Chapter 9
Advances in Molecular Simulation Studies of Clay Minerals

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Abstract The unique structure and behavior of swelling clay minerals, as observed in the laboratory and in the environment, present a challenge in understanding of the molecular details associated with these minerals. The chapter introduces the essence of classical methods involving empirically derived potential energy expressions that allow simulation of periodic cells representing bulk and interfacial clay mineral systems. The classical models provide the simulation and analysis of many thousands to more than a million atoms for evaluating structures, adsorption, diffusion, intercalation, physical, and other properties. Quantum chemical calculations, including molecular orbital methods and density functional theory, optimize the configuration of electrons about atoms from first principles, but require significant computational cost to examine many of the important topics in clay mineralogy. Molecular simulation methods such as energy minimization, molecular dynamics, Monte Carlo techniques, vibrational analysis, thermodynamics calculations, transition state analysis, and a variety of related computational methods are utilized to improve our understanding of clay minerals, and to better interpret traditional characterization and spectroscopic methods. An example showing the use of molecular simulation for clay minerals is presented for the process of montmorillonite's swelling as a function of interlayer water.

Application of computational chemistry and molecular simulation methods in clay mineralogy has increased steadily over recent years. The unique structure and behavior of clay minerals as observed in the laboratory and in the environment, present a challenge to improve our understanding of the molecular details associated with these common minerals. Classical-based methods involving empirically derived potential energy expressions allow simulation of periodic cells representing bulk and interfacial clay mineral systems. The classical models allow the simulation

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and analysis of many thousands to more than a million atoms for evaluating structures, adsorption, diffusion, intercalation, physical, and other properties. Quantum calculations, including molecular orbital methods and density functional theory, optimize the configuration of electrons about atoms from first principles, but require significant computational cost to examine many of the important topics in clay mineralogy. Molecular simulation methods such as energy minimization, molecular dynamics (MD), Monte Carlo techniques, vibrational analysis, thermodynamics calculations, transition state analysis, and a variety of related computational methods can be used to improve our understanding of clay minerals, and to better interpret traditional characterization and spectroscopic methods.

9.1 Basics of Molecular Simulation

Evaluation of the potential energy of a chemical system is the basic task of any molecular simulation whether one is using classical molecular mechanics or a quantum approach such as density functional theory (DFT). Fundamental to either method is the evaluation of the various contributing components of the total potential energy. For example, in classical-based molecular simulations, it is possible to evaluate each component of the potential energy by summing the nonbond and bond terms separately:

$$E_{\mathrm{total}} = E_{\mathrm{Coul}} + E_{\mathrm{VDW}} + E_{\mathrm{bond\ stretch}} + E_{\mathrm{angle\ bend}} + \cdots \qquad (9.1)$$

Electrostatics, as represented by the Coulombic energy E_{Coul} and van der Waals energy E_{VDW} comprise the bulk of the potential energy for most clay mineral systems. These two energy contributions correspond to the nonbond interactions associated with a molecular, crystal, or any particular arrangement of atoms. The nonbonded potential energy of interaction for atoms i and j is defined as:

$$E_{ij} = \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \qquad (9.2)$$

where the Coulombic term includes q_i which is the partial charge of the atom (or full charge of an ion), e is the charge of the electron, ϵ_0 is the dielectric permittivity of vacuum, and r_{ij} is the distance between atoms i and j. The van der Waals term represents the dispersive interaction of electrons between atoms and is significant only at relatively short distances. Empirical parameters $\varepsilon_{\mathrm{ij}}$ and σ_{ij} are typically determined from experimental and spectroscopic measurements or from high-level quantum calculations. The total nonbond energy of a chemical system requires summation of Eq. (9.2) for all atom pairs regardless of atomic positions. Calculations are typically performed for a simulation cell having periodic boundary conditions to represent a three-dimensional infinite-sized representation of a bulk clay mineral or one incorporating a two-dimensional interface to represent a clay mineral surface exposed to external water or aqueous solution.

