NE-M1-PRI12ENP – Integrated Nuclear Engineering Project

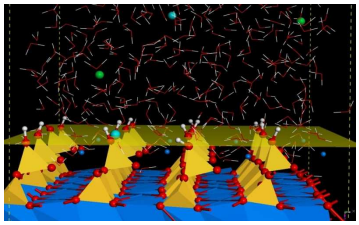
Molecular Modeling of Materials for Nuclear Engineering Applications

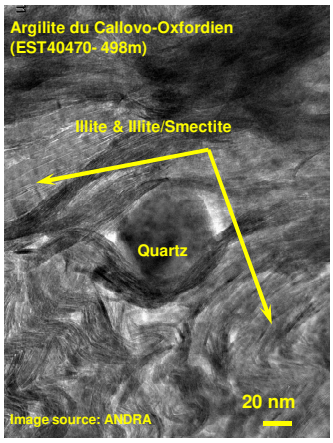
Lecture 1 – Introduction and Overview

Andrey G. Kalinichev

Laboratoire SUBATECH
Institut Mines-Télécom Atlantique

Office: H010

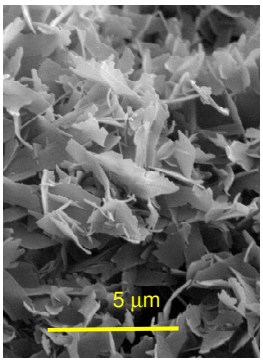




E-mail: ***kalinich@subatech.in2p3.fr***
https://www.imt-atlantique.fr/en/person/andrey-kalinichev

Objectives

- ***NE-M1-PRI12ENP (Integrated Nuclear Engineering Project)*** is an **overview course/project** for students in the SARENA international NE master program at the Institut Mines-Télécom Atlantique that introduces the methods and techniques of computational molecular modeling and their application to the fundamental understanding of the atomic- and molecular-level origins of physical and chemical properties of materials and processes related to nuclear engineering applications.
- The course is **particularly intended for students with relatively limited background in theoretical and molecular materials science**, but who need to know some fundamental basics of molecular modeling techniques in order to better understand modern approaches and current scientific literature on computational molecular modeling of materials relevant to nuclear waste management.
- **No previous experience in molecular modeling is required**



Syllabus

- Physico-chemical properties of materials relevant to nuclear engineering and environmental applications: metals, minerals, glasses, ceramics, cement, soil
- Brief introduction to statistical thermodynamics
  - Mechanical state *vs* thermodynamic state of a system; partition function
  - Macroscopic properties of materials from statistical thermodynamics
  - Egrodicity; time averages *vs* ensemble averages
- Monte Carlo (MC) molecular computer simulation techniques
- Molecular dynamics (MD) computer simulation techniques
- Periodic boundary conditions
- Intermolecular potentials (force fields) for atomistic simulations
  - Ab initio *vs* empirical potentials
  - Many body interactions
  - Molecular models of water
  - Hydrated ions

Syllabus (2)

- Calculation of macroscopic properties of materials from MC and MD simulations
  - Thermodynamic properties
  - Structural properties, radial distribution functions (RDFs), coordination numbers
  - Mean square displacement (MSD) and self-diffusion coefficients
  - Velocity autocorrelation functions (VACFs)
  - Power spectrum (density of states) of atomic motions
  - Dielectric properties
- Hydrogen bonding in aqueous systems
  - Geometric, energetic and other criteria of H-bonding
  - Donating and accepting H-bonds; local tetrahedrality of the water structure
  - Statistical analysis of H-bonding
  - Variations of H-bonding with thermodynamic state conditions and local molecular environment around ions and at interfaces

Syllabus (3)

- Interfaces of aqueous solutions with inorganic substrates
  - Molecular models of inorganic surfaces: oxides, hydroxides, clays, zeolites and other minerals
  - Rigid *vs* flexible substrate
  - Structure, energetics, and dynamics of aqueous interfaces and interlayers
  - Hydrophobic and hydrophilic surfaces
  - Local electrostatic fields and orientation of surface H_2O molecules
  - Ionic hydration and transport of H_2O and ions at the mineral surfaces
  - Energetics of adsorption at mineral surfaces
- Molecular models of organic matter and its interactions with metal cations
  - Molecular models of NOM (humic and fulvic acids)
  - Interaction of metal cations with NOM: Structure, energetics and dynamics
  - Molecular models of a generalized 3-component system: clay-metals-organics
  - Molecular modeling of bio-molecules
- Advanced simulation techniques: free energy calculations, ab-initio MD, metadynamics, etc.

