Clays and Clay Minerals, Vol. 43, No. 3, 285–293, 1995.

MONTE CARLO SIMULATION OF INTERLAYER MOLECULAR STRUCTURE IN SWELLING CLAY MINERALS. 1. METHODOLOGY

N. T. SKIPPER,[1] FANG-RU CHOU CHANG,[2] AND GARRISON SPOSITO[2]

[1] Department of Physics and Astronomy, University College, Gower Street, London WC1E 6BT, UK

[2] Department of Environmental Science, Policy, and Management
University of California, Berkeley, California 94720-3110

Abstract—Monte Carlo (MC) simulations of molecular structure in the interlayers of 2:1 Na-saturated clay minerals were performed to address several important simulation methodological issues. Investigation was focused on monolayer hydrates of the clay minerals because these systems provide a severe test of the quality and sensitivity of MC interlayer simulations. Comparisons were made between two leading models of the water-water interaction in condensed phases, and the sensitivity of the simulations to the size or shape of the periodically-repeated simulation cell was determined. The results indicated that model potential functions permitting significant deviations from the molecular environment in bulk liquid water are superior to those calibrated to mimic the bulk water structure closely. Increasing the simulation cell size or altering its shape from a rectangular 21.12 Å × 18.28 Å × 6.54 Å cell (about eight clay mineral unit cells) had no significant effect on the calculated interlayer properties.

Key Words—Clay-water systems, Monte Carlo simulation, Swelling clays.

INTRODUCTION

A central problem in the study of clay mineral surface chemistry is to deduce molecular mechanisms of surface reactions from experimental observations. Computer simulations can contribute significantly to achieving this goal by their synthesis of current understanding and data, and by their perspicacity in revealing critical conceptual issues whose resolution demands additional experimentation. Monte Carlo (MC) simulations of equilibrium molecular structure in condensed phases have been especially successful in this regard and are now well established in liquid-state physical chemistry (Allen and Tildesley 1987).

Bleam (1993) has reviewed the basic concepts of MC simulation as applied to describe molecular structure in the interlayers of 2:1 layer type clay materials that adsorb water. His evaluation of the half-dozen or so studies carried out since 1980 points to the rather primitive models of clay-water systems that were used prior to the present decade, and to the need for resolution of several computational questions to which MC simulations of these systems may be quite sensitive. Foremost is the choice of potential function to describe interactions between water molecules in a condensed, liquid-like phase. This choice, which must be made from a broad group of candidates (Spohr and Heinzinger 1988), affects not only the quality of the MC simulation of interlayer water structure, but also the selection of potential functions with which to describe interactions between water molecules and counter-ions or the clay mineral surface (Skipper *et al* 1989, 1991b, Delville 1991, 1992, Delville and Sokolowski 1993). Comparisons among leading models for water-water interactions should be made to ascertain their accuracy and any sensitivity to their differences that arise in MC simulations of clay mineral interlayers (Bleam 1993).

A second issue mentioned by Bleam (1993) relates to the technical problem of combining periodic boundary conditions with the long-range coulomb interactions caused by the presence of interlayer ions. Because of computational hardware limitations, only clay-water systems comprising up to a few hundred molecules and atoms can be simulated. In order to avoid artificial "edge effects" induced by finite system size, a practicable choice of simulation cell is made, and this cell is replicated periodically in space to mimic the system in nature. The molecules placed in each cell interact mutually and with their periodic images. Artifacts related to the imposition of a periodic lattice are obviated by applying an arbitrary cut-off to short-range interactions (e.g., the exponential terms in Eq. (1), below), usually limiting their extent to <10 Å (cf. Skipper *et al* 1993). This cut-off cannot be applied, however, to coulomb interactions without causing serious problems for the simulation of ion distributions (Bleam 1993). Skipper *et al* (1993b) have dealt with this important matter by using the Ewald sum in conjunction with three-dimensional periodic boundary conditions (Allen and Tildesley 1987) to represent long-range coulomb interactions beyond the cut-off distance, whereas Delville (1991) and Delville and Sokolowski (1993), on the other hand, used two-dimensional periodic boundary conditions and the device of a uniform, neg-

Copyright © 1995, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

Table 1. Parameters in the MCY potential function.

Sites	A_{ij}(kcal/mole)	B_{ij}(Å^{-1})	C_{ij}(kcal/mole)	D_{ij}(Å^{-1})
		water-water		
H-H	0.000E+00	0.000E+00	0.66633E+03	0.27608E+01
H-O	0.27359E+03	0.22333E+01	0.14554E+04	0.29619E+01
O-O	0.000E+00	0.000E+00	0.1088213E+07	0.51527E+01
		water-Na^+		
H-Na	0.88423E+03	0.19349E+01	0.20519E+04	0.236095E+01
O-Na	0.25948E+02	0.77461E+00	0.61888E+05	0.40849E+01
		water-clay or Na^+-clay[1]		
H-Si	0.2137E+01	0.122E+01	0.57723E+03	0.215646E+01
H-Al	0.2137E+01	0.122E+01	0.57723E+03	0.215646E+01
O-Si	0.13458E+04	0.22671E+01	0.13061E+05	0.32037E+01
O-Al	0.13458E+04	0.22671E+01	0.13061E+05	0.32037E+01
Si-Na	0.15054E+04	0.18652E+01	0.216454E+04	0.21209E+01
Al-Na	0.15054E+04	0.18652E+01	0.216454E+04	0.21209E+01

[1] Water-clay potential function includes water-water potential parameters for H-H, H-O, and O-O interactions; Na^+-clay potential includes water-Na^+ potential parameters for H-Na and O-Na interactions (see text).

ative background potential to compensate for the portion of the coulomb interactions lopped off beyond a finite distance.

