Mineralogical Magazine, October 1998, Vol. 62(5), pp. 657–667

Computer simulation of aqueous pore fluids in 2:1 clay minerals

N. T. Skipper

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

ABSTRACT

Monte Carlo and molecular dynamics computer simulations are now able to provide detailed information concerning the structure, dynamics, and thermodynamics of pore fluids in 2:1 clays. This article will discuss interparticle interaction potentials currently available for atomistic simulations of clay-water systems, and will describe how computational techniques can be applied to modelling of clay systems. Some recent simulation studies of 2:1 clay hydration will then be reviewed. Comparison with experimental data promotes confidence in the molecular models and simulation techniques, and points to exciting future prospects.

Keywords: Monte Carlo simulation, molecular dynamics, pore fluids, clay minerals.

Introduction

This contribution will discuss recent advances in statistical mechanical computer modelling of aqueous pore fluids in 2:1 clay minerals, such as smectites and vermiculites. The aim of this research is to provide molecular scale insight into fluid dependent processes, for example; clay hydration/dehydration, solute transport through clays, and clay compaction during burial. It is important to realise that, whichever simulation technique is used, the results depend intrinsically on the quality of the potential energy functions that are used to describe the interparticle interactions. We therefore begin with an overview of the generic types of molecular models, before moving on to the problem of clay–fluid interactions and the specific molecular models currently used in statistical mechanical simulations. At present the most successful of these models are based on empirical pair potentials originally designed for studies of water and aqueous solutions. For this reason they are not well suited to studies of chemical reactions at clay surfaces. Monte Carlo and molecular dynamics techniques are then discussed, with attention being paid to problematic areas such as the treatment of long-range interactions, representation of infinite systems, and choice of statistical ensemble. Finally, the current state-of-affairs is discussed, using the hydration/dehydration of smectites as an example. We conclude that a healthy synergistic relationship is developing between modelling and experiment.

Overview of interaction potential energy functions

Computer simulation studies of condensed matter aim to calculate the observable properties of systems in which the particles interact through a specified set of potential energy functions (Allen and Tildesley, 1987; Frenkel and Smit, 1996). These interaction potentials can be broadly classified according to the level of approximation they involve.

(i) *Ab Initio*: the properties of the system are calculated by solving the Schrödinger equation for all electrons and atomic nuclei (Bleam, 1993; Tossell, 1995). Computationally, quantum mechanical solution of the all-electron problem is extremely demanding, and is only feasible for systems containing fewer than ten or so atoms. For example, the interaction energy of a water dimer as a function of its geometry (Matsouka *et al.,* 1976), or simple molecules adsorbed onto small clay-like clusters (Delville, 1991; Bleam, 1993).

(ii) *Semi-empirical*: to reduce the computational cost of *ab initio* calculations, some knowledge of the electronic properties of the system can be used to simplify solution of the Schrödinger equation. For example, many important properties depend on the nature of the valence, rather than core, electrons. To economise, the nucleus plus core electrons can therefore be represented by a *pseudopotential,* which then acts on the valence electrons. At this level we can calculate the energy surfaces of systems containing more than a hundred atoms, and can study the thermodynamic properties of systems containing tens of atoms (Car and Parinello, 1985; Payne *et al.,* 1992; Lee *et al.*, 1992; Bleam, 1993; Tossell, 1995).

(iii) *Empirical*: to further increase the size of system that can be treated, a potential energy function can be chosen to represent the effective interactions between atoms and molecules. These effective interaction potentials will involve pairwise terms, and may also include higher order effects such as polarisation. In any case, the potential energy of a particular configuration is calculated from a set of empirical parameters. Examples include the Lennard-Jones model for interactions between noble gas atoms. Using empirical potential models the thermodynamic properties of systems containing thousands of atoms are routinely studied (Allen and Tildesley, 1987; Frenkel and Smit, 1996). This number of particles is sufficient to mimic the properties of liquids, such as water and aqueous solutions, in both the bulk phase (Enderby and Neilson, 1981; Finney *et al.*, 1986; Ohtaki and Radnai, 1993) and in clay pores (Guven, 1992; Bleam, 1993).

(iv) *Continuum*: certain aspects of some solutions are insensitive to the detailed molecular structure of the solvent. In this case the solvent can be represented as a structureless dielectric continuum; the so-called primitive model (Enderby and Neilson, 1981). This approach is currently used in studies of colloidal systems, including hydrated clays, where long-range electrostatic interactions are thought to be dominant (Guldbrand *et al.,* 1983; Israelachvili and Wennerström, 1996).

Interaction potentials of types (i) and (ii) will provide electronic structure/energy, through quantum mechanical solution of the Schrödinger equation. They can therefore be used to study chemical reactions of particular species at mineral surfaces (Bleam, 1993; Tossell, 1995). In this article, however, we are concerned with the statistical mechanical properties of liquids, particularly water and aqueous solutions, at clay surfaces. For a practical reason (current computer power) we must therefore concentrate on empirical potential models of type (iii). We note, however, that quantum statistical mechanical simulations of clay-water systems, using semi-empirical functions of type (ii) are on the horizon (Car and Parrinello, 1985; Remler and Madden, 1990; Bridgeman *et al.*, 1996).

Interaction of aqueous fluids with 2:1 clays

The 2:1 group of clay minerals includes talc and pyrophyllite, smectite, vermiculite, illite and mica (Brindley and Brown, 1980; Newman, 1987). The clay layers themselves are comprised of a sheet of octahedrally co-ordinated cations, for example magnesium or aluminium, sandwiched between two layers of tetrahedrally co-ordinated cations, for example silicon or aluminium. Unsaturated oxygen atoms form hydroxyl groups, which lie in hexagonal cavity sites recessed from the clay surface (Fig. 1). In all 2:1 clays, apart from talcs and pyrophyllites, ionic substitution among the tetrahedral and/or octahedral cations leaves the clay layers with an overall negative charge (Newman, 1987). This negative layer charge is balanced by positively charged interlayer counterions, such as sodium and calcium (common in smectites and vermiculites) or potassium (common in illites or micas).

