Study of Molecular Behavior in a Water Nanocluster: Size and Temperature Effect

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Temperature and size effects on the behavior of nanoscale water molecule clusters are investigated by molecular dynamics simulations. The flexible three-centered (F3C) water potential is used to model the inter- and intramolecular interactions of the water molecule. The differences between the structural properties for the surface region and those for the interior region of the cluster are also investigated. It is found that as the temperature rises, the average number of hydrogen bonds per water molecule decreases, but the ratio of surface water molecules increases. After comparing the water densities in interior regions and the average number of hydrogen bonds in those regions, we find there is no apparent size effect on water molecules in the interior region, whereas the size of the water cluster has a significant influence on the behavior of water molecules at the surface region.

Introduction

Besides its obvious significance to our life, water also exhibits many interesting and anomalous features in its physical and chemical properties. As a result, water usually plays an important role in chemical, physical, biological, and medical research areas. Although the properties of water have been examined by experimental methods,[1-3] theoretical approaches,[4-6] and computer simulations,[7-9] the structural properties of water are not yet well understood, especially the temperature and size effects on the properties.

In recent years, the problems concerning the temperature and size dependence of the physical properties of water have attracted much attention. Because of the complexity of the problems, there is still no well-established theory to deal with them, and computer simulation, such as the molecular dynamics (MD) method, seems to be an efficient approach. Some recent research efforts have focused upon the use of the MD method,[10-15] where different water models were invoked to study the temperature and size dependence of various properties of water. For example, rigid water models (e.g., SPC/E, TIP3P, or TIP4P) were used to explore the temperature and size effects on the structural,[10-12] dynamical,[11-13] or dielectric[14] properties of water. Levitt et al.[15] employed a flexible three-centered (F3C) water model for the investigation of structural and dynamical properties of water and obtained results which were well in agreement with experimental observations for different temperature and system sizes.

Although there were some advances made regarding the temperature and size effects on the structural properties of a water cluster, research concerning the near surface structural properties of water clusters was rarely considered. This problem is of significant importance for investigating the surface behavior of water clusters, such as the local structure and the surface

tension of water droplets.[8] Because of its potential in such applications as ink-jet printers[16] and surface wetting,[17] the topic of near surface structural properties of water clusters is worthy of examination.

In this paper we adopt the flexible three-centered (F3C) water model proposed by Levitt et al.[15] for the investigation of temperature and size effects on the properties of nanoscale water clusters. Because this model takes account of the flexible bonds and angles in the water molecules as compared with the rigid bonds and angles in the rigid models (e.g., SPC/E, TIP3P, or TIP4P), it not only accurately reflects the water structure detected by X-ray and neutron diffraction, but also yields values of the structural and dynamical properties which are in good agreement with those determined experimentally.[15] Table 2 in ref 15, which gave the comparison of properties calculated from the F3C model and other water models with experimental data, provides evidence for the above comment. Furthermore, since no periodical boundary conditions have been employed, the F3C model applies well for the small water droplets of the present study. A further advantage of this flexible water model is that it employs a short-range truncation, which largely reduces the necessary computational effort, and hence permits an MD simulation with a greater number of water molecules and/or with longer simulation duration. To examine the temperature and size effects, spherical water clusters of different sizes at various temperatures are analyzed and then hydrogen bond properties as well as the radial distribution functions of the water clusters are investigated in the present study. Moreover, the structural properties for the surface region are compared with those for the interior region.

Simulation Model

In the present research the flexible three-centered (F3C) water potential[15] is employed to model the inter- and intramolecular interactions of the water molecules in the clusters. The F3C

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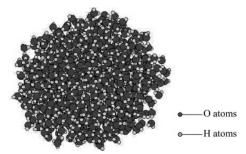*J. Phys. Chem. B, Vol. 110, No. 18, 2006* **9287**

Figure 1. Schematic diagram of a water cluster.

