Molecular dynamics simulation of dielectric properties of water

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The dielectric properties of liquid water are studied using an empirical potential model treating the monomers as flexible molecules with short-range interactions between oxygens and Coulomb interactions between charges situated on the individual atoms. Satisfactory results for the static dielectric constants at 259, 300, and 350 K are obtained from long simulation runs; these constitute a significant improvement over recent calculations using other potential models. Time correlation functions of dipole moment and single molecule orientation are evaluated. In the supercooled state an enhanced slowing down in the temporal decay of polarization fluctuations occurs, a behavior essentially absent in the single molecule reorientations. Good agreement is found in the self-diffusion coefficient over the entire temperature range.

I. INTRODUCTION

Although liquid water has been studied by computer simulations[1,2] for some 15 years, it is only recently that its dielectric properties have become the primary focus of investigations.[3-7] The calculation of the dielectric constant by molecular dynamics requires explicit considerations of a finite-size medium with periodic boundaries in the context of treating long-range interactions. Now that an equivalence has been established between the Ewald lattice summation method and the reaction field method,[8] proper calculations can be made with either method.

In the case of dielectric properties of water two considerations arise which appear not to have been sufficiently recognized previously. The first is a requirement that the potential function describes properly the orientational ordering of the molecules, the property which determines the polarization of the medium and hence the dielectric constant. A second consideration is that significantly longer simulation runs, relative to other property calculations, appear to be necessary because of large though infrequent fluctuations in the collective ordering of molecular orientations.

To date three different potential models of water have been used in the molecular dynamics study of dielectric properties of water, ST2,[9] MCY,[10] and TIP4P.[11] In all three the water molecules are treated as rigid monomers interacting through a Lennard-Jones potential between the oxygens and Coulomb potentials between charges situated at the hydrogens and at one or two auxiliary sites. In MCY and TIP4P, a single site is placed along the bisector of the HOH angle, at distances of 0.2677 and 0.15 Å, respectively, for the two potentials. In ST2 two sites representing the lone pair electrons are placed on the side of the oxygen away from the hydrogens.

In terms of the static dielectric constant ϵ_0 and the tem-

perature variation of the Kirkwood g factor, MCY gives a value for ϵ_0 at 293 K that is too low by more than a factor of 2.[6] For g the results at 293 and 370 K show slight increase with temperature which is in contradiction to experiment. For TIP4P the results at these two temperatures are closer to the experimental values, although they are also considered unsatisfactory.[7] In the case of ST2, the long-range interactions were not taken into account explicitly in the first simulation study of dielectric properties,[9] but a later calculation[3] showed the potential model gives results for ϵ_0 and g at 393 K in fair agreement with experiment.

In this work we report a molecular dynamics study of the dielectric properties of water using a simple point charge (SPC) model of intermolecular interactions that was constructed for simulation of protein hydration.[12] Recently intramolecular interactions have been added to the model for use in studying the high-frequency vibrational properties of water.[13] We are attracted to the SPC model in the latter form because of its simplicity and adaptability for our simulation algorithm,[14] and also because neither MCY nor TIP4P appear to be satisfactory for an application we have in mind, the study of dielectric behavior of aqueous solutions near charged surfaces. We find the SPC model gives considerably improved dielectric constant results compared to MCY and TIP4P. Not only are the magnitudes in satisfactory agreement with experiment, but also the temperature variation shows the correct behavior. We also find the self-diffusion coefficients to be given very well by the potential model at all three temperatures, an important contributing factor being the molecular flexibility. In calculating the time-dependent fluctuations of the dipole moment we find the results show a dramatic slowing down in the decay of correlations in the metastable state at 259 K. The relaxation time, although not well determined, is clearly increasing at a much more rapid rate than in the normal states of water.

