Advances in Clayff Molecular Simulation of Layered and Nanoporous Materials and Their Aqueous Interfaces

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ABSTRACT: As a general-purpose force field for molecular simulations of layered materials and their fluid interfaces, Clayff continues to see broad usage in atomistic computational modeling for numerous geoscience and materials science applications due to its: 1) success in predicting properties of bulk nanoporous materials and their interfaces; 2) transferability to a range of layered and nanoporous materials; and 3) simple functional form which facilitates incorporation into a variety of simulation codes. Here, we review applications of Clayff to model bulk phases and interfaces not included in the original parameter set, and recent modifications for modeling surface terminations such as hydroxylated nanoparticle edges. We conclude with a discussion of expectations for future developments.

1. INTRODUCTION

Among the most innovative advances in physical chemistry over the last fifty years has been the development of molecular models for evaluating structure, properties, dynamics, and behavior of chemical systems.[1-2] Not only have computational molecular simulation methods—including quantum-based approaches such as molecular orbital theory and density functional theory (DFT), and classical-based energy force fields—been successfully used to investigate molecules or molecular clusters, they have also been very effective in providing accurate models of layered inorganic materials, including clay minerals. The first research articles involving atomic simulations of clay minerals were published over thirty years ago[3-5] and this specialized

area of research has greatly expanded with advances in computational power and the availability of user-friendly software.

Clay minerals are layered hydrated aluminosilicates comprised of coordinated tetrahedral (T) silica sheets and octahedral (O) alumina sheets. These basic sheets are combined into TO and TOT layers, often with hydroxylated or hydrated interlayer regions. These layers stack to form nanoparticle platelets with dimensions on the order of hundreds of nanometers or a few microns for synthetic and natural samples, respectively. Layer charge can occur by substitution of Al^{3+} (or Fe^{3+}) for the tetrahedral Si^{4+}, or Mg^{2+} (or Li^{+}) for octahedral Al^{3+} which results in negatively-charged clay layers with charge-balancing hydrated cations, like Na^{+} and Ca^{2+}, occurring in the interlayer. Depending on the net layer charge, TOT layers can swell in aqueous environments resulting in nanoconfined fluids relevant to numerous environmental and industrial processes. Swelling clay minerals, known collectively as smectites, include Na-montmorillonite (idealized formula $Na_{0.5}(Al_{1.5}Mg_{0.5})Si_4O_{10}(OH)_2 \cdot nH_2O$) being one of the most common phyllosilicates. Figure 1 provides an example of Na-montmorillonite (Figure 1a), along with other layered or nanoporous materials, that can be accurately modeled using Clayff potentials.

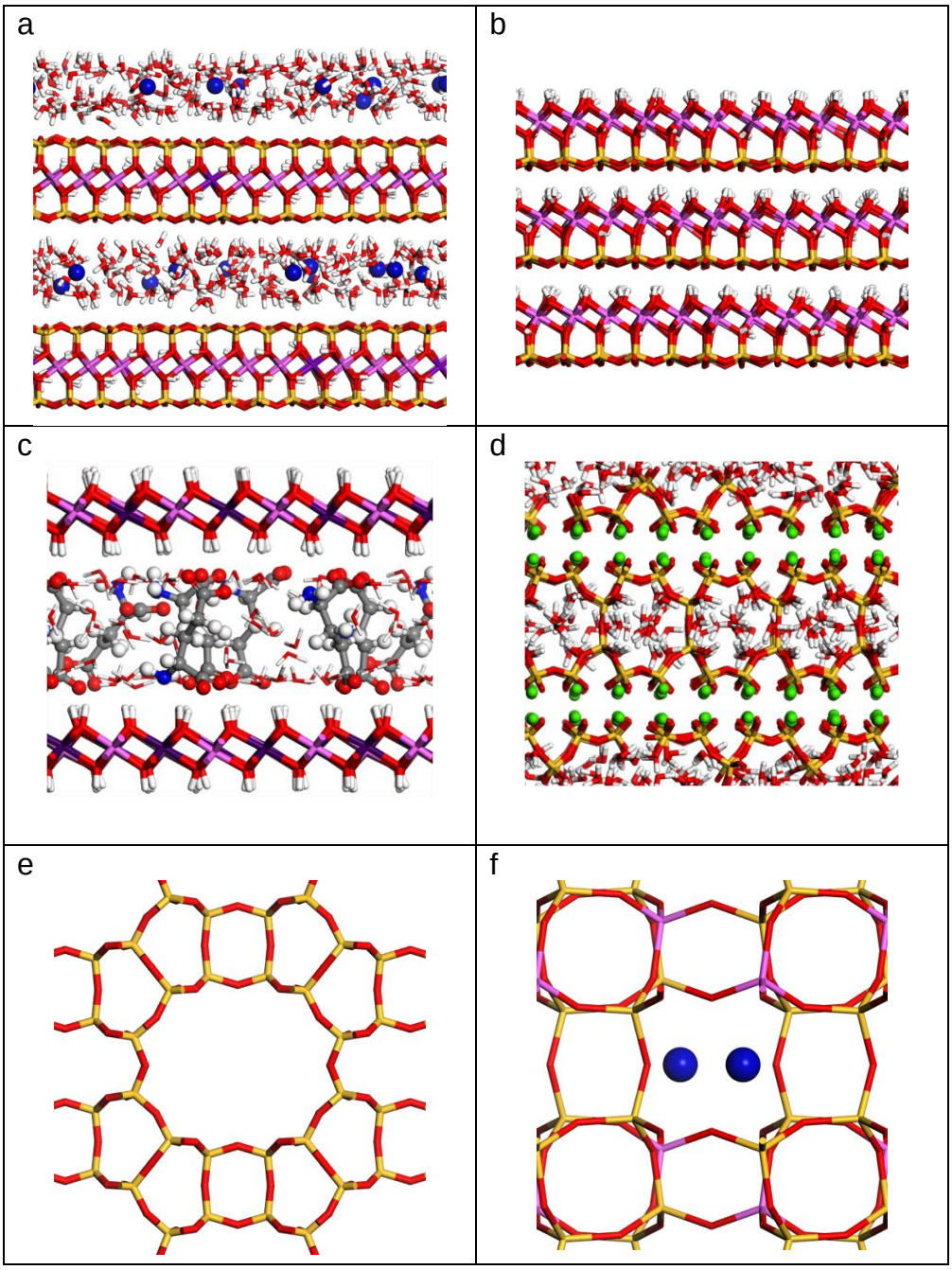

Figure 1. Models of layered and other phases that can be simulated using Clayff: a) Na-montmorillonite (TOT clay mineral); b) kaolinite (TO clay mineral); c) hydrotalcite (LDH) with interlayer gluconate; d) tobermorite, basis for calcium silicate hydrate model (C-S-H); e) endmember mordenite (zeolite); and f) K-feldspar (framework aluminosilicate).

Kaolinite, $Al_2Si_2O_5(OH)_4$, is a non-swelling TO clay mineral having no layer charge but has an interlayer characterized by hydrogen bonding of hydroxyl groups between the alumina O

sheet and the basal oxygens of the silica T sheet, to form TO-TO layers (Figure 1b). Many other clay minerals can be found in soils and sediments across many geological and environmental conditions, and can be classified by elemental composition, layer structure, layer charge, and morphology. Layered double hydroxides (LDH), also known as "anionic clays", which will be discussed briefly in this review, are similar to smectite clay minerals but have hydroxylated octahedral O sheets with structural cationic substitutions that result in positive layer charge and an interlayer region with hydrated anions (*e.g.*, Cl^-, CO_3^{2-}) rather than cations. Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot n(H_2O)$, is a representative of the LDH type of clay minerals (Figure 1c).

Because of the necessary large size of the simulation cells for many clay mineral systems, the number of atoms required for an accurate simulation range from many hundreds to several millions in order to properly capture the unique composition, morphology, edge structure, and interlayer chemistry. Although quantum-based simulation methods have become relatively common among computational chemists for investigating clay mineral structures and their reactivity, computational resources continue to limit the number of atoms that can be incorporated in such intensive electronic-structure-based simulations and the time scales of the dynamic processes that can be studied by such methods. Therefore, the practitioner typically relies on a set of empirically-derived interatomic potentials to accurately evaluate the interactions among the constituent atoms in the computer model.