water potential U is represented by

$$U = U_{\text{bond}} + U_{\text{bend}} + U_{\text{vdw}} + U_{\text{els}} \quad (1)$$

where the intramolecular potentials U_{bond} and U_{bend} represent the bond strength energy and the bending energy in a water molecule, respectively. These two potential functions are given by

$$U_{\text{bond}} = \sum K_b^{\text{OH}} (b_i - b_0^{\text{OH}})^2 \quad (2)$$

$$U_{\text{bend}} = \sum K_\theta^{\text{HOH}} (\theta_i - \theta_0^{\text{HOH}})^2 \quad (3)$$

where b_i, θ_i, b_0^{OH}, and θ_0^{HOH} are the ith O−H bond length, the ith H−O−H bending angle, the equilibrium length of the O−H bond in a water molecule, and the equilibrium angle of the H−O−H bending angle in a water molecule, respectively. The summations in eqs 2 and 3 are performed over all bond lengths and bond angles in the water molecules, respectively.

The van der Waals potential, U_{vdw}, is used to model the intermolecular energy of the water molecules. For nonbonded pairs i and j in the water cluster with an interatomic distance r_{ij}, the van der Waals potential is expressed as

$$U_{\text{vdw}} = \sum [A_{\text{sc}} \epsilon^{ij} (r_0^{ij}/r_{ij})^{12} - 2\epsilon^{ij}(r_0^{ij}/r_{ij})^6 - S_{\text{vdw}}(r_{ij})] \quad (4)$$

where the parameter A_{sc} is used to compensate for the interaction lost for small cutoff distances and has a value determined by the cutoff distance specified in the F3C model. In the present study, this cutoff distance is specified as 10 Å and the value of A_{sc} is assumed to be 1.0. The energy parameter ϵ^{ij}, the distance parameter r_0^{ij}, and the truncation shift function S_{vdw} for the van der Waals potential can be obtained from ref 15. We also carried out a convergence test with different cutoff radii of 6, 7, 8, 9, and 10 Å. The variation of the number of hydrogen bonds per surface water molecule is less than 3% when different cutoff radii are used. Consequently, the values of different cutoff radii used in our simulation model have no influence on the results in the current study.

The electrostatic potential, U_{els}, for atoms i and j in the water molecule with an interatomic distance r_{ij} is expressed as

$$U_{\text{els}} = \sum [q^i q^j / r_{ij} - S_{\text{els}}(r_{ij})] \quad (5)$$

where q^i and q^j represent the partial charges of the oxygen or hydrogen atoms of two water molecules within the cutoff distance. The truncation shift function S_{els} for the electrostatic potential can also be found in ref 15. The summations in eqs 4 and 5 are executed over all nonbonded pairs i and j closer than the cutoff distance. All parameters in the F3C water potential are listed in Table 1.

For the investigation of temperature and size effects on the molecular behavior of water clusters, a spherical water model,
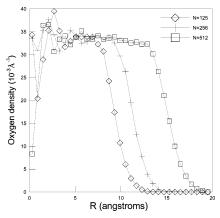

Figure 2. Oxygen density profiles for the F3C clusters of different sizes at room temperature (300 K).

TABLE 1: Parameters Used in the F3C Water Model

parameters and units	H₂O−H₂O
r_0^{OO} (Å)	3.5532
ϵ^{OO} (kcal mol⁻¹)	0.1848
r_0^{HH} (Å)	0.9000
ϵ^{HH} (kcal mol⁻¹)	0.01
r_0^{OH} (Å)	1.7883
ϵ^{OH} (kcal mol⁻¹)	0.0423
q^{O} (electron unit)	−0.820
q^{H} (electron unit)	0.41
b_0^{OH} (Å)	1.0000
θ_0^{HOH} (deg)	109.47
K_b^{OH} (kcal mol⁻¹Å⁻²)	250
K_θ^{HOH} (kcal mol⁻¹ rad⁻²)	60