In this paper, we address the issues identified by Bleam (1993) in the context of molecular MC simulations of the monolayer hydrates of swelling 2:1 clay minerals. We have chosen specifically to study low-water-content systems because there is a wealth of experimental data on their quasi-equilibrium properties (Sposito 1984), and because we expect them to offer a stern test of the quality of our MC simulation methodology. Comparison will be made between two leading choices of the potential function for describing water-water interactions, and the sensitivity of the MC simulations of clay mineral interlayers will be assessed relative to this choice and to the selection of simulation cell properties. Our results also will serve to examine further the validity of the basic approach taken by Skipper *et al* (1991b, 1993) in their MC simulations of multilayer hydrates of clay minerals.

METHODOLOGY

Intermolecular potential functions

In order to describe molecular interactions in a swelling clay-water system, six sets of intermolecular potential functions must be developed, viz., water-water, water-counter-ion (cation), cation-cation, water-clay mineral, cation-clay mineral, and clay-mineral-clay mineral. Our strategy for obtaining these functions, which necessarily involves several approximations, is as follows.

Water-water interactions. Much is understood about the water molecule in condensed phases (Neilson and Enderby 1986), and this information has led to a number of useful approximations for the intermolecular potential function in the bulk liquid (Finney *et al* 1986). Two of the most widely adopted and successful of these models are the MCY (Matsouka *et al* 1976, Lie *et al* 1976, Clementi 1976) and the TIP4P (Jorgensen *et al* 1983) potential functions. Both meet practical criteria of simplicity of mathematical form, rapidity of numerical evaluation, and accuracy of representation of the structure, dynamics, and energetics of bulk liquid water.

The MCY model was developed by fitting *ab initio* quantum chemical calculations of the potential energy, U_d, of various configurations of the water dimer to the expression (Table 1):

$$U_d = \sum_i \sum_j V_{if}MCY(r_{ij}) \equiv \sum_i \sum_j [q_iq_j/r_{ij} - A_{ij}e^{-B_{ij}r_{ij}} + C_{ij}e^{-D_{ij}r_{ij}}] \quad (1)$$

where the indices i and j run over four sites on each molecule, q_i is the effective charge on a site and r_{ij} is the intermolecular site separation. Interaction sites (A_{ij}, $C_{ij} \neq 0$) are placed on the H and O atoms. The first term thus represents coulomb interactions, while the second and third terms represent van der Waals attraction and electron-overlap repulsion, respectively. A charge (q_i) of $-1.43496e$ is located at a site 0.2677 Å along the C_2 axis, and balancing charges of $0.71748e$ are assigned to the H atoms. The dipole moment of the molecule is therefore 2.19D. For the present study, the MCY model is likely to have two main advantages. First, the dimer energies themselves were calculated using the configuration-interaction method (Clementi 1976), which gives accurately the electron-electron correlation and exchange energies that are neglected in semi-empirical estimates of U_d. Second, a wide range of dimer configurations was used in the fit to Eq. (1). This is important for water-water potentials in clay-water systems, wherein the tetrahedral network associated with bulk liquid water may be highly disordered. A problem with the MCY model, however, is that it

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

Table 2. Parameters in the TIP4P potential function.

Sites	A_{ij} (kcal Å^4/mole)	C_{ij} (kcal/mole)	D_{ij} (Å^{-1})	E_{ij} (kcal Å^6/mole)	F_{ij} (kcal Å^{12}/mole)
O-O	0.000E+00	0.000E+00	0.000E+00	0.610E+03	0.600E+06
H-Na	0.000E+00	0.2064E+04	0.3394E+01	0.000E+00	0.000E+00
O-Na	0.435E+03	0.27343E+05	0.35455E+01	−0.840E+03	0.000E+00
Si-Na	0.000E+00	951.71	2.1286	0.000E+00	0.000E+00
Al-Na	0.000E+00	951.71	2.1286	0.000E+00	0.000E+00

requires a large applied pressure to maintain liquid water at a density of 1 g cm^{-3} at 298 K (Lie *et al* 1976).

The TIP4P model was developed by fitting experimental thermodynamic and X-ray structural data for liquid water, at 298 K under 1 atm. pressure, to a four-site model of a water molecule, in which intermolecular site-site interactions are described by the expression (Table 2):

$$V_{ij}^{TIP}(r_{ij}) \times q_i q_j / r_{ij} - E_{ij}/r_{ij}^6 + F_{ij}/r_{ij}^{12} \qquad (2)$$

where the indices i and j again run over four sites on each molecule. The only interaction site (E_{ij}, $F_{ij} \neq 0$) is placed on the O atom, while a charge of 0.52e is assigned to each H atom, and a charge of −1.04e is located at a site 0.15 Å along the C_2 axis. The dipole moment of the molecule is therefore 2.17D. By contrast with the MCY model, TIP4P gives the correct liquid water density at 298 K and 1 atm. pressure. However, because its parameters were obtained by fitting to the experimental properties of bulk liquid water, it is possible that the model will not transfer well to more constrained molecular environments such as occur in clay mineral interlayers.

In both the MCY and TIP4P models, the water molecules are rigid. Polarization effects, therefore, are not dealt with directly; rather, they are lumped into the potential parameters. It is for this reason that the dipole moment of the model water molecules is about 2.2D, as compared to 1.8D for a single water molecule in the gas phase (Neilson and Enderby 1986). Including polarizability in the potential function is possible (Karin 1991, Corrungiu and Clementi 1992, Smith and Haynet 1992), but could add greatly to the complexity of the MC simulation from a computational point of view.