Hands-on Computer Exercises Using *Materials Studio 6.0* Modeling Software

- Building the models of clays and other materials interfaces for computational molecular modeling: Illite, smectite, quartz, calcite, cement phases, amorphous silicate glass.
- Selecting force fields for molecular simulations
- Using molecular mechanics, energy minimization and structure optimization techniques
- Preparing input parameters for molecular dynamics simulations of the selected systems for individual research projects

Hands-on Computer Exercises (2)

- Running MD simulations of the selected systems
- Quantitative analysis of the MD computer simulation results
  - Thermodynamic properties of aqueous solutions and hydrated interfaces
  - Structure of aqueous solutions in the bulk phase and at the interfaces
  - Diffusion and mobility of hydrated anionic, cationic and neutral species
  - Velocity autocorrelation functions and power spectra of atomic motions in aqueous solutions in the bulk phase and at the interfaces
  - Atomic density profiles and surface density maps of aqueous species from interfacial simulations

Grading Policy

- Participation in the class - 25%
- Exercises - 25%
- Individual research project - 50%

Web-page of the course and all materials:

https://moodle.imt-atlantique.fr/course/view.php?id=407

Literature

Relatively Introductory

- Hinchliffe A (2003) *Molecular Modeling for Beginners*, John Wiley & Sons Ltd, 410pp.
- Kubicki, J. D. (2016) *Molecular Modeling of Geochemical Reactions: An Introduction*. John Wiley & Sons, Inc., 440p.
- Schlick T (2002) *Molecular modeling and simulation: an interdisciplinary guide*, Springer, 634p
- Leach AR (2002) *Molecular Modelling: Principles and Applications*", 2d Ed., Prentice Hall, 744p
- Sainz-Díaz CI (ed.) (2021) *Computational Modeling in Clay Mineralogy,* AIPEA Educational Series, v.3, Digilabs Pub., Bari, Italy, 282p (**https://aipea.org/publications/**)

General Statistical Mechanics

- Chandler D (1987) *Introduction to Modern Statistical Mechanics*. Oxford University Press, 274p
- Hansen JP, McDonald IR (1986) *Theory of Simple Liquids*. Academic Press, 556p
- Landau LD, Lifshitz EM (1978) *Statistical Physics*. Pergamon Press, Oxford, 544p
- McQuarrie DA (1976) *Statistical Mechanics*. Harper & Row, New York, 641p

Molecular Simulations Theory

- Allen MP, Tildesley DJ (1987) *Computer Simulation of Liquids*. Oxford University Press, 385p
- Allen MP, Tildesley DJ (2017) *Computer Simulation of Liquids*. 2nd Ed., Oxford University Press, 626p
- Frenkel D, Smit B (2002) *Understanding Molecular Simulation: From Algorithms to Applications*. Academic Press, 638p
- Rapaport DC (2004) *The Art of Molecular Dynamics Simulation*. 2nd Ed., Cambridge Univ. Press, 549p

Internet Resources

General

- http://www.ccl.net/ - Computational Chemistry Web-Site
- http://www.lsbu.ac.uk/water/ - Water Structure and Behavior
- http://www.accelrys.com/sim/ - Molecular Modeling and Simulation
- http://www.fisica.uniud.it/~ercolessi/md/md/ - A Molecular Dynamics Primer (Furio Ercolessi, University of Udine, Italy)

Free MC & MD Software

- http://www.cse.clrc.ac.uk/msi/software/DL_POLY/ - DL_POLY
- http://www.gromacs.org/ - GROMACS
- http://lammps.sandia.gov/ - LAMMPS
- http://www.ks.uiuc.edu/Research/namd/ - NAMD
- http://www.emsl.pnl.gov/docs/nwchem/ - NWChem
- http://towhee.sourceforge.net/ - Towhee
- http://www.ccp5.ac.uk/librar.shtml - A library of MC & MD software

Visualization

- http://www.ks.uiuc.edu/Research/vmd/ - Visual MD
- http://alum.mit.edu/www/liju99/Graphics/A - AtomEye
- https://ovito.org/ - OVITO (open visualization tool)

Research Papers for Discussion (1)

- Cygan RT, Molecular Modeling in Mineralogy and Geochemistry. *Rev Mineral Geochem* **42**, 136.
- Guillot B (2002) A reappraisal of what we have learnt during three decades of computer simulations on water. *Journal of Molecular Liquids* **101**, 219-260.
- Cygan RT, Liang J-J, and Kalinichev AG (2004) Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. *J Phys Chem B* **108**, 1255-1266.
- Luzar A (2000) Resolving the hydrogen bond dynamics conundrum. *J.Chem.Phys.* **113**, 10663-10675.
- Kalinichev AG (2001) Molecular simulations of liquid and supercritical water: Thermodynamics, structure, and hydrogen bonding. *Rev Mineral Geochem* **42**, 83–129.
- Rustad JR (2001) Molecular models of surface relaxation, hydroxylation, and surface charging at oxide-water interfaces. *Rev Mineral Geochem* **42**, 169-197.
- Whitley HD, Smith DE (2004) Free energy, energy, and entropy of swelling in Cs-, Na-, and Sr-montmorillonite clays. *J Chem Phys* **120**, 5387-5395.
- Arab M, Bougeard D, Smirnov KS (2004) Structure and dynamics of interlayer species in a hydrated Zn-vermiculite. A molecular dynamics study. *PCCP* **6**, 2446-2453.
- Qiao R and Aluru NR (2004) Multiscale Simulation of Electroosmotic Transport Using Embedding Techniques. *International Journal for Multiscale Computational Engineering* **2**, 173-188.
- Enciso E, Almarza NG, Murad S, Gonzalez MA (2002) A nonequilibrium molecular dynamics approach to fluid transfer through microporous membranes. *Mol. Phys.*, **100**, 2337-49 (2002).
- Diallo MS, Simpson A, Gassman P, Faulon JL, Johnson JH, Goddard WA, Hatcher PG (2003) 3-D structural modeling of humic acids through experimental characterization, computer assisted structure elucidation and atomistic simulations. 1. Chelsea soil humic acid. *Env. Sci. Technol.* **37**, 1783-1793.
- Finney JL (2004) Water? What's so special about it? *Phil. Trans. R. Soc. Lond. B* **359**, 1145-1165.
- Sutton R, Sposito G, Diallo MS, Schulten HR (2005) Molecular simulation of dissolved organic matter. *Environmental Toxicology and Chemistry* **24**, 1902-1911.