A variety of interatomic potentials suitable for modeling clay minerals are found in the literature, and they typically involve analytical expressions describing the potential energy as a function of atomic distances, angles, or other geometric parameters.[6-8] Determination of the total potential energy of the chemical system involves the summation of Coulombic (electrostatic),

van der Waals (VDW), and related nonbonded interactions with contributions from explicit bonded interactions:

$$E_{Total} = E_{Coul} + E_{VDW} + E_{Bond} + \cdots \quad (1)$$

Additional potential energy terms representing hydrostatic pressure, directional stresses, electric fields, and other intensive conditions can be incorporated. This summation would also include any interlayer ions and water molecules associated with the layered material or interface.

As an example of a standard energy calculation for a material, the computer would evaluate the Coulombic interaction energy for all atoms with each other based on their partial charge assignments, which are typically part of the force field. Dispersive or VDW interactions, which are most effective at small atomic distances, would be similarly summed. Explicitly bonded components such as hydroxyl groups and interlayer water molecules would contribute a destabilizing energy based on their deviation from equilibrium bond distances and bond angles. Validation and accuracy of these force fields—as collections of interatomic potentials are commonly referred to—will depend on the quality of the structural data, physical properties, spectroscopic data, and quantum chemical methods used to derive the best fit of the empirical parameters for each interatomic potential of the force field.

2. ORIGINS OF CLAYFF

Clayff[9] was originally developed to provide a simple and straightforward set of potentials based primarily on the nonbonded potentials described by E_{Coul} (Equation 2) and E_{VDW} (Equation 3):

$$E_{Coul} = \frac{e^2}{4\pi\epsilon_\circ} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad (2)$$

where e is the fundamental charge of an electron, q_i and q_j are partial atomic charges, and r_{ij} is the distance between atoms i and j. A set of optimal and consistent values of atomic charges, based on local coordination, was derived for Clayff using electron density distributions obtained from DFT for experimental unit cell structures of a number of well-characterized simple metal oxides and hydroxides and for various molecular clusters involving hydrated metal ions. Bond stretch and three-body angle bends are also incorporated in Clayff to describe the potential energy E_{Bond} associated with explicit bonds, such as those of water molecules and hydroxyl groups.

A Lennard-Jones (L-J) potential, used to represent E_{VDW}, combines the short-range repulsion associated with atom-atom overlap and the short-range attraction associated with electron dispersion:

$$E_{VDW} = \sum_{i \neq j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{3}$$

where ε_{ij} is the depth of the potential energy well and σ_{ij} is the zero-crossing distance for the energy. ε_{ij} and σ_{ij} are treated as fitting parameters for the interactions between atoms i and j. For simplicity, L-J parameters in Clayff are presented for interactions between identical atom types ($i = j$), known as diagonal terms. Interaction parameters between different atom types ($i \neq j$), referred to as off-diagonal terms, are obtained using a combination of arithmetic and geometric (Lorentz-Berthelot) combining rules:[6]

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad \varepsilon_{ij} = \left(\varepsilon_i \varepsilon_j \right)^{1/2} \tag{4}$$

Examples of Clayff atom types for clay minerals and edges are shown in Figure 2.

Fundamental to the parameterization of Clayff potentials is the use of equivalent VDW parameters for all oxygen atoms based on the L-J parameters for the oxygen atom of the SPC

(simple point charge) water model.[10] This approach suggests that VDW parameters are the same for all clay oxygens including framework and edge oxygens, hydroxyl oxygens, and, of course, water oxygens. Only the atomic charges of these various oxygen types are different, dependent on the local bonding and coordination environment. Bond stretches associated with water molecules and hydroxyl groups are represented in Clayff by a harmonic potential where potential energy contributions increase as the square of the deviation of the bond length from its equilibrium value. Alternatively, such bond stretch can be described more accurately by a Morse potential as was done for hydroxyl bonds in serval clay minerals.[11]

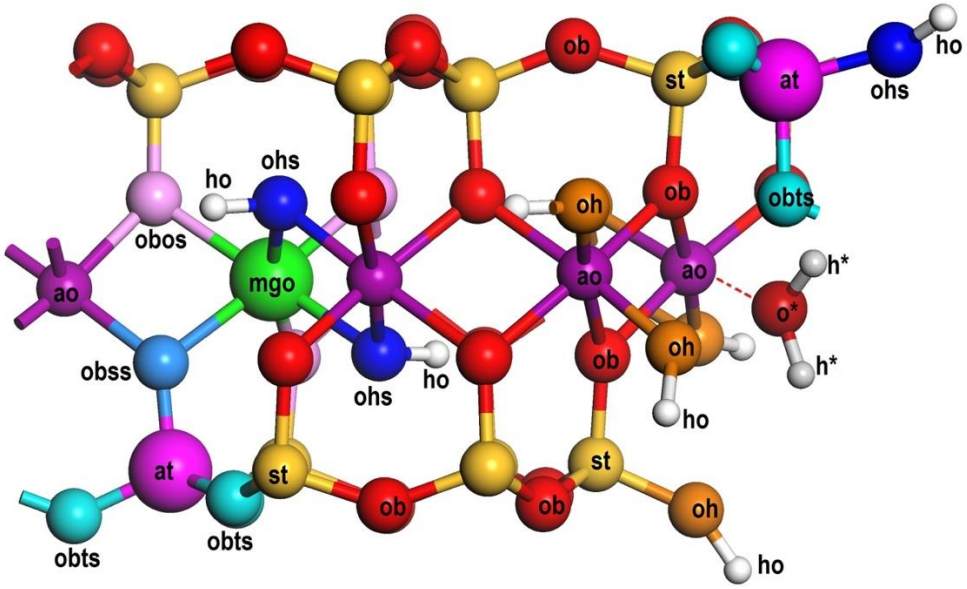

Figure 2. A fragment of a montmorillonite model with atom type parametrization according to Clayff. The complete list of atom types and their parameters is presented in Table S1. The (110) edge of the montmorillonite T-O-T layer is depicted on the right of the model.

Clayff has significantly contributed to improving bulk structure simulations of clay minerals, other environmental materials, and in predicting structural and dynamical behavior of hydrated clay interlayers and interfacial systems. The success of Clayff lies in the balanced combination of functional simplicity, relative accuracy, and transferability of the original

parameterization of the force field with the fitting to structural data for simple well-characterized metal oxides and hydroxides. Furthermore, Clayff parameters are consistent with standard models of water molecules and with respective models of various aqueous cations, anions, and organic species. Physical properties are well reproduced in Clayff simulations, including most second-derivative (of energy) properties such as elastic constants, bulk moduli, dielectric constants, and vibrational spectra (Figure 3).[9]

As originally designed, Clayff excels in atomistic simulations of environmental systems involving the hydration of clay minerals and related phases. Molecular simulation studies, using Clayff potentials involving clay minerals in energy and environment applications, include oil and gas extraction, and the sequestration of CO_2 and radionuclides in a variety of host materials.[12-18] Additionally, Clayff has been successfully used in the simulation of materials including zeolite and glass phases that are of particular use in technological and industrial applications.[19-22]

This review article provides a broad summary of Clayff and its use in the analysis of clay minerals, other clay-related and nanoporous materials, and their interfaces with aqueous solutions and other important fluids. In particular, the summary addresses recent modifications and advances in the use of Clayff since it was first introduced to the scientific community almost twenty years ago. The original authors, numerous collaborators, and other researchers have combined to improve Clayff in both practical implementations and novel applications. We first present general comments on Clayff and review the improvements made to the original interatomic potentials. We also discuss recent modifications for incorporating Clayff in the simulation of clay edge sites and how to properly implement these changes in standard molecular simulation software (Supporting Information).

Clayff was originally designed to be a general force field for the simulation of clay minerals and to have full atomic flexibility in energy optimizations and molecular dynamics (MD) simulations. Implicit in this approach was that simulations would approach accurate minimum energy configurations without the need for constrained atomic motions or fixed lattice parameters. Furthermore, dynamics simulations of aqueous interfaces involving clay surfaces, including interlayer regions of clays, would properly account for conservation of energy and momentum across the interface—for example, the interactions of clay surfaces with interlayer and interfacial cations and water molecules, and their impact on diffusional transport and vibrational/librational modes.