In the next section we define the flexible SPC model adopted for the present study. Details of the simulation procedure are briefly described in Sec. III. In Sec. IV results are

given for the self-diffusion coefficient, the proton vibrational frequency spectrum, the static dielectric constant, and the autocorrelation functions of the total dipole moment and the molecular dipole. Some implications of our work are discussed in the final section.

II. MODIFIED SPC POTENTIAL MODEL

The SPC[11] model was originally developed for water molecules with the monomer being a rigid structure with three interaction sites.[15] The intermolecular interactions consist of a Lennard-Jones potential between oxygens and a Coulomb potential between all possible pairs of positive charges on the hydrogens and negative charges on the oxygens. The placement of the negative charge is the essential difference between this potential and MCY and TIP4P. In the latter models the oxygen is treated as neutral and a negative charge is placed at an auxiliary site, which is different for each potential, along the H–O–H bisector on the side of the hydrogens. In terms of computational simplicity SPC has the advantage because the others involve four sites instead of three.

To allow the molecules to be flexible terms are added to the model which involve the intramolecular degrees of freedom.[13] The flexible SPC model is of the form

$$\phi = \phi_{intra} + \phi_{inter} , \qquad (1)$$

$$\phi_{intra} = D\{[1 - e^{-\alpha r_1^2}] + [1 - e^{-\alpha r_2^2}]\}$$
$$+ \tfrac{1}{2}K_\theta(r_3^2) + K_{r\theta}r_3(r_1 + r_2) + K_{rr'}(r_1 r_2) , \qquad (2)$$

$$\phi_{inter} = \sum_i \sum_j q_i q_j r_{ij}^{-1} + A r_{OO}^{-12} - C r_{OO}^{-6} , \qquad (3)$$

where r_1, r_2 are the O–H bond stretches, r_3 the deviation from equilibrium H–H separation, r_{ij} the interatomic separation between atoms i and j, r_{OO} the oxygen–oxygen separation, and q_i the charge on atom i. The constants in ϕ_{intra} are obtained by fitting the fundamental vibrational frequencies in the gas phase and the OH dissociation energy in liquid water, while the constants in ϕ_{inter} are determined using the interaction energy and pressure values for water at 300 K. Both sets of constants, along with the molecular geometry adopted for the present simulation, are given in Table I.

The rigid-molecule version of SPC, along with five other similar potential models including ST2, has been used to calculate structural and thermodynamic properties of water at 298 K and 1 atm.[15] SPC and ST2 were found to give reasonable results; SPC values for the density and energy are somewhat better, and the structure in the ST2 radial distribution function is too pronounced as a result of the tetrahedral charge distribution. On the other hand, comparison of the self-diffusion coefficients shows that the ST2 result is closer to the measurements. The flexible-molecule version of SPC has been used to study the effects of the liquid environment on the vibrational frequency spectrum[13]; otherwise very little is known about the properties of this potential model.

III. MOLECULAR DYNAMICS SIMULATION

The simulation system consists of 125 molecules confined to a cubic cell of constant volume with periodic boundaries. Simulations are carried out at 259, 300, and 350 K, all at a density of 1.0 g/cm^3. A spherical cutoff with radius equal to half the cell length, $L/2 = 7.7$ Å, is used for evaluating the short-range interactions. The Coulomb interactions are treated by the Ewald summation method,[16] with the real-space sum truncated at $L/2$ and in the sum over reciprocal lattice space approximately 100 vectors with magnitude less than 5 Å^{-1} are considered. The equations of motion are integrated using a fifth-order predictor–corrector algorithm at a time step size $dt = 3.9 \times 10^{-4}$ ps. For equilibration the molecules are placed on a cubic lattice and the temperature is rescaled at the desired level for the 20 ps. Then long simulation runs are made at 259 and 350 K for 200 and 175 ps, respectively, and two runs at 300 K carried out to 150 ps each. During these runs temperature rescaling is turned on for one time step every 500 to 1000 steps.