Research Papers for Discussion (2)

- Suter, J. L., Anderson, R. L., Greenwell, H. C., and Coveney, P. V., 2009. Recent advances in large-scale atomistic and coarse-grained molecular dynamics simulation of clay minerals. *Journal of Materials Chemistry* **19**, 2482-2493.
- Anderson, R. L., Greenwell, H. C., Suter, J. L., Coveney, P. V., and Thyveetil, M.-A., 2009. Determining materials properties of natural composites using molecular simulation. *Journal of Materials Chemistry* **19**, 7251-7262.
- Greenwell, H. C., Jones, W., Coveney, P. V., and Stackhouse, S., 2006. On the application of computer simulation techniques to anionic and cationic clays: A materials chemistry perspective. *Journal of Materials Chemistry* **16**, 708-723.
- Cygan, R. T., Greathouse, J. A., Heinz, H., and Kalinichev, A. G., 2009. Molecular models and simulations of layered materials. *Journal of Materials Chemistry* **19**, 2470-2481.
- Greathouse, J. A. and Cygan, R. T., 2006. Water structure and aqueous uranyl(VI) adsorption equilibria onto external surfaces of beidellite, montmorillonite, and pyrophyllite: Results from molecular simulations. *Environmental Science & Technology* **40**, 3865-3871.
- Skipper, N. T., Lock, P. A., Titiloye, J. O., Swenson, J., Mirza, Z. A., Howells, W. S., and Fernandez-Alonso, F., 2006. The structure and dynamics of 2-dimensional fluids in swelling clays. *Chemical Geology* **230**, 182-196.
- Sposito, G., Skipper, N. T., Sutton, R., Park, S. H., Soper, A. K., and Greathouse, J. A., 1999. Surface geochemistry of the clay minerals. *Proc Natl Acad Sci U S A* **96**, 3358-3364.
- Iskrenova-Tchoukova, E., Kalinichev, A. G., and Kirkpatrick, R. J., 2010. Metal Cation Complexation with Natural Organic Matter in Aqueous Solutions: Molecular Dynamics Simulations and Potentials of Mean Force. *Langmuir* **26**, 15909-15919.
- Wang, J. W., Kalinichev, A. G., and Kirkpatrick, R. J., 2006. Effects of substrate structure and composition on the structure, dynamics, and energetics of water at mineral surfaces: A molecular dynamics modeling study. *Geochimica et Cosmochimica Acta* **70**, 562-582.

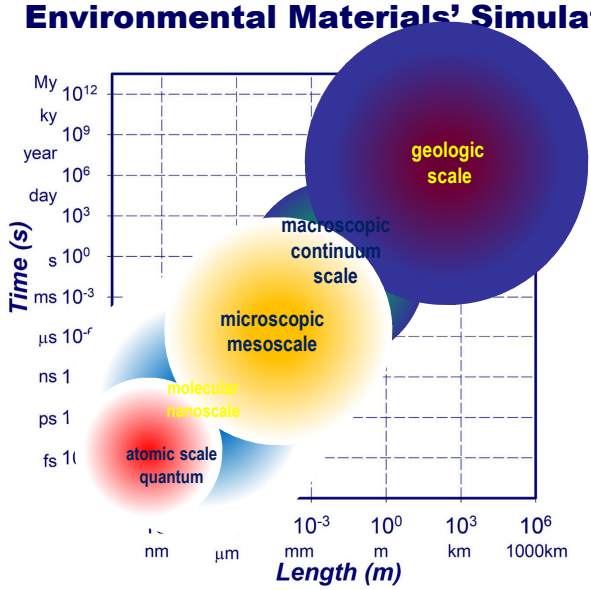
Research Papers for Discussion (3)

