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Tariq A. Andrea@f@f, William C. Swope@f@f, and Hans C. Andersen

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The role of long ranged forces in determining the structure and properties of liquid water^{a)}

Tariq A. Andrea,^{b)} William C. Swope,^{c)} and Hans C. Andersen

Department of Chemistry, Stanford University, Stanford, California 94305

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We have performed molecular dynamics calculations for liquid water using the revised central force model potential truncated at various distances and using two sizes of system, in order to study the effect of system size and range of the potential on the calculated thermodynamic and structural properties and to compare the results with those obtained by Ewald summation. All calculations were performed for a cubic system using periodic boundary conditions. Provided the side of the cube is equal to or greater than twice the range of the potential, the thermodynamic properties and distribution functions, including an orientational distribution function, are insensitive to the size of the system, for fixed range. Provided the range of the potential is equal to or greater than 6 Å, the thermodynamic energy and pressure are only slightly dependent on the range of the potential, to an extent that is, however, larger than that observed for dipolar hard spheres and the Stockmayer potential which do not have the tetrahedral structure similar to water. For potentials with ranges of 6 Å or greater, the atom-atom distribution functions are very insensitive to the range, but the orientational correlations are very sensitive to the range, as had been observed many times in studies of dielectric properties of simulated fluids. A potential with a range of 6 Å has thermodynamic and structural properties very similar to those of a longer ranged potential and similar to those obtained by Ewald summation. Use of such a model, which correctly describes interactions between nearest neighbors and next nearest neighbors but has no longer ranged forces, lead to significant increases in the speed of simulations.

I. INTRODUCTION

Molecular dynamics and Monte Carlo computer simulation studies of water and aqueous solutions have increased our understanding of the molecular nature of these important substances.¹⁻⁴ They have been applied to the study of structure and thermodynamics of pure water,⁵⁻¹³ solutions of nonpolar solutes,¹⁴⁻²¹ solutions of ions,^{22,23} and the solvation of a dipeptide molecule.²⁴

A major problem in performing these types of studies is that they require an extensive amount of computing. Solution of the computation problems posed by computer simulation methods will have to come from improvements in the speed and decrease in cost of computers, more efficient algorithms, new potential energy functions especially suited to computation, and perhaps development of entirely new computer simulation methods.

An important source of computing problems in the simulation of water and aqueous solutions is the long ranged dipolar nature of the intermolecular potential for water. In principle, every molecule interacts with every other molecule, and thus for N molecules the number of intermolecular interactions to be calculated is approximately $N^2/2$ for each time step in molecular dynamics and approximately N for each step in a Monte Carlo simulation (assuming single molecule moves). In addition, since the range of the interaction is longer than the size of the sample simulated, the long ranged interactions must be included in some approximate way or neglected in some systematic way.

A number of different methods are used to take long ranged interactions into account in simulations. Here we will restrict our attention to the case of methods that are used in conjunction with periodic boundary conditions on the particle positions. The first method involves calculating the interactions of a molecule with all periodic images of all the other molecules. (The Ewald summation method²⁵ is the traditional example, but there are other ways of implementing the summations, not all of which are equivalent to the Ewald method.²⁶) The second is the minimum image convention, in which the interaction of one molecule with the nearest periodic image of each other molecule is calculated. The third method, called spherical truncation of the potential, is to set the interaction potential equal to zero for distances beyond a certain cut-off distance when doing Monte Carlo calculations. The fourth, called the reaction field method, is based on a calculation of the polarization induced in distant molecules by the dipole moment of a molecule and the interaction of that polarization with nearer neighbors of the molecule.^{7,27} The fifth method, the spherical truncation of the force, is to set the intermolecular forces equal to zero for distances beyond a certain cut-off distance when doing molecular dynamics calculations.

Each of the first two methods requires approximately $N^2/2$ or N interactions to be calculated at each step for dynamics or Monte Carlo, respectively. (For the Ewald summation method, however, each of the interactions to be calculated is significantly more complicated than a simple two molecule interaction.) For the last three methods, the number of interactions to be calculated in each step is reduced to $Nz/2$ or z , where z is the average number of molecules within the cut-off distance of a molecule. For small enough values of z/N , these methods can result in significant increases in the speed of the computation.

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^{b)}National Institutes of Health Postdoctoral Fellow, 1978-80. Present address: Shell Oil Company, Modesto, Calif.

^{c)}Present address: IBM Instruments Inc., Danbury, CT.

