Molecular Dynamics Studies of Hydrated and Dehydrated Na⁺-Zeolite-4A

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Molecular dynamics simulations of fully hydrated and dehydrated Na⁺-zeolite-4A with a mobile zeolite framework at 298 K and a steepest descent energy minimization simulation on the dehydrated zeolite have been performed. The optimized structure yields bond lengths, bond angles, and positions of sodium ions in very good agreement with published X-ray data. The simulations at 298 K confirm that the Na(1) and Na(3) ions oscillate about their mean positions and that migration is slow. The Na(2) ions, located in the oxygen eight-rings, are much more mobile and move out of the plane of the ring as well as within the plane. Most water molecules in the α-cages are found to migrate between preferred sites on the inside of the cage. The preferred sites form a polyhedron with 44 vertices, differing from the interpretation of experiment. On average, 2.5 water molecules are found up to 3 Å from the α-cage center, with the remaining 21.75 water molecules at sites on the inside of the cage. Water molecules in the β-cages remain in the cages for 300 ps at 298 K and occupy six octahedral preferred sites. The water molecules in β-cages containing exactly four molecules are found to occupy planar sites.

I. Introduction

Zeolites are a class of aluminosilicates with considerable technological importance, particularly in the chemical industry. Zeolite crystals consist of SiO₄ and AlO₄ tetrahedra arranged in space to produce open structures consisting of interconnecting pores and cages.[1] Ions and small molecules can diffuse easily through the open crystal, and this phenomenon is responsible for many of their interesting and useful catalytic, ion-exchange, and molecular-sieve properties. The structure of a wide range of zeolites and the adsorption/absorption and motion of a variety of small molecules, from noble gases to aromatics, have been investigated over the years.

The present studies focus on the properties of water in Na⁺-zeolite-4A. Water is an important diffusant playing a critical role in many industrial and commercial processes. For instance, zeolite-4A is a major constituent of washing powder, and so the uptake, diffusion, and release of water are important processes to understand if new products with improved performance and stability are to be designed.

The true unit cell of zeolite-4A consists of 96 AlO₄ and 96 SiO₄ tetrahedra with each oxygen atom bonded to one aluminum atom and one silicon atom.[1] A schematic diagram is provided in Figure 1. Charge neutrality is provided by 96 sodium ions, and the full chemical formula of the unit cell is $Na_{96}Al_{96}Si_{96}O_{384}$. The cubic unit cell dimension is 24.555 Å.[2] The large cavities with a radius of approximately 5.7 Å and composed of 72 oxygen atoms are referred to as α-cages, while the smaller cavities with a radius of about 3.3 Å and composed of 36 oxygen atoms are the β-cages.[1] There are eight α-cages and eight β-cages per unit cell. The arrangement of oxygen atoms in zeolite-4A produces eight-membered, six-membered, or four-membered rings, referred to as 8R, 6R, and 4R, respectively, for brevity. Examples are illustrated by bold lines joining oxygen atoms in Figure 1. Each 6R contains three oxygen atoms approximately 2.3 Å from the ring center, conventionally labeled O(3), and three oxygen atoms about 2.9 Å from the
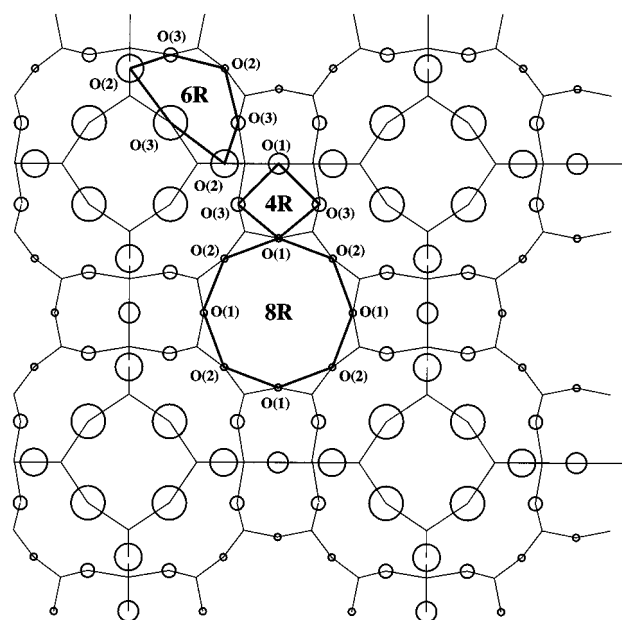

Figure 1. Schematic diagram of the zeolite-4A crystal. Only the oxygen atoms are shown and are represented by circles, with the size of circle indicating depth. Examples of an oxygen eight-, six-, and four-ring are illustrated by bold lines and labeled 8R, 6R, and 4R, respectively. The oxygen atoms are labeled O(1), O(2) and O(3) according to convention.

center, labeled O(2). All remaining oxygen atoms are labeled O(1). Each 8R is therefore composed of alternating O(1) and O(2) atoms, and each 4R is formed by alternating O(1) and O(3) atoms. These are labeled in the figure. The water molecules are located in the α-cages and β-cages and diffuse between the cages. The diffusion process at the microscopic level is complicated by the presence of sodium ions, which are also located in the cages and are presumed to be hydrated in the presence of water.