- Meleshyn, A., 2010. Adsorption of Sr2+ and Ba2+ at the cleaved mica-water interface: Free energy profiles and interfacial structure. *Geochimica Et Cosmochimica Acta* **74**, 1485-1497.
- Bougeard, D. and Smirnov, K. S., 2007. Modelling studies of water in crystalline nanoporous aluminosilicates. *Physical Chemistry Chemical Physics* **9**, 226-245.
- Joseph, S. and Aluru, N. R., 2006. Hierarchical Multiscale Simulation of Electrokinetic Transport in Silica Nanochannels at the Point of Zero Charge. *Langmuir* **22**, 9041-9051.
- Rotenberg, B., Marry, V., Malikova, N., and Turq, P., 2010. Molecular simulation of aqueous solutions at clay surfaces. *J. Phys.-Condes. Matter* **22**, 284114.
- Marry, V., Rotenberg, B., and Turq, P., 2008. Structure and dynamics of water at a clay surface from molecular dynamics simulation. *Physical Chemistry Chemical Physics* **10**, 4802-4813.
- Rotenberg, B., Marry, V., Vuilleumier, R., Malikova, N., Simon, C., and Turq, P., 2007. Water and ions in clays: Unraveling the interlayer/micropore exchange using molecular dynamics. *Geochimica et Cosmochimica Acta* **71**, 5089-5101.
- Bourg, I. C. and Sposito, G., 2010. Connecting the Molecular Scale to the Continuum Scale for Diffusion Processes in Smectite-Rich Porous Media. *Environmental Science & Technology* **44**, 2085-2091.
- Bourg, I. C., Bourg, A. C. M., and Sposito, G., 2003. Modeling diffusion and adsorption in compacted bentonite: a critical review. *Journal of Contaminant Hydrology* **61**, 293-302.
- Bonnaud, P. A., Coasne, B., and Pellenq, R. J. M., 2010. Molecular simulation of water confined in nanoporous silica. *J. Phys.-Condes. Matter* **22**, 284110.
- Kerisit, S. and Liu, C., 2010. Molecular simulation of the diffusion of uranyl carbonate species in aqueous solution. *Geochimica Et Cosmochimica Acta* **74**, 4937-4952.
- Spagnoli, D., Gilbert, B., Waychunas, G. A., and Banfield, J. F., 2009. Prediction of the effects of size and morphology on the structure of water around hematite nanoparticles. *Geochimica Et Cosmochimica Acta* **73**, 4023-4033.

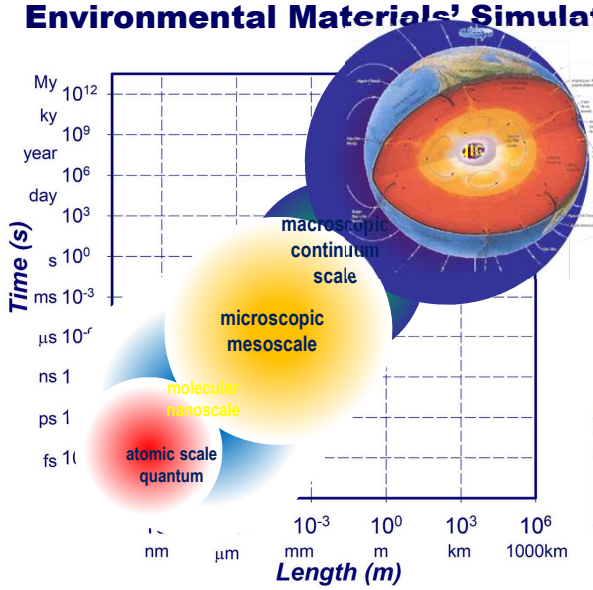
Research Papers for Discussion (4)

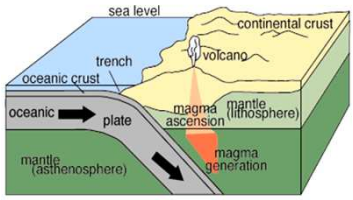
- Allen, J. P., Gren, W., Molinari, M., Arrouvel, C., Maglia, F., and Parker, S. C., 2009. Atomistic modelling of adsorption and segregation at inorganic solid interfaces. *Molecular Simulation* **35**, 584-608.
- Sakuma, H. and Kawamura, K., 2009. Structure and dynamics of water on muscovite mica surfaces. *Geochimica Et Cosmochimica Acta* **73**, 4100-4110.
- Wang, J., Kalinichev, A. G., and Kirkpatrick, R. J., 2009. Asymmetric Hydrogen Bonding and Orientational Ordering of Water at Hydrophobic and Hydrophilic Surfaces: A Comparison of Water/Vapor, Water/Talc, and Water/Mica Interfaces. *The Journal of Physical Chemistry C* **113**, 11077-11085.
- Sutton, R. and Sposito, G., 2006. Molecular simulation of humic substance-Ca-montmorillonite complexes. *Geochimica Et Cosmochimica Acta* **70**, 3566-3581.
- Kosakowski, G., Churakov, S. V., and Thoenen, T., 2008. Diffusion of Na and Cs in montmorillonite. *Clays and Clay Minerals* **56**, 190-206.
- Churakov, S. V., 2007. Structure and dynamics of the water films confined between edges of pyrophyllite: A first principle study. *Geochimica Et Cosmochimica Acta* **71**, 1130-1144.
- Pellenq, R. J. M., Kushima, A., Shahsavari, R., Van Vliet, K. J., Buehler, M. J., Yip, S., and Ulm, F.-J., 2009. A realistic molecular model of cement hydrates. *Proceedings of the National Academy of Sciences* **106**, 16102-16107.
- Perry, T. D., Cygan, R. T., and Mitchell, R., 2007. Molecular models of a hydrated calcite mineral surface. *Geochimica et Cosmochimica Acta* **71**, 5876-5887.
- Churakov, S. V. and Gimmi, T., 2011. Up-Scaling of Molecular Diffusion Coefficients in Clays: A Two-Step Approach. *Journal of Physical Chemistry C* **115**, 6703-6714.