as shown in Figure 1, containing N water (H₂O) molecules (with $N = 195$, 450, and 803) is invoked and five different temperature conditions (with $T = 273$, 285, 300, 310, and 320 K) are chosen in the simulations. The simulations are carried out in an NVT (canonical) ensemble. Initially, water molecules are distributed in the fcc arrangement. Then, the velocities of atoms in the model are randomly assigned according to a Maxwell distribution of 1 K by the Nosé−Hoover method.[18,19] The velocity Verlet's algorithm is then employed for time integration of Newton's equations of motion to obtain the new velocities and positions of each atom.[18,19] A time step equal to 10^{-15} s (1 fs) is used for time integration. After 5000 initial iterations for system equilibrium, the temperature was increased gradually and the simulations were iterated until the system reached the desired temperature. At this temperature, the simulations continued until equilibrium in energy had been reached. For the present cases, the equilibrium was accomplished in 10 ps. After the equilibrium check, the simulations were carried out for a further 50 ps and the time averages of simulation results for the last 20 ps were used for the investigation of water molecular properties of the clusters.

Results and Discussion

To demonstrate the validity of the present simulation, certain results determined from the present model are compared with previous works. Figure 2 displays the oxygen density profiles calculated from the present F3C model for a water cluster at room temperature (300 K) with size $N = 125$, 256, and 512. The oxygen density in the central region of the clusters is found to fluctuate about 0.0337 Å⁻³, which is very close to the bulk density (33.46 × 10^{-3} Å⁻³) for oxygen atoms in liquid water
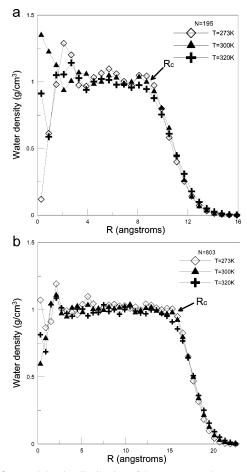
Figure 3. Local density distribution of the water nanocluster at different temperatures from the center to the surface: (a) 195 water molecules and (b) 803 water molecules in a water cluster.
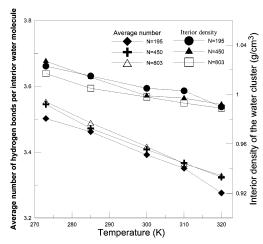

Figure 4. Variations of the average number of hydrogen bonds per interior water molecule and the average interior water density at different temperatures.

at room temperature and the value obtained from TIP4P clusters.[23] Moreover, peak and valley values of the O—O radial distribution function determined from the present simulation for a water cluster with $N = 803$ at room temperature are also very close to those values in Table 2 of ref 15.

Panels a and b of Figure 3 present the local density distributions of water molecules from the mass center of water clusters at different temperatures for the smallest and largest water clusters, respectively. The density distribution fluctuation is more apparent from the mass center to 8 Å because there are
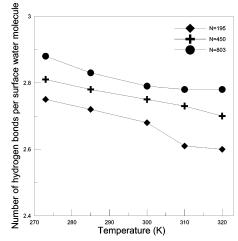

Figure 5. Variation of the average number of hydrogen bonds per surface water molecule at different temperatures.
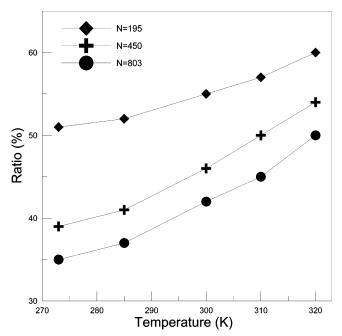

Figure 6. Variation of the ratio of the surface and all molecules of water clusters at different temperatures.