Water-sodium interactions. Several model potential functions have been proposed to describe the interaction between a water molecule and Na^+ (Kistenmacher *et al* 1973, Bounds and Bounds 1983, Bounds 1985, Delville 1991). In the present study, the choice of potential function was conditioned on the need to use an Ewald sum (*vide infra*) in order to compute long-range coulomb interactions in the MC simulations. This condition requires the water molecule to have exactly the same charge distribution in water-water, water-Na^+, and water-clay mineral interactions. The *ab initio* model of Bounds 1985, which gives a good account of the aqueous solvation of Na^+, thus was selected with parameterization (Tables 1 and 2) for the MCY (Skipper *et al* 1991b) water-water potential function in Eq. (1) or the TIP4P potential function (Bounds 1985):

$$V_{ij}^{TIP*}(r) \equiv q_i q_j / r_{ij} + C_{ij} e^{-D_{ij} r_{ij}} - A_{ij}/r_{ij}^4 - E_{ij}/r_{ij}^6 + F_{ij}/r_{ij}^{12} \qquad (3)$$

Interactions with the clay mineral. The development of high quality *ab initio* calculations of water molecule- or Na^+ clay mineral interaction energies remains a challenge for future research (Sauer 1989, Lasaga 1992, Bleam 1993). Semi-empirical estimates, for clusters comprising a water molecule or Na^+ interacting with a clay mineral fragment making up about two dozen atoms, are available (Sauer *et al* 1984, Delville 1991); but they do not yet give a good account of the electron-electron correlations and overlap that are expected to contribute to the short-range repulsions and van der Waals interactions important to H-bonded systems, such as interlayer water (Matsouka *et al* 1976, Lee *et al* 1992). Given this state of affairs, we shall take the view that, to capture efficiently and accurately the short-range interactions between a water molecule or Na^+ and a 2:1 clay mineral, it is necessary to reduce the size of the clay mineral fragment to one that can be described by the more rigorous *ab initio* calculations—in practice, perhaps three or four atoms. This step may seem drastic, but previous *ab initio* studies suggest that the valence electrons in OH, SiO_4, and AlO_4 groups are centered on the O atoms (Matsouka *et al* 1976, Allan and Teter 1987, Sauer 1989, Lasaga 1992) and, therefore, that the latter will dominate any short-range interaction with a clay mineral surface. We may then be justified in representing a clay layer solely by O atoms saturated by two H atoms (i.e., water molecules) to make optimal use of the model water-water and Na^+-water potential functions described above (Skipper *et al* 1989, 1991b).

To represent the siloxane surface, water molecules are placed at the sites of the O atoms on the basal planes of talc (Brindley and Brown 1980) with the H atoms generally directed toward the cation positions in the tetrahedral sheet. [See Skipper *et al* (1989) for details.] Structural OH groups also are represented by water molecules, but with one H atom removed and the OH bond inclined appropriately for a dioctahedral

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

Table 3. Atomic positions and effective charges in the unit cell of a dioctahedral clay mineral layer (MCY model).

Atom	x(Å)	y(Å)	z(Å)	q/e	Atom	x(Å)	y(Å)	z(Å)	q/e
O	2.64	0.0	3.28	−0.8	Al	7.04	6.09	0.0	3.0
O	1.32	2.28	3.28	−0.8	Al	7.04	3.05	0.0	3.0
O	3.96	2.28	3.28	−0.8	O	0.88	9.14	−3.28	−0.8
O	0.0	0.0	1.06	−1.7175	O	2.2	6.86	−3.28	−0.8
H	0.8815	0.0	1.434	0.7175	O	−0.44	6.86	−3.28	−0.8
Si	2.64	1.52	2.73	1.2	O	3.52	9.14	−1.06	−1.7175
Si	0.0	3.05	2.73	1.2	H	2.6385	9.14	−1.434	0.7175
O	2.64	1.52	1.06	−1.0	Si	0.88	7.62	−2.73	1.2
O	0.0	3.05	1.06	−1.0	Si	3.52	6.09	−2.73	1.2
Al	4.4	1.52	0.0	3.0	O	0.88	7.62	−1.06	−1.0
Al	4.4	−1.52	0.0	3.0	O	3.52	6.09	−1.06	−1.0
O	0.0	4.57	3.28	−0.8	O	3.52	4.57	−3.28	−0.8
O	3.96	6.85	3.28	−0.8	O	−0.44	2.29	−3.28	−0.8
O	1.32	6.85	3.28	−0.8	O	2.2	2.29	−3.28	−0.8
O	2.64	4.57	1.06	−1.7175	O	0.88	4.57	−1.06	−1.7175
H	3.5215	4.57	1.434	0.7175	H	−0.0015	4.57	−1.434	0.7175
Si	0.0	6.09	2.73	1.2	Si	3.52	3.05	−2.73	1.2
Si	2.64	7.62	2.73	1.2	Si	0.88	1.52	−2.73	1.2
O	0.0	6.09	1.06	−1.0	O	3.52	3.05	−1.06	−1.0
O	2.64	7.62	1.06	−1.0	O	0.88	1.52	−1.06	−1.0