Interlayer counterions and charged clay surfaces interact strongly with polar solvents. As a result many 2:1 clays, notably smectites and vermiculites, expand in the presence of water and aqueous solutions (Brindley and Brown, 1981; Sposito and Prost, 1982; Newman, 1987). Typically the expansion begins as a series of discrete steps, corresponding loosely to one-, two- and three-layers of water molecules. Further colloidal swelling may then take place, depending on the particular clay and external conditions.

For a given fluid, therefore, the precise nature of clay–fluid interactions is mainly determined by: (i) the valence, radius and number density of the interlayer counterions, and; (ii) the number density and origin (octahedral or tetrahedral substitution) of the clay layer charges (Brindley and Brown, 1980; Newman, 1987). If anything, the former is generally regarded as the most important factor. For example, clay hydration is more sensitive to whether the interlayer counterions are potassium or magnesium, than whether the sheets are vermiculite or smectite. In order of priority, therefore, a successful molecular model of clay–water–cation systems must capture: (i) water–water; (ii) counterion–water; (iii) water–clay/counterion–clay, and; (iv) clay–clay interac-

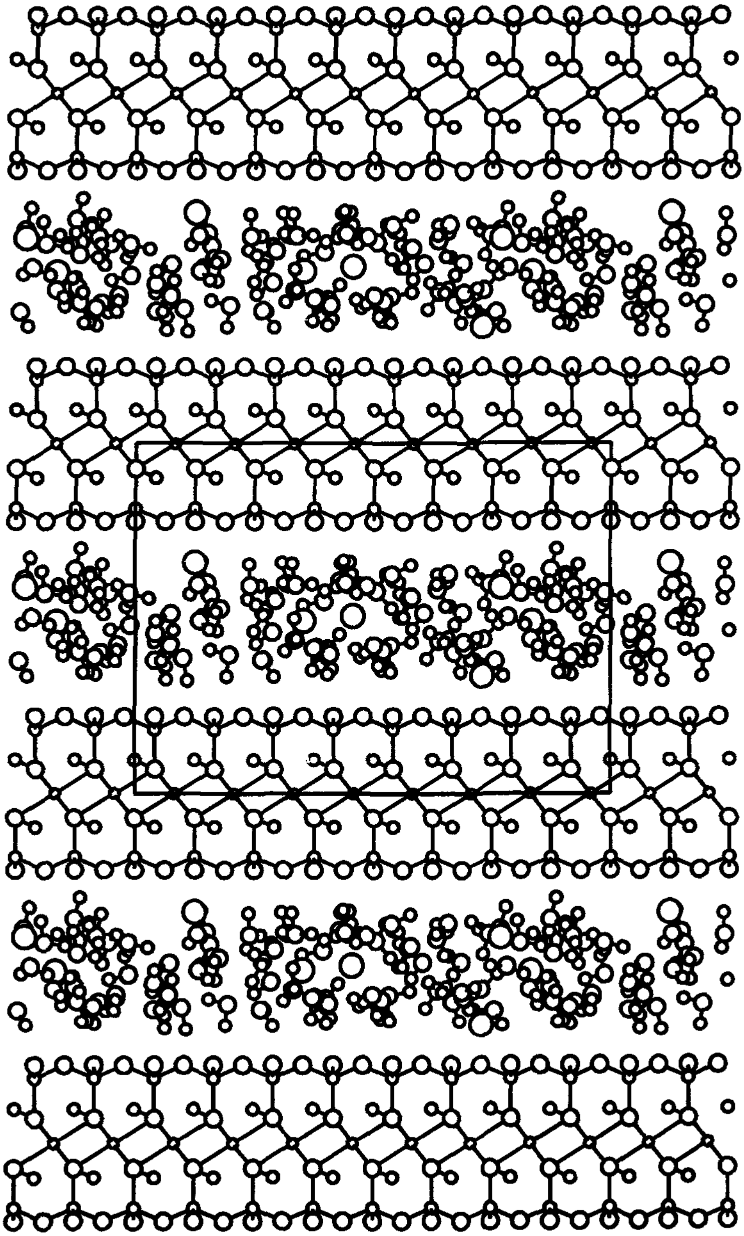

FIG. 1. A 'computer-eye' view of a clay–water–cation system. The figure shows an equilibrated molecular configuration of a periodically repeated two-layer hydrate of a sodium substituted smectite clay mineral, viewed in the *yz*-plane. The rectangular box encloses the simulation cell, which, when repeated in all three directions, approximates to a macroscopic sample. In this particular case the simulation cell is comprised of a 21 × 18 Å section of clay sheet, 64 water molecules, and 6 sodium cations. The clay layer spacing is 15.28 Å, in good agreement with experimental data for this water content (Chang *et al.*, 1995). Within the smectite sheet itself the central layer is made up of octahedrally co-ordinated cations, such as Al^{3+} or Mg^{2+}. These are sandwiched between two layers of tetrahedrally co-ordinated cations, Si^{4+} or Al^{3+}. Clay sheet hydroxyl groups are recessed below the tetrahedral ions, and are at an angle of about 70° to the normal (Brindley and Brown, 1980; Newman, 1987).

tions. For this reason the starting point for molecular models of clay-water systems has been those designed for water and aqueous solutions (Skipper *et al.*, 1991, 1995*b*; Delville, 1991, 1992).

