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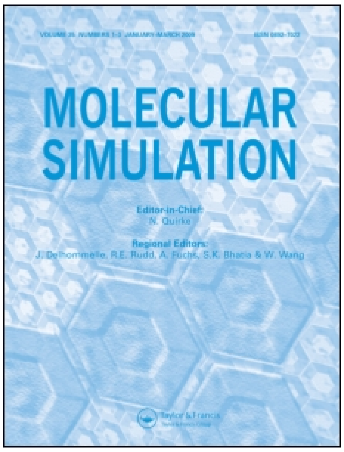

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THE DIELECTRIC PROPERTIES OF SIMULATED WATER DROPLETS

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Simulation of a droplet system has been suggested as a way to study local molecular processes in aqueous solution. To be valid, such a simulation should reproduce the results of simulations on an infinite solution. While it has been shown that the structural and thermodynamical features in the central part of a pure water droplet are very much like those of bulk water, no study has been done on the dielectric properties of a water droplet. Here, we report the estimation of the dielectric constants of SPC water droplets. We find that the dielectric constant of a droplet as a whole is very low. However, the dielectric constant of the central part of the water droplet can be as high as 50. Apparently, the molecules in the surface layer preferentially assume orientations so as to compensate the instantaneous dipole moment of the core volume. The influence of the surface layer extends over circa 6 Å.

KEY WORDS: Water droplets, dielectric properties, molecular dynamics simulation, boundary effects.

1 INTRODUCTION

An important technical problem in molecular dynamics simulation is how to simulate a finite system and at the same time incorporate the long-range interactions [1]. Such simulations can focus on an interesting part of a system and greatly reduce the computational time. An interesting scheme is to do the simulations on a finite droplet system [2–6] and incorporate the long-range interactions by, for example, the reaction field method [4–6]. There have been some efforts to study the behavior of such a system in molecular dynamics simulations [2, 3, 5, 6].

To be valid, such a simulation should be able to mimic major aspects of an infinite system. Despite the existence of boundary effects in simulations of droplet systems, it has been found that the structural and thermodynamic features in the central part of a water droplet are very much like those of bulk water [2, 3, 5, 6]. Therefore, this method promises to reproduce the properties of a bulk aqueous solution if a solute is placed at the center of the droplet. We present here a study of the dielectric properties of these water droplets.

We have estimated the dielectric constants of SPC water [7] droplets. We find that the dielectric constant of the droplets as a whole is very low (of the order of 10 for our water droplets). Also, the dielectric constant is not very sensitive to the size of the droplet and the boundary condition. However, the dielectric constant of the droplet interior is much higher than the whole droplet, reaching a value of about 50 for large droplets.

2 METHOD

All simulations were done with the CEDAR [8] molecular dynamics simulation package. The SPC water model [7] was used with the SHAKE procedure [9] to constrain the geometry of the water molecules. Because the geometry of the water molecules is rigid, a time step of 4 fs could be used, longer than a more conventional 2 fs time step. This has been shown to be appropriate in previous simulations of liquid water [10]. The mean temperature of each simulated droplet was maintained at 300 K by coupling the system to an external heat bath [11]. No cutoff on nonbonded interactions was used in any simulation.

The simulations were done on three different sizes of water droplets, with radius of 9.5 Å, 11.5 Å and 14.5 Å and 119, 215, 426 water molecules, respectively. The radius of each droplet is the radius of a sphere with the same number of water molecules but having the density of pure water under standard conditions (0.0334611/Å^3). The actual radius of the simulated droplet is larger than this size because the water molecules slightly spread out near the boundary.

To keep water molecules from escaping from the droplet, a soft wall restraint was applied. The potential function of the wall takes the form:

$$U_{\text{wall}} = \frac{A}{(R_{\text{wall}} - r)^{12}} - \frac{B}{(R_{\text{wall}} - r)^6} \tag{1}$$

Here $R_{\text{wall}} - r$ is the distance between the center of mass of a water molecule and the soft wall. In most of our simulations, we chose $A = 2048$ kcal/mol Å^{12} and $B =$ 64 kcal/mol Å^6. This is equivalent to the potential of a Lennard-Jones particle with radius, σ of 1.8 Å and the depth of potential well, ε of -0.5 kcal/mol. In most cases, R_{wall} was chosen to be the radius of that droplet plus 2.5 Å to avoid excessive compression of the droplet by the wall. Other choices of A and B and other forms of soft wall potential function are possible. However, according to our experience, this does not change the general features of the results.