The bond terms of Eq. (9.1) represent the covalent interactions of a chemical system and are typically represented in classical-based models by harmonic analytical expressions for bond energy about an equilibrium bond distance

$$E_{\text{bond stretch}} = k(x - x_0)^2 \tag{9.3}$$

or equilibrium three-body bend angle

$$E_{\text{angle bend}} = k(\theta - \theta_0)^2 \tag{9.4}$$

where x and θ are bond distance and bend angle, respectively, and x_0 and θ_0 are the corresponding equilibrium values, with k representing the associated force constants. Additional bond terms can exist for four-body interactions, such as for dihedral torsions and out-of-plane atomic motions, and for coupling among the various stretch and bend modes. Bond terms for clay mineral systems often include all nearest-neighbor metal-oxygen bonds in coordination polyhedra or for just water molecules and hydroxyl bonds.

The convenience of simple analytical expressions in classical models to describe the potential energy for an assembly of atoms makes it relatively easy to use computers to repetitively evaluate the potential energy functions and obtain the lowest total energy configuration (i.e., energy minimization). This is especially the case in deterministic MD simulations where Newton's equations of motion are evaluated over many iterations often involving many millions of time steps, or in simulations relying on stochastic methods such as Monte Carlo methods where hundreds of thousands to millions of configurations are evaluated to determine the most energetically favored geometries. The practical success of any set of potential energy functions—referred to collectively as a force field—ultimately relies on the quality and accuracy of the energy expression in reproducing experimental chemical structures, physical properties, and spectroscopic observations. There are several successful force fields designed specifically for modeling clay minerals and environmental processes (Teppen et al., 1997; Kawamura et al., 1998; Sainz-Diaz, Hernández-Laguna, & Dove, 2001; Cygan, Liang, Kalinichev, 2004; Heinz et al., 2013). Such force fields are typically implemented with specific H_2O models (SPC, TIP3P, etc.) to accurately model hydrated clay interlayers and interactions with aqueous solutions (van der Spoel, van Maaren, & Berendsen, 1998).

Force fields developed for application to clay mineral systems typically rely on fitting of force constants and other parameters for the interatomic potentials to structural, physical properties, and spectroscopic data, or, in some cases, to results of quantum mechanical calculations. The Kawamura et al. (1998) force field involves nonbonded interactions as given in Eq. (9.2) but with additional two-body parameters to explicitly account for the Pauli exclusion of electrons. Covalent, or bonded, terms based on an exponential dependence of atom-atom distances are incorporated to describe the potential energy of metal-oxygen polyhedra and hydroxyl groups of the clay and for O-H interactions in water molecules. A complex three-body term is also needed to reproduce the structural and physical properties of water, ice, and related structures. Teppen et al. (1997) developed a conventional bonded force field using bond stretch, angle bend, and torsional terms parameterized for the common tetrahedral and octahedral linkages of metal-oxygen polyhedra associated with clay minerals. Additionally, this particular force field includes bonded potentials to describe the difference in energy of Al occurring in either tetrahedral or octahedral coordination. Partial charges were assigned to clay atoms by a combination of deformation electron densities from X-ray diffraction measurements and from electrostatic potentials fitted to high-level ab initio calculations.

A different approach, involving predominantly nonbonded interactions, was taken by Sainz-Diaz et al. (2001) using exponential-based potentials for two-body interactions and a harmonic core-shell potential to account for electronic polarization associated with O ions. Three-body terms are incorporated to improve polyhedral geometries, and formal charges of ions are used for evaluating electrostatics. Cygan et al. (2004) expanded such an approach with the development of Clayff, a primarily nonbonded force field (Eq. 9.2) that includes optimized charge distributions for metals and coordinating oxygens in either tetrahedral or octahedral coordination based on quantum calculations and stoichiometric constraints. Harmonic and Morse potentials describe covalent bonds of hydroxyl groups and water molecules. Clayff was developed to accurately model a variety of oxide, hydroxide, oxyhydroxide, and clay mineral systems and their interactions with aqueous solutions, and has been used to successfully model molecular interactions associated with numerous environmental applications. Recently, Heinz et al. (2013) optimized parameters for two-, three-, and four-body harmonic potentials to accurately reproduce a large set of crystal structures, thermodynamics, and physical properties of mineral and oxide phases. The INTERFACE force field enables molecular simulations of clay minerals and of organic and biochemical molecules interacting with clay interlayers and external surfaces.