Empirical molecular models for clay–fluid interactions

To model a clay–fluid system we require three complete sets of interaction potential functions: fluid–fluid, fluid–clay and clay–clay (for the purposes of this section, we will assign interlayer counterions to the fluid, rather than the clay). For the reasons given in the previous section the most popular starting point is to exploit the models developed for studies of water and aqueous solutions. Fluid–clay and clay–clay potentials of the same functional form are then obtained empirically, or by fitting to *ab initio* energy surfaces.

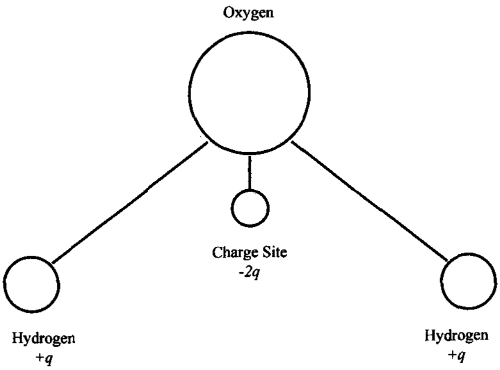

FIG. 2. The four-site model of water. This geometry is common to both the MCY model (Matsouka *et al.*, 1976) and TIP4P model (Jorgensen *et al.*, 1983), that are frequently used in simulations of clay-water systems. In these two water 'molecules' the value of the charge q and position of the charge site result in a dipole moment of about 2.2 D. This value is larger than the 1.8 D for an isolated water molecule, and reflects polarisation of one molecule by its neighbours in the liquid.

Fluid–fluid interactions

A number of potential models have been proposed for the interaction between two water molecules (Jorgensen *et al.*, 1983; Finney *et al.*, 1986; Watanabe and Klein, 1989). Of these, the two that are currently most popular for studies of clay–fluid systems are the MCY and TIP4P models, due to Matsouka *et al.* (1976) and Jorgensen *et al.* (1983) respectively.

Both the MCY and TIP4P models represent a water molecule as a rigid entity comprised of four interaction sites (Fig. 2). Three of these sites are placed on the atomic oxygen and hydrogen. The fourth site is a (negative) charge that lies on the C_2 axis of the molecule, as shown in Fig. 2. Both the MCY and TIP4P 'molecules' meet the demands of relatively simple functional form, and accurate representation of the energetics, hydrogen bonded structure, and dynamics of bulk water (Finney *et al.*, 1986; Watanabe and Klein, 1989).

The MCY model of Matsouka *et al.* (1976) was obtained by fitting the total potential energy, V, for a wide range of configurations of the water dimer to *ab initio* potential energy data.

$$V = \sum_{i=1}^{4} \sum_{j=i+1}^{4} U_{ij}(r_{ij}) \tag{1}$$

where sites i and j are separated by r_{ij}, and for the MCY model,

$$U_{ij}^{MCY}(r_{ij}) = q_i q_j / r_{ij} - A_{ij} e^{-b_{ij} r_{ij}} + C_{ij} e^{-D_{ij} r_{ij}} \tag{2}$$

In this function q_i is the partial charge in site i, and A_{ij}, B_{ij}, C_{ij} and D_{ij} are fitted constants. The first term therefore represents Coulomb interactions, the second term van der Waals attraction, and the third term short range Pauli repulsion. Interaction sites (A_{ij} and $C_{ij} \neq 0$) are placed on the O and H sites. A partial charge of 0.71748e is placed on each hydrogen atom, and a balancing charge of −1.4349 e on the site located 0.2677 Å down the C_2 axis (Fig. 2). The dipole moment of the molecule is therefore 2.19 D. At this point we note that the dipole moment of an isolated water molecule is 1.8 D. The difference is due to polarisation of a molecule in the liquid by its neighbours. MCY endeavours to capture these many-body effects within the sum of pair-wise terms, and is therefore an example of an effective pair potential.

The strength of the MCY model is the fact that it is based on *ab initio* energy data for a wide range of configurations. It is therefore likely to be accurate for water in non-tetrahedral environments, such as clays. The main disadvantage is that a large pressure is required to maintain the liquid at a density of 1 g cm^{-3} at 298 K (Lie *et al.,* 1976).

The TIP4P model Jorgensen *et al.* (1983) was obtained by refining the parameters in equation 3 by reference to thermodynamic and X-ray data for liquid water at STP:

$$U_{ij}^{TIP}(r_{ij}) = q_i q_j / r_{ij} - E_{ij}/r_{ij}^6 + F_{ij}/r_{ij}^{12} \quad (3)$$

The geometry of the TIP4P model is very similar to that of MCY. A single interaction site is placed on the O atom. A charge of 0.52e is placed on each H site, balanced by -1.04 e located 0.15 Å down the C_2 axis. The dipole moment of the molecule is therefore 2.17 D. Importantly, the TIP4P model reproduces the density of bulk water, at STP (Jorgensen *et al.*, 1983) and beyond (Brodholt and Wood, 1993). However, because the parameters were fitted to data for bulk water at STP, it might be expected to be less apposite in confined, non-tetrahedral, environments.

There are numerous potential functions available to describe the interactions of ions with MCY and TIP4P water. These models have been collated and compared with experimental data by Enderby and Neilson (1981), Neilson and Enderby (1989) and Ohtaki and Radnai (1993). The general conclusion is that the hydration of monovalent ions (such as Li^+, Na^+, and K^+) can be well represented by rigid molecule effective pair potential models. Small di- and trivalent cations (such as Mg^{2+} and Al^{3+}) are more problematic (Bounds, 1985). These ions are strongly polarising, and may therefore require flexible/polarisable model of the solvent molecules (Lybrand and Kollmann, 1985; Smith and Haymet, 1992).