The method of spherical truncation of the force in molecular dynamics is potentially pathological for molecules that are not spherically symmetric, because the motions generated by truncated forces do not conserve energy.²⁸ (A truncated force is not the negative gradient of a truncated potential or of any other conservative potential, for molecules lacking spherical symmetry.) For long enough runs the temperature rises secularly unless artificial means are used to remove the excess energy. The rate at which the temperature rises depends on the magnitude of the discontinuities in the force at the truncation distance. This makes it advisable to have the truncation distance be large, but this in turn makes z to be large and decreases the computational advantage of this method.

The choice of method cannot be based solely on considerations of computational ease, however. There is a fundamental theoretical problem involved, namely, that of deciding what method in principle gives the proper thermodynamic and structural properties of a fluid whose molecules interact via long ranged dipolar forces. It is not known, e.g., whether the Ewald summation method gives thermodynamic properties and structures for finite sized systems that approach a thermodynamic limit as the system size increases to infinity. Even if one is willing to assume the existence of such a limit, there are no proofs that the limiting results are the same as those for a system with physical boundaries and without periodic boundary conditions.

In the absence of analytic guidance, there has been a large amount of empirical work of testing and comparing the various methods for molecular fluids in order to guide future simulations of interesting materials.^{7,13,28-40} Four conclusions have clearly emerged from this work:

- (1) Calculated dielectric properties and some orientational correlation functions are very sensitive to the way in which the long ranged forces are included in the calculation.
- (2) Some other properties, such as the internal energy and atom-atom radial distribution functions, are much less sensitive to the way in which long ranged forces are included.
- (3) The magnitude of the effect of long ranged dipolar forces depends on the behavior of the potential at short distances, being larger, e.g., for dipolar hard spheres than for hard spheres with both dipoles and quadrupoles.
- (4) The minimum image method is the least trustworthy of the various methods.

For two simple models of dipolar fluids, namely dipolar hard spheres^{33,34,36} and the Stockmayer potential,³⁹ there has been an extensive amount of comparison of the results of different methods for including the long ranged forces. It was found that the internal energy calculated by Ewald summation is insensitive to the size of the system simulated. Also, for the spherical truncation methods, the dependence of the energy on the truncation distance is very small. The two methods give closely agreeing results for the internal energy.

For the case of water, which is of special interest in this paper, empirical comparisons of the results of various methods have been less extensive and the results somewhat different. Such comparisons have been performed for the Rowlinson potential,⁷ the Ben-Naim Stillinger potential,⁷ the Watts potential^{13,37} and for the ST2 potential.^{32,40} Especially disturbing is the comparison, for the ST2 potential, of the molecular dynamics results obtained by spherical truncation of the force⁶ and Monte Carlo results obtained using a multipole summation method³² similar to Ewald summation. The oxygen-oxygen radial distribution functions for the two simulations are significantly different in the vicinity of the second peak. The location of the second peak in the oxygen-oxygen radial distribution function for water is a signature of the characteristic tetrahedral structure of that fluid. The spherical truncation molecular dynamics results have the peak positioned properly, but the multipole summation Monte Carlo results have a peak that is broader and centered at much larger distances. Also somewhat disturbing are the findings that in some cases the calculated thermodynamic energy depends significantly on the size of the system simulated. This was found by Watts⁷ for the BNS potential by Monte Carlo calculations using spherical truncation of the potential and by Ladd³² for the ST2 potential. On the other hand, an insensitivity of the energy to the system was found by Pangali *et al.*³⁷ for the ST2 potential by Monte Carlo calculations using spherical truncation of the potential. The ST2 and BNS potentials are especially important for those interested in water, since they both give structures that have the local tetrahedral ordering characteristic of water.

Another model for water that has this tetrahedral structure is the revised central force (RCF) model of Stillinger and Rahman,¹⁰ who have performed molecular dynamics calculations using Ewald summation to study its properties. In this paper, we report the results of molecular dynamics calculations for the revised central force model using a type of spherical truncation and compare them with the Ewald summation results of Rahman and Stillinger. We performed studies with the potential truncated at various distances and for two different sized systems to obtain information separately about the size dependence of the calculated properties and their dependence upon the range of the potential. The comparisons show that provided the potential is truncated at distances of about 6 Å or greater, the two simulation methods give good agreement for the energy and the atom-atom correlation functions. A potential truncated at 6 Å gives a model for water that is qualitatively as good as the revised central force model itself but that lends itself to much more efficient computing because of the smaller number of interactions that each molecule participates in. The limitations of such a model are discussed in the light of our simulation results and the results are also compared with results on other potential models.