Time and Length Scales of Geologic and Environmental Materials' Simulation



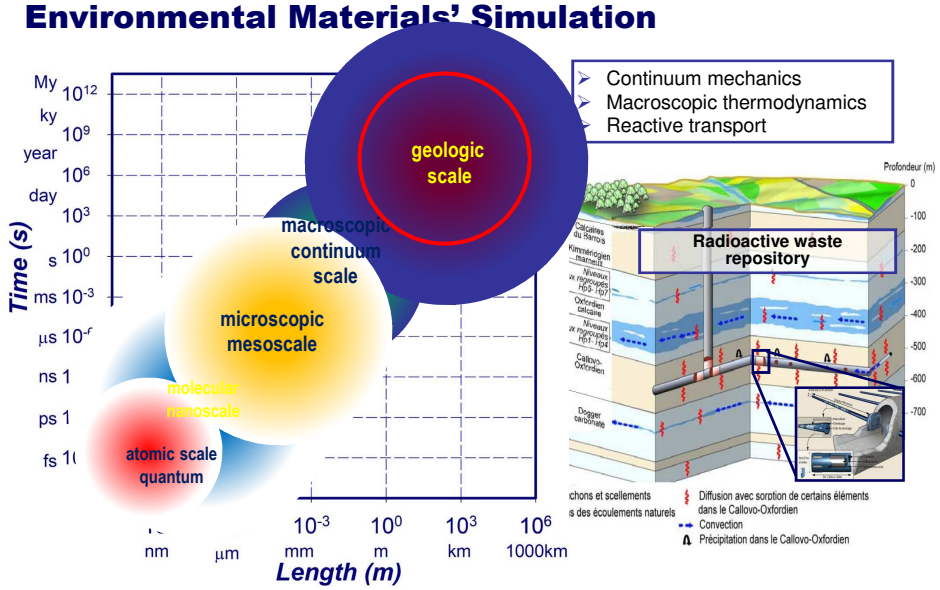
Time and Length Scales of Geologic and Environmental Materials' Simulation



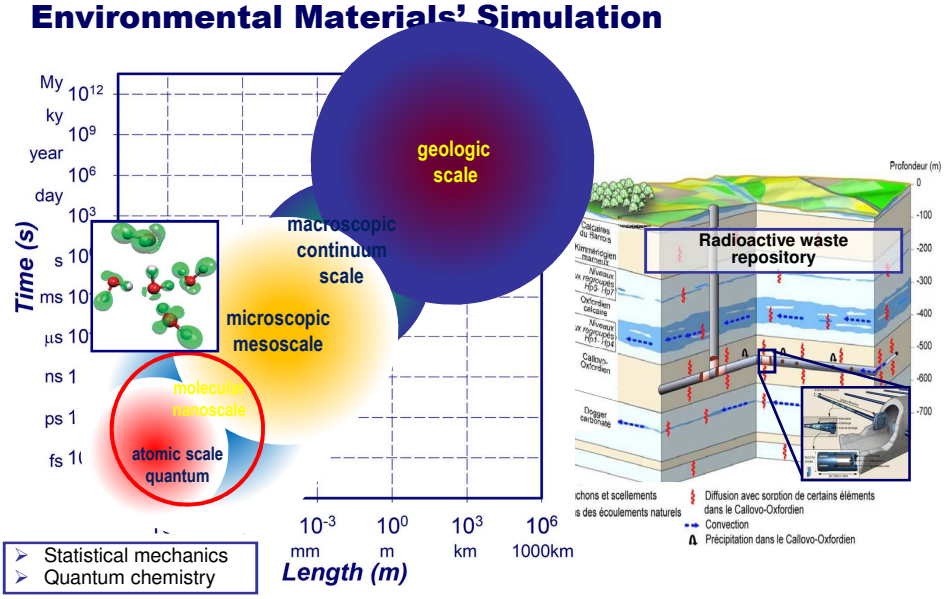


IMT Atlantique Bretagne-Pays de la Loire École Mines-Télécom
Subatech
NE-M1-PRI12ENP – Integrated Nuclear Engineering Project, February-June 2025
"Molecular modeling of materials for nuclear engineering applications"