relatively fewer water molecules in this region which have been sampled to calculate the local density on time average. As the distance becomes larger than 8 Å, the density profiles fluctuate less, and then start to drop significantly after a specific distance in both the smallest and the largest cases. For convenience in investigating the respective behaviors of interior and surface water molecules of the water cluster, this specific distance R_c is used to divide water molecules of the cluster into the interior region and the surface region. The specific distance R_c, as labeled in Figure 3 for the highest temperatures, is defined as the point where the local density starts to gradually decrease to zero. Clearly, the interior water molecules distribute inside a close spherical space with a radius of R_c and the surface water molecules arrange upon the outside surface of this spherical space. It is obvious from Figure 2 that variation of the local density for the surface water molecules is much larger than that for the interior water molecules. The difference between the behavior of the interior water molecules and that of the surface water molecules is the main concern of the current study. This is the reason R_c is so defined rather than the equimolar dividing surface or the "90-10" rule, for example.
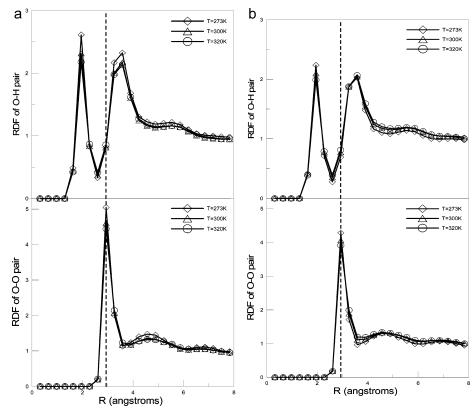
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Figure 7. Radial distribution functions of O−H and O−O pairs for surface water molecules: (a) 195 water molecules and (b) 803 water molecules in a water cluster.

Figure 4 shows the variation of interior water densities and the average number of H-bonds per interior water molecule, n_{HB}, at different temperatures. In determining the value of n_{HB}, the present study adopts the geometric criterion[20] that a hydrogen bond will be formed if the distances between two oxygen atoms and the oxygen and hydrogen atoms of a pair of water molecules are less than the first minimum[21] of the F3C O−O radial distribution function (3.4 Å) and the F3C O−H radial distribution (2.4 Å).[21] In addition, this study specifies that the angle between the O−O and O−H vector directions must be less than 30°. Because the local density fluctuation is more apparent in the interior region, the interior density is defined as the ratio of the number of total water molecules in the interior region divided by the spherical volume with radius R_c on time average. At higher temperatures, a single water molecule will possess higher kinetic energy and counteract more attractive energy including the hydrogen bonding and van der Waals interaction between water molecules, resulting in the increase of the average distance between two water molecules. This also leads to the decrease of the interior density and n_{HB}. As is observable in Figure 4, it is clearly evident that the interior density and n_{HB} are independent of the cluster size. In previous studies,[22,23] the orientation of water molecules in a nanocluster was observed by monitoring the variation of the dipole moment orientation against the distance from the cluster center. The authors concluded the dipole moment of interior water molecules orientated randomly, as in the bulk water. Since the orientation of bulk water still remains random, there is no size effect in the interior region. Consequently, the variation of interior densities and n_{HB} at different temperatures for different cluster sizes is almost the same.

The value of n_{HB} for a surface water molecule is shown in Figure 5. This value is smaller than that of the interior molecules shown in Figure 4. An interior water molecule stays in the interior portion of a closed spherical volume and is surrounded by its neighbor water molecules with the same probability in all directions. However, for a surface water molecule, there are fewer neighbor water molecules in the outer radial direction of the reference water molecule because the density of surface water in the outer region is decreasing toward zero as shown in Figure 3. Consequently, a surface molecule has fewer opportunities to form a hydrogen bond with a water molecule in the outer shell than an interior molecule, resulting in a lower average number of hydrogen bonds than for the interior water molecules. Hydrogen bonding is the main reason water has particular material properties such as higher melting and boiling points than other nonpolar molecules. This hydrogen bonding is also responsible for surface tension that arises from the intermolecular attractive forces at the water surface. Since the strength of a hydrogen bond is 10 to 100 times higher than that of van der Waals energy, the hydrogen bonding that forms between surface water molecules is responsible for the surface tension. In Figure 5, the average number of hydrogen bonds for a larger cluster is larger than the average number for a smaller water cluster at the same temperature. This also means the average intermolecular attractive energy at the surface for a larger size cluster is higher, leading to a higher surface tension at the surface. The current result is also in agreement with previous studies.[23] As regards the effect of temperature, the average number of hydrogen bonds decreases with the temperature. The lower average number of hydrogen bonds also leads to the reduction in surface tension, a tendency also investigated in bulk water. From a microscopic viewpoint, higher temperature indicates that a molecule possesses more kinetic energy to overcome the attractive energy by hydrogen bonding between surface water molecules, resulting in a lower surface tension.

