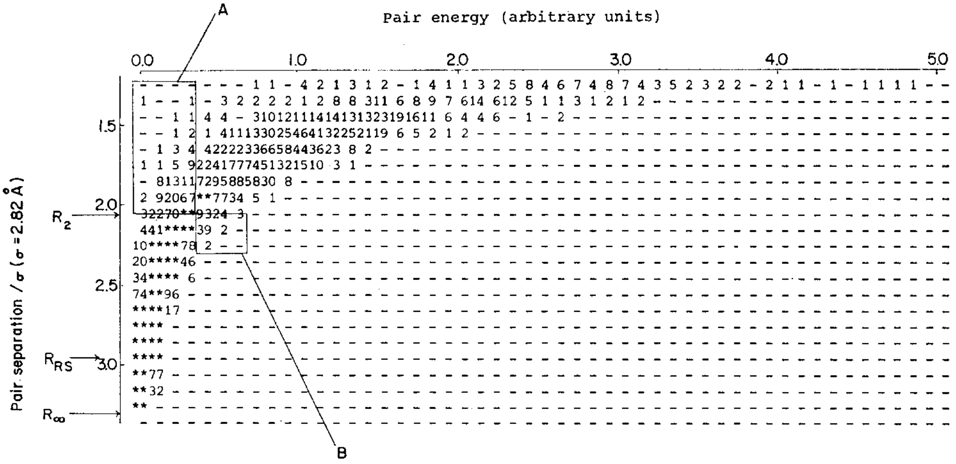

FIG. 5. Force–distance histogram of all pair interactions in shell $S_{1\infty}$ for configuration 1 ($t = 0$). The number of interactions within given ranges of force and distance are shown. ** indicates >99. The boundary between spheres 1 and 2 is indicated (R_2), as are the cutoff distances used here (R_∞) and by Rahman and Stillinger (R_{RS}). Regions A and B are referred to in the text.

5. CHOICE OF CUTOFF CRITERION

Figure 5 indicates how pair forces correlate with distance for *all* pairs between R_1 and R_∞ for configuration 1. Forces for the approximately four pair separations less than R_1 are generally much larger. This cumulative histogram demonstrates a correlation between force and separation distance, suggesting that a straight distance cutoff criterion is reasonable, especially for the larger cutoff R_2.

Comparing individual force–distance histograms for a single center with increasing time shows only small force changes for pair separations between R_2 and R_∞ (shell $S_{2\infty}$); moreover, the numbers (60 to 80) and small force changes involved result in very small total force changes. For the 15 to 25 molecules lying within shell S_{12}, individual force changes of $10\Delta t$ of up to 1 % of the average force are observed. The individual force changes within the explicitly calculated shell defined by R_1 may reach to 10 % of the average, the larger variations occurring for the shortest neighboring distances. Thus, the distance criterion generally assigns the most rapidly varying forces into the explicitly calculated shell.

Two alternative choices of criterion are thereby suggested. First, we could specifically identify the pairs giving rise to the most rapidly varying forces with respect to the average force. This, however, would require at least two explicit calculations over R_∞ to partition neighbors into two sets, and thus considerably reduce the potential time saving. There is, however, correlation between force magnitude and *the signifi-*

TABLE II

Time Factors Theoretically Obtainable over a Cutoff Distance $R_\infty = 9.31$ Å (Equivalent to 80 to 90 Pair Interactions) in Calculating Forces and Torques[a,b]

		Correction recalculated every n time steps					
		n					
Criterion	Average number of explicit pairs	5	10	20	50	100	∞
Sphere 1	4	4.2	7.0	10.5	14.9	17.4	20.8
		(4.0)	(6.4)	(9.0)	(12.1)	(13.7)	15.7
Sphere 2	21	2.6	3.2	3.6	3.9	4.0	4.2
		(2.2)	(2.6)	(2.8)	(3.0)	(3.1)	3.1
Force 0.4	19	2.7	3.4	3.9	4.3	4.4	4.6
Force 0.5	16	2.9	3.8	4.5	5.0	5.2	5.4

[a] Explicit pair calculations are made within spheres 1 ($R_1 = 3.38$ Å) and 2 ($R_2 = 5.78$ Å) corresponding to minima in the PDF. Note that the marginal increase possible after 20 time steps is relatively low.