II. CALCULATIONS AND RESULTS

We performed molecular dynamics calculations for liquid water using various truncations of the revised

central force (RCF) model potential of Stillinger and Rahman.¹⁰

The intermolecular potential used in the simulations was the RCF model multiplied by a switching function of the form $S(r/r_0^2)$, where r_0 is the distance between the oxygens on the two molecules. $S(x)$ is a function satisfying

$$S(x) = 1 \text{ for } x < R_L^2 \\ = 0 \text{ for } x > R_U^2$$

and $S(x)$ falls smoothly from 1 to 0 as x increases from R_L^2 to R_U^2 . This use of a switching function to cut off the interactions at large distances was introduced by Adams *et al.*^{28,41} In the present calculations, $S(x)$ between R_L^2 and R_U^2 was equal to the unique fifth order polynomial that makes S and its first two derivatives continuous at the endpoints of the interval. Switching off the potential smoothly in this manner and calculating the corresponding forces is superior to merely truncating the forces of the RCF model at a particular distance, because the latter method does not lead to conservative Hamiltonian dynamics whereas the former does.

The intramolecular potential we used was a set of atom-atom potentials, each of which was a harmonic function of distance, with a minimum and a curvature that matched those of the RCF atom-atom potentials. (This relatively minor change from the calculations of Rahman and Stillinger was made for simplicity. It should have no effect on the results because in these simulations the molecules do not dissociate, but stay in a conformation near their intramolecular minimum potential.)

All calculations were performed at constant volume and constant temperature. The constant temperature dynamics method used was that of Andersen⁴² with one modification. The stochastic collisions that served to establish the temperature were applied simultaneously to all molecules at time intervals of 0.375 ps, rather than at random times as discussed in the original presentation of the method. Periodic boundary conditions were used. In all cases, the temperature of the bath was 29.5 °C and the volume was chosen to give a mass density of 1.000 g/cm³. This matches the conditions of the Ewald summation simulation of Stillinger and Rahman.¹⁰ Three of the calculations were for 512 molecules, and one was for 64 molecules. The velocity form of the Verlet algorithm⁴³ was used to integrate the equations of motion, using a time step of 7.5×10^{-16} s. (We verified that this large a time step gave thermodynamic

TABLE I. Binding energy (in kcal/mol) for various truncations of the potential and for Ewald summation.

Number of molecules	Range of the potential		
	Short	Medium	Long
512	9.079 ± 0.022	10.179 ± 0.017	9.848 ± 0.015
64		10.147 ± 0.059	
216	Ewald summation ^a	9.478	

^aReference 10.

TABLE II. pV/NkT for various truncations of the potential and for Ewald summation.

Number of molecules	Range of the potential		
	Short	Medium	Long
512	0.172 ± 0.068	2.132 ± 0.031	2.345 ± 0.061
64		2.314 ± 0.107	
216	Ewald summation ^a	0.1 ± 0.1	

^aReference 10.

properties equal to those obtained with time steps as small as 1×10^{-16} s.)

The calculations were performed on a Floating Point Systems AP120B array processor, which operated with a Digital Equipment Corporation PDP 1134A computer as a host. The intermolecular and intramolecular force calculations, which require the bulk of the computational effort, were performed by programs written in the assembly language for the array processor. A new table lookup and interpolation method was used to evaluate the intermolecular potentials and forces as functions of distance. See the Appendix for a description of the algorithm. For the 512 molecule system and the medium ranged potential, the computations require 2.0 s of computer time per time step and with our algorithms the computation time is approximately proportional to the number of interacting pairs of molecules.

We used three different switching functions, leading to a short ranged, a medium ranged, and a long ranged potential. The R_L and R_U were 3 and 3.5 for the short ranged potential, 5.5 and 6 for the medium ranged potential, and 11.9 and 12.4 for the long ranged potential. For the short ranged potential, the forces between molecules that are near neighbors is the same as for the infinite ranged potential. For the medium ranged potential, the forces between first neighbors and between second neighbors is the same as for the infinite ranged potential. The long ranged potential is the longest range potential whose range is less than half the length of the cubic box for 512 molecules. For the medium ranged potential, the range is slightly less than half the length of the cubic box for 64 molecules.

For the molecular dynamics calculations, the starting configuration was a configuration of 512 water molecules equilibrated to 303 K at a density 1% lower than the density desired. The coordinates were scaled to the desired density and constant temperature molecular dynamics calculations were performed with the medium ranged potential for 30 ps. The resulting configuration was the starting point for calculations with all three potentials. For each potential, the dynamics were continued for another 30 ps equilibration period and then for a 45 ps period during which the thermodynamic properties were calculated and averaged. During the last 45 ps, one configuration was analyzed every 0.375 ps to determine the distribution functions and the results were averaged. We also performed the same calculation for a fluid of 64 molecules for the medium ranged potential only.