Time and Length Scales of Geologic and Environmental Materials' Simulation

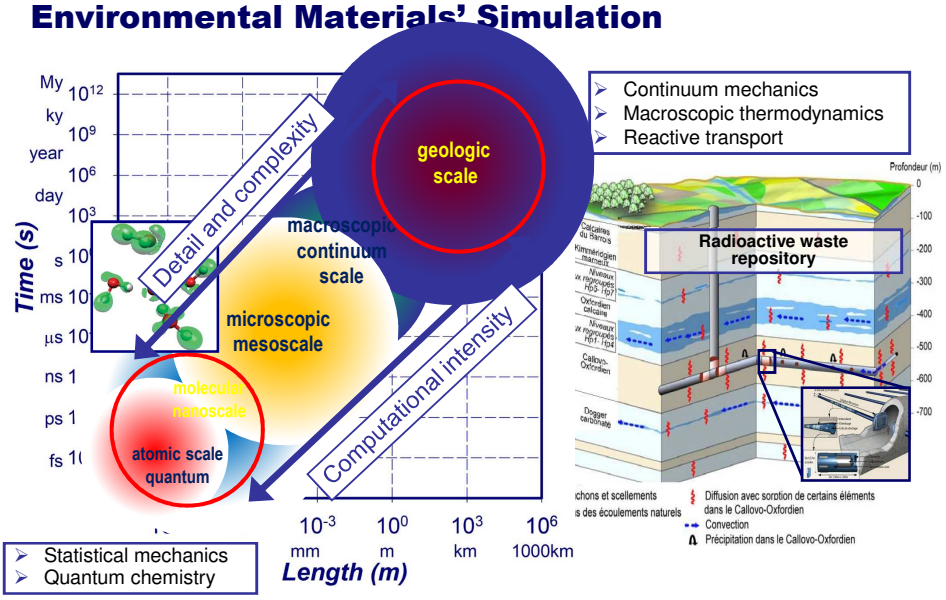


Time and Length Scales of Geologic and Environmental Materials' Simulation

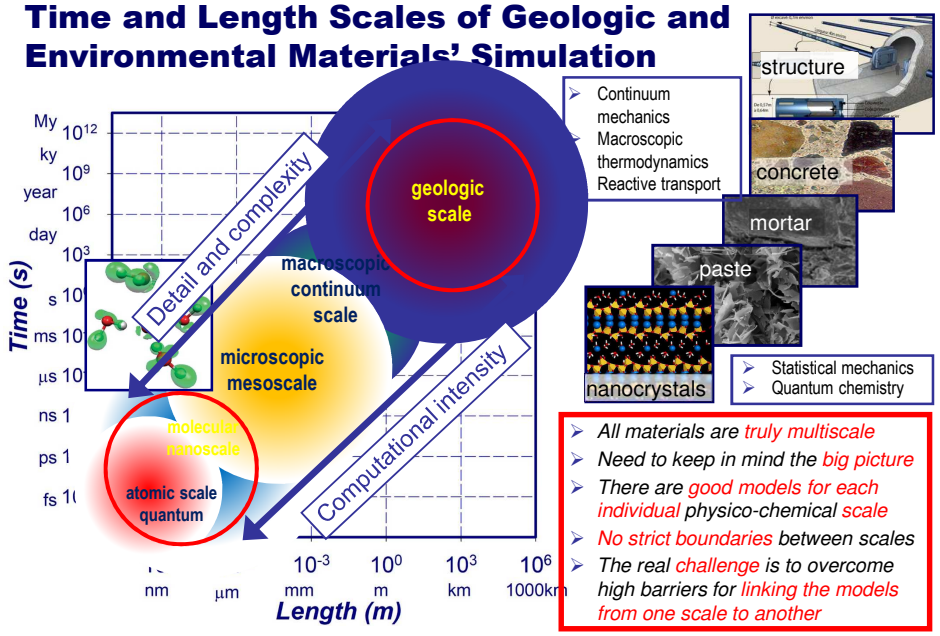


NE-M1-PRI12ENP – Integrated Nuclear Engineering Project, February-June 2025
"Molecular modeling of materials for nuclear engineering applications"

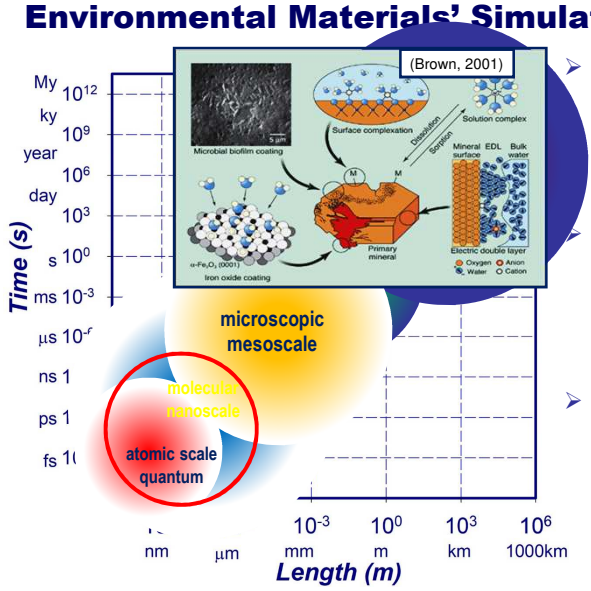
Time and Length Scales of Geologic and Environmental Materials' Simulation



Time and Length Scales of Geologic and Environmental Materials' Simulation



Time and Length Scales of Geologic and Environmental Materials' Simulation



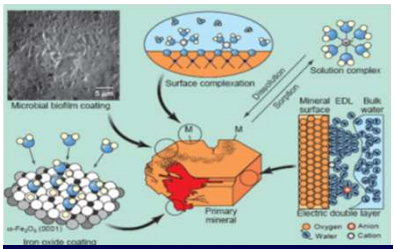
- Nano-structure of materials and their interfaces with water and aqueous solutions, reactions on their surfaces are greatly important, poorly understood and difficult to study
- Molecular-scale understanding of these properties are crucial to understanding and prediction of the radionuclide mobility and toxicity in the environment on a much larger scale
- Computational chemistry and atomistic computer modeling can provide atomic and molecular scale understanding of the structure, energetics, dynamics, mobility, reaction mechanisms, etc.