IV. RESULTS

Although our main interest in this study is the dielectric properties, it is pertinent to also examine other properties in order to have a more complete assessment of the ability of the flexible SPC model to describe the various physical properties of water. We will therefore briefly consider diffusion and vibrational properties as part of our assessment. The self-diffusion coefficient and the vibrational frequency spectrum are familiar quantities in molecular dynamics studies of liquids. Since each involves a different aspect of the dynamics, both are relevant in measuring the characteristics of the potential model.

Prior to the calculation of dynamic and dielectric properties the equilibrium properties are first obtained.[17] The configurational energy at 300 K is found to be 32.8 kJ/mol, about 20% lower than the observed value of 41.5. This is because the parameters of the intermolecular part of the potential, which contributes an energy of 42.6, have not been readjusted after the addition of the intramolecular part. No major differences are found in the structural properties between the flexible and the rigid-molecule models of SPC.

A. Self diffusion

The molecular self-diffusion coefficient D can be calculated from the velocity autocorrelation function of the mo-

TABLE I. SPC water potential parameters.

Intermolecular potential parameters (Ref. 12)	Intramolecular potential parameters (Ref. 13)
$A = 629\,400$ kcal mol^{-1} Å^{12}	$k_\theta = 2.283$ mdyn Å^{-1}
$C = 625.46$ kcal mol^{-1} Å^6	$k_{r\theta} = -1.469$ mdyn Å^{-1}
$q_O = -0.82e$	$k_{rr'} = 0.776$ mdyn Å^{-1}
$q_H = +0.42e$	$D = 0.708$ mdyn Å
Equilibrium geometry:	$\alpha = 2.567$ Å^{-1}
r_e (OH) $= 1.0$ Å	
θ_e (HOH) $= 109.47°$	

TABLE II. Simulation results for dielectric constants and diffusion coefficients (experimental results given in parentheses).

$T(K)$	Sim. Time (ps)	$\sqrt{\langle \mu^2 \rangle}$ (D)	G_k	g_k	ϵ_0	$D(10^{-5}\,cm^2/s)$
259	175	2.42	4.8 ± 0.2	3.2 ± 0.2	109 ± 5 (94.1) (Ref. 22)	0.76 (0.80) (Ref. 19)
300	200	2.42	4.2 ± 0.2	2.8 ± 0.2	82.5 ± 4 (77.6) (Ref. 22) (80.0) (Ref. 23)	2.54 (2.20) (Ref. 20)
350	150	2.41	4.2 ± 0.2	2.8 ± 0.2	70.5 ± 4 (61.8) (Ref. 22)	5.60 (6.1) (Ref. 20)

lecular centers-of-mass. Alternatively, it can be obtained from the mean-squared displacement of the center-of-mass. We have followed the latter method in determining the values of D which are given in Table II. These results are seen to be in quite good agreement with the experimental values over the entire range of temperature that we have investigated. The present results are somewhat better than those obtained using the ST2 model[9] and also an improvement over the central force model[18] which consistently underestimates D. It is worth noting that in contrast to our value of D at 300 K, the rigid-molecule version of SPC gives a value of 3.6.[12] Thus the flexibility of the molecule has an appreciable effect in the proper description of self-diffusion.

B. Proton vibrations

The velocity autocorrelation function also provides a convenient route to the analysis of vibrational motions since its Fourier transform gives the generalized frequency distribution, the amplitude-weighted vibrational density of states. Using the proton velocities $v(t)$ we have evaluated

$$\psi(t) = \frac{1}{N_h} \sum_{i=1}^{N_h} \frac{\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle}{\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle}, \qquad (4)$$

where N_h is the number of protons in the simulation cell. The function shows a highly oscillatory behavior indicating the presence of many more frequency components than in the same function for an atomic liquid. The corresponding frequency spectrum is shown in Fig. 1 for the high temperature state and the supercooled state. One can discern a lowering of the peak frequencies with increasing temperature in the HOH angle bending vibrations at 1800 cm^{-1}, the broad distribution of hindered rotations around 600 cm^{-1}, and in the hindered molecular translations around 50 cm^{-1}. Also, there is a small amount of broadening with increasing temperature, as is to be expected.