It is also noteworthy that Clayff incorporates primarily nonbonded potentials whereby most metal-oxygen interactions in the crystal structure are assumed to be quasi-ionic and described simply by a combination of Coulombic and L-J potentials. Only hydroxyls and water molecules in Clayff incorporate bond stretching and bond-angle bending terms, using either harmonic or Morse potentials. The implementation of nonbonded potentials is helpful for describing some bond-breaking and bond-forming M-O reactions which may occur at elevated temperatures as expected in some molten and quenched glass materials involving coordination changes.[23-24] However, such reactivity of clay minerals was not an objective in the original Clayff development, especially since the parameterization of the potentials was based on room-temperature structures of the simple oxide and hydroxide phases.

There are other force fields that have been introduced for the simulation of layered minerals.[7, 25-31] Some of the early efforts in developing force fields did not treat the clay framework as fully flexible and typically relied on rigid or constrained atom arrangements. Several of the force fields developed later use a bonded form of potential to describe explicit M-

O bonds in the crystal structure, and thereby focus on improving vibrational properties associated with the simulation. Other force fields have incorporated polarizable bonds to better reproduce electronic structure and the charge distribution among atoms.[32-35] As discussed in detail below, several studies have chosen to make modifications to Clayff potentials to significantly improve the accuracy for one specific class of layered or nanostructured materials. In general, each force field has its own strengths and each, including Clayff, has its own imperfections. Nonetheless, caution must be exercised when software choice and convenience preclude accuracy in the selection of an energy force field for investigating a particular material system.

3. APPLICATIONS OF CLAYFF

Clayff has been cited well over a thousand times since the parameters were first published in 2004. Clayff was initially used to simulate bulk crystal phases and aqueous interfaces of layered minerals, but an inspection of citing articles reveals that it has been used for a variety of other applications,[36] including other oxide phases, mineral-organic interactions, including contaminants, hydrocarbons,[12] natural organic matter,[37-38] biomolecules,[39-41] and polymers.[42] Clayff has also been used to model mineral phases and interfaces beyond the original training set.[43-47]. Note that the following discussion is a non-exhaustive list; Clayff continues to be used and adapted into new applications. We refer the reader to previous review papers on molecular simulation of layered materials.[15, 36, 48-51]

Figure 3 highlights several applications using Clayff to examine properties of clay minerals. These include simulations of the mechanical response of a montmorillonite nanoparticle,[52] the hydration and swelling behavior of Na-montmorillonite at various interlayer water contents,[53] the diffusion rates of water and cations as impacted by the clay surface,[54] and

the vibrational behavior of water-siloxane interactions at various water loadings of a Na-montmorillonite.[55]

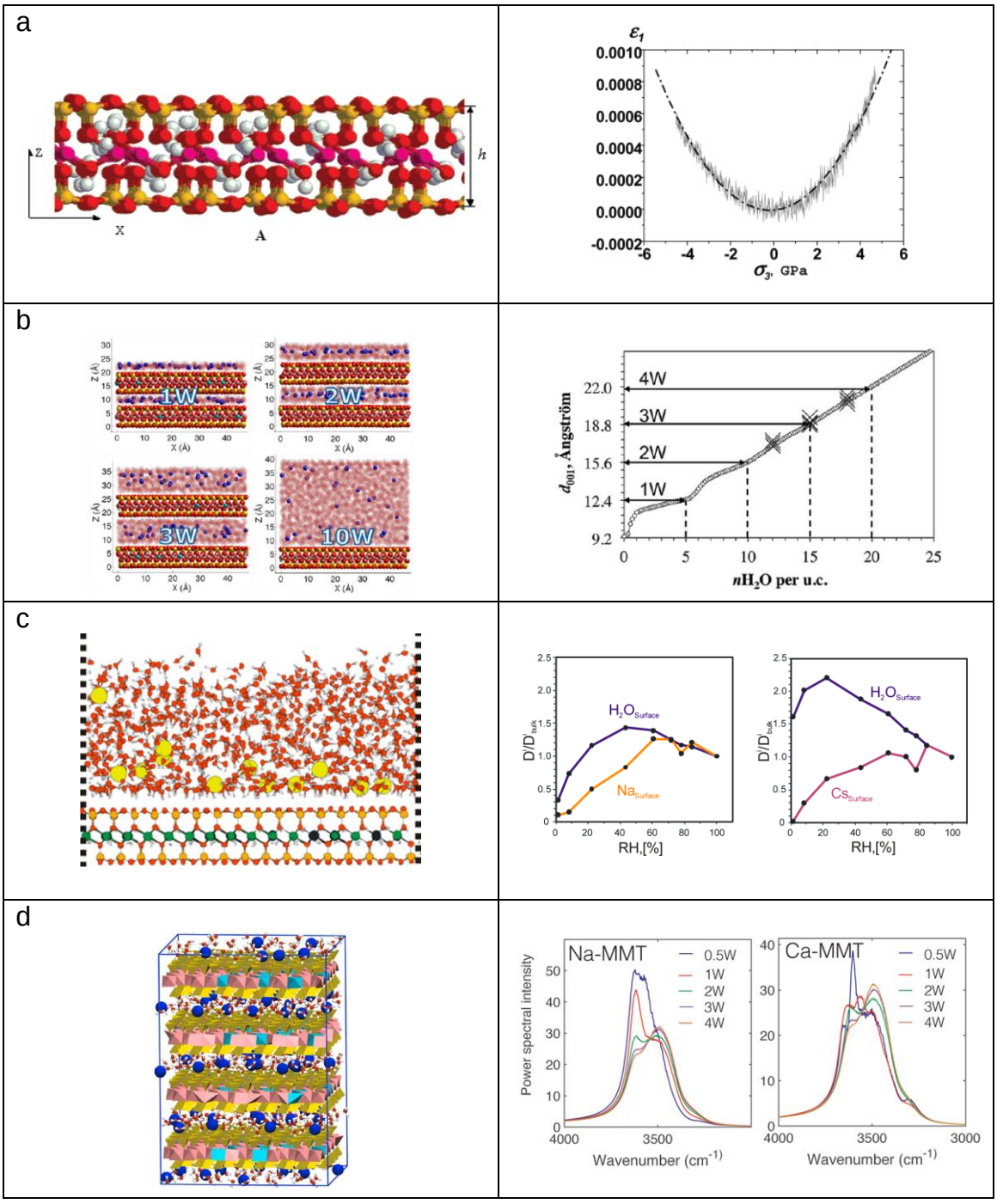

Figure 3. Material properties obtained from MD simulations using Clayff: a) variation of pyrophyllite elastic constant under uniaxial deformation transverse to the TOT layer (*z*-direction);[52] b) comparison between simulation (lines) and experiment (crosses) of basal (001) *d*-spacing of Na-montmorillonite with increasing water content from one water layer (1W) to four water layers (4W);[53] c) simulated diffusion coefficients relative to bulk values for water and cations at an external surface of montmorillonite;[54] and d) simulated vibrational spectrum (O-H stretch region) of Na- and Ca-montmorillonite at different water contents.[55] Images reprinted with permission from the cited references: (a) Copyright 2008 American Chemical Society; (b)

3.1. Clay Minerals

Many atomistic simulations have contributed new insights to the structure and dynamics of clay minerals, their interlayers, and associated nanopores. Montmorillonite, as the most common swelling clay of the smectite mineral group, has been the subject of many of these efforts[9, 53, 56-62] Successful Clayff-based models of montmorillonite have been developed to evaluate crystalline structure, hydration, interlayer structure, interlayer cation environments, swelling behavior, adsorption, and diffusion processes. Many of these efforts are related to understanding model systems for environmental applications and to advance chemical and nuclear waste remediation and repository methods. Montmorillonite with highly expanded interlayers provides a unique model for understanding nanopores and the impact of multiple charged surfaces.

Models of kaolinite developed using Clayff potentials have also contributed to understanding TO clay structures[9, 63-64] and mechanisms of cation adsorption.[65-67] Kaolinite provides two unique surface environments, where the siloxane sheet is relatively hydrophobic in contrast to the Al-octahedral sheet, which is terminated by hydroxyl groups and is hydrophilic in nature.