The molecular dynamics results were used to calcu-

TABLE III. Maxima and minima of the RCF oxygen-oxygen $g(r)$ and distances at which it passes through unity, calculated in various ways and compared with experiment.^a

	S-512	M-64	M-512	L-512	Ewald	Expt.
$g=1$ at	2.64	2.62	2.61	2.61	2.6	
$g=\max$ at	2.84	2.82	2.82	2.82	2.85	2.85
value	3.51	3.18	3.08	3.00	3.1	1.96
$g=1$ at	3.13	3.10	3.10	3.11	3.1	
$g=\min$ at	3.25	3.31	3.30	3.30	3.3	3.3
value	0.47	0.58	0.58	0.65	0.6	0.73
$g=1$ at	3.47	3.95	3.95	4.05	4.0	
$g=\max$ at	3.49	4.54	4.54	4.60	4.5	4.4
value	1.02	1.17	1.22	1.21	1.2	1.24
$g=1$		5.11	5.13	5.19	5.3	
$g=\min$ at	4.00	5.80	5.77	5.83	5.8	
value	0.90	0.86	0.79	0.85	0.8	
$g=1$ at	5.11		6.42	6.51	6.3	
$g=\max$ at	5.52		7.00	7.05	7.0	
value	1.11		1.07	1.07	1.1	

^aS, M, and L, refer to truncation at short, medium, and long distances, respectively. The numbers 64 and 512 refer to the number of molecules in the system simulated. Ewald refers to the Ewald summation results of Ref. 10. Most of the numbers were read from a figure to one decimal place. Expt. refers to the experimental results (see Ref. 45). All distances are in Å.

TABLE IV. Maxima and minima of the RCF oxygen-hydrogen $g(r)$ and distances at which it passes through unity, calculated in various ways and compared with experiment.^a

	S-512	M-64	M-512	L-512	Ewald	Expt.
$g=1$ at	1.82	1.75	1.76	1.76	1.7	
$g=\max$ at	1.98	1.90	1.90	1.90	1.85	1.97
value	1.50	1.44	1.50	1.45	1.5	1.19
$g=1$ at	2.13	2.04	2.03	2.05	2.0	
$g=\min$ at	2.46	2.48	2.47	2.45	2.4	2.4
value	0.28	0.16	0.15	0.14	0.2	0.0
$g=1$ at	2.89	2.97	2.98	2.98	2.9	
$g=\max$ at	3.14	3.18	3.18	3.15	3.2	3.0
value	1.47	1.49	1.49	1.49	1.5	1.78
$g=1$ at	3.88	4.04				
$g=\min$ at	4.13	4.09	4.12	4.02		
value	0.88	1.00	1.02	1.02		
$g=1$ at	5.24					
$g=\max$ at	5.74	4.46	4.40	4.23		
value	1.03	1.02	1.031	1.03		
$g=1$ at	6.31	4.75	4.90	4.80		
$g=\min$ at	6.83	4.94	5.07	5.06		
value	0.99	0.99	0.99	0.99		
$g=1$ at	7.52	5.13	5.17			
$g=\max$ at	8.33		5.27	5.31		
value	1.00		1.00	1.00		
$g=1$ at	9.12		5.36			
$g=\min$ at			6.13	6.14		
value			0.95	0.96		
$g=1$ at			6.78	6.84		
$g=\max$ at			7.44	7.57		
value			1.04	1.03		
$g=1$ at			8.25	8.30		

^aSee footnote to Table III.

TABLE V. Maxima and minima of the RCF hydrogen-hydrogen $g(r)$ and distances at which it passes through unity, calculated in various ways and compared with experiment.^a

	S-512	M-64	M-512	L-512	Ewald	Expt.
$g=1$ at	2.13	2.12	2.14	2.13	2.1	
$g=\max$ at	2.19	2.21	2.19	2.19	2.2	2.4
value	1.98	1.79	1.81	1.80	1.8	1.42
$g=1$ at	2.91	2.70	2.69	2.69	2.7	
$g=\min$ at	3.21	3.07	3.04	3.05	3.0	2.9
value	0.81	0.71	0.69	0.73	0.7	0.01
$g=1$ at	3.50	3.47	3.46	3.48	3.4	
$g=\max$ at	3.60	3.62	3.66	3.71	3.6	3.5
value	1.10	1.17	1.17	1.12	1.2	1.50
$g=1$ at	3.87					
$g=\min$ at	4.22	4.21	4.27	4.25		
value	0.96	1.01	1.03	1.04		
$g=1$ at	4.57					
$g=\max$ at	5.03	4.79	4.75	4.62		
value	1.03	1.05	1.06	1.07		
$g=1$ at	5.68	5.16	5.34	5.18		
$g=\min$ at	6.36		6.16	5.75		
value	0.98		0.95	0.96		
$g=1$ at	6.95		6.90	6.82		
$g=\max$ at	7.55		7.48	7.48		
value	1.01		1.04	1.02		