Although each may use a different set of analytical functions to describe the potential energy, these validated force fields are useful in providing accurate classical-based descriptions of clay mineral structures and molecular behavior. Use of bonded force fields require constrained metal-O polyhedra while nonbonded force fields allow metal-O bond breaking and bond forming—and therefore support formation of new coordination polyhedra—under extreme or nonequilibrium conditions. Nonbonded force fields are typically used for modeling amorphous and glassy materials where it is not uncommon to have atoms change coordination dynamically throughout the simulation. Accurate nonbonded force fields, usually with limited number of analytical expressions for the potential energy, are also attractive by reducing the computational cost of large-scale molecular simulations when many millions of atoms and time steps (or atomic configurations) require repetitive evaluations. Of course, due to the variety of clay mineral structures and compositions, it is beneficial to utilize a general force field that is accurate and suitable for a wide range of clay mineral applications.

A recent challenge in modeling clay systems is the refinement of force fields to accurately model the edge sites of clay minerals where acid-base reactions can change the protonation state and charge of the clay mineral and therefore impact adsorption phenomena. Depending on the pH of the aqueous solution and the surface properties of the clay mineral, negatively-charged O, neutral hydroxyl groups, or positively-charged groups with doubly-protonated O would be exposed to the solution. Recent efforts by Zeitler et al. (2014), Newton and Sposito (2015) using modified versions of Clayff have developed new approaches to improve modeling these edge sites.

Several interatomic potentials for CO_2 are available for modeling gas, liquid, and supercritical states (Zhang & Duan, 2005; Aimoli, Maginn, & Abreu 2014). Flexible CO_2 potentials incorporate bond stretch and bend modes that assist in the analysis of interfaces involving intercalation processes and adsorption of CO_2 (Harris & Yung, 1995; Zhu, Zhang, Liu, & Zhang, 2009; Cygan, Romanov, Myshakin, 2012). Molecular behavior in carbon sequestration applications, in particular, requires compatible force fields that can collectively model interactions among CO_2, H_2O, and mineral phases, especially clay minerals which can effectively capture CO_2. Accurate and reliable potentials/force fields are important in providing realistic MD and Monte Carlo simulations especially when the clay-H_2O-CO_2 systems are comprised of many tens of thousands to millions of atoms.

9.2 DFT Methods for Clay Systems

First-principles methods offer more precise estimations of thermodynamic, spectroscopic, mechanical, and other parameters of clay systems compared to empirical force field-based molecular simulations. However, even with the use of modern supercomputers, first-principles Density Functional Theory (DFT) methods would be computationally expensive to model complex clay systems due to the size of the simulation cell that must be employed. As a result, first-principles MD calculations on clays systems were limited to perfect bulk systems, and the dynamics were limited to pico-second scale. In those simulations, potential energy of the interacting particles and forces are computed using DFT methods; and evolution of the system is governed by Newtonian dynamics similar to classical molecular dynamics simulations. That means that at each time step, the first-principles method is involved to compute a potential energy of a system. Given that a typical time step is 1 *femto*-second (or even smaller, if a power spectrum for high-frequency modes is of interest) a simulation of 10 *pico*-seconds would require 10,000 single-point calculations of potential energy.