[b] The figures in parentheses are possible time-saving factors over Rahman and Stillinger's 8.46 Å cutoff. Also shown are estimated time savings using a force criterion for cutoff (Section 5).

cance of its rate of change to the central molecule. Thus, a *force criterion* should offer both improvements in "prediction" and a reduced number of calculations. Referring again to Fig. 5, we might define our inner "shell" by a force cutoff of 0.4, or even 0.5, units. This would allow those pairs presently within shell S_{12} contributing less than this threshold force to be removed from the explicit-calculation set (set A, Fig. 5). Even allowing for the extra pairs requiring transfer from shell $S_{2\infty}$ to S_{12} (set B), this would reduce the number of explicit calculations by 10 % with expected increased reliability. An increased force cutoff of 0.5 units would offer a 24 % reduction, although the reliability of corrections at this level would require reassessment. Table II illustrates the speedups expected from these refinements.

6. APPLICATION TO MOLECULAR DYNAMICS

The sphere 2 predictions involve only about 20 explicit pair force calculations compared with the normal 50 to 90 which have been used in calculations to date; the accuracy is good for the forces even over 20 or more timesteps. The torque predictions are less favorable, but still yield a ±5 % accuracy for 90 % of the centers. As Table II shows, by using a 5.78 Å cutoff, the time factor improvement over Rahman's 8.46 Å cutoff (60 to 70 molecules) is likely to be about 2.6 using $10\Delta t$, or 2.8 using the still excellent $20\Delta t$ approximation.

The force predictions using shell 1, which involve explicit calculations over the very small number of about four molecules, seem surprisingly good; the torque predictions are less encouraging. However, as using sphere 1 is likely to give a more dramatic increase in speed over using sphere 2, even for time intervals of only $5\Delta t$ (Table II), the possibilities of this very low cutoff may be worth pursuing.

The effects of making these approximations during a full molecular dynamics calculation can be reasonably assessed. Macdonald [3] has shown that Rahman and Stillinger's cutoff for water results in errors in force calculations (compared with a full Ewald sum) symmetrically distributed about zero mean. In only about 1 % of the cases does the magnitude of the difference between the Ewald sum and the cutoff calculated forces exceed 5 % of the root mean square force. With this error, it is known that energy drifts of ±5 % over $\sim 200\Delta t$ are observed, thus necessitating periodic rescaling [1]. These figures are comparable to the sphere 2 data after $20\Delta t$ (Table I and Fig. 4), and thus the corresponding time-saving factor of 2.8 (Table II) should be immediately achievable in a full MD calculation without significant loss. The marginal increase in time saving achievable when correcting for times greater than $20\Delta t$, compared to the significant fall in accuracy, suggests that sphere 2 calculations at $20\Delta t$ may be an effective limit to the method.

This assessment of the potential application of the method holds irrespective of the significantly worse torque data which are automatically accounted for in Macdonald's calculations. A greater inaccuracy in torque data is in fact expected, the rotation of the water molecule forcing the use of a time step shorter than the natural time step for the forces. Indeed, Rahman and Iacucci [5] have found it possible to increase the elementary time step by a factor of 4 by artificially increasing the moment of inertia of the water molecule. Thus, it is in any case possible to effectively "normalize out" the inaccuracies in torque predictions.

The method as it stands seems capable of speeding up *full* molecular dynamics calculations on water by an overall factor of 2 to 4 without significant decrease in accuracy or exacerbation of energy conservation problems. It is complementary to other recently developed procedures [5, 6], so combination with them is unlikely to further decrease significantly the overall computation time. Particularly useful applications include a very significant speedup to the approach to equilibrium using the severe sphere 1 approximation rather than uncorrected low R cutoffs. Moreover, several thermodynamic and time-dependent properties depending upon very long-range forces beyond the 9 Å range could be tackled without significant increase in computer time. As R_i increases, the approximate method described becomes more accurate, and provides a possible rapid approach to the continuum without making continuum approximations. It is thus particularly suited to probing those properties (e.g., dielectric) which require an accurate assessment of long-range forces.

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