^aSee footnote to Table III.

late the binding energy of the liquid, which is the energy of the ideal gas at that temperature minus the energy of the liquid and pV/NkT , where N is the number of molecules. The results are shown in Tables I and II, together with the Ewald summation results of Stillinger and Rahman.¹⁰ (The error estimates in these tables were obtained by breaking the 45 ps runs into six sections of length 7.5 ps. Averages over each of these six sections were calculated. The average of these averages is the result quoted, and the standard deviation of the averages, divided by the square root of 6, is the error quoted. This would be the actual statistical error if averages calculated over 7.5 ps intervals were statistically independent. This is likely to be the case since 7.5 ps is longer than the rotational relaxation time of water.)

Tables III, IV, and V contain information about the OO, OH, and HH radial distribution functions for the three ranges of potential calculated for the 512 molecule system, for the medium ranged potential calculated for a 64 molecule system, for the Ewald summation results, and for real water. The medium range, long range, and Ewald results are so alike one another that a tabular rather than graphical comparison is needed to demonstrate the quantitative nature of the similarity.

We calculated another correlation function that is a measure of the orientational correlations between the molecules. The function calculated is the average value of the cosine of the angle between the HOH angle bisectors of pairs of molecules whose oxygen-oxygen distance is between r and $r + dr$. The angle bisector is approximately the direction of the dipole moment of the molecule, and so this function is proportional to the

distance dependent dipolar correlation function defined with the oxygen as the center of the molecule. The function plotted $\langle \cos \theta \rangle$ is related to the h_Δ function of Levesque *et al.*³³ by

$$\langle \cos \theta \rangle = h_\Delta(r)/3g_{00}(r).$$

The results for the 512 molecule fluid are shown in Fig. 1. These functions are very different for the three ranges of potential. The sensitivity of this particular correlation function to the long range forces is well

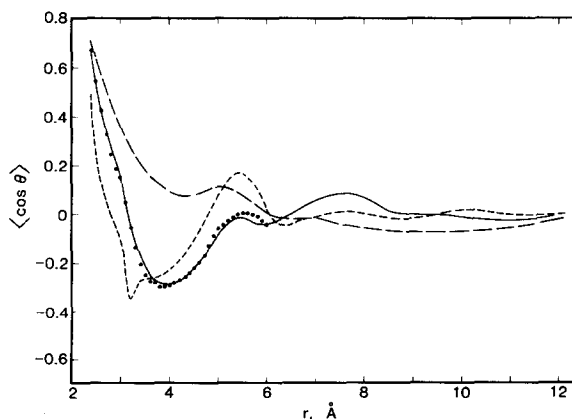


FIG. 1. Dipole correlation function $\langle \cos \theta \rangle$ as a function of distance. See the text for the definition. All results are for the revised central force model potential at the same density and temperature. Dots: medium ranged potential, 64 molecule system. Big dashes: long ranged potential, 512 molecule system. Solid curve: medium ranged potential, 512 molecule system. Small dashes: Short ranged potential, 512 molecule system.

known from other simulations. We also calculated this function for a 64 molecule fluid using the medium ranged potential (see Fig. 1). Within statistical error, the results were the same as for the medium ranged potential for 512 molecules, except for distances between R_L and R_U , which are just less than half the length of the periodic box for the smaller system.

III. DISCUSSION

The short ranged potential has thermodynamic and structural properties that are significantly different from those of the medium and long ranged potential and from the Ewald summation results. Neglect of the part of the potential between 3 and 6 Å does qualitative harm to the model.

For the medium ranged potential, for which we have results for different sized systems (64 and 512 molecules), the internal energy and pressure are independent of the system size. The same is true for the atom-atom distribution functions and even the $\langle \cos \theta \rangle$ orientational distribution functions. This indicates that the results are close to the thermodynamic limit for the finite ranged potential, even when the system is just large enough that half the side of the cubic box is the cut off distance. It is reasonable therefore to expect that our results for the long range potential for the 512 molecule system are also close to the thermodynamic limit results for that finite ranged potential.