Even though Clayff was primarily developed for robust atomistic simulations of clay minerals and their aqueous interface, it was almost immediately applied to a broader range of materials, such as layered double hydroxides,[68-70] zeolites,[19] and mineral phases of cement,[43] which, similar to clay minerals, are characterized by incompletely or poorly characterized crystal structures and composition, often have large unit cells, low symmetry, and frequently occur as

only sub-micron size particles.[43, 60, 71-72] In fact, the first attempt of applying a Clayff-based approach in such simulations featured hydrocalumite (Friedel's salt), known in cement chemistry as the AFm phase.[73] The early models of layered materials, sometimes involving a few unit cells, have evolved to greater dimensions with more complex structure and chemistry. This is, in part, due to access to greater computational power but also to the simplicity of Clayff potentials and their ability to scale with system size.

3.2. Cement Phases.

Over the last ten to fifteen years, Clayff has been successfully tested in numerous molecular simulations of cementitious materials.[43, 70-72, 74-75] Despite its simplicity, Clayff was proven to quite accurately reproduce the crystallographic parameters of such cement-related phases as tobermorite, ettringite, hydrocalumite, tricalcium aluminate, kanemite, and gypsum. In addition to structural properties, Clayff has shown to reproduce quite accurately the energetics of swelling for a wide range of cement-related silicates and hydroxides.[43, 74] Not unexpectedly, the MD-simulated energetics of water adsorption in Na- and K- kanemite, [(Na,K)$HSi_2O_5 \cdot nH_2O$], is in very good agreement with the observed X-ray diffraction, water adsorption, TGA/DTA, and ^{29}Si NMR data.[72] Kanemite-like local structures represent a realistic model of gels produced during the so-called alkali-silica-reaction (ASR) in concrete that occurs primarily due to incorporation of H_2O molecules between silicate nanoparticles, rather than within their interlayer galleries.[72]

Clayff has been shown to also well reproduce ion and water adsorption and diffusional dynamics at the surfaces of several typical cementitious materials, including hydrous calcium aluminates and the C-S-H phase represented by a tobermorite model (Figure 1d).[43, 71] Good

quantitative agreement between the MD-simulated diffusion coefficients of water on the surface of tobermorite, and the hopping mechanisms of longer timescale mobility of interfacial H_2O molecules, with the values obtained for hydrated cement pastes and mortars from proton field cycling NMR spin-lattice relaxation measurements provides strong support for the molecular scale interpretation of such experimental measurements probing the behavior of water in cement nanopores.[76-77]

Even though classical approaches, such as Clayff, cannot model chemical reactions, they can still be successfully applied to simulate the systems at various equilibrium states, that is, before and after the reaction. Androniuk and Kalinichev[78] have recently applied this approach to develop a series of classical models for calcium silicate hydrates (C-S-H) corresponding to different Ca/Si ratios and different degrees of surface protonation, using experimental ^{29}Si MAS NMR data[79-80] and accurate quantum chemical results[81] as guidance. The models were then successfully applied to simulate adsorption of uranyl ion at the hydrated C-S-H surfaces as a function of Ca/Si ratio and solution pH, the effects of organic molecules, such as gluconate, on these adsorption and complexation processes, and to interpret the experimentally observed behavior of these systems on a fundamental atomistic scale.[78]

3.3. Layered Double Hydroxides.

Layered double hydroxides (LDHs), also known as anionic clays, represent another important class of layered materials successfully simulated using Clayff. LDHs possess positive charge on their layers and exhibit large exchange capacities for inorganic and organic anions. They have found a great variety of applications as catalysts, bio-nanocomposites and carriers for drugs, non-viral vectors for gene therapy, media for molecular separation, environmental

remediation and many other technological purposes.[82-83] The positive charge of LDH layers provides important contrast with the negative layer charges typical of aluminosilicate clay phases, which also makes LDHs useful in the investigations of the fundamental molecular scale structural and thermodynamic properties of hydrated anions in concentrated aqueous solutions.

Over the years, Clayff has been successfully applied to study the intercalation, hydration and swelling of various LHD phases with many inorganic[70] and organic[51, 68] anions (Figure 1c), including amino acids[69, 84], and even larger fragments of DNA and RNA.[85-89]

3.4. High-Charge Mineral Phases.

Clayff was originally parameterized to simulate layered minerals that are either electrostatically neutral or that bear a slight negative (*e.g.*, smectite clay minerals) or slight positive (*e.g.*, layered double hydroxides) charge. In those cases, charge delocalization predicted by quantum chemical calculations can be adequately described by smearing the net charge (±1 *e*) among the four or six oxygen atoms coordinated to the substitution site. When the total layer charge is relatively low, there is little or no overlap of these smeared charges; that is, a layer oxygen atom coordinated to two charge sites. However, Clayff has also been used to simulate layered minerals with higher permanent charge, such as muscovite, saponite, vermiculite, illite, and micas. Saponite and vermiculite are swelling minerals whose interlayers expand to accommodate a few monolayers of water. Those studies have therefore focused on interlayer properties.[59, 90] Illite and the mica class of clay minerals are non-swelling, so studies have been limited to bulk mineral properties[91-92] or aqueous interfaces at the external basal surface.[47, 57, 93-98]

3.5. Birnessite Structures.

Phyllomanganate minerals, perhaps best represented by the hydrated phase birnessite, often control many geochemical processes involving trace and heavy element distribution in groundwater and in sediments. The high-cation exchange capacity of birnessite facilitates water purification. These phases are also important materials used in catalysis and battery applications. Birnessite has a general formula of $M_xMn_2O_4 \cdot nH_2O$, where M is one or more hydrated interlayer cations and Mn occurs in either tri- or tetravalent oxidation state, typically with a mean valency of +3.75. Charge analysis of manganese atoms in a geometry-optimized Na-birnessite system from DFT calculations[99] indicate a delocalization of charge for Mn consistent with the classical models of a fully-occupied Na-birnessite. However, Newton and Kwon[100] suggest that some biogenic birnessites with octahedral vacancies may not exhibit such delocalization of electrons due to the vacancies.

Expanded unit cells of Na-birnessite have been used to develop and dynamically equilibrate Na-birnessite, K-birnessite, and Ba-birnessite systems to assess the structure and dynamics of interlayer water.[99] Clayff parameters for these simulations included octahedral Fe parameters (feo atom type) as a proxy for octahedral Mn in the birnessite structure. The MD simulations indicate a strong correspondence of atomic contour maps of interlayer water with observed structures obtained by synchrotron X-ray diffraction and difference electron Fourier mapping of the interlayer region (Figure 4). In particular, contour maps for K-birnessite indicate diffuse regions for much of the interlayer water consistent with the low hydration enthalpy for K^+ compared to the other interlayer cations.

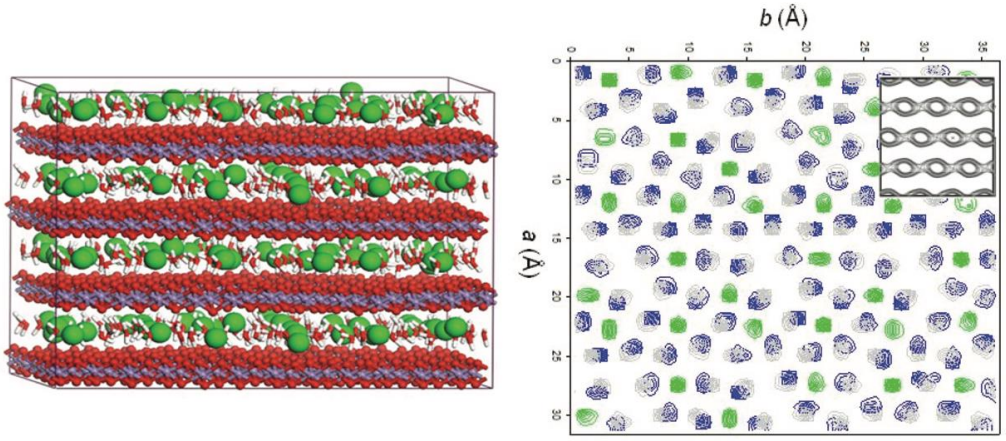

Figure 4. Simulation cell of MD-equilibrated Na-birnessite model (left) with corresponding density map (right) of interlayer species Na^+ (green), water oxygen (dark blue), and water hydrogen (gray).[99] Inset shows difference electron Fourier map obtained by synchrotron X-ray diffraction and indicating positional ordering of interlayer species. Reprinted with permission from ref. 99. Copyright 2012 Mineralogical Society of America.