The clays minerals as layered systems provide space for interlayer species like counter-balancing ions and molecules. For example, energy gain resulting from hydration of the interlayer ions serves as a driving force for clay swelling. The interactions between the interlayer molecules themselves, interlayer molecules and clay layers, and between the neighboring clay layer units are non-bonding in nature. For such interactions, the van der Waals dispersion correction to a total energy is important. In classical molecular dynamics, that correction is accounted for through the Lenard-Jones part of the interatomic potential describing van der Waals forces. In standard DFT calculations, an explicit correction must be added to the DFT energies as the local and semi-local exchange correlation functionals are short ranged and cannot describe the nonlocal interactions. Several approaches have been proposed for correcting DFT for dispersion, including the DFT-D2 (Grimme Antony, Schwabe, & Mück-Lichtenfeld, 2007), DFT-D3 (Grimme, Antony, Ehrlich, & Krieg, 2010), and vdW-TS (Tkatchenko & Scheffler, 2009) methods at an atom-atom level, the DCACP (dispersion-corrected atom-centered pseudopotential) method (Tavernelli, Lin, & Rothlisberger, 2009) at atom-electron level, and explicit consideration of non-local interactions as in the vdW-DF method (Lee et al., 2010).

Dispersion corrections to the DFT energies are important in characterizing clay surfaces (Voora, Al-Saidi, & Jordan, 2011, 2012). This was demonstrated by Voora et al. (2011) who investigated lattice constants, bond lengths, and bulk moduli of pyrophyllite and montmorillonite with alkali and alkali earth metal ions, using density functional theory with and without dispersion corrections. Both the DFT-D2 and vdW-TS methods were used to adjust representations of the layered structures of montmorillonite and pyrophyllite. For pyrophyllite, it was found that inclusion of the dispersion correction significantly improves agreement between the calculated and experimental values of the lattice parameters and bulk modulus. For montmorillonite, the calculations predict that the interlayer spacing varies approximately linearly with the cation radius. Inclusion of the dispersion correction leads to a sizable shift to lower values of the interlayer spacing.

Subtle features in interatomic interactions may be responsible for experimentally observed changes in IR and Raman spectra of intercalated species in clay systems. DFT-based molecular dynamics simulations with DFT-D2 dispersion correction were used to interpret the origin of the observed shift in asymmetric stretch vibration of CO_2 trapped in montmorillonite (Myshakin et al., 2013). The atomic velocities were collected from production runs and used to calculate the velocity autocorrelation functions (VACF) which, in turn, were used to calculate the power spectra. The spectra computed for selected CO_2/H_2O compositions were compared with the experimental FT-IR spectra including the asymmetric stretch fundamental for CO_2 intercalated in sodium-exchanged montmorillonite. The results provide strong evidence that the observed red shift is due to geometry distortions of the CO_2 molecules induced by the water molecules. The data explain why classical MD simulations were unable to predict a red shift for the intercalated carbon dioxide. The force field employed in classical MD only uses a harmonic C–O stretch term, whereas it is necessary to include an anharmonic C–O stretch term to account for the frequency shift accompanying the stretching of CO bonds upon hydration. The results also suggest a way of how to rectify that deficiency by adopting a Morse-type potential to describe the C–O stretch bond.

9.3 Hydration of Montmorillonite

An instructive example in the use of molecular simulation for clay minerals is provided by the swelling of montmorillonite using energy minimization and MD approaches and a classical force field (Cygan et al. 2004) to describe the potential energy of the clay system as a function of interlayer water. In a simple analysis of this system one can evaluate the electrostatic energy for a relatively small periodic simulation cell comprised of a single Na-montmorillonite interlayer in which the layer charge is associated with a Mg^{2+} site in the dioctahedral sheet resulting in a layer charge of −0.5 per $O_{10}(OH)_2$. Figure 9.1 presents a summary of the energy-minimized smectite model without interlayer water and for two different interlayer water contents. The optimized anhydrous model exhibits a collapsed smectite layer in which the interlayer Na^+ exists adsorbs to at a hexagonal hole of the siloxane sheet near the octahedral substitution. The strong Coulombic interactions between charged layers and the interlayer Na^+ control the long-range structure of the collapsed smectite model. However, the clay layers can be expanded with the introduction of nominal number of water molecules into the interlayer to form a monolayer hydrate. The resulting clay structure is stabilized by the partial hydration of the interlayer Na^+ by the water molecules and by the formation of hydrogen bonds among the water molecules and with the clay surfaces of the interlayer. The energy benefit amounts to about 70–80 kJ/mol for each water molecule that is introduced into the clay interlayer. The electrostatic stabilization in the monolayer