The dielectric constant of a droplet was estimated by the Clausius-Mosotti formula [12]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi\rho\mu^2}{9k_B T} g_K \tag{2}$$

and the dielectric constant of the interior part of a droplet was estimated by the Kirkwood-Fröhlich [12] equation

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = \frac{4\pi\rho\mu^2}{9k_B T} g_K \tag{3}$$

In (2) and (3), $\rho = N/V$ is the number density of water molecules of a droplet, μ is the dipole moment of a SPC water molecule (2.3 Debye), $g_K = \langle M^2 \rangle / (N\mu^2)$ is the Kirkwood g-factor and $\langle M^2 \rangle$ is the mean square dipole moment of the whole water droplet or its interior part. A molecular dynamics simulation of 800 ps (200000 steps) was performed to calculate each dielectric constant.

The R-dependent Kirkwood g-factor, $G_K(R)$, is calculated with [12]

$$G_K(R) = \frac{\langle \sum_{r_{ij}<R}^{j} \vec{\mu_i} \bullet \vec{\mu_j} \rangle}{\mu^2} \tag{4}$$

where $\vec{\mu_i}$ is the reference dipole and the summation is over all the dipoles (including $\vec{\mu_i}$) within distance R of the reference dipole. In our simulations one water molecule was held near the center of the droplet by a weak positional restraint on the oxygen atom of the water molecule, and was used as the reference dipole. A test simulation indicated that this weak positional restraint has negligible influence on the orientation of the reference water dipole.

3 RESULTS AND DISCUSSION

The estimated Kirkwood g-factors and dielectric constants of the 9.5 Å, 11.5 Å and 14.5 Å water droplets are listed in Table 1. For the 11.5 Å droplet (case b in Table 1), the estimated Kirkwood g-factors and dielectric constants of the interior parts of the droplet are listed in Table 2 and the convergence of the Kirkwood g-factor during the simulation is shown in Figure 1. The estimated dielectric constants of the interior parts of different droplets are shown in Figure 2.

From Table 1 and Table 2, we can see that the Kirkwood g-factors have been determined with an error of around 4 – 5%. This is lower than in other reports of calculations of the dielectric constant of water models, which give an error of about 10% in the g-factor [13–17]. However, we believe that this is a fact because long simulations (800 ps) were used in this study to ensure the convergent of the results and from Figure 1, it can be seen that the g-factors converge well in the course of simulation time. In addition, as will be discussed below, a simulated water droplet

Table 1 The dielectric constant, ε of different water droplets[a].

label	*radius*	*A*	*B*	R_{wall}	g_K	ε
a	9.5	2048	64	12.0	0.24 ± 0.01	7.8 ± 0.9
b	11.5	2048	64	14.0	0.23 ± 0.01	10.2 ± 1.6
c	11.5	2048	0	13.2	0.21 ± 0.01	14.9 ± 3.7
d	14.5	2048	64	17.0	0.22 ± 0.01	15.0 ± 3.4

[a] A, B and R_{wall} are the parameters for the soft wall restraint in *QE.* (1). The radius and R_{wall} are in Å. A is in kcal/mol Å^{12} and B is in kcal/mol Å^6. The error in g_K was calculated with the method of Straatsma *et al.* [18] and converted into the error in ε.

Table 2 The dielectric constants of different interior parts of the 11.5 Å water droplet[a].

radius	g_K	ε
9.5	0.96 ± 0.03	25.9 ± 0.7
8.5	1.31 ± 0.04	35.2 ± 1.0
7.5	1.50 ± 0.04	40.3 ± 1.1
6.5	1.66 ± 0.05	44.4 ± 1.3
5.5	1.67 ± 0.05	44.6 ± 1.3
4.5	1.62 ± 0.04	43.2 ± 1.2

[a] For the boundary conditions of the droplet, see case b in Table 1. The radius is in Å. The error in g_K was calculated with the method of Straatsma *et al.* [18] and converted into the error in ε.