or trioctahedral mineral (Giese 1979). Lastly, the apical O atoms in SiO_4 or AlO_4 tetrahedra are represented in the same way as the basal plane O atoms. Metals in the octahedral sheet are assigned unscreened ionic charges (e.g., Mg and Al are represented by point charges of +2e and +3e, respectively). We balance this charge by placing −1e on each of the co-ordinating O atoms (apical O of the SiO_4 tetrahedra). The H atoms in structural OH groups are assigned the same positive charge as H in a water molecule. This charge, in turn, is balanced by an equal and opposite charge on the bonding O atoms. Semi-empirical estimates of the gross atomic charge on surface O atoms in uncharged silicate clusters suggest the range −0.7e to −0.9e (Hass *et al* 1981, Delville 1992); we have selected the value −0.8e, which has been adopted successfully for MC simulations of the talc-water system (Skipper *et al* 1989, 1991b). Electroneutrality then dictates a gross atomic charge of +1.2e for Si in the tetrahedral sheet. With this assignment of effective charges, the H_4 group representing cation sites in the tetrahedral sheet is replaced by a single interaction site, whose potential functions with structural O and H or with Na^+ can be parameterized as in Eq. (1) (Skipper *et al* 1991b). The resulting parameters are listed in Table 1. Since the MCY and TIP4P water molecules have very similar effective dipole moments, we shall use the same assigned charges and potential parameters, irrespective of the particular model of the water-water or water-Na^+ interactions used.

Negative charges resulting from isomorphic substitutions in the octahedral or tetrahedral sheets are placed on specific cation sites within the sheets. To substitute an octahedral Al by Mg in a given site, we simply reduce the charge on that site from +3e to +2e, whereas substitution of Si by Al in the tetrahedral sheet results in a reduction in the charge on the site from +1.2e to +0.2e. The configuration of the layer is not altered to accommodate a cation substitution, but the positions of the tetrahedral substitution sites are chosen so that the top ($z > 0$) and bottom halves ($z < 0$) of the clay layer are structurally equivalent (see Table 3). It is our expectation that the isomorphic substitution sites will dominate the electrostatic potential surface of the clay sheet (Bleam 1993). By decreasing the positive charge on cation sites, we have effectively placed all the net negative charge on the neighboring O atoms, consistent with quantum chemical calculations for the case of the tetrahedral cations (Bleam 1993). The details of the charge distribution at octahedral substitution sites differ, but should be of much less importance, since these sites are >3 ÅA away from the basal plane surfaces of the clay mineral.

This representation of the interactions between water molecules or Na^+ ions and the clay mineral structure does involve significant approximation, but it identifies what we believe to be the most important contributions to the electrostatic potential at the clay mineral surface. It also has the advantage of permitting a facile use of three-dimensional periodic boundary conditions and the Ewald sum technique in the MC simulations. Skipper *et al* (1989, 1991b, 1993) found good agreement between experimental data and predictions based on the present approach for the talc-water system and for both tri- and dioctahedral Na-smectite-water systems.

Monte Carlo simulations

Monte Carlo simulation of the detailed molecular structure of the interlayer region was implemented by

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

the computer program MONTE (Skipper 1992). This program has been described by Skipper *et al* (1991b, 1993), and the general principles of Monte Carlo methods are covered in detail by Allen and Tildesley (1987). The present discussion therefore is limited to specific issues arising in connection with the application of MC simulation to monolayer hydrates of 2:1 clay minerals.

Choice of ensemble. As is typical in Monte Carlo simulations, the temperature (T) is fixed. Since the density of interlayer water is initially unknown, and clay minerals tend to swell in discrete steps, the layer spacing must be allowed to reach equilibrium during the simulation. We therefore keep the stress normal to the clay mineral layers (σ_{zz}) constant and allow the system volume (V) to vary. The simulation then will predict the layer spacing. Ideally, the chemical potentials of water and counter-ions also would be kept constant during a simulation and the numbers of these molecular species would be predicted. However, in our view, it is not possible currently to obtain satisfactory equilibration of a constant-stress grand ensemble simulation for such clay-water systems. For example, in their two-dimensional, grand ensemble MC simulations of clay-water systems, Delville (1991, 1992) and Delville and Sokolowski (1993) reported that equilibration was complete; but long-range coulomb interactions were dealt with in a manner that is inappropriate to the present study. For reliable calculations of equilibrium counter-ion distributions, inclusion of these long-range interactions is essential (Allen and Tildesley, 1987). Thus we have elected to keep constant the number of water molecules (N_w) and counter-ions (N_c). A particular advantage of the resulting isothermal-isobaric ensemble (N_w, N_c, σ_{zz}, T) is that the properties of the clay mineral without interlayer water can be simulated easily as a reference.

Simulation cell. A typical simulation cell for a monolayer hydrate is shown within a box in Figure 1. This cell encloses a 21.12 Å by 18.28 Å patch of the basal-plane surface, 32 water molecules [corresponding to a water content of 0.1 g water per g clay (Newman 1987)], and 6 Na^+ cations. Each of the molecules interacts with the others through the effective potential functions described above. Clearly, if this system were to be studied in isolation, "edge effects" would be important. Periodic boundary conditions, therefore, are imposed so that the simulation cell is repeated infinitely in all directions. Every atom interacts with all other atoms in a cell and with their (infinite number of) periodic images, simulating a three-dimensional clay mineral as would occur in nature, not two clay layers in isolation. Indeed, two-dimensional periodic boundary conditions would seem inconsistent with the existence of isomorphic substitutions among octahedral-sheet cations, since each simulation cell would have to be assigned half the actual octahedral charge in the clay mineral.