In this article we will focus on aqueous fluids. However, there is increasing demand for accurate modelling of clay-water-organic systems. For example, to predict hydrocarbon and pollutant migration. There is now a realistic prospect that computer simulation will provide an important contribution to these fields. To illustrate this, the TIP4P model forms part of a complete set of models for studying aqueous-organic fluids, the so-called OPLS potential parameters (Jorgensen, 1981, 1984; Jorgensen *et al.*, 1983). This set of potentials is eminently suitable for incorporation into model clay–fluid systems (Boek *et al.*, 1995*a,b*).

Fluid–clay interactions

Within the realm of atomistic empirical models there are two common routes to fluid-clay interaction potential functions (Bleam, 1993), (i) fitting to *ab initio* potential energy surface calculations (Delville, 1991,1992), and (ii) direct transfer of parameters from fluid-fluid potential functions (Skipper *et al.*, 1991, 1995*a*). In either case, the functional form should be consistent with the choice of fluid-fluid interactions, and be able to represent octahedral and/or tetrahedral substitution within the clay sheet (Fig. 1).

To date the clays sheets themselves have been treated as rigid entities, with a structure based on atomic co-ordinates derived from X-ray diffraction (Brindley and Brown, 1980). The main weakness of this procedure is that the orientation of clay surface hydroxyl groups is poorly resolved, and is also assumed to be independent of the hydration state of the clay. A priority for future work is therefore to allow rotational freedom among the hydroxyl groups on the clay surface.

Clay–clay interactions

The final piece in the jigsaw is clay–clay interactions. In the current context this is a simple matter: when we choose parameters, such as partial charges, to describe clay–fluid interactions we have necessarily chosen clay–clay parameters as well. Studies of dry clays and monolayer hydrates have shown that this description of the clay sheets can capture clay–clay interactions rather well (Skipper *et al.*, 1995*b*).

Mimicking an infinite system: periodic boundary conditions

By using effective pair potentials it is possible to calculate the energy of simulation cells containing up to a few thousand particles. In the case of a clay–water–cation systems, the cell might contain a 20 × 20 Å section of clay sheet, 6 cations, and 64 water molecules (Fig. 1). If such a system was studied in isolation edge effects would, of course, dominate. Before we hand the cell to our computer we must therefore disguise the small simulation cell so that it looks like an infinite system. To do this we normally repeat the simulation cell infinitely in all three directions, using so-called periodic boundary conditions (Fig. 1; Allen and Tildesley, 1987; Frenkel and Smit, 1996). By casting the system as an infinite number of repeats of a finite cell we have created two potentially embarrassing problems.

First, we have, in principle, to sum energy over an infinite number of pairwise terms to obtain the total potential energy of the system: each molecule interacts with the others in the unit cell, but also with all their images. To reduce this summation to manageable proportions we only consider short-range interactions (terms 2 and 3 in equations 2 and 3) below a certain cut-off, typically 10 Å. Long-range coulombic interactions (term 1 in equations 2 and 3) do not converge under this scheme. An Ewald sum (or equivalent) is therefore used to evaluate charge–charge interactions in our periodic system (Allen and Tildesley, 1987; Skipper *et al.*, 1995*a*; Frenkel and Smit, 1996).

The second problem lies in the periodic system itself, and in particular whether periodicity manifests itself in the data generated. One must therefore vary the size of the simulation cell, and check for unwanted size dependent effects. In practice, a simulation cell such as that shown in Fig. 1 is generally found to be sufficiently large for most practical purposes (Skipper *et al.* 1995*a*).

Computational techniques

Two methods of computer simulation are currently available to calculate the equilibrium thermodynamic properties of a system in which the particles interact through a set of potential energy functions: Monte Carlo and molecular dynamics (Fig. 3; Allen and Tildesley, 1987; Frenkel and Smit, 1996). Both methods can be used to calculate time-averaged quantities, such as the structure and density. Molecular dynamics, though more time consuming, can also give time-dependent quantities, such as diffusion coefficients.

Monte Carlo

At the start of a Monte Carlo simulation the particles are placed in a disordered configuration within the simulation cell. The total energy of this initial state is then calculated, by summing over all pairwise interactions (of the form given in equations 2 or 3 for example). A molecule is then chosen at random, and moved a small amount. If the total energy of this new state is lower than the original one, then the move is accepted. If the new energy is higher, then it is accepted with a Boltzmann probability:

$$P = e^{\Delta E/kT} \tag{4}$$

where ΔE is the change in energy of the system (consistent with the choice of sampling ensemble; Allen and Tildesley, 1987; Frenkel and Smit, 1996), k is Boltzmann's constant and T is temperature. New moves are then attempted until; (i) the system has reached satisfactory equilibrium, and following this; (ii) statistically significant thermodynamic averages have been obtained. In practice, the system shown in Fig. 1 might require 1,000,000 attempted moves for equilibration, and 2,000,000 for sampling of energetic and structural properties. Inadequate equilibration sampling is a common pitfall of computer simulations, and can best be avoided by comparing data obtained from different starting configurations and different length runs (Skipper *et al.*, 1995*a*).

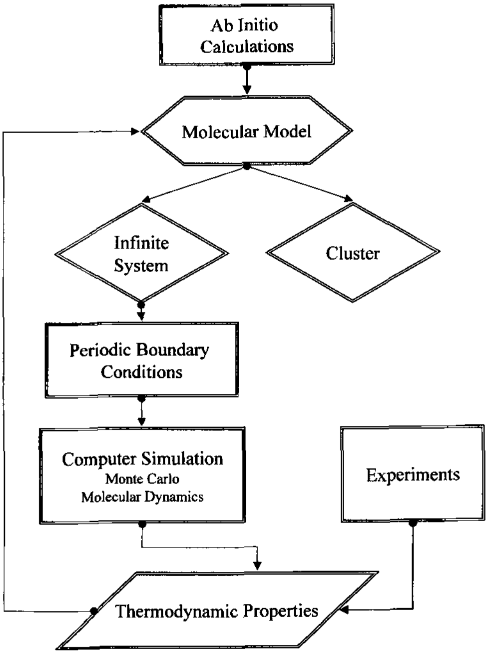

FIG. 3. Flow diagram to show the role of statistical mechanical computer simulation in studies of condensed matter. Note that refinement of the molecular model should involve comparison of calculated thermodynamics properties with data measured by experiment.

