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MOLECULAR COMPUTER SIMULATIONS OF
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RECENT PROGRESS, CHALLENGES, AND
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INTRODUCTION TO A SPECIAL ISSUE ON MOLECULAR COMPUTER SIMULATIONS OF CLAYS AND CLAY–WATER INTERFACES: RECENT PROGRESS, CHALLENGES, AND OPPORTUNITIES

ANDREY G. KALINICHEV^{1,*†}, XIANDONG LIU^{2,†}, AND RANDALL T. CYGAN^{3,†}

¹ Laboratoire SUBATECH (UMR 6457), Ecole des Mines de Nantes, 44307 Nantes, France

² State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, P.R. China

³ Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

Over recent years, a steady increase has been noted in the publication of research articles in *Clays and Clay Minerals* which have included the use of molecular simulation methods. Based on a keyword search of *Web of Science*, the number of molecular simulation papers has increased from zero during the first four decades of the journal to five during the late 1990s, to 14 in the 2000s, to 36 so far in the 2010s including those published in this special issue. Most research papers using computational molecular modeling approaches to study the properties of clays and clay-related systems and their practical applications are published in the broader materials science and chemical engineering literature.

The clay-minerals community has taken quite a long time to embrace the technical insights associated with using a molecular modeling approach. Not only does a molecular basis help to develop and test crystallographic models of clay structures, it provides critical insight into understanding the fundamental mechanisms that control many physical and chemical properties, thermodynamics, kinetic processes, and reactivity. Molecular simulations help in the interpretation of spectroscopies and microscopies, and in many other critical issues associated with the behavior and dynamics of clay mineral systems. Though clearly not a panacea for all technical challenges in clay mineralogy, molecular models and simulations provide a solid theoretical context to enable us to delve deeper into the fundamental mechanisms of our science.

The physical nature of clay minerals presents the challenge for examining clay mineral systems from a molecular perspective. A combination of micron-scale character of clay minerals and the stacking disorder of clay platelets limits our technical ability to fully evaluate atomic positions and crystal structures of these common materials found in soils and sediments. The low crystal symmetry of clays and their multi-component compositions, atomic defects, atomic site and

layer stacking disorder, variable water content, and related issues present significant challenges for the characterization of clays and clay minerals with atomic-scale detail. Fortunately, computational chemistry methods involving classical potential energy force fields and first principles (*i.e. ab initio*) methods provide a practical alternative for evaluating the structure and behavior of clay minerals on an atomistic and electronic basis.

The so-called classical methods of molecular simulations can be roughly divided into two groups: deterministic and stochastic. Accordingly, they are often referred to as methods of molecular dynamics (MD) and Monte Carlo (MC). In both cases the simulations are typically performed for a relatively small number of interacting particles (atoms, ions, and/or molecules; $1000 < N < 1,000,000$) confined in a box (the simulation cell). Molecular computer simulations generate a large number of instantaneous atomic configurations, and with the help of statistical mechanics, yield directly many useful thermodynamic, structural, and transport properties from the microscopic information about instantaneous atomic positions and velocities. These simulations make possible the calculation of pressure, temperature, internal energy, heat capacity, interatomic distances, coordination numbers, radial distribution functions, diffusion coefficients, and the spectra of vibrational, rotational, and translational atomic motions for the simulated systems (*e.g.* McQuarrie, 2000).

In MD simulations, all individual particles in the simulation box are given initial positions and velocities, and the Newtonian equations of motion are integrated numerically over time for all interacting particles in the simulated system. The size of the time step for integration depends on temperature, density, the masses of the particles, the interparticle potentials, the detail of information sought, and the numerical stability of the integration algorithm. For clay-related systems the time step is typically of the order of a femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$), and the dynamic trajectories of the particles are usually followed for 10^5 – 10^7 time steps after a period of thermodynamic pre-equilibration. The resulting record of the trajectories of the particles (*i.e.*

* E-mail address of corresponding author:

kalinich@subatech.in2p3.fr

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† Guest editors

their positions and velocities, and if they are molecules, their orientations and angular velocities) is a complete description of the system in a classical mechanical sense. The thermodynamic, structural, spectroscopic, and transport properties of the system can then be calculated from the ‘time averages’ of these parameters.

In MC simulations new atomic configurations in the system are generated randomly, but are then selected in a specific way that ensures that each new microscopic configuration of atoms represents the same macroscopic thermodynamic state. Usually, many millions of such configurations are generated, and the thermodynamic and structural properties of the system simulated are then calculated as ‘averages over the ensemble of configurations.’

In quantum-based simulations the potential energy of the model is calculated iteratively by approximate solutions of the Schrödinger equation describing the quantized energies of electrons in the system, rather than considering an empirical ball-and-spring model of atoms as used in classical models. The price to pay in quantum-based approaches is the much greater computational cost to derive iterative solutions and obtain convergence, but advances in supercomputing hardware and software are systematically reducing the computational cost of these quantum-based methods.

This special issue of *Clays and Clay Minerals* brings together a large group of researchers currently active in using molecular simulations to understand the electronic and molecular behavior of clay minerals and clay mineral processes. They illustrate and summarize many of the most recent developments in the field that happened over the last 10–15 years since the previous such publication of The Clay Minerals Society (Kubicki and Bleam, 2003). The research articles include authors from numerous countries, and represent a diversity of topics and simulation methods. Research highlights include the analysis of the structure and dynamics of water and cations in the interlayer (Escamilla-Roa, 2016; Ferrage, 2016; Scholtzova *et al.*, 2016; Szczerba *et al.*, 2016; Tournassat *et al.*, 2016; Zhou *et al.*, 2016), adsorption onto external surfaces of clay minerals including an analysis of the significance of edge sites (Kerisit *et al.*, 2016; Kremleva and Krüger, 2016; Underwood *et al.*, 2016; Zhang *et al.*, 2016), intercalation of organic molecules (Scholtzova *et al.*, 2016; Szczerba and Kalinichev, 2016), multiscale modeling with links to macroscopic properties of clay (Ebrahimi *et al.*, 2016; Tournassat *et al.*, 2016). Based on the comparisons with X-ray and neutron diffraction, NMR and IR spectroscopy, the authors are also suggesting ways to improve the accuracy of classical force fields for molecular simulations of clays (Ferrage, 2016; Szczerba and Kalinichev, 2016; Szczerba *et al.*, 2016). The editors hope that this diversity of research topics and presentation of state-of-the-art simulation methods will help the clay-minded reader recognize the wealth of molecular

detail that can be obtained by these theoretical approaches. As the content of this special issue reveals, molecular simulation in clay mineralogy has matured to an established and, perhaps, indispensable part of the scientific toolbox. The clay mineralogy community will continue to benefit by participating in its use.

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