The effects of the liquid phase environment on the intramolecular vibrations of water have been recently studied by inelastic neutron scattering,[21] and a simulation introducing the flexible SPC model, with intramolecular interactions represented in different forms, was carried out at temperatures of 250, 325, and 375 K.[13] It was found that using the Morse potential form as in Eq. (2) one obtains a peak value of 541 cm^{-1} for the libration band, whereas the neutron data show a peak frequency at about 597. In Fig. 1 we see a broad band centered about 650 cm^{-1}. Our result for the HOH vibration agrees well with the earlier simulation,[13] both being

too high compared to the observed peak at 1670 cm^{-1}. It therefore appears that some adjustments of the intramolecular potential parameters are necessary to achieve a proper description of the vibrational modes in water.

C. Dielectric constant

The static dielectric constant ϵ_0 of a fluid of N molecules can be expressed in terms of the dipole moment

$$\mathbf{M} = \sum_{j=1}^{N} \mu_j, \qquad (5)$$

where μ_j is the dipole moment of molecule j;

$$\mu_j = \sum_s q_s \mathbf{r}_s, \qquad (6)$$

with q_s and $\mathbf{r}_s$ being the charge and position of atom s in the molecule. For a system with periodic boundaries and the long-range interactions treated by the lattice summation method, ϵ_0 is given by[8]

$$\frac{4\pi \langle \mathbf{M}^2 \rangle}{3VT} = \epsilon_0 - 1, \qquad (7)$$

where V is the system volume and T is the temperature in units of the Boltzmann's constant. The angular bracket $\langle \ \rangle$ denotes an ensemble average; as is usual in molecular dynamics calculation it is replaced by a time average over the system trajectories after equilibration.
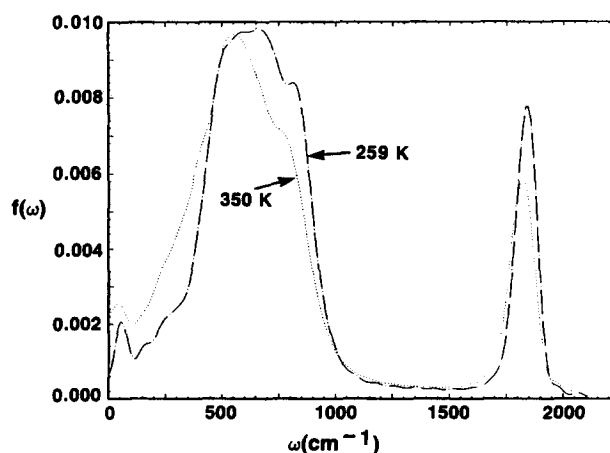