A recent molecular simulation study of birnessite utilizing Clayff potentials has demonstrated the role of interlayer Ni^{2+} as an electrocatalyst for water oxidation.[101] Andersen and coworkers[102] examined the adsorption of a small model protein on the basal surface of birnessite using MD simulations with Clayff to investigate the disruption of the protein structure in response to the birnessite surface. The modeling suggests the birnessite surface is more efficient at unraveling the α-helix and β-sheet structures of the protein compared to kaolinite or montmorillonite surfaces, perhaps leading to catalyzed oxidation or hydrolysis of the protein. Recent MD simulations[100, 103] have used modified Clayff potentials to improve accuracy of simulations of birnessite and related phyllomanganate structures over a range of Mn^{3+} and vacancy content. Another recent MD study[104] investigated the hydration of K-birnessite nanoparticles and successfully distinguished between intercalated (interlayer) water and externally-adsorbed surface water.

Birnessite, and the previously discussed layered materials, demonstrate the versatility and robustness of Clayff molecular simulation to investigate materials that were not originally targetted in the early development of Clayff. More recent examples of the novel use of Clayff potentials to study a diverse range of materials and processes are illustrated in Figure 5.

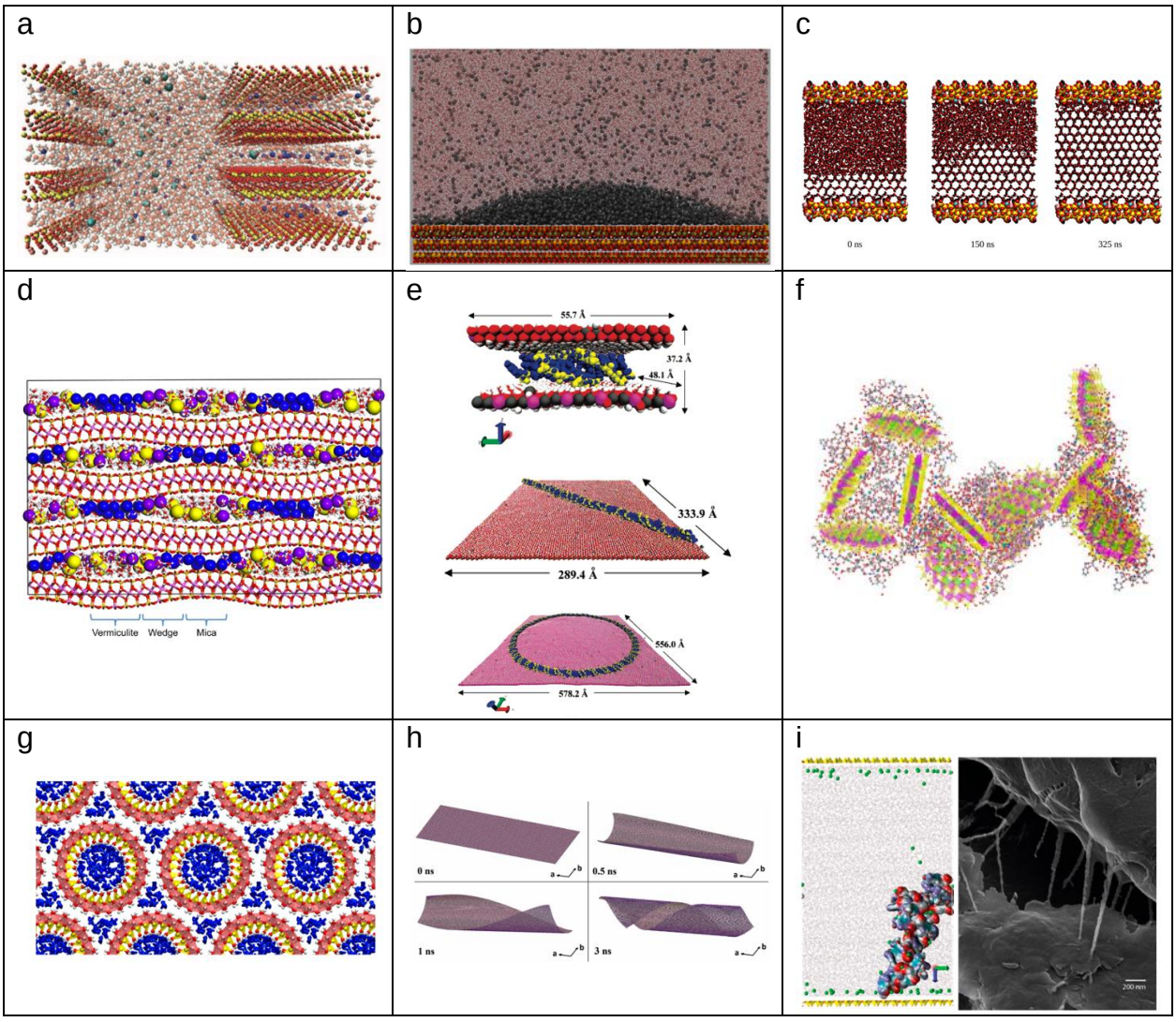

Figure 5. Selected models of layered and nanoporous phases and surfaces that have used Clayff interatomic potentials: a) aqueous mesopore bounded by clay edges;[105] b) supercritical CO_2 droplet in water on siloxane surface of kaolinite;[106] c) ice nucleation in feldspar nanopore;[107] d) transitional mica-vermiculite structure showing enhanced adsorption of cations;[90] e) various types of DNA strands intercalated in LDH;[87] f) hydrated aggregate of NOM and clay platelets;[108] g) imogolite nanotubes saturated with water;[109] h) evolution of kaolinite sheet into halloysite nanoribbon;[110] and i) NOM aggregate adsorbed onto smectite nanopore with SEM image of natural sample.[38] Images reprinted with permission from the cited references: (a) Copyright 2016 Clay Minerals Society; (b) Copyright 2014 American Chemical Society; (c) Copyright 2019 AIP Publishing; (d) Copyright 2015 American Chemical Society; (e) Copyright 2008 American Chemical Society; (f) Copyright 2020 Elsevier; (g) Copyright 2018 American Chemical Society; (h) Copyright 2018 Royal Chemical Society; (i) Copyright 2020 American Chemical Society.

3.6. Nanoporous Materials with Channels.

Clayff was originally designed to simulate minerals with planar symmetry, but it has proven successful for nanoporous phases with one-dimensional (1D) or two-dimensional (2D) channels. Zeolites are cage-like aluminosilicate minerals consisting of 1D channels connected by cages (Figure 1e). The endmember siliceous zeolites do not bear a permanent charge, but substitution of aluminum ions at tetrahedral silicon sites results in a net negative charge. This charge is balanced by counterions. Charged zeolites readily adsorb water within the nanoscale cages, which hydrate the counterions much the same way that smectite clays expand in humid environments. The nanoscale size of zeolite cages combined with the presence of negative charge sites make zeolites extremely valuable materials for separation and catalysis applications.[111] Although unique force field parameters have been developed specifically for zeolites,[112] Clayff has also been used to model structural and dynamic properties of adsorbed species, both aqueous[19, 113] and organic.[114-115] In another study, Bushuev and Sastre[21] added angle bending terms to Clayff to study the role of water in forming structural defects in a siliceous zeolite. Additionally, zeolites and fibrous clays such as palygorskite and sepiolite also contain 1D channels that are ideal environments to investigate the properties of nanoconfined water using both molecular simulation and spectroscopy.[116-117]

Clayff has also been used to simulate aluminosilicate nanotubes such as imogolite (Figure 5g) and halloysite (Figure 5h). These phases consist of TO layers similar to kaolinite, but the sheets are curved to form single walled nanotubes (imogolite) or scrolls (halloysite). The curvature of these sheets results in additioal strain applied to the octahedral and tetrahedral layers, representing an accute test of Clayff parameters. Clayff has been used to study the effect

of nanotube diameter on phase stability,[118], as well as the properties of water or gases at the interior and exterior walls (Figure 5g).[109, 119-121]