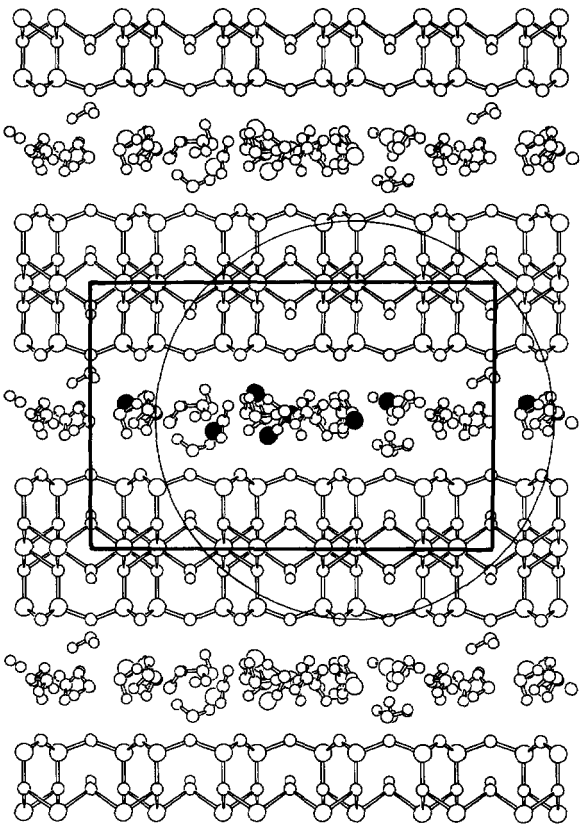


Figure 1. Equilibrated molecular configuration of a periodically-repeated, monolayer hydrate of a 2:1 dioctahedral clay mineral, viewed in the yz-plane. The rectangular box encloses the simulation cell. The black circle centered on a Na^+ site has a radius of 9 Å, indicating the real-space cut-off distance.

The potential energy of a configuration of the periodically-repeated system is given by a sum over all atom pairs in the simulation cell and over all of their (infinite number) of periodic images:

$$U = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} V_{ij}(r_{ij}) \qquad (4)$$

where i and j index atoms in the infinite system and $V_{ij}(r)$ is given by Eqs. (1), (2) or (3). To make this infinite sum manageable, we shall make several well-established approximations (Allen and Tildesley 1987).

First we apply a cut-off to the short-range contributions to the potential energy $V_{ij}(r)$ [e.g., terms 2 and 3 on the right side of Eq. (1)]. At site separations greater than this cut-off, we do not count atom pairs individually, but instead make the approximation that the number of pairs is given by the average number density. This cut-off is typically made between 7.5 Å and 10 Å; we use 9 Å. Note that, for monolayer hydrates, the layer spacing is less than 13 Å. This means that we

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

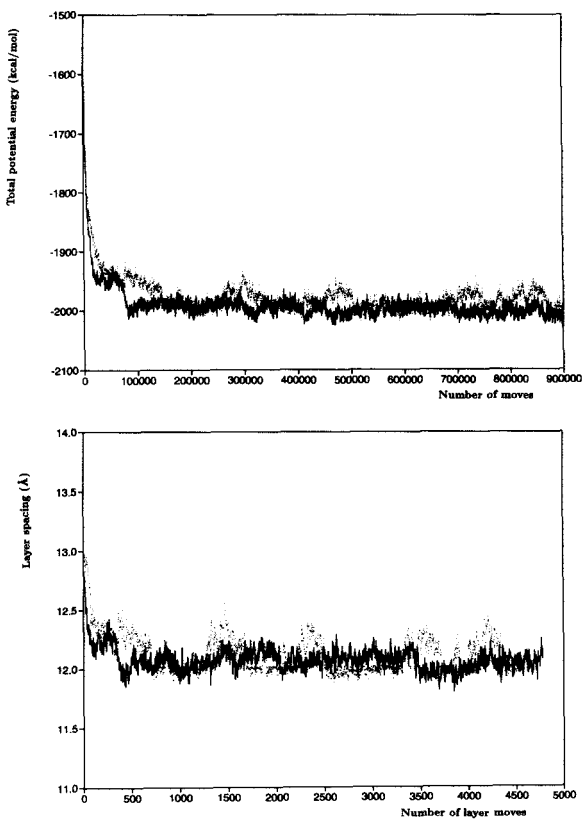


Figure 2. Convergence profiles for total potential energy (a) and layer spacing (b) during MC simulation of the monolayer hydrate of a Wyoming-type montmorillonite using a rectangular (solid line) or parallelpiped (dotted line) simulation cell.

cannot use the customary minimum-image convention to count all pairs of atoms within the cut-off distance (Allen and Tildesley 1987). Instead, we must consider all images of each atom (see the large circle in Figure 1).

Second we evaluate the long-range coulomb interactions [term 1 in Eq. (1)]. As with the short-range parts of the interaction energy, we are faced with a sum over an infinite number of pairs. However, the coulomb potential falls off much more slowly (as $1/r_{ij}$) and the summation will not converge if we simply apply a real-space cut-off. We therefore use the Ewald technique (Adams 1983, Allen and Tildesley 1987). In the Ewald sum we separate the coulomb interaction energy, U_c, exactly into two parts:

$$U_c = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} [\mathrm{erf}(\kappa r_{ij}) q_i q_j / r_{ij} + \mathrm{erfc}(\kappa r_{ij}) q_i q_j / r_{ij}] \quad (5)$$

where

$$\mathrm{erf}(\kappa r_{ij}) + \mathrm{erfc}(\kappa r_{ij}) \equiv 1 \quad (6)$$

κ is a constant, chosen to minimize computational time, and erf(x) and erfc(x) are the error function and complementary error function, respectively, used here as "window functions." By an appropriate choice of κ, the sum involving erf(κr) will converge as closely as desired in real space and the sum involving erfc(κr) will do the same in reciprocal space, both within feasible cut-off distances. In the present study, we used $\kappa = 0.4$ Å^{-1}, thus including all $k < \sqrt{5}$ Å^{-1} in the reciprocal-space sum and all $r_{ij} < 9$ Å in the real-space sum. This choice leads to an inaccuracy of <0.1% in the Ewald sum energy.