FIG. 1. Fourier transform of the proton velocity autocorrelation function of SPC water at 259 K (dashed-dotted curve) and 350 K (dotted curve). The OH vibrations centered about 3500 cm^{-1} are not shown.
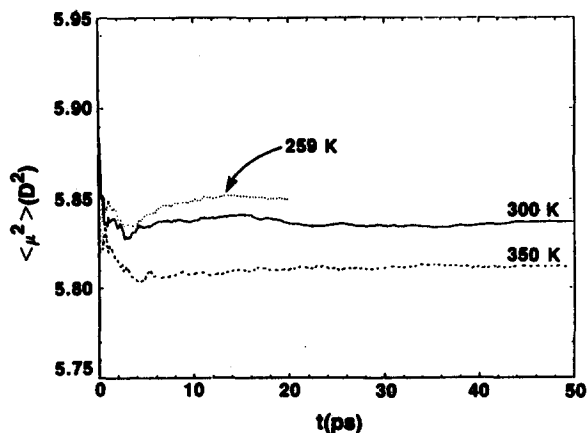
FIG. 2. Cumulative time average of the mean-square dipole moment of SPC water at 259 K (dotted curve), 300 K (solid curve), and 350 K (dashed curve).
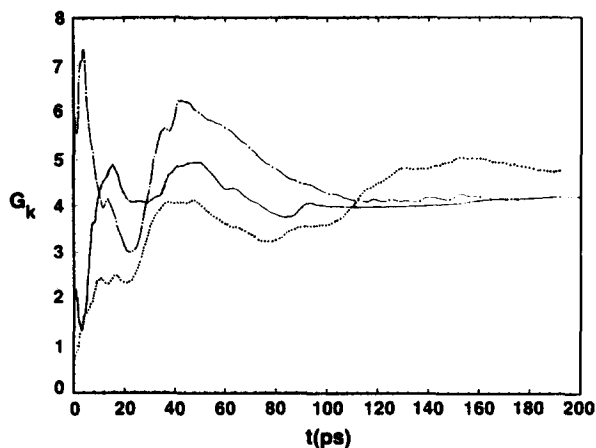

FIG. 3. Cumulative time average of the finite-system g factor G_k of SPC water at 259 K (dotted curve), 300 K (solid curve), and 350 K (dashed-dotted curve).

In practice the quantity directly calculated is

$$G_k = \frac{\langle M^2 \rangle}{N \langle \mu^2 \rangle}, \qquad (8)$$

where $\langle \mu^2 \rangle$ is the mean-squared molecular dipole moment. Combining Eqs. (7) and (8) gives

$$G_k = \frac{3T(\epsilon_0 - 1)}{4\pi\rho\langle \mu^2 \rangle}, \qquad (9)$$

where $\rho = N/V$ is the number density. The quantity G_k is the finite-system analog of the Kirkwood g factor defined for an infinite system[24]

$$g_k = \frac{T}{4\pi\rho\langle \mu^2 \rangle} \frac{(\epsilon_0 - 1)(2\epsilon_0 + 1)}{\epsilon_0}. \qquad (10)$$

Comparing Eqs. (9) and (10) one has the relation

$$g_k = G_k \frac{(2\epsilon_0 + 1)}{3\epsilon_0}. \qquad (11)$$

For water ϵ_0 is sufficiently large that the ratio g_k/G_k is given to a good approximation by just 2/3.

The calculated $\langle \mu^2 \rangle$ and G_k at the three temperatures studied in this work are shown in Figs. 2 and 3, respectively. It can be seen that $\langle \mu^2 \rangle$ is well converged within a simulation duration of 10 ps, and its variation with temperature is resolvable, though extremely weak. As a measure of convergence, the values for $\langle \mu^2 \rangle$ at 259 K after 20 and 175 ps of simulation agree to within one part in 500. The rms molecular dipole moment is given in Table II; the value of 2.41 holds for the entire temperature range. The value, 2.35, is generally accepted for the liquid, while the gas-phase value is well known to be 1.85.[22]

In contrast to $\langle \mu^2 \rangle$, the convergence of G_k is seen to be markedly slower in Fig. 3. The present simulation runs have already extended out to times about an order of magnitude longer than previous simulation studies of other properties. Although the results appear to have stabilized, still they should be regarded with some reserve. It has been shown by Neumann[6,7] who has reported simulation runs to times of 1 to 2 ns that exceptionally long runs are necessary to establish convergence in G_k.