Molecular dynamics

Molecular dynamics simulations solve the classical equations of motion for all the particles in the system, under the force field of interactions with the other particles (Allen and Tildesley, 1987; Frenkel and Smit, 1996). Exact solution of this problem is not practical, but numerical solution of the required accuracy can be achieved by extrapolating the position, velocity and acceleration of each particle from a record of the past. The extrapolation time (known as the timestep) is chosen so that the changes to the state of the system are small. A typical value for the timestep is 0.25×10^{-15}s, with the simulation itself extending over 200×10^{-12}s. Integration algorithms are discussed in the texts by Allen and Tildesley (1987) and Frenkel and Smit (1996).

Thermodynamic quantities can be calculated by averaging over instantaneous values for many timesteps. Time-dependent quantities can be calculated directly from the trajectories of the particles. In the current context, an important example is the mobilities of interlayer species. These can be obtained from the 2-dimensional Fick's Law, which relates the self-diffusion constant to the mean square displacement of each particle as a function of time:

$$4Dt = \langle r^2 \rangle = \langle |r(t) - r(0)|^2 \rangle \qquad (5)$$

Current molecular dynamics simulations of clay-water-cation systems have extended to about 200×10^{-12}s (Refson *et al.*, 1994; Chang *et al.*, 1995, 1997), providing a lower calculable limit of $D = 1 \times 10^{-11}\mathrm{m}^2\mathrm{s}^{-1}$. For reference, the calculated self-diffusion coefficients for water molecules and sodium counterions in a two-layer smectite hydrate are about $1.4 \times 10^{-9}\mathrm{m}^2\mathrm{s}^{-1}$ and $5.1 \times 10^{-11}\mathrm{m}^2\mathrm{s}^{-1}$ respectively (Chang *et al.*, 1995).

Statistical mechanical simulations of smectite–fluid interactions

In this section we discuss some recent computer simulations of clay–water–cation systems. The broad aim is to compare and contrast simulation and experimental data, thereby highlighting the successes and failures of the modelling studies. We will therefore begin by discussing the options for, and implications of, the statistical sampling ensemble. We then describe the current state of affairs concerning simulation of aqueous fluids in smectites. We are particularly concerned with establishing the current consensus and future challenges.

Choice of sampling ensemble

The equilibrium thermodynamic state of the system is usually defined by a small set of state parameters. For example, in the canonical ensemble these are the number of particles, *N*, volume, *V*, and temperature, *T*. Before we start a lengthy simulation we must therefore decide which parameters are relevant to the system and conditions of interest.

For a clay–water–cation system in contact with an external bath of fluid, held at temperature *T*, equilibrium occurs when the chemical potential of the interlayer fluid, μ, is equal to that of the external fluid. Since the clay can, in general, expand or contract to accommodate the interlayer fluid the final state depends also on the applied pressure, *p*. In principle, therefore, the preferred statistical ensemble is constant (μpT). In practice, however, the computational cost of sampling this ensemble is prohibitive. The main reasons are that setting μ requires us to create/destroy water molecules, and sampling of both *N* and *V* is therefore very slow (Allen and Tildesley, 1987; Delville, 1991, 1992; Frenkel and Smit, 1996; Karaborni *et al.*, 1996). For this reason look for a less time consuming alternative.

Delville (1992) and Karaborni *et al.* (1996) have opted for a series of simulations in grand canonical (μVT) ensembles, covering a range of volumes, *V*, relevant to hydrated clays. This approach has the important advantage that it can predict water content for a given clay-layer spacing. The drawback is that sampling of the number of water molecules, *N*, is still extremely slow. To date results for interlayer density and structure have not been entirely consistent with experiment or other simulations (Chang *et al.*, 1995; Boek *et al.*, 1995*b*), suggesting perhaps a need to refine the choice of μ or allow even longer equilibration/simulation.

To side-step the problems inherent to constant μ sampling, Skipper *et al.* (1991, 1995*a*) have conducted a series of simulations in the (NpT) ensemble, covering a suitable range of water contents, *N*. In these simulations the pressure is applied normal to the clay surfaces, and is therefore equivalent to the stress, σ_{zz}. This choice provides contact with experiment by predicting the clay-layer spacing as a function of water content, but has the disadvantage that it cannot predict water content *a priori*.

A third option is sampling in (NVT) ensembles over a range of both *N* and *V*. This choice has applications when water is absorbed onto exposed clay surfaces, but is not ideal for studies of clay swelling, except when used to follow (μVT) equilibration (Delville and Sokolwoski, 1993).

A final important question concerns sampling of non-equilibrium processes: there is considerable interest in the kinetics of clay hydration/dehydration following a change in external conditions. During burial compaction, for example, the rate of fluid loss from expanded clays may not be sufficient to establish equilibrium with the external fluid (North, 1990). The time-scale of such processes is typically seconds to M-years, clearly not accessible to molecular simulations. For this reason the best compromise is probably a series of (*NpT*) simulations that span the initial and final states (Siqueira *et al.*, 1997).

Monte Carlo study of smectite hydration/dehydration

Monte Carlo simulations have provided detailed insight into the energetics and microscopic structures involved in the hydration/dehydration of smectite. Smectite is the archetypal swelling clay mineral: in the presence of water it has the ability to swell to many times its original dry volume (Brindley and Brown, 1980; Sposito and Prost, 1982; Newman, 1987). In addition to external water activity, controlling factors in the expansion include; (i) interlayer counterion, (ii) clay-layer charge density, and (iii) clay-layer charge position (octahedral or tetrahedral substitution).