There have been a number of experimental investigations into the properties of water in zeolite-4A.[3−5] These have elucidated some aspects of the macroscopic and microscopic behavior of water, but it is difficult in some cases to interpret the

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experimental results. The magnetic resonance imaging experiments of Hughes *et al.*[4,5] are measurements of long-range water transport, but their results are interpreted in terms of short-range interparticle and intraparticle diffusion. The macroscopic quantities are intrinsically linked to microscopic processes.

The computer simulation has an important role to play in establishing the relationship between microscopic and macroscopic quantities. Studying zeolite systems under a controlled environment provides insight into the behavior of small molecules at the microscopic level, thereby leading to a greater understanding of the overall behavior of these materials. Early computational studies involved potential energy minimization to obtain structural information on zeolites and to identify preferred sites for adsorbates (for example, refs 6, 7). Later work employed Monte Carlo methods, both to determine the preferred adsorbate orientation and, secondly, to simulate the macroscopic diffusion of adsorbed species (ref 8 and references therein). With the advent of more available computer power it has been possible to attempt molecular dynamics (MD) studies of zeolite structures. Some notable work has been performed by Catlow, Parker, Nowak, and others.[6,9−12] These authors have demonstrated the value of MD modeling, and most importantly, they show that it is possible to obtain good agreement with experiment of macroscopic quantities derived from the simulation.

We present the results from a series of MD simulations designed to investigate the behavior of water in Na$^+$-zeolite-4A. Simulations are performed at 298 K for the dehydrated and fully hydrated crystal. In addition, a steepest descent energy minimization simulation is performed on the dehydrated zeolite for structure optimization, and we refer to this, for simplicity, as a 0 K simulation. Only one group has performed MD simulations of water in Na$^+$-zeolite-4A.[9] These authors employed a rigid zeolite lattice and performed a MD simulation on the fully hydrated crystal at 298 K. Their work provides a useful comparison, but the diffusion of small molecules is likely to be sensitive to the lattice motion, and so the framework lattice is mobile in the present work. To our knowledge, these are the first MD simulations of water in Na$^+$-zeolite-4A incorporating a mobile framework.

The present simulations are only useful if the chosen interatomic potentials provide a reasonable reproduction of known structural properties. The present work therefore concentrates on the structural properties of Na$^+$-zeolite-4A and the water and sodium ions contained in its pore network. The 0 K simulation is compared to X-ray data on dehydrated Na$^+$-zeolite-4A and with previous computational work. The MD simulations of hydrated zeolite at 298 K provide new information on the possible preferred sites of water within the cages. These results are discussed fully in section III. Section II outlines the model and simulation, and section IV contains the discussions and general conclusions.

II. Model

The Interatomic Potentials. Transferring interatomic potentials optimized for one system to a second closely related system has generally proved successful. Jackson and Catlow employed potentials derived for α-quartz, for instance, in their lattice-energy-minimization studies of Na$^+$-zeolite-4A and obtained a very satisfying agreement with crystallographic data.[6] Other authors have applied the same set of potentials to a range of different zeolite structures.[13,14] We similarly adopt, where possible, potentials derived for closely related systems while remaining cautious as to their general validity for the Na$^+$-zeolite-4A system.

TABLE 1: Potential Energy Functions and Parameters

Coulombic:	$q_1 q_2/(4\pi\epsilon_0 r)$
Buckingham:	$Ae^{-r/\rho} - Cr^{-6}$
Lennard-Jones:	$Br^{-12} - Cr^{-6}$
Harmonic:	$k(\theta - \theta_0)^2/2$

2-body	A	ρ	B	C
OZ–OZ	22764.000	0.1490		21.250
Si–OZ			1150.000	50.000
Al–OZ			1300.000	0.000
Na–OZ	5836.840	0.2387		0.000
Na–OW	5836.840	0.2387		0.000
OW–OW			27320.000	27.060
Si–OW			10.644	0.586
Al–OW			11.758	0.500
OZ–OW			5645.172	23.429
Si–HW			0.552	0.089
Al–HW			0.626	0.075
OZ–HW			660.778	5.413

Atom	Charge q (e)
OZ	-1.86875
Si	3.70000
Al	2.77500
Na	1.0000
OW	-0.8476
HW	0.4238

3-body	k	θ_0
Al-OZ-Si	4.5815	109.47
Si-OZ-Al	4.5815	109.47

OW-HW Intramolecular distance 1.00000 Å
HW-HW Intramolecular distance 1.63299 Å

The interatomic potentials used in the present simulations are the sum of two-body Coulombic, Lennard-Jones, Buckingham, and three-body harmonic potentials. The functional forms of the potentials and the parameters are given in Table 1. Where confusion is possible, the symbols OZ and OW are used to distinguish between oxygen atoms forming part of the zeolite cage and in water molecules, respectively. For consistency, the water hydrogen atoms are labeled HW.