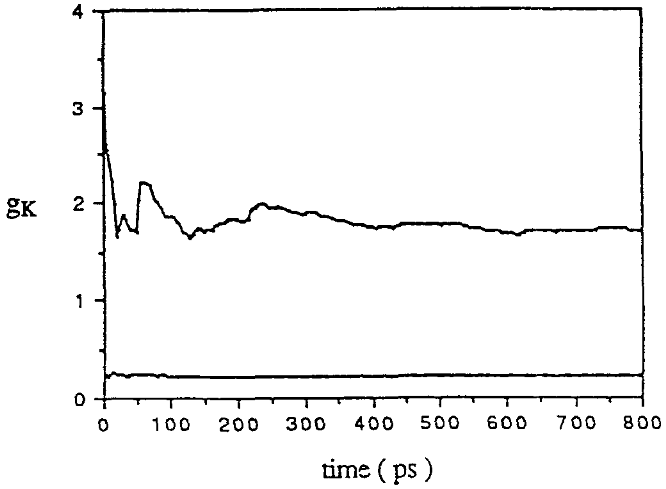

Figure 1 The cumulative average of the Kirkwood g-factor, g_K as a function of simulation time for a 11.5 Å water droplet (case b in Table 1). The upper curve is the g-factor of the inner sphere with radius of 6.5 Å. The lower curve is the g-factor of the whole droplet.

behaves differently from a sphere of water in a system with periodic boundary conditions, for which most of the other calculations of water dielectric constants were performed [13–17].

The error estimates of the g-factor reported in Tables 1 and 2 have been evaluated from time series of the square of the total dipole moment, M^2 according to the method of Straatsma *et al.* [18], for estimating the error of the mean of quantity from a correlated time series. For example, for the 11.5 Å droplet, the mean and mean-square deviation of M^2 were found to be 11.05 and 83, respectively. Using the method of ref. 17, the correlation time was estimated to be 0.5 ps; this method then gives .04 for the relative root-mean-square deviation of $\langle M^2 \rangle$ over a total simulation time of 800 ps (This is also the relative error in g_K). According to Equation (2) the relative error of ε is very sensitive to the relative error in g_K, as for large ε

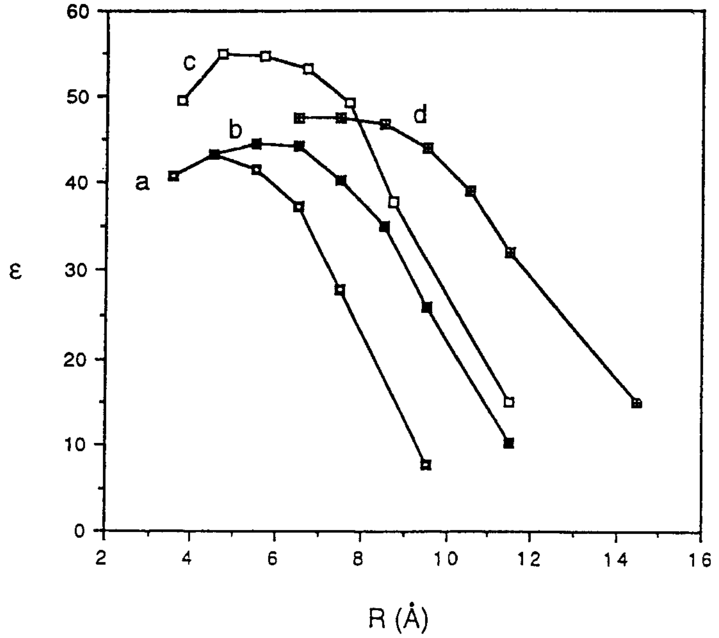

Figure 2 The dielectric constant of the interior parts of water droplets of different radii. a, b, c, d: see Table 1.

$(d\varepsilon/\varepsilon)(dg_K/g_K) \sim \varepsilon/3$. Thus, it is an advantage that the droplets have small ε (see next paragraph). There is no particular problem with use of Equation (3), for which $(d\varepsilon/\varepsilon)/(dg_K/g_K) \sim 1$.

From Table 1, we can see that the estimated dielectric constant of all water droplets is small. Even for the largest droplet, it reaches a value of only 15.0, much lower than the calculated dielectric constants of bulk water with periodic boundary conditions, which are above 60 for SPC water [14–17]. The dielectric constant of the droplet is not very sensitive to the modification of the parameters for the boundary restraint. In case c of Table 1, greatly increasing the repulsiveness of the boundary restraint increases the dielectric constant of the whole droplet by only 4 and the interior part by about 10. Modification of boundary conditions (case c) caused a larger change in dielectric constant than changes of droplet size (case a, b, d). Thus, the calculated dielectric constant appears to be more sensitive to the boundary conditions than to the size of the droplet. We have also tried other parameters for the boundary restraint, but this did not change the dielectric constant significantly.