In a series of modelling studies of the clay–water interface Delville (1991, 1992, 1993) and Delville and Sokolowski (1993) have studied the hydration of mica-like clay sheets and their associated counterions. Their method involves 2-dimensional periodic boundary conditions, which precludes isomorphic substitution among the octahedral cations of the clay layers (Skipper *et al.*, 1995*a*). Long-range coulombic interactions are handled by the continuous field method, rather than an Ewald sum. For a fixed clay–clay separation they prosecute equilibration in the (μVT) ensemble, and then sample from the resulting (*NVT*) ensemble. This choice of mineral and ensemble is most closely resembles surface force apparatus and atomic force microscope measurements. Models are based on MCY (Delville, 1991) and subsequently TIP4P water (Delville, 1992, 1993; Delville and Sokolowski, 1993). For both interlayer Na^+ (Delville, 1991, 1992; Delville and Sokolowski, 1993) and K^+ (Delville, 1993) agreement with experimental heat of immersion and adsorption data is acceptable. Analysis of interlayer structure reveals strong hydrogen bonding of water to the clay surfaces, resulting in water layering. Both Na^+ and K^+ ions prefer to hydrate as they would in aqueous solution, rather than bind to the clay surface.

Simulations in the (*NpT*) ensemble have been conducted by Skipper *et al.* (1991, 1995*a,b*), Chang *et al.* (1995, 1997), Boek *et al.* (1995*a,b*), and Siqueira *et al.* (1997). Comparison of the MCY and TIP4P models suggests that the former provides a more realistic structural picture of the interlayer region in a variety of swelling 2:1 clays (Skipper *et al.* 1995*a,b*), leading to good prediction of clay swelling curves (Chang *et al.*, 1995, 1997). Energetic data is also encouraging. Comparison between Li^+, Na^+ and K^+ counterions show that the smaller counterions prefer to hydrate in the presence of water, rather than remain attached to the clay surface. K^+, on the other hand, is rather weakly hydrated, and is therefore reluctant to leave the charged clay surfaces (Boek *et al.*, 1995*a*). Even in low hydrates the interlayer counterion–oxygen coordination numbers are remarkably similar to those found in bulk solutions, due to the ability of oxygen atoms on the clay surface to replace lost water molecules. Observation of events at the clay surface points to an important distinction between isomorphic substitution among (i) octahedral and (ii) tetrahedral layer cations (Fig. 1). The latter are located at the clay surface, and therefore interact more strongly with interlayer counterions (Chang *et al.*, 1995, 1997).

Siqueira *et al.* (1997) have modelled smectite hydration/dehydration at elevated pressures and temperatures (Fig. 4). They find rather poor packing of water at low porosities, and link the resulting density increase to the loss of water during the final stages of compaction.

A recent series of (μVT) simulations by Karaborni *et al.* (1996) have calculated the swelling pressure as a function of layer spacing, for an MCY based model. Their conclusion is that one- and three-layer hydrates are stable, while two- and four-layers are not. This conclusion is at odds with current experimental data (Sposito and Prost, 1982; Newman, 1987), and may be due to the difficult choice of chemical potential for the MCY model, or problems associated with obtaining an unbiased, statistically significant, sample within the grand canonical ensemble (Frenkel and Smit, 1996). Nevertheless, their approach involving rotational biasing of water molecule insertion/deletion is extremely promising.