The OZ−OZ Buckingham potential and the Si−OZ−Al three-body harmonic potential parameters are taken from Jackson and Catlow[6] with the attractive term of the OZ−OZ potential modified for the choice of electrostatic charge on the OZ atom according to Baram and Parker.[15] It was not possible to stabilize the crystal structure with full nominal charges on the silicon, aluminum, and oxygen atoms of the zeolite crystal. Reduction of the charges by 7.5% stabilized the crystal and yielded a lattice energy consistent with published results.[6] Simple Lennard-Jones potentials are chosen for the Si−OZ and Al−OZ interactions. These parameters are adjusted to maintain stability of the structure and to obtain reasonable agreement for bond lengths and bond angles obtained from X-ray data.[2] The Lennard-Jones parameters are very similar to those employed by Jackson and Catlow.[6]

The water−zeolite interaction parameters are taken from Leherte *et al.*, who performed MD studies of water in ferrierite and obtained good agreement with experiment for the heat of adsorption and self-diffusion coefficient.[16,17] The SPC/E model is used to describe the water−water interactions.[18] Here the water molecule is rigid, with a HW−OW bond length of 1.000 Å and a HW−HW bond length of 1.632 99 Å. The water molecules interact via the OW−OW Lennard-Jones potential with parameters presented in Table 1. This potential is simple and provides reasonable agreement with experiment for a range of properties, including the diffusion coefficient,[18] although more recent work suggests that the strength of the hydrogen bonding is underestimated.[19] Finally, the Na−OZ potential is taken from Jackson and Catlow, who calculated the potential using the electron gas method.[6] The Na−OW potential is assumed to be of the same form.

TABLE 2: Bond Lengths and Distances (in Å) between Ring Centers and the Surrounding Zeolite Oxygen Atoms

source	Si–O	Al–O	6R(c)–O(3)	6R(c)–O(2)	8R(c)–O	4R(c)–O
Yanagida *et al.*	1.66	1.66	2.31	2.89		1.93
Pluth and Smith	1.597	1.731	2.313	2.907	3.64	1.97
Jackson and Catlow	1.549	1.757				
this work	1.580	1.722	2.40	2.88	3.56	1.90

TABLE 3: Angles (in deg) Subtended at (a) Oxygen Atoms by Silicon/Aluminum Atoms and (b) at Silicon/Aluminum Atoms by Oxygen

(a)

source	(Si,Al)–O(1)–(Si,Al)	(Si,Al)–O(2)–(Si,Al)	(Si,Al)–O(3)–(Si,Al)
Yanagida *et al.*	145	166	144
Pluth and Smith	142.2	164.7	144.8
Jackson and Catlow	142.2	165.1	144.6
this work	147	166	150

(b)

source	O(1)–Si–O(2)	O(1)–Si–O(3)	O(2)–Si–O(3)	O(3)–Si–O(3)	O(1)–Al–O(2)	O(1)–Al–O(3)	O(2)–Al–O(3)	O(3)–Al–O(3)
Yanagida *et al.*	110.4	110.3	106.8	112.1	110.4	110.3	106.8	112.1
Pluth and Smith	108.8	111.3	107.2	110.9	108.1	112.3	106.0	111.6
Jackson and Catlow	106.2	110.9	107.7		118.0	108.4	105.2	
this work	112	110	108	109	113	109	109	109

TABLE 4: Distances of the Sodium Ions from the Zeolite Oxygen Atoms and from the Center or Plane of Oxygen Rings

source	Na(1)–6R(p)	Na(1)–O(2)	Na(1)–O(3)	Na(2)–8R(c)	Na(2)–O(2)	Na(2)–O(1)	Na(3)–4R(p)	Na(3)–O(3)
Yanagida *et al.*	0.20	2.90	2.32	1.23	2.40	2.64		2.47
Pluth and Smith	0.21	2.915	2.323	1.26	2.38	2.615	1.70	2.60
Jackson and Catlow		2.993	2.378			2.456		
this work	0.17	2.89	2.41	1.31	2.44	2.66	1.65	2.46

Molecular Dynamics Simulations. A single true cell of Na$^+$-zeolite-4A, formula Na$_{96}$Al$_{96}$Si$_{96}$O$_{384}$, was used in all simulations. The space group is *FM$\bar{3}$c*, and the cubic cell dimension is 24.555 Å.[2] The silicon and aluminum atoms alternate so that each oxygen atom is bonded to one atom of each type, and the sodium ions were initially placed at approximate X-ray sites within the crystal. The Ewald summation technique was used to determine the long-range Coulomb interactions. This is essential in MD studies of zeolites.[17] The Ewald convergence parameter α is determined by calculating the configuration energy as a function of α and locating the midpoint of the plateau, at which the configuration energy is a maximum. The value of α was 0.32 Å^{-1}, which was used in conjunction with a real space potential cutoff of 12 Å and a reciprocal space cutoff of 1.54 Å^{-1}. These parameters give a converged electrostatic energy to about ±0.005%.