Simulation sampling. At the start of each simulation, the layer spacing is set at 13 Å. The counter-ions then are placed in two planes, at z = 5.5 Å and 7.5 Å, and the water molecules are placed in a disordered configuration. The energy of the initial state is calculated and a chosen molecule is moved a small distance. If the energy of the resulting state is lower than that of the initial one, the move is accepted with unit probability; otherwise, it is accepted with a Boltzmann factor. Moves involving a change in the layer spacing (z_L) are allowed, and the probability of acceptance is (Wood 1968, Allen and Tildesley 1987):

$$P = e^{\Delta E / k_B T} \quad (7)$$

if $\Delta E < 0$, where

$$\Delta E \equiv U_1 - U_2 - p\Delta V + Nk_B T \ln(V_1/V_2) \quad (8)$$

k_B is the Boltzmann constant, U_1 and U_2 are the initial and final potential energies, N is the total number of molecules, and V_1 and V_2 are the initial and final volumes, with

$$\Delta V \equiv V_1 - V_2 \quad (9)$$

Moves for which $\Delta E > 0$ are always accepted with unit probability. Moves involving a change in the layer spacing, dz_L, are accompanied by a displacement, dz_i, of the interlayer ions and water molecules:

$$dz_i = dz_L(z_i/z_L) \quad (10)$$

where z_i is the z-co-ordinate of the i^{th} interlayer molecule. The magnitude of the attempted move is chosen from a gaussian distribution, whose width, σ_i, is adjusted to give an acceptance probability of 50% for each molecule. To reduce the chance of any of the interlayer molecules becoming trapped in a local potential energy minimum, however, we set the condition $\sigma_i > 0.1$ Å.

In addition to allowing z_L to vary during the simulation, moves involving only a change in the simulation cell angles, α and β, are permitted. (The unit-cell vectors, $\vec{a}$, $\vec{b}$, and $\vec{c}$, are along the x, y and z directions, respectively, at the start of each simulation; α, β and γ are the angles between $\vec{b}$ and $\vec{c}$; $\vec{a}$ and $\vec{c}$; and $\vec{a}$ and $\vec{b}$, respectively.) By allowing the simulation cell to change shape, adjacent clay mineral layers may registrate. A move involving a change in the shape of the unit cell

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

was attempted with an average frequency equal to 0.2 that of moves involving any interlayer species in the simulation cell. This definition of "layer move" means that density profiles will be slightly broader at larger z.

Equilibration. For a system containing a 21.12 Å by 18.28 Å patch of hydrated siloxane surface, equilibration was as follows. First, 5000 moves were attempted in which only water molecules were selected. This was followed by an equilibration involving about 150,000 attempted moves in which any molecular species could be chosen. Equilibration was judged to have taken place when the average total potential energy of the system and z-dimension of the layer had reasonably constant values (cf. Figure 2). The simulations were then allowed to proceed for at least 200,000 moves. Data were collected for averages after every 200 attempted moves. Averages over consecutive runs of about 50,000 steps are within the calculated root-mean-square deviation. Systems containing skew or rectangular simulation cells and 32 water molecules, or a rectangular cell with 96 water molecules, were run for over 500,000 moves to determine whether there were any longer-term variations in the simulation output. None was found; but this does not rule out the possibility that, because of the imposed periodicity a system could form some long-term registration after, say 5,000,000 steps. We believe that this type of registration, if it did exist, would be less representative of a clay mineral in nature than are the results presented in this paper.

All simulations were performed on a Cray Y-MP8/864 at the San Diego Supercomputer Center.

RESULTS AND DISCUSSION

Effects of simulation cell size and shape

It is important to know whether the properties of a relatively small, periodically-repeated simulation cell are representative of the macroscopic system and whether they are strongly influenced by the artificial long-range symmetry of the imposed periodic lattice. A particular problem for the monolayer hydrate is that the z-axis dimension of the simulation cell is comparable to the layer spacing. This means that, in a rectangular cell, each molecule is only about 10 Å from its nearest images in neighboring cells (Figure 1). We address the question of cell size effects in two alternative ways, using the monolayer hydrate of a Wyoming-type montmorillonite as an example. For this system, Figure 1 is illustrative, since 6 Na^+ per 21.12 × 18.28 $Å^2$ patch corresponds to a layer charge of 0.72, typical of this class of smectite (Newman 1987). One-third of the layer charge was assigned to the tetrahedral sheet, since Wyoming-type montmorillonite has between 15 and 50% of its layer charge in the tetrahedral sheet. The temperature and applied normal stress were 300 K and 10^5 Pa, respectively.

First, we increased the number of interlayer molecules in the system by a factor of three (i.e., from 32 to 96 water molecules). This was accomplished by increasing the size of the siloxane surface patch to 31.68 × 36.56 $Å^2$ from 21.12 × 18.28 $Å^2$. The result of this change on the average potential energy per water molecule was a decrease by only 2.36%. This effect is quite consistent with the results of Jorgensen *et al* (1983) for the decrease in the average potential energy per water molecule with increasing system size in bulk liquid water. Bearing in mind that the efficiency of Ewald sum computation decreases as the simulation cell is increased in this way, we conclude that the use of a 21.12 × 18.28 $ÅA^2$ simulation cell is justifiable.