A further investigation about the ratio of surface molecules in a water cluster of different sizes and at different temperatures is shown in Figure 6. The vertical axis represents the ratio of

surface water molecules to all water molecules in a water nanocluster, and this value is used to examine the variation of the surface molecule ratio with the cluster size at different temperatures. For a smaller size cluster, the ratio of surface molecules is higher, and the ratio becomes smaller in a larger water cluster. Similar results are also found in other nanoclusters,[24] which reveal that the surface−volume ratio continuously increases as the nanocluster size decreases. From the observation of Figure 5 and Figure 6, for the larger size cluster at each temperature, the average number of hydrogen surface water molecules is higher while the ratio of surface molecules is lower. Consequently, the internal energy will increase with the cluster size.[22]

To investigate the distribution of surface water molecules, radial distribution functions (RDF) of O−H and O−O pairs for the smallest and largest cases at 273, 300, and 320 K are shown in Figure 7, panels a and b, respectively, where the radial distribution functions are properly normalized to make them approach unity at large *R*. The oxygen atoms of the surface water molecules are referred to as the reference atoms in all RDF profiles. The upper and lower panels in Figure 7 show the O−H and O−O radial distribution profiles of surface water molecules, respectively. The dashed lines connecting upper and lower panels are used to indicate the distribution of hydrogen and oxygen atoms relative to the referenced oxygen atoms. For both the smallest and largest water clusters, there are two prominent peaks for O−H RDF profiles and one O−O peak apparent between the O−H RDF peaks. The first O−H RDF peak arises from the hydrogen bond between the reference oxygen atom and the hydrogen atoms covalently bonded to the oxygen atoms which are arranged within the O−O RDF peak. The oxygen atoms distributed within the O−O RDF peak also cause the hydrogen atom distribution of the second O−H RDF peak. In Figure 7, the values of all RDF peaks decrease with the cluster temperatures, which indicates that the number of neighbor atoms for surface oxygen atoms decreases as the temperature increases. At a higher temperature, the kinetic energy of a water molecule has more ability to overcome the hydrogen bonding and reduce the average number of hydrogen bonds for surface water molecules, as shown in Figure 5. With a close inspection of the first O−H peak values at different temperatures, it is clear that the variation of the first O−H peak for a smaller water cluster is more sensitive to temperature than that of the larger cluster, reflecting that the variation of the average number of hydrogen bonds per surface water molecule is more sensitive to temperature, as shown in Figure 5. The distribution of hydrogen atoms within the first O−H RDF peak has an influence on the distribution of the first neighbor oxygen atoms within the O−O RDF peak, and the distribution of these oxygen atoms has a further influence on the distribution of the hydrogen atoms within the second O−H RDF peak. Consequently, the variation of the first O−H peak of a larger size cluster at different temperatures is not as apparent as the variation of a smaller cluster, so the distributions of first neighbor oxygen atoms and second hydrogen atoms are not as sensitive to the variation of temperature as for a smaller cluster. This can be attributed to the average number of hydrogen bonds per surface water molecule in different size clusters. The average number of hydrogen bonds for a larger size cluster is higher and this means a surface water molecule of a larger cluster bonds more strongly with neighbor molecules than the surface water molecule of a smaller cluster does. More kinetic energy is needed to change the surface molecular arrangement in a larger water cluster.

Conclusions

The influences of water cluster size and temperature on the behavior of water molecules in a water cluster are investigated by molecular dynamics simulation. Each water nanocluster can be divided into two regions according to the variation of the local density profile. The region where water molecules behave as bulk water is in the interior portion of the water cluster, which is termed the interior region. Since water molecules in the interior region still keep random orientation, there is no size effect on the arrangement of water molecules within this region. However, for water molecules outside the interior region, the size of the water cluster has an influence on the distribution of water molecules. For a larger size cluster, a surface water molecule has a higher average number of hydrogen bonds, leading to a higher surface tension. Considering a smaller water cluster, however, there are fewer hydrogen bonds forming between surface water molecules, which results in a lower surface tension. It is found that as the temperature rises, the average number of hydrogen bonds formed per water molecule decreases in both regions but the ratio of surface molecules in a water cluster increases. The dynamic behavior of a water molecule is directly influenced by the environment where the water molecule resides. For example, the dynamic properties of water molecules for bulk water are different from those of water molecules interacting with particular molecules[25] or in a confined space.[26] Consequently, the study on the dynamic behavior of surface water molecules is an interesting topic and worthy of further investigation.