The calculated dielectric properties are summarized in Table II. The indicated uncertainties are estimates based on the fluctuations during the last 20 to 25 ps portion of the trajectory. The ϵ_0 values are seen to be within 10% of the experiment at 300 and 350 K, and within about 15% in the supercooled state. This is a considerable improvement over the recent results obtained using the potential models MCY[6] and TIP4P.[7]

Some insight into the temperature dependence of G_k may be gained by considering the quantity

$$G_k(R) = \sum_{\substack{i,j \\ r_{ij} < R}} \frac{\langle \mu_i \cdot \mu_j \rangle}{N \langle \mu^2 \rangle}, \qquad (12)$$

where the summation extends over only pairs of molecules with separation distance less than R. Apart from a normalization, $G_k(R)$ is the average total dipole moment of a sphere of radius R centered about a reference molecule. Figure 4 shows that the qualitative behavior of $G_k(R)$ is similar at
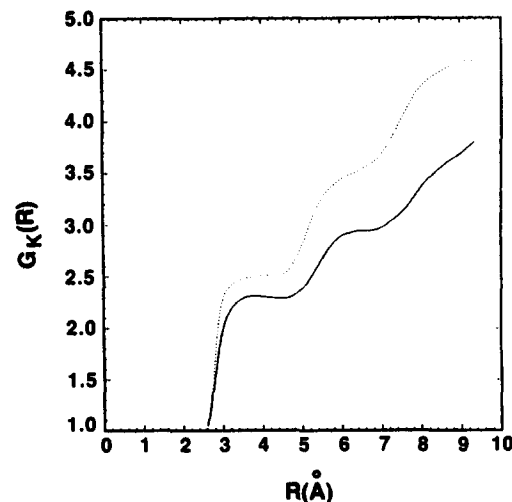

FIG. 4. R-dependent finite-system g factor $G_k(R)$ of SPC water at 259 K (dotted curve) and 350 K (solid curve).

both temperature extremes. The fact that contribution to the total dipole moment from the first hydration shell is temperature insensitive indicates that orientational ordering at this separation is primarily determined by short-range repulsive interactions. At larger distances thermal agitation is seen to disrupt the tendency to antiparallel alignment, thus $G_k(R)$ increases with temperature. At $R = (3/2)L = 13.4$ Å, where L is the simulation cell length, $G_k(R)$ must have the same value as G_k. The difference between Figs. 3 and 4 lies in that G_k in Fig. 3 is a cumulative time average, whereas $G_k(R)$ in Fig. 4 refers to the value obtained using only a 25 ps portion of the trajectory data. The fact that in Fig. 4 $G_k(R)$ reaches essentially the same value at 259 and 350 K indicates that to obtain satisfactory values of G_k one really needs to average over long runs.

D. Dielectric relaxation

The relaxation of the collective orientational ordering can be studied through the total dipole moment autocorrelation function

$$\Phi(t) = \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle}{\langle \mathbf{M}^2 \rangle}. \tag{13}$$

A knowledge of $\Phi(t)$ gives the frequency-dependent dielectric constant. The long-time decay of $\Phi(t)$ is shown in Fig. 5 where the persistence of correlations in the metastable
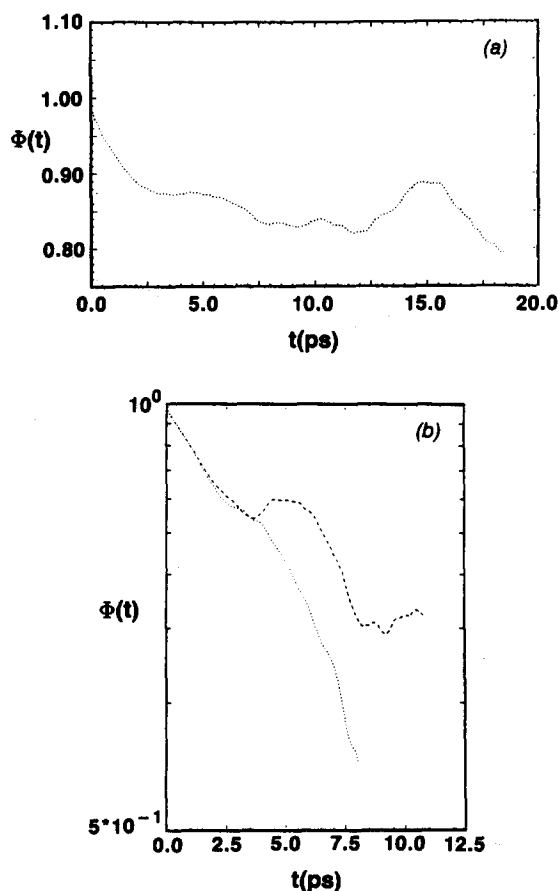
TABLE III. Simulation results for dipole moment and single molecule reorientation times (experimental values given in parentheses).