Second, we increased the distance between a molecule and its own images in neighboring simulation cells by using a parallelpiped cell (Allen and Tildesley 1987). For the case of a 10 Å layer spacing, the separation between a molecule and its nearest self-image is then increased from 10 Å to just above 15 Å. We found that increasing the image separation in this way had no significant effect (Figure 2) on the calculated layer spacing, average potential energy, or predicted molecular structure. This result gives us confidence that the simulation results are not distorted by the existence of small layer spacings.

Effects of potential function model

To compare the MCY and TIP4P potential functions, we focused on three clay-water systems of widely varying layer charge: talc (0.00), Wyoming-type montmorillonite (0.72), and vermiculite (1.5). These systems have been the subject of detailed experimental studies (Brindley and Brown 1980). Our strategy was as follows. First, we compared calculated results and experimental data for the full-dehydrated clay minerals, thereby assessing the clay-clay and clay-absorbed cation interactions. Second, we compared calculated results and experimental data for the hydrated systems, thereby assessing the clay-water, water-water, and water-adsorbed cation potential functions.

Talc is uncharged and, therefore, its layer spacing depends only on the clay-clay interaction. The MCY model gave a layer spacing of 9.10 ± 0.02 Å, about 2.7% *smaller* than the experimental value of 9.34 Å (Brindley and Brown 1980), whereas the TIP4P model gave 9.53 ± 0.02 Å, 2% *greater* than the experimental value. We find this agreement rather encouraging, for the following reason. When two talc layers approach one another, their respective siloxane surface oxygen atoms come into very close contact. This is a configuration rarely observed in either bulk water or aqueous solution, the systems from which we transferred our potentials. We would expect that, because of all of the approximations we made in the clay-water-cation model, the clay-clay interactions would be the *least* accurate.

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

The calculated layer spacings for fully dehydrated Wyoming-type montmorillonite and vermiculite will be sensitive to the clay-clay potential functions, and, to a greater extent, to the clay-counter-ion cation interaction. The experimental layer spacings for Wyoming-type montmorillonite and vermiculite are 9.8 Å (Mooney *et al* 1952) and 10 Å (Brindley and Brown 1980), respectively. Both the MCY and TIP4P models gave satisfactory agreement with these experimental data: 9.86 ± 0.02 Å and 9.82 ± 0.02 Å, respectively, for the montmorillonite and 9.96 ± 0.03 Å and 9.88 ± 0.03 Å, respectively, for vermiculite.

The measured properties of the monolayer hydrates of Wyoming-type montmorillonite and vermiculite provide good tests of all the terms in the potential functions, but most particularly for the clay-water, water-water, and water-cation interactions. The experimentally measured layer spacings for monolayer hydrates of montmorillonite and vermiculite are 12.2–12.5 Å (Mooney *et al* 1952, Brindley and Brown 1980) and 11.8–12.6 Å (Brindley and Brown 1980, Skipper *et al* 1991a), respectively. Those calculated using the MCY model are 12.1 Å and 11.6 Å; using the TIP4P model we obtained 11.7 Å and 11.6 Å.

On the strength of these results, the MCY model would seem to provide a closer approximation to the behavior of 2:1 clay mineral interlayers than does the TIP4P model. We believe that this is due to the quality of the *ab initio* calculations and the large number of molecular configurations used to obtain the MCY potential function. That the TIP4P model may underestimate layer spacings by as much as 0.5 Å is probably because it is strictly an empirical potential fitted only to experimental data for bulk liquid water. Therefore, it may not transfer readily to more constrained water environments, such as those in clay mineral interlayers. In structural terms, the difference between the TIP4P and MCY models can be related to the closest clay layer-to-water (oxygen-oxygen) distance: It is 6.0 Å for MCY and 5.8 Å for TIP4P. Based on our comparison of layer spacings, we favor the use of the MCY model potential functions for MC simulations of swelling clay-water systems.

ACKNOWLEDGMENTS

The research reported in this paper was supported in part by NSF grant EAR-9206052. The first author thanks Pembroke College, Cambridge University, and British Gas for their support through the award of the Sir Henry Jones Research Fellowship. Gratitude is expressed to Joan Van Horn for excellent typing of the manuscript and to the San Diego Supercomputer Center for an allocation of Service Units on the Cray Y-MP8/864 supercomputer.

REFERENCES

Adams, D. J. 1993. On the use of the Ewald summation in computer simulation. *J. Chem. Phys.* **78**: 2585–2590.

Adams, D. J., and G. S. Dubey. 1987. Taming the Ewald sum in computer simulation of charged systems. *J. Comput. Phys.* **72**: 156–176.

Allan, D. C., and M. P. Teter. 1987. Nonlocal pseudopotentials in molecular-dynamical density-functional theory. Application to SiO_2. *Phys. Rev. Lett.* **59**: 1136–1139.

Allen, M. P., and D. J. Tildesley. 1987. *Computer Simulation of Liquids.* Oxford: Clarendon Press, 110–139.

Bleam, W. F. 1993. Atomic theories of phyllosilicates. *Rev. Geophys.* **31**: 51–73.

Bounds, D. G. 1985. A molecular dynamics study of the structure of water around the ions Li^+, Na^+, K^+, Ca^{2+}, Ni^{2+}, and Cl^-. *Mol. Phys.* **54**: 1335–1355.