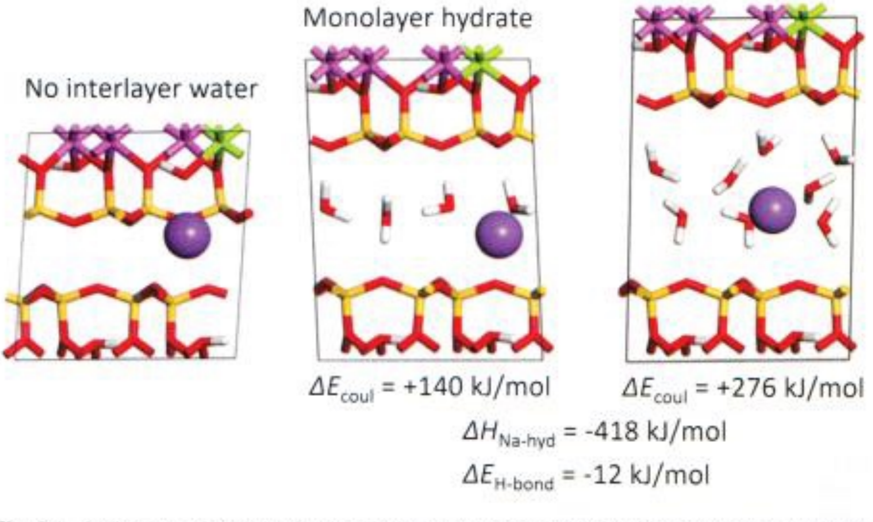

Fig. 9.1 Optimized periodic molecular models of an idealized Na-montmorillonite exhibiting expansion as a function of interlayer water content, and the corresponding changes in the electrostatic energy relative to the anhydrous model. Hydration enthalpy for Na^+ and energy associated with hydrogen bonds are indicated

hydrate is reduced by 140 kJ/mol in this example, but this amount is easily offset by the energy gained through hydrating the Na^+ and the development of a hydrogen bond network.

Further expansion of the smectite interlayer to a bilayer hydrate leads to further reduction in the Coulombic contribution (+276 kJ/mol) and is accompanied by increased hydration of the Na^+; a fully hydrated Na^+ can lead to an energy gain (enthalpy of hydration) of about −418 kJ/mol (Burgess 1999). Such outer-sphere complexes are preferred in Na-montmorillonite rather than the direct adsorption of Na^+ to the clay surface (inner-sphere complex) that would be more likely for a beidellite where the layer charge is localized at the interlayer in the tetrahedral sheet (Teich-McGoldrick, Greathouse, Jové Colón, & Cygan, 2015).

These simple examples demonstrate how important the energy balance for the various atomic and molecular interactions is to the stability of a hydrated clay mineral system. Such simulations allow the modeler to extract very detailed snapshots of the atomic structure and of the thermodynamics to better assess molecular behavior, especially for complicated structures as associated with clay minerals. The significance of water and the development of hydrogen bonds among water molecules and mineral surfaces are crucial to the unique adsorption and swelling properties of clay minerals. The enthalpy of a hydrogen bond—approximately −12 kJ/mol based on an average of 3.5 bonds per tetrahedral coordination of water molecules—can contribute significantly to the stability of clay interlayers and interfaces.

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