T(K)	τ(ps)	τ_s (ps)
259	103 ± 10	12.9 ± 0.5
	(33.5) (Ref. 23)	(8.0) (Ref. 26)
300	11.0 ± 1.0	5.0 ± 0.5
	(7.7) (Ref. 25)	(2.1) (Ref. 27)
350	5.1 ± 0.5	2.0 ± 0.2
	(3.0) (Ref. 25)	(0.9) (Ref. 27)

state can be noted. By fitting the portion of the function after about 2 ps to an exponential, we obtain the relaxation time τ whose values are given in Table III. Compared to the experimental dielectric relaxation times the values at 300 and 350 K are slightly higher, but the temperature variation is well reproduced. Going into the supercooled state both simulation and experiment show a rapid increase in τ. The enhancement effect appears to be exaggerated by the simulation; however, one should ascribe only qualitative significance to the calculated value of τ for at least two reasons. The first is that there is considerable statistical uncertainty in the determination of $\Phi(t)$. The result shown in Fig. 5 is obtained from the portion of the trajectory data from 150 to 175 ps. Secondly, the simulation is carried out at a density of 1 g/cm^3, whereas at 259 K the density of water is 0.992 g/cm^3. If nearest-neighbor interactions and local structural effects are important in the relaxation slowing down, then one would expect a higher value of τ at a higher density.

A related quantity is the correlation function of single molecule orientation

$$\Phi_s(t) = \sum_j^N \frac{\langle \boldsymbol{\mu}_j(0) \cdot \boldsymbol{\mu}_j(t) \rangle}{\langle \boldsymbol{\mu}_j^2 \rangle}. \tag{14}$$

FIG. 5. Normalized autocorrelation function of the total dipole moment of SPC water, (a) $T = 259$ K, (b) $T = 300$ K (dashed curve), and $T = 350$ K (dotted curve).

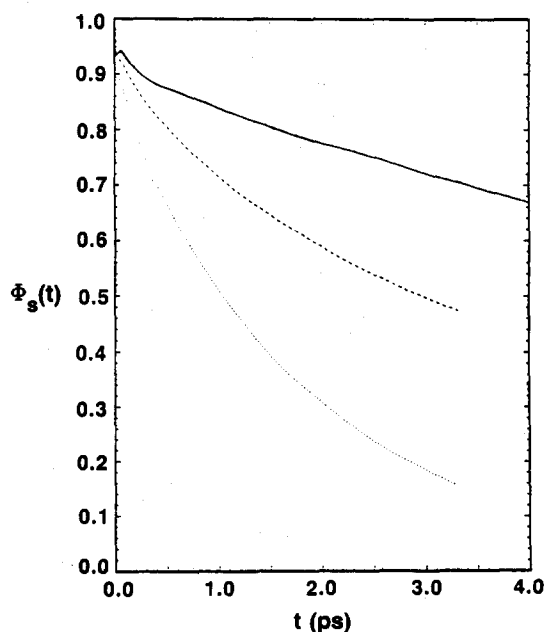
FIG. 6. Normalized autocorrelation function of the single molecule dipole moment of SPC water at $T = 259$ K (solid curve), $T = 300$ K (dashed curve), and $T = 350$ K (dotted curve).