The thermodynamic limit results for energy and pressure are different for the medium ranged and long ranged potentials, but the differences are small (about 0.3 kcal/mol or 3% in the binding energy and 0.2 in pV/NkT). This range dependence is larger than the essentially negligible range dependence found for dipolar hard spheres³⁵ and the Stockmayer potential.³⁹ However, it is smaller but in the same direction as that found by Watts⁷ for the BNS potential, which like the RCF model gives a fluid with true tetrahedral ordering. Ladd,³² using a method related to the Ewald summation, also found a size dependence for the tetrahedral ST2 model that is in the same direction as the range dependence we find but with a larger magnitude. Thus, it appears to be the case that, for thermodynamic properties, convergence to the thermodynamic limit (for Ewald methods) and to the infinite range results (for spherical truncation) is slower for the tetrahedral models of water than for simple dipolar fluids.

The binding energy is smaller for the longer range, and if this trend continues we expect the binding energy for the infinite ranged potential to be less than 9.84 kcal/mol. The Ewald summation result for 216 molecules is 9.478, and we do not know its size dependence for this potential. These results are consistent with the possibility that both the Ewald summation and spherical truncation give the same results for the energy in the thermodynamic limit. When the Ewald summation results of McDonald and Klein⁴⁴ for the Watts potential are compared with the potential truncation results of Reimers *et al.*⁴⁵ and of Berens *et al.*,¹³ it is seen that, for this potential also, Ewald summation gives smaller binding energies than potential truncation for systems

of finite size.

The thermodynamic limit pressure is a slightly increasing function of the range in our simulations. If this trend continues, the value of pV/NkT for the infinite ranged potential is greater than 2.35. The Ewald summation result for 216 molecules is 0.1 and its size dependence is not known.⁴⁶ The pressure is a more sensitive function of the structure than the internal energy, and so we do not know whether the difference between the Ewald and truncation results are due merely to a small difference between the structures generated by these two methods for small finite systems or whether it is a reflection of a discrepancy between these two methods for infinite ranged potentials in the thermodynamic limit.

The atom-atom correlation functions for the medium and long ranged potential for 512 molecules are identical to within the noise of the calculations for all distances. They are also identical to the Ewald summation results to within the accuracy that the latter were given. The results for the medium ranged potential for a 64 molecule system are also the same as for the larger system for distances less than 6 Å, which is half the size of the box for a 64 molecule system. This type of insensitivity of the atom-atom correlation functions to the method of simulation, the range of the potential, and the size of the system has been noted for the BNS potential,⁷ the Rowlinson potential,⁷ the ST2 potential,³⁷ the Watts potential,³⁷ and for dipolar hard spheres,³³ and thus it appears to be a general property of dipolar fluids, applying both to those that have and those that do not have a tetrahedral structure.

The $\langle \cos \theta \rangle$ correlation functions, unlike the atom-atom correlation functions, are different for the three different ranges of potential. The largest difference between the medium and long ranged results occurs in the vicinity of the second neighbor distance of 4.5 Å, where the correlations are predominantly negative for the medium range and positive for the long range. The first and second neighbor shells in liquid water are presumably similar to distorted versions of the corresponding shells for the low pressure phases of ice. Rahman and Stillinger⁴⁷ have studied the orientational correlations in models of ice Ic and ice Ih constructed using the Bernal-Fowler rules.⁴⁸ In both structures, the average value of the cosine of the angle between the dipoles of second neighbors is very close to zero, but the distribution of cosines is very broad, consisting in both cases of a set of discrete values extending from -1 to +1. A similarly broad but continuous distribution presumably exists in liquid water and in our simulated models, and the long ranged forces have the capability of both distorting the angle for each type of second neighbor as well as shifting the balance among the various types of second neighbors. This happens without any observable change in the atom-atom distributions and without significant change in the energy or pressure. It has an enormous effect, however, on calculated dielectric properties.

A small system of 64 molecules with the medium ranged cutoff provides a good estimate of the energy and

the pressure of the infinite ranged potential in the thermodynamic limit. The results are good in the sense that they are about the same as the estimate provided by a simulation with eight times as many molecules and twice the range of the potential and not very different from the Ewald summation results for a system with three times as many molecules. This is an optimistic note for the use of small simulations to calculate thermodynamic properties. The reliability and absolute accuracy of either of the methods when applied to small systems is still an open question, because of the size and range dependence discussed above. Nevertheless, for some model studies devised to give qualitative insight into the properties of aqueous systems, small systems may be entirely adequate.