3.7. Other Silicate Phases.

Like clay minerals, the local structure of framework silicates (*e.g.*, quartz, silica) and aluminosilicates (*e.g.*, feldspars; Figure 1f) is dominated by tetrahedrally coordinated silicon and aluminum atoms. Not surprisingly, Clayff is well suited to simulate these structures and their fluid interfaces (Figure 5c). However, modifications to Clayff parameters (atomic charges and L-J parameters) or additional constraints (*e.g.*, fixed atomic positions) are needed for atomic environments not included in the original force field. Many of these surfaces are terminated with hydroxyl groups, using the same harmonic O-H bond stretch term used for SPC water and layer hydroxyl groups. Kerisit and co-workers used Clayff to model orthoclase feldspar ($KAlSi_3O_8$) and forsterite (Mg_2SiO_4) and their fluid interfaces, with several modifications to Clayff for improved agreement with experimental structures.[44-45, 122] Quartz and silica phases (including amorphous silica) have also been simulated using Clayff, although some studies fixed the coordinates of silicon and oxygen atoms while allowing surface hydrogen atoms to move freely.[22, 123-127]

3.8. Mesoscale Structures.

Shortly after its introduction, MD simulation studies using Clayff for expanded interlayers began to appear in the literature.[66, 128-129] These model systems are often referred to as external surfaces or clay nanopores,[105, 130] and they serve as useful platforms to investigate the effect of fluid chemistry or pore size on adsorption and diffusion (Figures 5a and 6), and to help

better understand the structure of the electric double layer (EDL). For example, Greathouse and Cygan[128] studied the effect of carbonate concentration on U(VI) adsorption onto montmorillonite surfaces, and Kerisit and Liu[122] studied the effect of pore size on water diffusion near orthoclase surfaces. Water diffusion coefficients from Clayff simulations have also been used in multi-scale modeling of mesoscale clay structures.[131] Numerous Clayff studies based on nanopore models continue to be published each year for interfaces involving basal surfaces as well as hydroxylated edge surfaces. Almost all of the silica interfacial studies discussed previously used nanopore models. In recent years, such simulation studies are arguably more prevalent than those involving bulk interlayers.

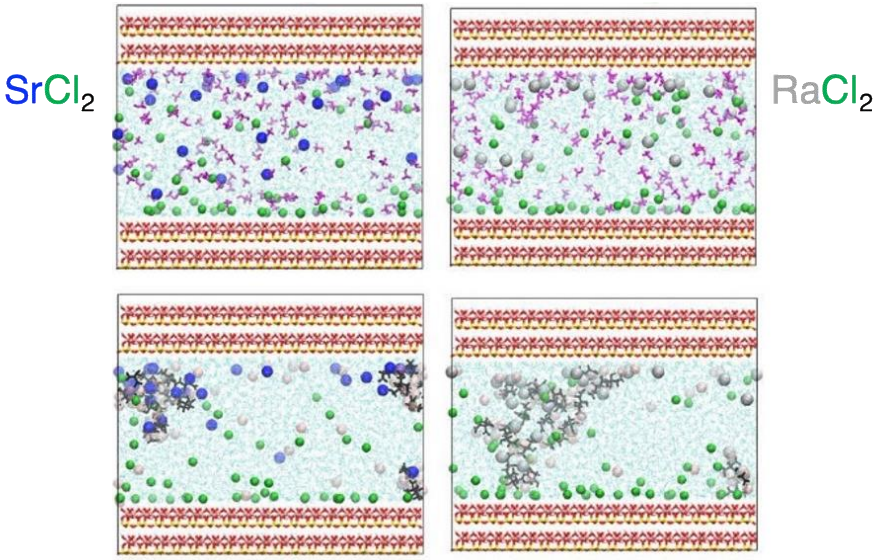

Figure 6. Snapshots of the equilibrated water-based fracturing fluids examined with methanol (top) and citric acid (bottom) additives in kaolinite mesopores, $SrCl_2$, and $RaCl_2$ salts at approximately 0.3 M concentration. Reprinted with permission from ref 67. Copyright 2018 American Chemical Society.

3.9. Mechanical Properties.

The nonbonded nature of Clayff also facilitates its use in modeling the response of layered minerals to mechanical stimuli. Fully-bonded force fields usually employ rigid harmonic

bond stretch and angle bending terms, resulting in more rigid layers that are less responsive to stress and strain.[26, 132-133] The assumption of most bonded interactions in Clayff as quasi-ionic, using a "softer" combination of L-J interaction and electrostatic attraction, results in a more dynamic response to stress and strain. For such a simple principally non-bonded force field, Clayff gives reasonable estimates of the cleavage and surface energy of layered materials[134] but leads to less accurate estimates of elastic properties.[20, 60, 135]

Rutledge and co-workers were the first to investigate mechanical properties of montmorillonite clay minerals using Clayff, initially investigating the strain dependence on vibrational frequencies,[136] and then determining elastic constants of a single clay particle (Figure 3a),[52] as well as expanded clays.[137-138] Coveney and co-workers used large-scale models (more than 100,000 atoms) of montmotillonite[139] and Mg-Al LDH[140] to calculate mechanical properties including bending moduli. More recently, similar methods have been applied to investigate mechanical properties of nonswelling clays,[91] cement-graphene nanocomposites,[141] aluminosilicate nanolayers and nanotubes,[142-143] and clay-polymer nanocomposites.[144] In another application invovling second-derivative properties, Clayff was recently used for atomistic simulations of the dielectric properties of swelling clays and their dependence on water saturation and frequency.[145]

3.10. Large-Scale Moleular Simulations.

Accessibility to larger and faster computational resources through massively parallel clusters and grid-exascale computing has allowed researchers to model clay mineral systems and properties that were previously considered impossible using fully-atomistic simulation methods. System sizes of a few nanometers are adequate for modeling many interfacial properties such as

adsorption geometries and energies, but the studies discussed below require system sizes of at least 10 nm and often simulation times of many tens of nanoseconds in order to thoroughly sample equilibrium properties. The large-scale models used by Coveney and co-workers to study mechanical properties of clays also served to illustrate undulatory behavior of individual clay layers.[139-140] They used similar system sizes to model polymers and biomolecules (RNA, DNA, and proteins) intercalated in clay mineral interlayers[85, 87-88, 146] (Figure 5e) and on mineral surfaces.[86, 102] Simulations used to obtain contact angles between hydrophobic (hydrophilic) fluid phases near hydrophilic (hydrophobic) mineral surfaces require system sizes on the order of 10 nm (Figure 5b),[18, 106, 147] while the temperature effects on rolling of kaolinite sheets into halloysite nanotubes has been modeled at length scales up to 200 nm (Figure 5h).[110] More recently, individual clay particles consisting of single TOT layers[148] (Figure 7) or multiple TO layers[149] have been used to model the aggregation of these phases under different sedimentation environments.

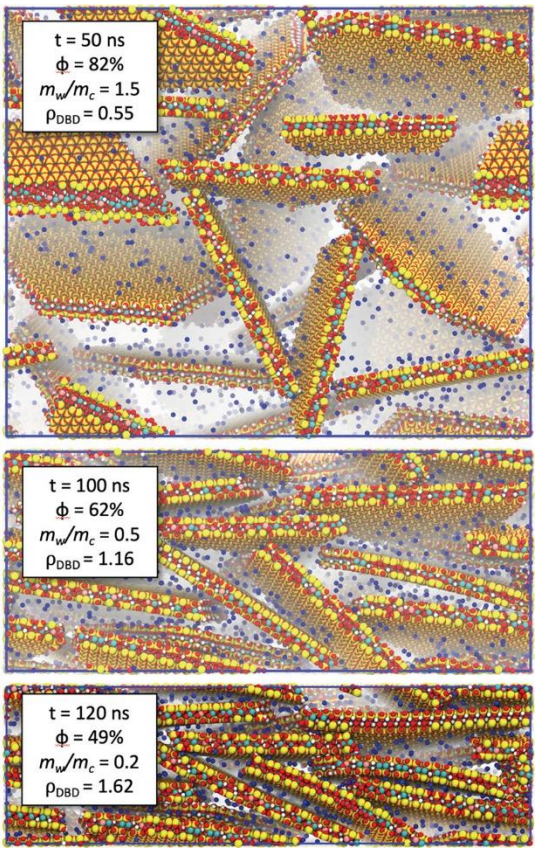

Figure 7. Snapshots of configurations predicted via MD simulation during the dehydration and compaction of a Na-montmorillonite clay suspension (water molecules not shown). The initial configuration (top) had minimal orientational correlations between clay particles, while the final structures present stacking features and correlations representative of the clay matrix. Reprinted with permission from ref 148. Copyright 2020 American Chemical Society.