MD simulations were performed at constant volume and temperature using the program DLPOLY, version 1.1. In the 0 K simulation all atoms move in the direction of the computed force and the crystal is allowed to equilibrate until the total energy is constant to five significant figures for a time of 100 ps. For the hydrated zeolite, 224 water molecules were placed at random within the crystal to the desired concentration and allowed to equilibrate at 298 K. In all simulations, the time step was 2 fs.

III. Results

Zeolite Framework. The crystal structure obtained from the 0 K simulation on the dehydrated Na$^+$-zeolite-4A is compared to X-ray data due to Yanagida *et al.*[20] and Pluth and Smith[2] and with the lattice energy minimization results of Jackson and Catlow[6] in Tables 2, 3, and 4. Jackson and Catlow employed five different potential refinements, and we take their model e (their most sophisticated model) for comparison. All structural results from the 0 K simulation are within the statistical error of those from the simulation at 298 K.

Table 2 presents the mean Si–O and Al–O bond lengths and distances between the oxygen ring centers and the zeolitic oxygen atoms. The mean Si–O and Al–O bond lengths are found to be 1.580 and 1.722 Å, respectively, compared to the averaged values of 1.597 and 1.730 Å obtained by Pluth and Smith. These results are in good agreement. Unfortunately Yanagida *et al.* do not present bond lengths for Si–O and Al–O separately, but their averaged value is consistent with Pluth and Smith.

The distances from the ring centers to the oxygen atoms forming the ring are also presented in Table 2 and are compared to other data where available. The 6R is puckered so that the three O(3) atoms are closer to the ring center than the three O(2) atoms. It has been suggested that the puckering arises from the attraction of the oxygen atoms to the sodium ion located at the center of the ring, but the presence of the sodium ion only has a small influence on the strong Si–O and Al–O bonds, and the puckering is simply a property of the crystal geometry. The mean value of the distance from the 6R center to the O(3) atoms is overestimated by about 0.09 Å, but the mean 6R(c)–O(2) distance is in good agreement with experiment. The mean 8R(c)–O and 4R(c)–O distances are also in good agreement with the experimental values. We note that the value of 3.64 Å included in Table 2 for the 8R(c)–O distance is half the O(2)–O(2) ring diameter indicated by Pluth and Smith in their Figure 3.

The angular data are presented in Tables 3 and 4. Again, the agreement with X-ray data is good, with angles obtained from the simulation differing from the experimental results typically by at most 3°. The only exception is the (Si,Al)–O(3)–(Si,Al) angle, which is overestimated by about 6° by the simulation.

The total lattice energy of the true cell was found to be −21 590 eV, slightly lower than the range −20 650 to −21 250 eV obtained by Jackson and Catlow.[6] Finally, the mean distance from the center of the α-cages to the centers of the oxygen atoms that form the cage is found to be 7.078 Å.

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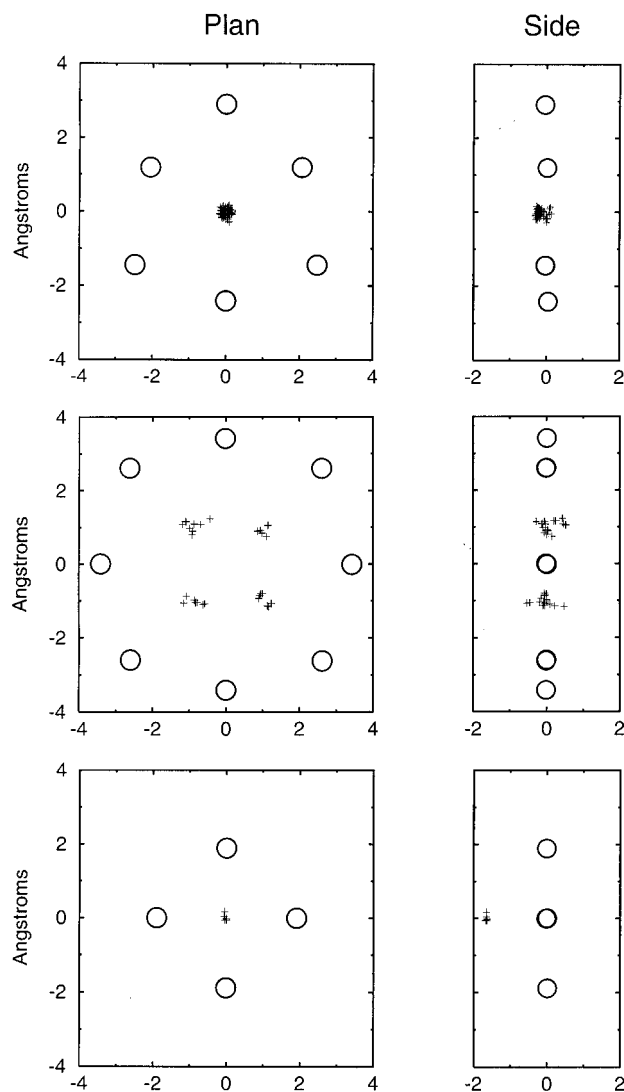*J. Phys. Chem. B, Vol. 101, No. 10, 1997* **1765**

Figure 2. Plan and side views of the oxygen (O) and the Na(1) ions (+) associated with the six-rings, eight-rings, and four-rings in the dehydrated zeolite.