Role of Molecular Modeling in Materials Science

- Fundamental understanding of the atomic- and molecular-level origins of many important physical and chemical properties and processes
- Prediction of properties and processes under extreme conditions or other conditions that are difficult or impossible to reach experimentally
- Connection with experiment
  - Interpretation of observations
  - Test of fundamental theories
  - Guidance for new experiments
- Molecular modeling as "computer experiments"

Molecular-Scale Geochemistry of Reactive Environmental Interfaces

- Most environmental reactions take place at ***substrate-solution interfaces***
- ***Adsorption and transport*** of contaminants in soil and water
- ***Corrosion*** of metal, glass, concrete
- ***Geological CO_2 sequestration / Shale gas***
- Mineral ***weathering*** processes



G. Brown, *Science* **294**, 67-70 (2001)

- Interaction with ***organics***: Geochemical mechanisms of primitive metabolism and the ***origin of life***
- ***Our primary focus – molecular level understanding of the materials and processes related to nuclear engineering (waste disposal and storage)***

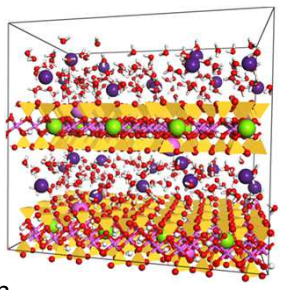
Molecular scale is, in fact, ***inherently multi-scale*** in time and distance

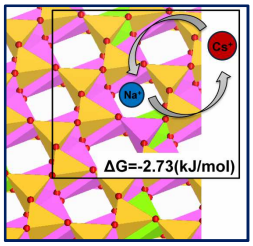
Structure
Dynamics
Reactivity

} at hydrated mineral interfaces are ***inherently coupled with each other***, and none of them can not be adequately understood without the others

Molecular-Scale View of Aqueous Interfaces

- Recent progress of the surface-sensitive experimental techniques:
  - ✓ Synchrotron X-ray reflectivity, EXAFS
  - ✓ Inelastic and quasielastic neutron scattering
  - ✓ Sum-frequency vibrational spectroscopy (SFVS)
  - ✓ Multi-nuclear multi-dimensional NMR spectroscopy
- Probe the properties of H_2O molecules and dissolved species adjacent to mineral surfaces, provide direct molecular-scale information on the structure and dynamics of hydrated interfaces
- However, these complex experimental data are often difficult to interpret unambiguously

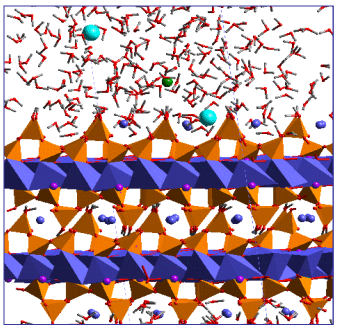




Molecular computer simulations can provide a complementary powerful quantitative tool to facilitate the atomic-scale interpretation of the observed interfacial phenomena, the effects of substrate structure and composition on the structure, dynamics, and composition of the interfacial aqueous solution

What is Computational Molecular Modeling?

- Use powerful computers to calculate properties of materials, represented by *N* interacting particles (atoms, molecules, ions, etc.)
- *Time* ~ 0.1 - 1.0 ns
- *L* ~ 10 - 100 nm
- *N* ~ 1,000 – 1,000,000 atoms



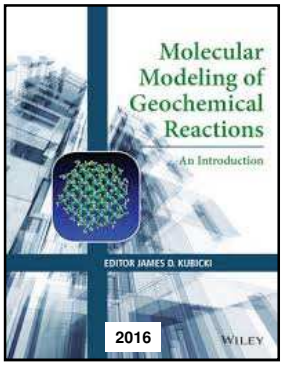
- Use **statistical mechanics** to dynamically model such processes as *hydration, adsorption, intercalation, expansion, diffusion, and the behavior of water and ions.*
- **Objective**: Quantitative understanding of the *molecular- and nano-scale structure and dynamical behavior of materials*

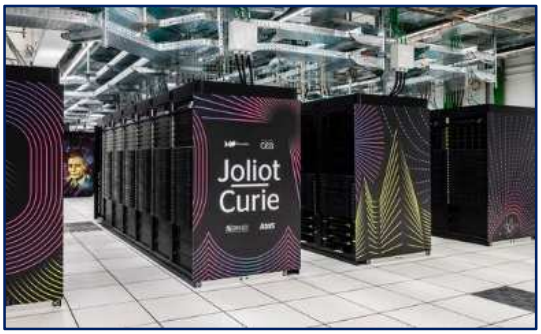
Classical Monte Carlo (MC) and Molecular Dynamics (MD) Molecular Modeling - Details