The properties of the core and the boundary region of a simulated water droplet have been shown to be very different [3, 19]. Accordingly, we have estimated the dielectric constants of spherical volumes inside the droplets by Equation (3), which is only an approximation. According to our knowledge, there is, at present, no formula derived for the calculation of the dielectric constant of the internal part of a droplet.

Equation (3) is usually applied to calculate the dielectric constant of a droplet embedded in an infinite continuum with the same dielectric constant as the droplet. In principle, Equation (3) should be a good approximation of the dielectric constant of the internal parts of large droplets and give progressively poorer results for small droplets. In practice; we have found in another study [20] that for the inner part of a droplet, the dielectric constant calculated with Equation (3) is similar for the droplet in a reaction field, where use of Equation (3) should be appropriate, and for the droplet in vacuum. Therefore, this appears to be a valid approximation of the dielectric constant of the inner parts.

From Table 2 and Figure 2, it can be seen that the dielectric constant of the central part of a droplet is much higher than that of the whole droplet, varying from 43 to 56. For all cases, as the size of the interior region becomes smaller, the dielectric constant increases to a maximum, then decreases. (In the limit of one water molecule, g_K will be 1, which, according to Equation (3), formally corresponds to a dielectric constant of about 26. When the number of water molecules is very small, this dielectric constant has no physical meaning). For all cases, the maximum dielectric constant of the inner sphere was found at a distance between 5.5 and 6.0 Å from the droplet surface, which corresponds to two layers of water molecules. For the three different sizes of droplets with similar boundary restraints (a, b, d), the larger droplet has a higher maximum of the dielectric constant.

It is also interesting to look at the R-dependent Kirkwood g-factor. In Figure 3, we have listed the G_K (R) of the 11.5 Å droplet. The curve can be separated into two parts. In the first part ($0 < R < 6$ Å), $G_K(R)$ rises to about 2.5 as R increases. This behavior is very similar to the result obtained from simulations of water with periodic boundary conditions and with Ewald summation [16], *i.e.*, very much like the behavior in infinite bulk water. In the second part of the curve ($R > 6$ Å), $G_K(R)$

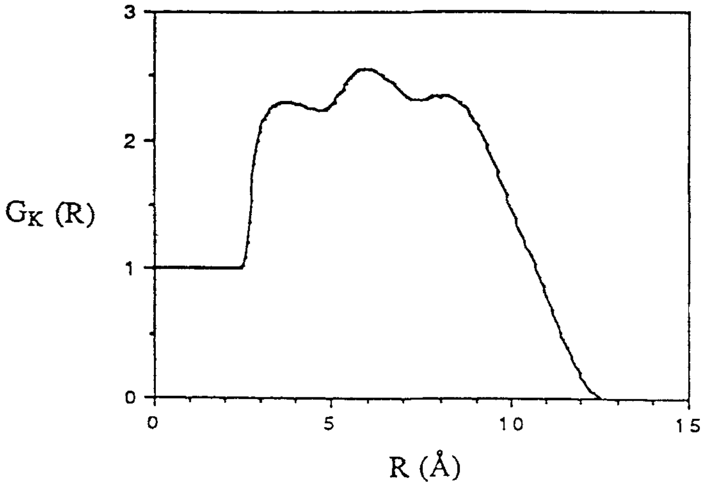

Figure 3 The R-dependent Kirkwood g-factor of 11.5 Å droplet from a 800 ps simulation (case b in Table 1). One water molecule was restrained at the center of the droplet as the reference.

does not increase, as in the simulations of water with periodic boundary condition and with Ewald summation, but goes down to zero because of boundary effects.

It is clear from the above discussion that the boundary has a strong influence on the dielectric properties of the water droplets. While it has been shown before that the boundary effect is limited to about one layer of water molecule away from the surface of the droplet [3, 19], we have found here that the boundary layer that adversely influences the dielectric properties includes about two layers of water molecules. The boundary effect observed here correlates with the strong orientational preference of water molecules near the surface of the droplet. Water molecules in the surface layer tend to have their dipole moments pointing in directions parallel to the surface, as is also the case in liquid water near planar hydrophobic surfaces [19, 21]. In addition, the boundary layer apparently compensates the instantaneous dipole of the interior volume and, as a result, the net dielectric constant of the droplet becomes very low. It would be desirable to make the simulations on droplet systems realistic by eliminating or at least reducing the boundary effect. At present this has still not been achieved. Our experience [22] in simulations with Friedman's image charge method [23] shows that plausible remedies are insufficient or significantly perturb the boundary layer in new and undesirable ways.

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