4. ADVANCES IN CLAYFF

4.1. Truncated Surfaces and Edges.

A systematic effort to improve Clayff parameterization is currently ongoing along two directions important in view of future application: 1) making Clayff fully compatible with more complex and more accurate models of H_2O in order to improve the accuracy of description of the structural and dynamic behavior of substrate-water interfaces, and make it compatible with common force fields for organic substances;[150-151] and 2) the development of additional explicit

metal-O-H bending terms (Si-O-H, Al-O-H, etc.) which facilitate the accurate description of hydroxylated inorganic nanoparticle edges, including, for instance the edges of C-S-H particles.[152-153]

Molecular modeling of truncated mineral surfaces presents a unique challenge for classical forcefields that do not accommodate bond breaking or forming between adsorbed species and surface sites (*e.g.*, proton transfer). The structure and net charge of hydroxylated mineral surfaces often varies with pH, which in turn affects the properties of many mineral-fluid interfaces.[154-156] The pH-dependent adsorption behavior of clay minerals is attributed to interactions at edge surfaces due to the presence of hydroxyl groups from the octahedral sheet or from dissociative water adsorption at unstable surface sites resulting from crystal growth or dissolution processes. Accurate modeling of such interfaces is needed to predict the adsorption and transport of important solute species in the subsurface.[157-158]

A growing number of studies have used Clayff to model edge surfaces of clays and other layered minerals. Typical applications include the distribution of water and solute between pore fluids and interlayers,[23, 96, 159-161] adsorption at edge surfaces,[16, 162-164] and the simulation of nanoparticles.[148-149]

Once a molecular model for the desired edge surface is created, any dangling bonds must be repaired, typically by creating edge hydroxyl groups by adding –H (–OH) groups to MO– or M– sites, respectively. Unless surface atoms are simulated with fixed atomic position or restricted movement, these newly created edge hydroxyl groups must be simulated with additional intramolecular terms (bond stretch and/or angle bending) to prevent nonbonded hydroxyl groups from drifting into the fluid region. To accurately describe the O-H bond stretch in bulk clays or at hydroxylated surfaces, a Morse potential provides increased sensitivity to the

local environment which is important when simulating vibrational properties. Morse O-H bond parameters have been developed to replace the SPC harmonic term for H_2O in Clayff.[11] However, one can still use the original SPC water harmonic term for simplicity and when the O-H bond term is not likely to affect the results (*e.g.*, structural or transport properties at basal surfaces where layer hydroxyl groups have minimal impact on the interlayer).

Additional stability at cleaved surfaces and edges is achieved by using a three-body M-O-H angle bending term (M represents layer cations such as Al or Si). Importantly, such an angle term can be implemented while still maintaining the nonbonded pair interactions of Clayff. Parameters have been derived for cations in octahedral (Mg-O-H and Al-O-H) and tetrahedral (Si-O-H) coordination.[152-153, 165] The new Clayff parameterization of the Al-O-H bending terms[152] has been recently successfully used to accurately reproduce the complex phase-sensitive vibrational sum frequency generation spectra of water on a fully hydroxylated (0001) surface of alumina.[166] Zhang and coworkers[108] have recently used the extended potentials(Pouvreau et al., 2017) of Clayff to model the interaction of soil organic matter with basal and edge surfaces of clay nanoparticles (Figures 5f and 5i).

The other important consideration for newly created edge surfaces is the assignment of appropriate atomic charges. Atom types for edge hydroxyl groups were not included in the original parameter set. Three approaches have been used to assign atomic charges for neutral edge surfaces: 1) use existing Clayff charges;[159, 165] 2) assign new charges for hydroxyl groups and connecting atoms based on a bond valence approach;[44, 96] and 3) assign charges by comparing with quantum (DFT) calculations.[163, 167] In the case of octahedrally coordinated edge cations (*e.g.*, Mg, Al), a neutral surface is obtained from original Clayff charges if one edge hydroxyl group is removed. However, physisorption of a water molecule completes the six-fold

coordination. As suggested in Figure 2, deprotonated octahedral edge sites can then be created by removing a H atom from an adsorbed water molecule and making slight adjustments, if necessary, to the hydroxyl O charge.[164]

4.2. Interlayer and Pore Fluids.

Clayff has been used to simulate the interaction of many fluid and gaseous species near basal and edge surfaces. In many instances, bulk properties of the fluid are well described by a self-consistent set of force field parameters, but interaction parameters between fluid species and mineral surfaces have not been derived for specific fluid-surface pairs. Since many force fields also use a L-J expression to describe van der Waals interactions, parameters for specific fluid-surface interactions between unlike atom types (off-diagonal parameters) can be obtained using the standard Lorentz-Berthelot combining rules (Equation 4).

Clayff was originally parameterized to be consistent with the simple point charge (SPC) water model[10] with a simplest harmonic approximation for the intramolecular motions.[168] However, later its more accurate version SPC/E[169] was also successfully used.[53, 59] More complex anharmonic terms can also be used to describe the bond bending and stretching terms of the structural –O-H groups and interfacial H_2O molecules for accurate simulation and interpretation of their vibrational properties.[11, 151, 165] There were also attempts to use a more complex four-point-charge TIP4P model of H_2O[170] together with Clayff.[107, 171] Improved and more accurate L-J parameters for monovalent and divalent cations compatible with SPC, SPC/E, and other water models have recently been published,[172-173] and can be successfully implemented in Clayff to describe cation-water and other metal cation interactions.

Several recent studies have demonstrated a very good agreement of the 2-D and 3-D interfacial aqueous solution structures at heterogeneously charged basal and edge surfaces of clay nanoparticles simulated with Clayff with results from experimental atomic force microscopy (AFM) observations.[174-177] These studies illustrate the value of using molecular simulations as a tool in the atomistic-scale interpretation of complex AFM results.

One of the most common applications of Clayff is the simulation of organic species near mineral surfaces. Clayff was originally developed for compatibility with the Consistent Valence force field (CVFF),[178] which also uses the flexible SPC water model. Thus, the early Clayff simulations of mineral-organic systems combined Clayff for the surface atoms and CVFF for the organic molecules. Other mineral-organic systems have included polymers[89, 138, 179] and biological compounds, including constituents of amino acids and natural organic matter (Figures 5f and 5i).[38, 68, 108] Figure 8 shows stages in the polymer intercalation process from coarse-grained MD simulation.[179] This multiscale modeling approach incorporates properties from quantum calculations and Clayff simulation.

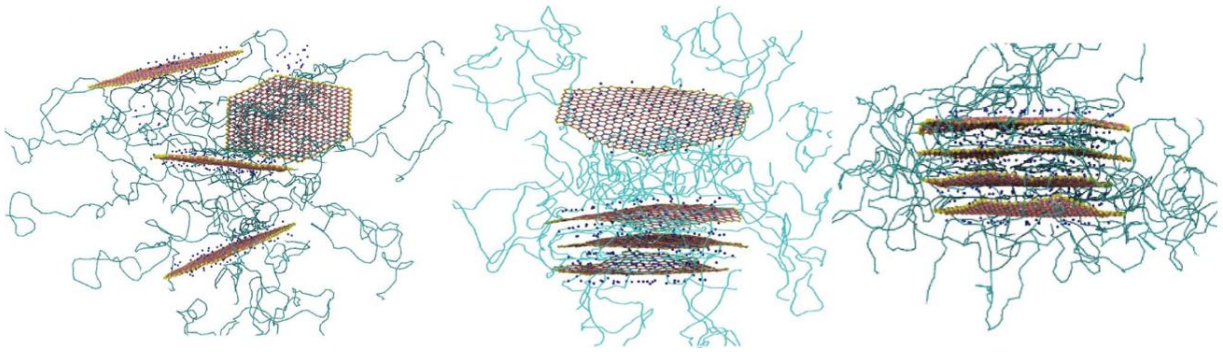

Figure 8. Snapshots from coarse-grained MD simulation showing the intercalation of polyethylene glycol (turquoise strands) in Na-montmorillonite interlayers. Each hexagonal clay particle has lateral dimensions of approximately 100 Å. Reprinted with permission from ref 179. Copyright 2015 Wiley-VCH.