For the β-cage the mean distance is 4.780 Å. Both are in good agreement with accepted values.[1]

Overall it can be concluded that the zeolite framework potentials employed in the MD simulations yield structural parameters that are in good agreement with X-ray data and confirm that the simple Lennard-Jones Si$-$O and Al$-$O potentials are satisfactory for this purpose. We have not, at present, examined vibrational or other data, and it is likely that more sophisticated potentials would be required to reproduce a range of properties.

Sodium Ions. Previous experimental and theoretical studies indicate that the sodium ions occupy three main sites.[1] Ions in these sites are referred to as Na(1), Na(2), and Na(3) and correspond to locations associated with the 6R, 8R, and 4R, respectively. There are 64 6Rs, 24 8Rs, and 96 4Rs in the true unit cell. Previous workers have concluded that each 6R and each 8R contain approximately one sodium ion, accounting for 88 of the 96 ions in the cell.[1] The remaining eight Na(3) ions are found at random 4R sites.

The positions of the sodium ions are best illustrated through plan and side views of portions of the crystal. For instance, if we focus on the location of the Na(1) ions close to the 6R, every 6R in the unit cell can be rotated and viewed on the same diagram with the plane of the ring in the plane of the diagram. Thus the plan view presented in Figure 2 is a simultaneous plot

of the atomic positions of all the sodium ions in the cell together with the mean positions of the oxygen atoms forming the 6Rs. Each 6R contains exactly one sodium ion, and so there are 64 sodium ions plotted in the figure. A side view is also presented so that the displacement of the Na(1) ions away from the plane of the ring can be seen. The Na(1) ions are located at the centers of the 6Rs, and the side view shows a very small displacement away from the plane of the ring toward the α-cage. These observations concur with experiment. The mean displacement of 0.17 Å into the α-cage is shown in Table 4 and compares well with values of 0.20 and 0.21 Å obtained from X-ray data. It is interesting to note that the side view indicates a small buckling of the oxygen 6R away from the plane of the ring.

The Na(2) ions are located at sites associated with the 8Rs. Twenty one of the 24 8Rs contain a single sodium ion and three 8Rs contain two ions. Diffusion of sodium ions has clearly occurred during the equilibration of the crystal at 298 K, before the steepest descent energy minimization was executed. The plan and side views of the 8Rs and the 27 sodium ions are presented in Figure 2. In agreement with previous work, we find that the Na(2) ions are located in the plane of the ring but offset from the ring center. The mean distance from the center is found to be 1.31 Å, once again in good agreement with the experimental values of 1.26 and 1.23 Å. Figure 2 also shows the presence of four equivalent sites. In each equivalent site the Na(2) ion is interacting with three oxygen atoms in the ring. The distance between the Na(2) ion and the closest oxygen atom, which is an O(2) atom, is 2.44 Å, compared to X-ray results of 2.38 and 2.40 Å. Pluth and Smith and Jackson and Catlow quote values for the distance between Na(2) ion and its second and third oxygen neighbors, both O(1) atoms. Thus two values for the Na(2)$-$O(1) distance are quoted in their work. Here we average their values and present these in Table 4 together with the result from the present simulation. The mean Na(2)$-$O(1) distance is found to be 2.66 Å, close to the range 2.61$-$2.64 Å obtained from experiment but about 0.2 Å larger than the value obtained by Jackson and Catlow. The side view confirms that the Na(2) ions are approximately in the plane of the ring.

The final five sodium ions are located in random 4Rs and are referred to as Na(3) sites. Figure 2 shows the mean positions of the oxygen atoms forming the 4Rs and the five Na(3) ions. The side view shows that the Na(3) ions are displaced from the plane of the ring by a mean distance of 1.65 Å. The mean Na(3)$-$O(3) distance is found to be 2.46 Å. Both results once again compare well with experiment.