Figure 6 shows the behavior of Φ_s and the relaxation times τ_s derived in the same manner are given in Table III. The calculated values are again higher than the values deduced from quasielastic neutron scattering at 259 K[26] and proton NMR relaxation measurements at the higher temperatures,[27] but the temperature variation is satisfactory. Relative to the determination of $\Phi(t)$ the problem of statistical fluctuations is much less severe in the evaluation of $\Phi_s(t)$. This is understandable from the fact that $\Phi_s(t)$ involves an average of N molecules.

In contrast to the SPC model the MCY[6] and TIP4P[7] results for τ are lower than the experimental values. At 300 K these two models give 6.5 and 3.84 ps, respectively, and at 350 K they give 2.1 and 1.36 ps. For τ_s the MCY and TIP4P results are 3.3 and 3.8 ps, which are higher than the NMR data.

V. DISCUSSION

Using a potential model which stresses simplicity rather than refinement we have calculated the dielectric properties of water at three temperatures including a supercooled state at -14 °C. We find values for the static dielectric constant which are in quite good agreement with measured data. This may appear surprising at first sight since recent calculations using more sophisticated potential models have yielded rather unsatisfactory results. We believe the good results given by the flexible SPC model are not fortuitous. Indeed, Neumann has pointed out that based on his results for MCY and TIP4P it appears that the placement of the charges can have an important effect on the dielectric constant and suggested that models such as SPC and ST2 may provide a better description.[7] Our findings here show that this hypothesis is correct.

It should be noted that because of the slow convergence of G_k any determination of ϵ_0 will require long simulation runs. We have seen in Fig. 3 that substantial fluctuations can still occur after 100 ps. To our knowledge this phenomenon is not understood at the molecular level. Since it occurs at all three temperatures the underlying process is not likely to be associated with slowly varying structural rearrangements that are thermally activated. It is clear that the effect is a collective behavior since $\langle \mu^2 \rangle$ converges much more rapidly as shown in Fig. 2. There is also little doubt that long-range interactions and strong dipolar coupling effects play an important role. Simulation can be used to investigate this problem; however, considerable computation resources will be required.

A significant observation of the present study is the persistence of intermolecular angular correlations in the supercooled state as seen in the dramatic slowing down of the time decay of $\Phi(t)$. Unlike the problem of G_k this collective phenomenon has the familiar characteristic of supercooling, a freezing in of the local structure. While we believe the simulation has demonstrated the existence of such an effect, the value of the relaxation time should not be considered well determined. More work is clearly needed to ascertain whether the SPC model is capable of describing quantitatively dielectric relaxation in supercooled water. To reduce statistical uncertainties, more averaging is necessary. Also, the

possibility of being trapped in a particular metastable state should be investigated by repeating the simulation to probe different regions of the phase space. Furthermore, it may be useful to study $\Phi(t)$ in a manner analogous to the recent analysis of density fluctuations in atomic fluids undergoing a glass transition.[28,29]

Although self-diffusion and vibrational properties are not the primary focus of our study, we find them useful measures of the goodness of the potential model at least in a complementary way. That the SPC model is capable of giving accurate values of the self-diffusion coefficient over a wide range of temperatures is a pleasant surprise; apparently the importance of the molecular flexibility has not been previously appreciated. In its present form the model does not give a satisfactory description of the intramolecular vibrational frequencies. This is not a serious defect since the potential parameters have not been adjusted after the addition of the intramolecular interactions.

Considering the simplicity of SPC relative to other existing models and the fact that the intermolecular part was only fitted to pressure and energy data at 300 K, the success of the potential model is quite remarkable. It appears that the original expectation[12] that the potential model be suitable for simulation of large systems with water being only one of several molecular constituents is justified. In a future report we will present a study of the concentration effects of an aqueous solution on the dielectric constant where the potential model also gives sensible results.

ACKNOWLEDGMENTS

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