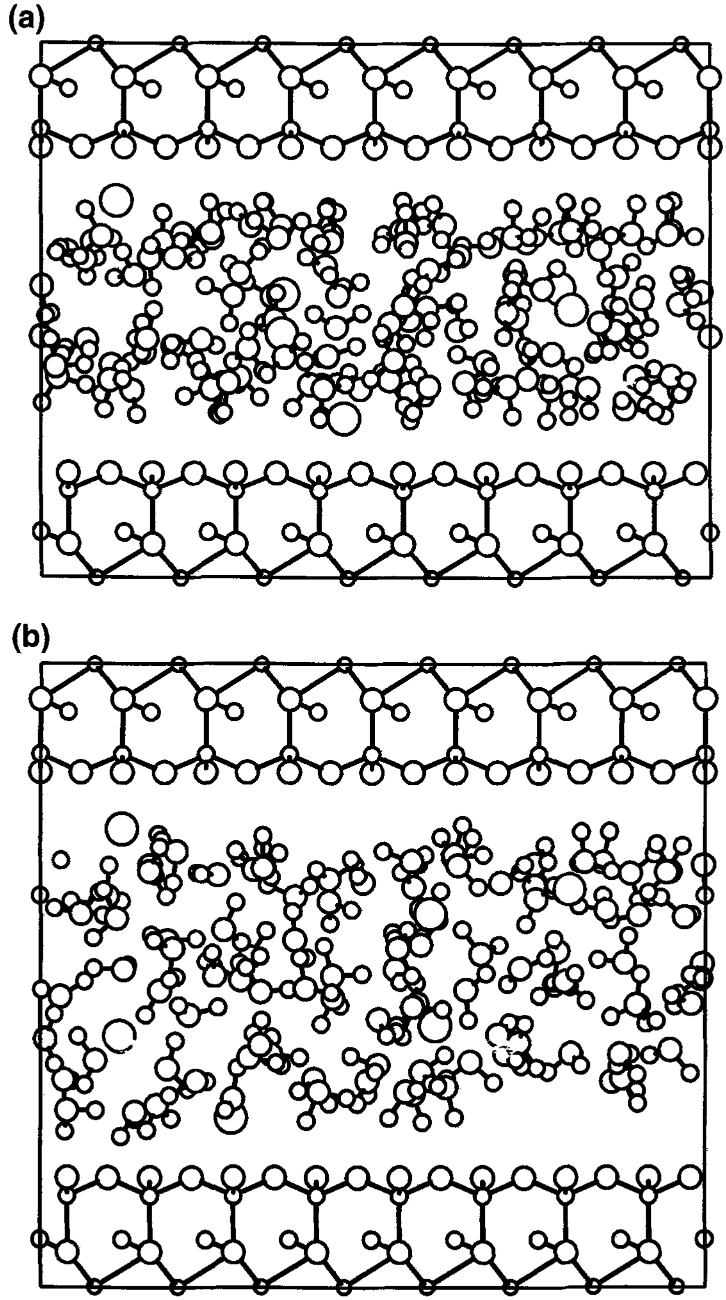

FIG. 4. The effect of 'burial' on a computer model of a three-layer hydrate of a sodium substituted smectite clay mineral, in which the simulation cell contains a 21 × 18 Å section of clay sheet, 96 water molecules, and 6 sodium cations. (*a*) A snapshot of the simulation cell equilibrated at surface conditions, namely 1×10^5 Pa and 277 K. In this case the clay layer spacing is 17.07 Å. (*b*) A snapshot of the simulation cell after equilibration at a depth of 9 km, 1.35×10^8 Pa and 547 K. In this case the clay layer spacing is 18.49 Å (Siqueira *et al.*, 1997). The simulations therefore show that, due to the geothermal gradient, the interlayer pore fluid expands during burial.

Molecular dynamics studies of water and cation mobility in smectites

In spite of their potential, molecular dynamics simulations of clay–water systems have been less numerous than Monte Carlo. Interest in solute and counterion mobility through clays, and the environmental implications, will undoubtedly lead to more studies in the future.

To reduce computational demands the starting point for molecular dynamics simulations is generally an equilibrated configuration generated by a Monte Carlo run. Within this scheme Refson *et al.* (1994) and Chang *et al.* (1995, 1997) have studied water and counterion diffusion in Li-, Na- and Mg-smectites through molecular dynamics simulations of about 200ps duration. They find that the mobility of interlayer water rises rapidly as the interlayer water content is increased, but even in the three-layer hydrates rises to only about 75% of the value in the bulk ($2.0 \times 10^{-9} m^2 s^{-1}$). The diffusion properties of interlayer counterions present practical problems: these ions are less mobile and more dilute than the interlayer water. In one-layer hydrates the mobility of sodium ions is close to the calculable limit in a 200 ps simulation, $D = 1.0 \times 10^{-11} m^2 s^{-1}$, rising to a value of $D = 1.8 \times 10^{-10} m^2 s^{-1}$ in the three-layer hydrate (Chang *et al.,* 1995). These conclusions are in satisfactory agreement with experiment, promoting confidence in the molecular models and points to exciting future prospects.

Conclusion

Monte Carlo and molecular dynamics computer simulations are proving to be powerful techniques in the study of clay–fluid interactions and clay swelling. Using molecular models developed originally for studies of water and aqueous solutions these methods have provided detailed molecular insight into processes occurring at the clay–fluid interface. In many cases simulations have suggested new experiments, and a healthy synergistic relationship is developing between modelling and experiment. Future challenges include the development of polarisable and flexible models, implementation of (μpT) ensemble algorithms, studies of non-aqueous fluids and solutes, and systematic investigation of clay–fluid interactions at elevated pressures and temperatures.

Acknowledgements

I would like to acknowledge the contributions made by a number of my co-workers: Keith Refson, Desmond McConnell, Garrison Sposito, Fang-Ru Chang, Edo Boek, Peter Coveney and Ascenso de Siguiera.

References

Allen, M.P and Tildesley, D.J. (1987) *Computer Simulation of Liquids*. Clarendon Press, Oxford, UK.

Bleam, W.F. (1993) Atomic theories of phyllosilicates: quantum chemistry, statistical mechanics, electrostatic theory, and crystal chemistry. *Rev. Geophysics*, **31**, 51–73.

Boek, E.S., Coveney, P.V. and Skipper, N.T. (1995*a*) Molecular modelling of clay hydration: a study of hysteresis loops in the swelling curves of sodium montmorillonites. *Langmuir*, **11**, 4629–31.

Boek, E.S., Coveney, P.V. and Skipper, N.T. (1995*b*) Monte Carlo molecular modelling studies of hydrated Li-, Na-, and K-smectites: understanding the role of potassium as a clay swelling inhibitor. *J. Amer. Chem. Soc.*, **117**, 12608–17.

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**, 1335–55.

Bridgeman, C.H., Buckingham, A.D., Skipper, N.T. and Payne, M.C. (1996) Ab initio total energy study of uncharged clays and their interaction with water. *Mol. Phys.*, **89**, 879–88.

Brindley, G.W. and Brown, G. (1980*) Crystal Structures of Clay Minerals and their X-ray Identification*. Mineralogical Society, London, UK.

Brodholt, J. and Wood, B. (1993) Simulations of the structure and thermodynamic properties of water at elevated pressures and temperatures. *J. Geophys. Res: Solid Earth*, **98**, 513–36.

Car, R. and Parrinello, M. (1985) Unified approach for molecular dynamics and density functional theory. *Phys. Rev. Lett.*, **55**, 2471–4.

Chang, F-R.C., Skipper, N.T. and Sposito, G. (1995) Computer simulation of interlayer molecular structure in sodium montmorillonite hydrates. *Langmuir*, **11**, 2734–41.

Chang, F-R.C., Skipper, N.T. and Sposito, G. (1997) Monte Carlo and molecular dynamics simulations of interfacial structure in lithium montmorillonite hydrates. *Langmuir*, **13**, 2074–82.