Finally, it is interesting to examine the motion of the sodium ions obtained from the simulation at 298 K. Figure 3 shows the location of the Na(1) ions in the 6R in the plan and side view. The positions are plotted every 5 ps for 300 ps and show that these ions vibrate about the mean position but do not migrate away from the 6R during the time of the simulation. By contrast, Figure 3 also presents the positions of the Na(2) ions in the 8R at 298 K over the same time period. The Na(2) ions are mobile and able to move out of the plane of the ring. Shin *et al.*[21] report movement of Na(2) ions of about 1.5$-$1.7 Å during 20 ps at 300 K and suggest that the ions are migrating between degenerate positions within the plane of the ring. Our results clearly show movement out of the plane of the ring as well as within the plane. Shin *et al.* reported significant mobility of Na(1) and Na(3) ions about their X-ray positions at room temperature but little migration. They also noted the high mobility of the Na(2) ions, and the present simulations therefore support these observations.
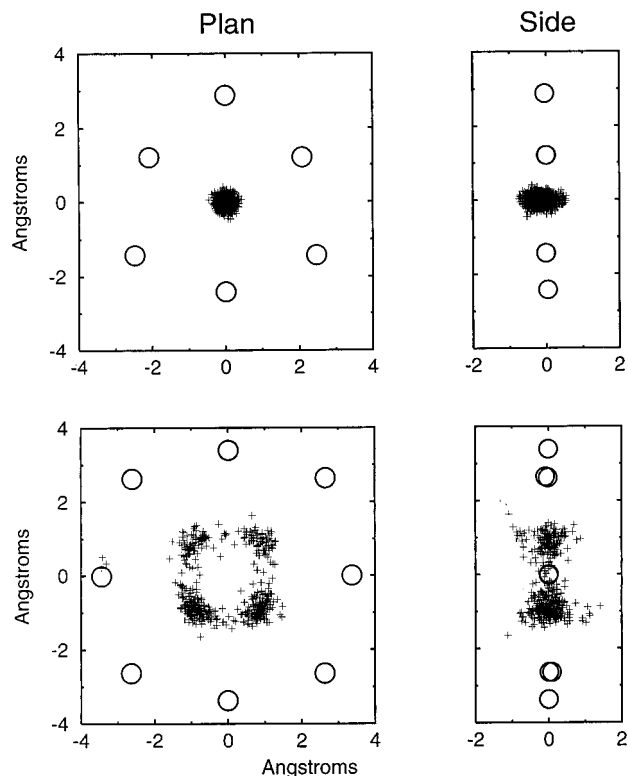
Plan   Side

Figure 3. Plan and side views of the oxygen (○) and the Na(1) ions (+) associated with the six-rings and eight-rings, plotted every 5 ps, in the dehydrated zeolite at 298 K.
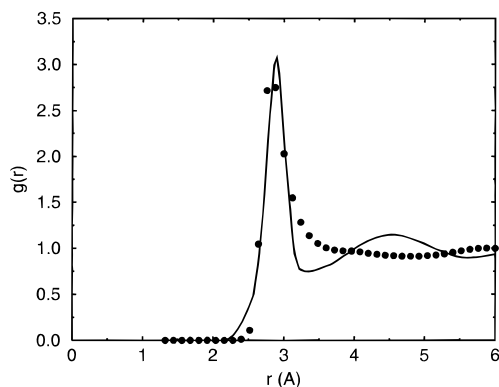

Figure 4. OW−OW radial distribution function from the MD simulation of fully hydrated zeolite-4A at 298 K (●) and the experimental radial distribution function (−) for bulk water at 300 K.[23]

Water. A total of 224 water molecules are placed randomly into the simulation cell and equilibrated at 298 K for about 200 ps. The 224 water molecules are chosen because this number corresponds approximately to full hydration as reported in the literature.[1] The full simulation is then performed for 300 ps with time steps of 2 fs. The random placement of water molecules into the crystal results in 30 molecules in the β-cages, or 3.75 molecules per cage on average, with the α-cages containing the remaining 194 water molecules with an average occupancy of 24.25 per cage. The cage occupancies are in broad agreement with the X-ray measurements of Gramlich and Meier,[3] who note 5.5 and 22.9 water molecules per cage, respectively. There is no migration to or from the β-cages during the course of the simulation at 298 K, confirming that diffusion into and out of the β-cages is very slow.

Figure 4 presents the OW−OW radial distribution function. This function represents the density of OW atoms at a distance r from a single OW atom normalized to the average density of
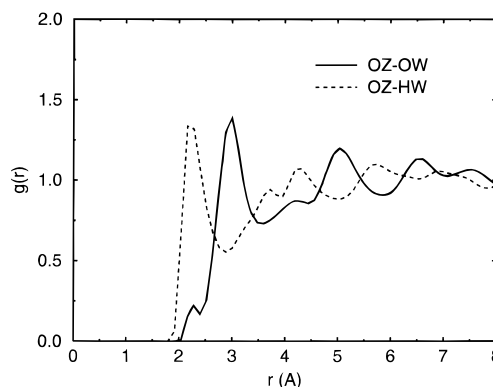

Figure 5. OZ−OW (—) and OZ−HW (- - -) radial distribution function from the MD simulation of fully hydrated zeolite-4A at 298 K.

OW atoms in the system. The results are consistent with the distribution function obtained for bulk water[23] and for vicinal water at silicate surfaces[24] at short distances, but there is a different structure for $r > 3.5$ Å which arises due to the existence of preferred sites in the α-cages and β-cages, as will be discussed shortly. Figure 5 presents the OZ−OW and OZ−HW radial distribution functions. The hydrogen atoms of the water molecules are generally closer to the zeolite cage walls than the OW atoms. The minimum OZ−OW and OZ−HW distances are approximately 2.1 and 1.8 Å, respectively, in reasonable agreement with values of 2.2 and 1.9 Å presented by Leherte et al.[22] in their MD studies of water in ferrierite.