The medium ranged potential provides a good model for water, i. e., a model that is almost as good as the RCF model itself. It has radial distribution functions that are indistinguishable from those of the RCF model. Thus it has the tetrahedral structure characteristic of water. The thermodynamic properties are somewhat different, but probably could be adjusted with a minor change in the potential. The major deficiency, compared with the RCF model, is the orientational correlations in the second neighbor shell, which are biased slightly towards antiparallel rather than parallel correlations of the molecular dipole moments. The main obvious deficiencies of both models when compared with experiment are that the first peak of the oxygen-oxygen radial distribution function is higher than experimentally observed.

IV. CONCLUSIONS

The thermodynamic and gross structural properties of liquid water can be adequately modeled using an intermolecular potential whose range is long enough to include interactions with only first and second neighbors (about 6 Å). The longer ranged dipolar interactions have a minor effect on the pressure and energy and a negligible effect on the atom-atom distribution functions. They affect the quantitative details of the orientational distribution functions and hence have an enormous effect on the calculated dielectric constant. But for properties and problems that do not depend on a quantitative modeling of dielectric behavior, a short ranged potential model is about as good as a potential with an infinite range. We believe that such a truncation procedure can be successfully applied to other potential models as well.

This has important consequences for the speed of computer simulations. The number of molecules that a molecule interacts with is proportional to the cube of the cut-off distance. Calculations performed with a potential truncated at about 6 Å will be about three times faster than those performed with a cut-off of 8.46 Å, as was used in the first simulations of ST2 water.⁶ The average number of water molecules in a sphere of radius 6 Å at normal liquid density is about 30. Calculations in which each molecule interacts with about 30 others will be much faster than Ewald summation calculations in which each molecule interacts with every image of every other molecule, to an extent that is very

dependent on system size. The results presented above also show that for thermodynamic properties and for the short ranged part of the atom-atom distribution functions, it is adequate to perform simulations with only 64 molecules for such a short ranged potential.

It might be argued that the neglect of longer ranged forces and of their effect on orientational correlations should be a matter of concern even in studies not directly related to dielectric properties. However, statistical error and uncertainties about adequate equilibration are also major concerns in current day simulations, and only long simulations can eliminate this source of error. Moreover, many potential simulation problems in the field of water and aqueous solutions, such as hydration of small solutes, hydration of polymers, hydrophobic interactions, and chemical reactions in solution, require so much computation that statistical error and equilibration are the major computational concerns, second in importance only to the basic uncertainty of what the fundamental intermolecular potentials are. The use of a water-water potential with a range of about 6 Å would contribute toward the efficiency and hence the precision of such calculations.

There have been encouraging recent developments,^{35,39,40} in the use of reaction fields to model the effect of the long ranged forces on the structure of water. Perhaps some combination of a short ranged water potential with a theoretical or empirical reaction field will provide a way of obtaining fast simulations without sacrificing the effect of long ranged forces on short ranged orientational correlations.

APPENDIX: INTERPOLATION PROCEDURE FOR CALCULATION OF INTERATOMIC FORCES AND POTENTIALS

The time consuming part of a typical molecular dynamics calculation is the inner loop in which the forces acting between the $N(N-1)/2$ pairs of molecules are calculated. Any increase in speed in calculating this inner loop results in an almost proportionate decrease in the amount of computation required to achieve a desired result. Intermolecular forces are usually expressed in terms of formulas containing transcendental functions and other operations whose calculation by a digital computer is much slower than the more basic operations of addition and multiplication. Thus considerable savings in computer time could be achieved if transcendental functions could be avoided in the inner loop.

This suggests the use of a table look-up procedure in which numerical values of the force and energy are tabulated. This can be very efficient in terms of speed, but it may require an excessive amount of memory. If the tabulation procedure is such as to lead to a force that is a discontinuous function of position or has a discontinuous derivative, this may be incompatible with the algorithm used to integrate the equations of motion numerically.

These considerations led us to develop a table look-up procedure, described below, that can be executed

rapidly without requiring prohibitively large amounts of memory and that generates forces with desirable continuity properties. The procedure is especially efficient on the Floating Point Systems AP120B array processor, which was used in the present work and which is used by several groups for computer simulation studies of liquids.^{49,13,11,21} Preliminary studies for this research were done using a Digital Equipment Corporation PDP1170 computer, and the table look-up procedure led to considerable savings in computation time on this machine as well.