Potentials for organic compounds from the OPLS force field[180] can also be implemented with Clayff. Geoscience applications have included interlayer CO_2,[181] and methane,[182-183] as well as methane hydrates.[184-185] Several computational studies have investigated CO_2 and H_2O mixtures in smectite interlayers to better assess the role of carbon sequestration in mitigating climate change.[17, 186-187]

In most cases, when modeling such hybrid systems, the resulting off-diagonal L-J terms governing adsorption and other nonbonded interactions have not been explicitly validated, although comparisons between Clayff-CVFF and quantum chemical methods have been made.[65] Off-diagonal parameters have been derived for specific interfaces,[163, 188] but this involves a great deal of quantum chemical calculations and fitting. Nonetheless, when combining Clayff with other general force fields or atom types, it is important to check that both force fields use the same combining rules (Equation 4). It is worth noting that Heinz and coworkers have streamlined the process of developing off-diagonal parameters for modeling organic species near silicate surfaces based on the INTERFACE force field.[26]

Some researchers have modified Clayff parameters in order to fit experimental or DFT-calculated properties for specific minerals or interfaces. Kerisit and coworkers have made several adjustments to Clayff L-J parameters and partial charges to improve agreement with experiment for feldspar[44], hematite,[189] and forsterite,[45] and gibbsite.[167] Adjustments to the bridging oxygen (ob) L-J parameters have been made to improve agreement with X-ray diffraction data.[59, 151] Recently, Ho et al.[190] showed that thermodynamic properties of interlayer hydration and clay swelling are quite sensitive to the L-J parameters describing the interaction of aqueous cations with bridging oxygen atoms of the surface (ob). Adjustments to a subset of Clayff parameters are usually not checked for validity with other phases in the original training set, so they are not

considered to be implicitly transferrable. Recently, Findley and coworkers[191] have successfully used Clayff as a basis for the development of a specifically transferable force field for predicting adsorption and diffusional mobility of hydrocarbons and small molecules in silica zeolites.

5. FUTURE DIRECTIONS

The last thirty years have seen a rapid and continuous growth in the use of computer simulation tools to investigate the molecular structure and behavior of layered materials and their interfaces that are critical to understanding the safe treatment and long-term isolation of chemical contaminants, including radionuclides, in the environment.[157, 192] The physical and chemical properties of clay minerals, in particular, suggest their significant role in controlling adsorption processes and in limiting metals and organics into natural water systems that could potentially impact the quality of drinking waters. Advances in microscopy, spectroscopy, and new analytical methods have helped researchers to better evaluate the mechanisms of these complex processes; however, details derived from molecular simulations are often required to supplement these methods and, in some cases, due to nano-sized and disordered or impure nature of natural clay samples, remain the only basis for understanding such processes.

Use of the Clayff energy force field in molecular simulations of layered materials has proven to be a valuable approach in these efforts. However, there remain several unique challenges for researchers in expanding and improving the accuracy of such simulations using Clayff, or other sets of potentials. One such area is the accurate simulation of the siloxane sheet structure that comprises the basal surface of many clay minerals. Results from Clayff simulations of clay phases typically exhibit hexagonal symmetry for the ring structure of the siloxane sheet. Polarizability is not the only way to introduce asymmetry. Adding bond-angle terms and

adjusting VDW sigma diameters can also induce asymmetry. Even with Al substitution for Si atoms on this sheet, as found in some smectite minerals, one would expect to reduce the symmetry of the ring to ditrigonal while collapsing the size of the ring. Cation adsorption onto the basal siloxane surface may be overestimated by the more open ring structure observed in the molecular simulations.[190] Incorporation of polarization terms in classical potentials, based on DFT calculations, has led to recent improvements in modeling the rotation and tilt of tetrahedra in the tetrahedral sheet of montmorillonite, and in predicting the ditrigonal symmetry for the ring structure.[32-33, 193] Nonetheless, more work is needed to properly account for ionic and electronic polarization mechanisms within the framework of Clayff potentials.

Incorporating Clayff parameters in various molecular simulation codes is a straightforward process due to the nonbonded nature of the potentials. This leads to a practical and less costly approach for MD simulations that avoids having to describe bonded atom pairs that require continuous monitoring and updating during a simulation run. Although no bond between a metal and a single oxygen is explicitly defined, the Clayff interatomic potential derives a total "bond" energy in assuming the proper coordination of oxygens about the charged metal center and calculating the "bond" energy of the cluster (*e.g.*, SiO_4, MgO_6, etc.). As long as the interatomic potentials are accurately derived from the empirical fits based on refinements of simple oxide and hydroxide crystal structures, this approach can be efficient and practical, although less analogous to defining an explicit M-O bond.

Clayff was developed using a consistent set of partial charges for each atom type in the force field. Values were initially derived from quantum chemical calculations and then adjusted accordingly to accommodate substitutional schemes, the stoichiometry of simulation cells for bulk phases, and to make the entire charge distribution scheme consistent with the model for

H_2O molecules and aqueous species. However, simulations involving surface species (*e.g.*, edge sites), where metal coordination changes from that of the bulk environment, can become problematic when assigning partial charges. We have summarized some of the recent work in developing new Clayff potentials for these edge sites and recognize the difficulty in maintaining universal partial charges. Future development of Clayff for such sites may help guide further work on a partial charge scheme that could be easily applied to all surface sites and help guide improved potentials for protonation-deprotonation structures.

There are additional improvements that could be made to Clayff potentials. The original parameters for the nonbonded potential terms (i.e., ε and σ of the 6-12 L-J potential) could be scaled by reducing the size of the sigma terms to be consistent with physical L-J radii. In addition, it would be beneficial to practitioners to avoid combining rules when identifying L-J parameters for specific atom-atom interactions, the off-diagonal terms. This would require reporting explicit pair-interaction parameters rather than relying on diagonal terms and combining rules. Such an approach is now easier to implement with the increased use of preprocessing scripts to prepare input files. Explicit inclusion of the off-diagonal terms would also help avoid the pitfalls in using automated software to define such interactions that often confuse the user and lead to improper simulation results. Nonetheless, in part because of convention, we continue to report nonbonded potentials in terms of single atom types (diagonal format). Simulations of organic-mineral systems (*e.g.*, clay-polymer composites) are often limited by the lack of appropriate nonbonded potentials thereby requiring users to arbitrarily combine Clayff potentials with general organic force fields by means of various combining rules. Such an approach requires a critical eye to properly judge the worthiness of the simulation results.

Further development of Clayff should include how best to improve bonded potentials, especially for modeling metal-hydroxyl behavior in either bulk or surface structures. Our recent work has demonstrated that angle bending potentials involving metal hydroxyls need to be customized for specific hydroxyl environments.[152-153, 165] Can bulk Clayff terms be simply reparameterized for surface or interfacial structures or do completely new potentials need to be developed? Additional development work is required to accurately model Fe-O-H and Ca-O-H potentials for clay edge environments.

Lastly, much effort has been spent by van Duin and others in the development of ReaxFF[194-195] to explicitly incorporate chemical reaction dynamics into classical atomistic simulations. Incorporation of acid-base reactions such as the protonation and deprotonation of edge sites of clay minerals, or the reaction of interlayer species, would greatly broaden the predictive capabilities of such simulations for many environmentally complex and technologically important processes. Mapping potential reaction pathways associated with the interaction of aqueous solutions and clay minerals will involve substantial quantum chemical calculations coupled with machine learning methods to develop validated parameters for Reaxff.[196-197] Nonetheless, combining the reactivity of ReaxFF, or machine-learned potentials, with Clayff potentials would significantly improve simulation accuracy and greatly expand the general application of these predictive methods.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

SUPPORTING INFORMATION

A short discussion of Clayff, including analytical expressions and parameters for interatomic potentials parameters, is provided in the Supporting Information section. Nonbonded and bonded parameters are tabulated, and include values for surface/edge sites. Sample computer input files with Clayff parameters are presented for several commonly-used molecular simulation programs.

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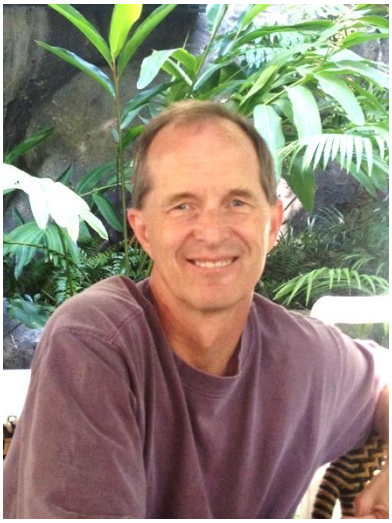
Biographies



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