Delville, A. (1991) Modelling the clay-water interface. *Langmuir*, **7**, 547–55.

Delville, A. (1992) Structure of liquids at a solid interface: an application to the swelling of clay by water. *Langmuir*, **8**, 1796–805.

Delville, A. (1993) Structure and properties of confined liquids: a molecular model of the clay-water inteface. *J. Phys. Chem.*, **97**, 9703–12.

Delville, A. and Sokolowski, S. (1993) Adsorption of vapour at a solid interface: a molecular model of clay wetting. *J. Phys. Chem.*, **97**, 6261–71.

Enderby, J.E. and Neilson, G.W. (1981) The structure of electrolyte solutions. *Rep. Prog. Phys.*, **44**, 593–643.

Finney, J.L., Quinn, J.E., and Baum, J.O. (1986) The water dimer potential surface. *Water Science Reviews*, **1**, 93.

Frenkel, D. and Smit, B. (1996) *Understanding Molecular Simulation.* Academic Press, San Diego, USA.

Guldbrand, L., Jonsson, B., Wennerstrom, H. and Linse, P. (1983) Electrical double layer forces. A Monte Carlo study. *J. Chem. Phys.*, **80**, 2221–8.

Guven, N. (1992) Molecular aspects of clay-water interactions. In *Clay Water Interface and its Rheological Implication*, (N. Guven and R.M. Pollastro, eds.) Volume 4, CMS Workshop Lectures, The Clay Minerals Society, Boulder, Colorado, USA.

Israelachvili, J.N. and Wennerström, H. (1996) The role of hydration and water structure in biological and colloidal systems. *Nature*, **379**, 219–25.

Jorgensen, W.L. (1981) Transferable intermolecular potential functions for water, alcohols and ethers. Application to liquid water. *J. Amer. Chem. Soc.*, **103**, 335–40.

Jorgensen, W.L. (1984) Optimised intermolecular potential functions for liquid hydrocarbons. *J. Amer. Chem. Soc.*, **106**, 6638–46.

Jorgensen, W.L., Chandrasekhar, J., Madura, J., Impey, R.W. and Klein, M.L. (1983) Comparison of simple potential functions for modelling water. *J. Chem. Phys.*, **79**, 926–35.

Karaborni, S., Smit, B., Heidug, W., Urai, J. and van Oort, E. (1996) The swelling of clays: molecular of the hydration of montmorillonite. *Science*, **271**, 1102–4.

Lee, C., Vanderbilt, D., Laasonen, K., Car, R. and Parrinello, M. (1992) Ab initio studies on high pressure phases of ice. *Phys. Rev. Lett.*, **69**, 462–5.

Lie, G.C., Clementi, E. and Yoshimine, O. (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**, 2314–23.

Lybrand, T.P. and Kollman, P.A. (1985) Water-water and water-ion potential functions including terms for many body effects. *J. Chem. Phys.*, **83**, 2923–33.

Matsouka, O., Clementi, E. and Yoshimine, M. (1976) CI study of the water dimer potential surface. *J. Phys. Chem.*, **64**, 1351–61.

Neilson, G.W. and Enderby, J.E. (1989) Co-ordination of metal aquaions. *Adv. Inorg. Chem.*, **34**, 196–218.

Newman, A.C.D. (1987) *Chemistry of Clays and Clay Minerals.* Wiley, New York, USA.

North, F.K. (1990) *Petroleum Geology.* Unwin-Hyman, Boston, USA.

Ohtaki, H. and Radnai, T. (1993). Structure and dynamics of hydrated ions. *Chem. Rev.*, **93**, 1157–204.

Payne, M.C., Teter, M.P., Allan, D.C., Arias, T.A. and Joannopoulos, J.D. (1992) Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.*, **64**, 1045–97.

Refson, K. Skipper, N.T. and McConnell, J.D.C. (1993), Molecular dynamics simulation of water mobility in smectites. In *Geochemistry of Clay-Pore fluid interactions*, (D.A.C. Manning and P.L. Hall, eds.) Mineralogical Society, Chapman and Hall, London, UK.

Remler, D.K. and Madden, P.A. (1990) Molecular dynamics without effective pair potentials via the Car-Parrinello approach. *Mol. Phys.*, **70**, 921–66.

Siqueira, A. de, Skipper, N.T., Coveney, P.V. and Boek, E.S. (1997) Computer simulation evidence for enthalpy driven dehydration of clays under sedimentary basin conditions. *Mol. Phys.*, **92**, 1–6.

Skipper, N.T., Refson, K. and McConnell, J.D.C. (1991) Computer simulation of interlayer water in 2:1 clays. *J. Chem. Phys.*, **94**, 7434–45.

Skipper, N.T., Chang, F-R.C. and Sposito, G. (1995*a*) Monte Carlo simulation of interlayer molecular structure in swelling clay minerals. 1. Methodology. *Clays Clay Minerals*, **43**, 285–93.

Skipper, N.T., Chang, F-R.C. and Sposito, G. (1995*b*) Monte Carlo simulation of interlayer molecular structure in swelling clay minerals. 2. Monolayer Hydrates. *Clays Clay Minerals*, **43**, 294–303.

Smith, D.E. and Haymet, A.D.J. (1992) Structure and dynamics of water and aqueous solutions: the role of flexibility. *J. Chem. Phys.*, **96**, 8450–9.

Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites. *Chem. Rev.*, **82**, 553–73.

Tossell, J.A. (1995) *Mineral Surfaces: Theoretical Approaches* (D.J. Vaughan and R.A.D. Pattrick, eds.). Chapman and Hall, London, UK.

Watanabe, K. and Klein, M.L. (1989) Effective pair potentials and the properties of water. *Chem. Phys.*, **131**, 157–67.

[*Manuscript received 2 May 1998*]