There has been some debate concerning the location of the water molecules in the cages of Na⁺-zeolite-4A. Breck[1] provides a summary of findings to 1974. The only X-ray analysis of hydrated zeolite-4A appears to be due to Gramlich and Meier.[3] They indicate some evidence for a pentagonal dodecahedral arrangement of 20 water atoms in the α-cages, noting that a similar structure has also been observed in clathrate compounds,[1] and a distorted tetrahedral arrangement of four water molecules in the β-cages. Nuclear magnetic resonance studies have produced conflicting evidence concerning the possible relationship between bound and nonbound water and revealed long and short components of the relaxation time.[5] Interpretation of the experimental data is difficult, however, and there is clearly a need to relate simulation results to NMR experiments in future work.

We now focus on the water located in the α-cages. It is noted that generally *more* than 20 water molecules are located in the α-cages. For example, Gramlich and Meier report an average of 22.9 water molecules per cage, and the present simulations show between 20 and 28 water molecules per cage with an average occupancy of 24.25. Figure 6 shows the positions of the OW atoms every 5 ps during the simulation of 300 ps. The results from all α-cages have been superposed onto the same figure, which can therefore be interpreted as a density plot. The water molecules move within the α-cages and also between cages. There is, however, clear evidence of regions in which the water molecules spend more time. There are found to be 44 preferred sites in each α-cage. The approximate positions of these sites with respect to the center of the α-cage are permutations of the vectors (±0.86, ±0.86, ±4.80), (±0.00, ±3.24, ±3.24), and (±2.26, ±2.26, ±2.26), with all distances in angstroms. This arrangement is illustrated for greater clarity in Figure 7. The square arrangement of four preferred sites face the 8R openings between α-cages and are only about 1.7 Å apart. Thus we find that only two of the four sites, those diagonally opposite, may be simultaneously occupied. This reduces the number of sites that may be simultaneously occupied
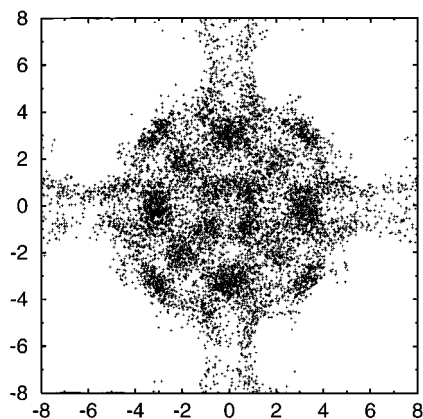
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Figure 6. Position of the OW atoms (+) located in the α-cages plotted every 5 ps from the MD simulation of fully-hydrated zeolite-4A at 298 K. The results from all α-cages have been superposed. Distances are in angstroms.
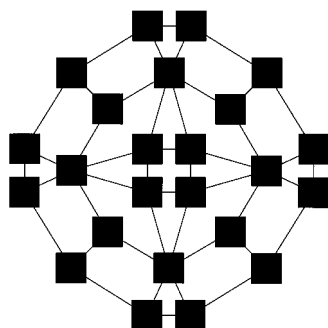

Figure 7. Schematic diagram of the arrangement preferred sites for water molecules in the α-cages obtained from the simulation of fully hydrated zeolite-4A at 298 K.

Figure 8. Radial distribution function of OW atoms (—) and HW atoms (- - -) as a function of distance from the center from the α-cage from the MD simulation of fully hydrated zeolite-4A at 298 K. The radius of the α-cage is approximately 5.7 Å.

Figure 9. Position of the OW atoms (+) located in the β-cages plotted every 5 ps from the MD simulation of fully hydrated zeolite-4A at 298 K. The results from all β-cages have been superposed. Distances are in angstroms.

to 32 per α-cage. This result is new and appears to contradict interpretations of available experimental data. However we note that the key X-ray data are that of Gramlich and Meier,[3] and their deduction of a pentagonal dodecahedral arrangement of preferred water sites may have been influenced by other systems. The pentagonal dodecahedral arrangement of water molecules does not place the water molecules at consistent positions with respect to the oxygen atoms of the α-cage and does not allow occupancies in excess of 20 water molecules unless the remaining molecules are found toward the center of the cage. Lee *et al.* in their MD simulations of water in a fixed-frame zeolite-4A find no evidence of a dodecahedral arrangement of water molecules in the α-cages and do not state which structure, if any, they observe. The new polyhedral arrangement contains 32 preferred sites on the inside of each α-cage, and each preferred site is approximately equidistant from two or three zeolitic oxygens atoms.

Figure 8 presents the radial distribution function of the OW and HW atoms from the center of the α-cage. These results coupled with the time-lapse positional data presented in Figure 6 indicate that the water molecules spend the majority of their time migrating between preferred sites on the inside of the α-cages but that there are also a few water molecules toward the center of the cage. Examination of Figure 8 reveals that, on average, there are 2.5 water molecules in the volume within 3 Å of the center of the α-cage and about 21.75 water molecules between 3 and 6 Å of the cage center.