References and Notes

(1) Narten, A. H.; Thiessen, W. E.; Blum, L. *Science* **1982**, *217*, 1033.
(2) Pugliano, N.; Saykally, R. J. *J. Chem. Phys.* **1992**, *96*, 1832.
(3) Kropman, M. F.; Bakker, H. J. *Science* **2001**, *291*, 2118.
(4) Palinkas, G.; Kalman, E.; Kovacs, P. *Mol. Phys.* **1977**, *34*, 525.
(5) Stillinger, F. H. *Science* **1980**, *209*, 4455.
(6) Xantheas, S. S.; Dunning, T. H. *J. Chem. Phys.* **1993**, *99*, 8774.
(7) Gregory, J. K.; Clary, D. C.; Liu K.; Brown, M. G.; Saykally, R. J. *Science* **1997**, *275*, 814.
(8) Brodskaya, E. N.; Eriksson J. C.; Laaksonen, A.; Rusanov, A. I. *J. Colloid Interface Sci.* **1996**, *180*, 86.
(9) Silvestrelli, P. L.; Parrinello, M. *Phys. Rev. Lett,* **1999**, *82*, 308.
(10) Luzar, A. *Chem. Phys.* **2000**, *258*, 267.
(11) Sokol, M.; Dawid, A.; Dendzik, Z.; Gburski, Z. *J. Mol. Struct.* **2004**, *704*, 341.
(12) Egorov, A. V.; Komolkin, A. V.; Chizhik, V. I.; Padro, K. A.; Gvardia E. *J. Phys. Chem.* **2000**, *74*, 1650.
(13) Yeh, I. C.; Hummer, G. *J. Phys. Chem. B* **2004**, *108*, 15873.
(14) Guàrdia, E.; Martý, J. *Phys. Rev. E* **2004**, *69*, 011502.
(15) Levitt, M.; Hirshberg, M.; Sharon, R.; Laidig, K. E.; Daggett, V. *J. Phys. Chem. B* **1997**, *101*, 5051.
(16) Furbank, R. J.; Morrisa, J. F. *Phys. Fluids* **2004**, *16*, 1777.
(17) Heine, D. R.; Grest, G. S.; Webb, E. B. *Phys. Rev. Lett.* **2005**, *95*, 107801.
(18) Haile, J. M. *Molecular Dynamics Simulation*; Wiley-Interscience: New York, 1992; Chapter 4.
(19) Rapaport, D. C. *The Art of Molecular Dynamics Simulations*; Cambridge University Press: Cambridge, UK, 1997; Chapter 3.
(20) Gordillo, M. C.; Marti, J. *Chem. Phys. Lett.* **2000**, *329*, 341.
(21) Michael, L.; Miriam, H.; Ruth, S.; Keith, E. L.; Valerie, D. *J. Phys. Rev. B* **1997**, *101*, 5051.
(22) Brint, C. L.; Burton, J. J. *J. Chem. Phys.* **1975**, *63*, 3327.
(23) Zakharov, V. V.; Brodskaya, E. N.; Laaksonen, A. *J. Chem. Phys.* **1997**, *107*, 10675.
(24) Erkoc, S. *Phys. E* **2000**, *8*, 210.
(25) Lin, S. T.; Maiti, P. K.; Goddard, W. A. *J. Phys. Chem. B* **2005**, *109*, 8663.
(26) Ju, S. P.; Chang, J. G.; Lin, J. S.; Lin, Y. S. *J. Chem. Phys.* **2005**, *122*, 154707.