Bounds, D. G., and P. J. Bounds. 1983. Potential surfaces derived from gradient calculations. New potentials for Li^+/H_2O, Na^+/H_2O, and K^+/H_2O. *Mol. Phys.* **50**: 25–32.

Brindley, G. W., and G. Brown. 1980. *Crystal Structures of Clay Minerals and their X-ray Identification.* London: Mineralogical Society, 1–123.

Clementi, E. 1976. *Determination of Liquid Water Structure.* Berlin: Springer-Verlag, 1–88.

Corrungiu, G., and E. Clementi. 1992. Solvated water molecules and hydrogen-bridged networks in liquid water. *J. Chem. Phys.* **98**: 2241–2249.

Delville, A. 1991. Modeling the clay-water interface. *Langmuir* **7**: 547–555.

Delville, A. 1992. Structure of liquids at a solid interface: An application to the swelling of clay by water. *Langmuir* **8**: 1796–1805.

Delville, A., and S. Sokolowski. 1993. Adsorption of vapor at a solid interface: A molecular model of clay wetting. *J. Chem. Phys.* **97**: 6261–6271.

Finney, J. L., J. E. Quinn, and J. O. Baum. 1986. The water dimer potential surface. *Water Sci. Rev.* **1**: 93–170.

Giese, R. F. 1979. Hydroxyl orientations in 2:1 phyllosilicates. *Clays & Clay Miner.* **27**; 213–223.

Hass, E. C., P. J. Mezey, and P. J. Plath. 1981. A non-empirical molecular orbital study on Lowenstein's rule and zeolite composition. *J. Mol. Struc.* **76**: 389–399.

Jorgensen, W. L., J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein. 1983. Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.* **79**: 926–935.

Karin, O. A. 1991. Simulation of an anion in water: Effect of ion polarizability. *Chem. Phys. Lett.* **184**: 560–565.

Kistenmacher, H., H. Popkie, and E. Clementi. 1973. Study of the structure of molecular complexes. II. Energy surfaces for a water molecule in the field of a sodium or potassium cation. *J. Chem. Phys.* **58**: 1689–1699.

Lasaga, A. C. 1992. Ab initio methods in mineral surface reactions. *Rev. Geophys.* **30**: 269–303.

Lee, C., D. Vanderbilt, K. Laasonen, R. Car, and M. Parrinello. 1992. *Ab initio* studies on high pressure phases of ice. *Phys. Rev. Lett.* **69**: 462–465.

Lie, G. C., E. Clementi, and M. Yoshimine. 1976. Study of the structure of molecular complexes. XIII. Monte Carlo Simulation of liquid water with a configuration interaction pair potential. *J. Chem. Phys.* **64**, 2314–2323.

Matsouka, O., E. Clementi, and M. Yoshimine. 1976. CI study of the water dimer potential surface. *J. Chem. Phys.* **64**: 1351–1361.

Mooney, R. W., A. G. Keenan, and L. A. Wood. 1952. Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction. *J. Am. Chem. Soc.* **74**: 1371–1374.

Neilson, G. W., and J. E. Enderby. 1986. *Water and Aqueous Solutions.* Boston: Adam Hilger, 284 pp.

Newman, A. C. D. 1987. *Chemistry of Clays and Clay Minerals.* New York: Wiley, 1–128.

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press

Newman, A. C. D. 1987. The interaction of water with clay mineral surfaces. In *Chemistry of Clays and Clay Minerals.* A. C. D. Newman, ed. New York: Wiley, 237–274.

Sauer, J. 1989. Molecular models in ab initio studies of solids and surfaces. *Chem. Rev.* **89**: 199–255.

Sauer, J., C. Morgeneyer, and K.-P. Schröder. 1984. Transferable analytical potential based on nonempirical quantum chemical calculations (QPEM) for water-silica interactions. *J. Phys. Chem.* **88**: 6375–6383.

Skipper, N. T. 1992. *MONTE User's Manual.* Technical Report, Department of Chemistry, University of Cambridge, UK.

Skipper, N. T., K. Refson, and J. D. C. McConnell. 1989. Computer calculation of water-clay interactions using atomic pair potentials. *Clay Miner.* **24**: 411–425.

Skipper, N. T., A. K. Soper, and J. D. C. McConnell. 1991a. The structure of interlayer water in vermiculite. *J. Chem. Phys.* **94**: 5751–5760.

Skipper, N. T., K. Refson, and J. D. C. McConnell. 1991b. Computer simulation of interlayer water in 2:1 clays. *J. Chem. Phys.* **94**: 7434–7445.

Skipper, N. T., K. Refson, and J. D. C. McConnell. 1993. Monte Carlo simulations of Mg- and Na-smectites. In *Geochemistry of Clay-Pore Fluid Interactions.* D. C. Manning, P. L. Hall, and C. R. Hughs, eds. London: Chapman and Hall, 40–59.

Smith, D. E., and A. D. J. Haynet. 1992. Structure and dynamics of water and aqueous solutions: The role of flexibility. *J. Chem. Phys.* **96**: 8450–8459.

Spohr, E., and K. Heinzinger. 1988. Computer simulations of water and aqueous electrolyte solutions at interfaces. *Electrochim. Acta* **33**: 1211–1222.

Sposito, G. 1984. *The Surface Chemistry of Soils.* New York: Oxford University Press, 47–77.

(Received 9 September 1993; accepted 27 September 1994; Ms. 2414)

https://doi.org/10.1346/CCMN.1995.0430303 Published online by Cambridge University Press