We now turn our attention to the β-cages. Figure 9 shows the positions of the OW atoms in the β-cages plotted at 5 ps intervals. There are six preferred sites at locations that are approximate permutations of the vector (±1.9, 0, 0) with respect to the center of the cage. The maximum occupancy of a single
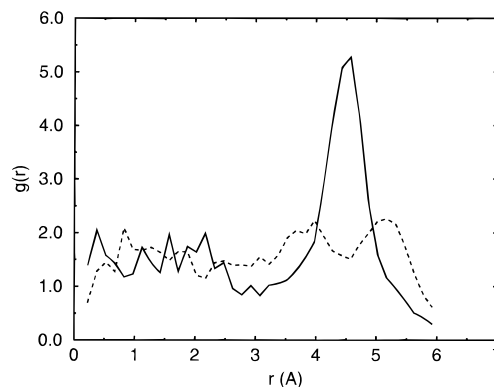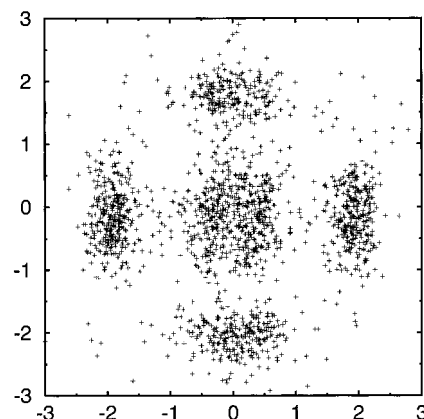
β-cage in the present simulations is four, and so the OW atoms will tend to occupy four of the six preferred sites. Gramlich and Meier found that the four water molecules form a distorted tetrahedral arrangement with four edges of 2.9 Å and two edges of 3.3 Å. Lee *et al.*[9] found that these distances are constantly changing and that the mean value of the four shortest distances was 2.82 ± 0.16 Å and the mean value of the two longest distances was 3.29 ± 0.21 Å, in very good agreement with the X-ray data.

In the present simulations, the distances between pairs of OW atoms for those β-cages containing exactly four water molecules were measured and values of 2.90 ± 0.21 and 3.98 ± 0.30 Å were found. The first is in good agreement with the published data; the second is not. To understand this, we need to look more carefully at the arrangement of the four water molecules in the β-cages. Only those β-cages in the simulation that contain four water molecules are examined, and these are found to predominantly occupy four planar sites forming a square arrangement. The four shortest distances between pairs of OW atoms are therefore the sides of the square, and the two longest distances correspond to the diagonals of the square. This explains the distances obtained from the present simulations. However, Gramlich and Meier observe a distorted tetrahedral arrangement of four water molecules. They also record an average of 5.5 water molecules per β-cage, indicating approximately equal numbers of cages containing five and six water molecules with, presumably, very few β-cages containing exactly four water molecules. The results from the present simulations suggest that five water molecules would occupy sites
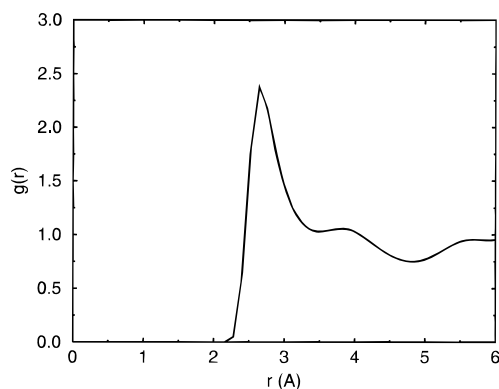
Figure 10. Na−OW radial distribution function from the MD simulation of fully hydrated zeolite-4A at 298 K.

in the β-cage, forming a square-based pyramid, and that six water molecules would occupy all six sites, forming an octahedron. In this case, groups of four water molecules would indeed form a distorted tetrahedron but with five short sides and one long side. The mean value of the four shortest distances would be about 2.7 Å (based on the average position of the preferred sites), and the mean value of the remaining two distances would be 3.3 Å, values which agree with the X-ray data and with Lee *et al*. Note that Lee *et al.* do not state whether their analysis is based on β-cages with an occupancy of four or whether they simply extract the four shortest and two longest distances from groups of four water molecules in the β-cages.

Finally, Figure 10 presents the Na−OW radial distribution function. A peak occurs at about 2.7 Å, indicating that the sodium ions are hydrated. The magnitude of the peak suggests that there exists, on average, between two and three water molecules hydrating each sodium ion.

IV. Conclusions

The first MD simulations of water in Na$^+$-zeolite-4A with a mobile zeolite framework have been performed at 298 K for the dehydrated and fully hydrated material, and a steepest descent energy minimization simulation has been performed on the dehydrated crystal. Bond lengths, bond angles, and positions of sodium ions and their distances with respect to the oxygen rings are in good agreement with published experimental data. The good general agreement with experiment for structure provides confidence in the choice of potentials for this system.

The majority of the water molecules in the α-cages appear to migrate between preferred sites close to the cage walls, with only a small proportion of the water toward the center of the cage. The water molecules in the β-cages occupy six octahedral preferred sites. A detailed examination of the dynamical properties of water in Na$^+$-zeolite-4A will be presented in a future publication.

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