Consider an atom-atom potential $u(r)$ which in general is represented by a formula describing a smooth function of r (typically analytic or piecewise analytic). The force associated with this potential is the negative of the gradient of u , which can be written as

$$\nabla u(r) = \mathbf{r}[u'(r)/r],$$

where $u'(r)$ is the derivative of u with regard to the scalar distance r . In a typical molecular dynamics calculation, the vector positions of two particles are subtracted and the result is squared to give r^2 . The numerical problem then is: given the functional form of u and a value for r^2 , calculate $u(r)$ and $u'(r)/r$. Let

$$z = r^2$$

and define

$$w(z) \equiv u(z^{1/2}) = u(r).$$

Then

$$\begin{aligned} w'(z) &= u'(z^{1/2})/2z^{1/2} \\ &= u'(r)/2r. \end{aligned}$$

Thus the problem mentioned above is: Given the functional form of w and a value of z , find $w(z)$ and $w'(z)$. The basis of our procedure is to pick a set of grid points z_0, z_1, z_2, \dots , etc, such that

$$z_0 < z_1 < z_2 \dots < z_N.$$

Within each interval between the grid points, we approximate the function $w(z)$ as a fifth order polynomial in z ; more specifically, for

$$z_i \leq z < z_{i+1},$$

let

$$\delta = z - z_i.$$

We represent $w(z)$ as

$$w(z) = c_0 + c_1\delta + c_2\delta^2 + c_3\delta^3 + c_4\delta^4 + c_5\delta^5. \quad (\text{A1})$$

The six coefficients $c_0 \dots c_5$ are chosen so that the value, first derivative, and second derivative of w at both ends of the interval z_i and z_{i+1} are equal to those of the correct function w at these two points. The six restrictions are sufficient to determine the coefficients uniquely as

$$\begin{aligned} c_0 &= w(z_i), \quad c_1 = w'(z_i), \\ c_2 &= w''(z_i)/2, \\ c_3 &= [10A - 12B + 3C]/6, \quad c_4 = [-15A + 21B - 6C]/6\Delta, \\ c_5 &= [2A - 3B + C]/2\Delta^2, \end{aligned}$$

where

$$\Delta = z_{i+1} - z_i, \quad A = (6/\Delta^3)[w(z_{i+1}) - C_0 - c_1\Delta - c_2\Delta^2],$$

$$B = (2/\Delta^2)[w'(z_{i+1}) - c_1 - 2c_2\Delta],$$

$$C = (1/\Delta)[w''(z_{i+1}) - 2c_2].$$

By differentiating the polynomial approximation for w we obtain a polynomial approximation for w' :

$$w'(z) = c_1 + 2c_2\delta + 3c_3\delta^2 + 4c_4\delta^3 + 5c_5\delta^4. \quad (\text{A2})$$

To implement this procedure, it is necessary to store the values of the grid points in memory (or, in the case of equal size intervals, the grid spacing and one grid point must be stored) and to store the values of the six coefficients for each interval. (If storage permits, it is useful to store not only $c_0 \dots c_5$, but also $2c_2, 3c_3, 4c_4$, and $5c_5$.)

This method has four important characteristics and advantages:

(1) The polynomial approximation to the potential has exactly the correct value, derivative, and second derivative at the grid points. The error in the interior of each interval is of the order $(z_{i+1} - z_i)^6$ for analytic potentials. By choosing narrow enough intervals, the error in the polynomial approximation can be made arbitrarily small. Similarly, the polynomial approximation to the force has exactly the right value and first derivative at the grid points, and the error in the interior of each interval is of order $(z_{i+1} - z_i)^5$.

(2) If the potential is analytic, then the polynomial approximation is continuous and has two continuous derivatives everywhere, including at the grid points, which are the boundaries between regions where different polynomial approximations are used. This is especially advantageous when integrating the equations of motion using the Verlet algorithm or other algorithms that assume that the force is continuous or differentiable (see Ref. 4).

(3) The force obtained from the polynomial approximation (A2) is exactly (except for computer roundoff error) equal to the gradient of the potential obtained from the polynomial approximation (A1) at all distances. Thus, use of these approximate forms does not contribute to the lack of conservation of energy. (Monitoring the fluctuations in the total energy is a very useful way of checking a calculation for programming errors, for too large a time step in numerical integration, and for roundoff and other computational errors. Thus, it is worthwhile if the approximations made in representing the force and the potential do not contribute to the energy fluctuations).

(4) The only floating point operations needed in the inner loop for the implementation of this procedure are addition and multiplication. Division, extraction of a square root, or calculation of transcendental functions are not required, no matter what the form of the potential. This makes the calculations faster on many types of computers. This feature is especially significant for calculations performed on the Floating Point Systems AP120B array processor.

In the present work, we used this procedure with variable interval spacing to fit the O-O, O-H, and H-H interaction potentials. We needed 14, 25, and 26 intervals, respectively, to obtain polynomial functions that differed from the analytic formulas by a maximum of 0.001 kcal/mol.

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