- *N* ~ 1,000-1000,000 atoms / *t* ~ 1-10 ns / n ~ 10^6-10^7 conf.
- Typically, constant *T*,*P* or *T*,*V* **statistical ensembles**
- Many molecular modeling software packages currently available.
- **Most important**: develop efficient numerical tools for the analysis of MD-generated trajectories or MC-generated ensembles of configs.
- *Coordinates* → Equilibrium thermodynamic properties
  - → Atom-atom radial distribution functions
  - → Coordination numbers, hydration numbers
  - → Fluid structure, hydration shells
  - → Molecular cluster formation and sorption environments
- *Velocities* → Diffusion
  - → Velocity autocorrelation functions
  - → Power spectra; dynamic details of atomic motions
- Comparison and interpretation of spectroscopic measurements: NMR, IR, Raman, X-ray.
- Molecular mechanisms controlling the behavior of aqueous species in solution and at substrate interfaces.

Atomistic Modeling: Computational Tools

N ~ 1,000-1000,000 atoms
t ~ 1-10 ns
τ ~ 10^6-10^7 time steps
n ~ 10^6-10^7 configurations





Atomistic computer simulations can be used today as any other tool of materials research, the same way all other physical and chemical methods are used (IR, Raman, NMR, Brillouin spectroscopies, X-ray and neutron diffraction, mass spectrometry, etc.)

First Atomistic Modeling of Fluids (1953-1959)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 6 JUNE, 1953

Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico
AND
EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*

(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

J. Chem. Phys. 27, 1208 (1957); doi:10.1063/1.1743957 (2 pages)

Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright
University of California Radiation Laboratory, Livermore, California map

(Received 12 August 1957)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 31, NUMBER 2 AUGUST, 1959

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT
Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

First Molecular Simulations of Water (1969-1971)

64 H_2O molecules in both cases

Volume 3, number 3 CHEMICAL PHYSICS LETTERS March 1969

STRUCTURE OF WATER; A MONTE CARLO CALCULATION *

J. A. BARKER and R. O. WATTS

Departments of Applied Mathematics and Physics, University of Waterloo, Waterloo, Ontario, Canada

Received 10 February 1969

An *a priori* calculation of the energy, specific heat and radial distribution function of liquid water at 25°C is made using the Monte Carlo technique and an intermolecular pair potential determined by Rowlinson from the properties of ice and steam. Agreement with experiment is sufficiently good to demonstrate the feasibility of this approach to water.

Notes

Monte Carlo Calculation of Some Thermodynamic Properties of Steam Using a Dipole–Quadrupole Potential*

R. J. BESHINSKE

Department of Chemistry, St. John's University, New York, New York

AND

M. H. LIETZKE

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 6 February 1969)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 7 1 OCTOBER 1971

Molecular Dynamics Study of Liquid Water*

ANEESUR RAHMAN

Argonne National Laboratory, Argonne, Illinois 60439

AND

FRANK H. STILLINGER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974

(Received 6 May 1971)

A sample of water, consisting of 216 rigid molecules at mass density 1 g cm^{-3}, has been simulated by computer using the molecular dynamics technique. The system evolves in time by the laws of classical dynamics, subject to an effective pair potential that incorporates the principal structural effects of many-

First Molecular Simulations of Clay and Cement Phases (1989-1996)

Clay Minerals (1989) **24**, 411–425

COMPUTER CALCULATION OF WATER–CLAY INTERACTIONS USING ATOMIC PAIR POTENTIALS

N. T. SKIPPER, K. REFSON AND J. D. C. MCCONNELL

Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR

(*Received 27 June 1988;*

ABSTRACT: Existing data on interatomic po
between an uncharged clay sheet and a water m
surface is relatively hydrophobic, with binding e
kcal mol^{-1}. There is, however, a low-energy site

Langmuir 1991, *7*, 547–555

Modeling the Clay–Water Interface

Alfred Delville†

Laboratoire de chimie fine, biomimétique et aux interfaces, Ecole Polytechnique, 91128 Palaiseau Cédex, France

Received February 22, 1990. In Final Form: May 9, 1990

iption of the solvent and clay sheet. The
n calculations. These potentials are used
ite sheets and their interlamellar sodium
ater orientation in agreement with the
ation of the interlamellar cations on the

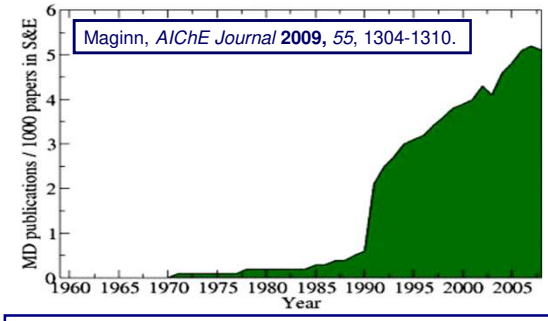
J. Chem. Soc., Faraday Trans., 1996, **92**(5), 831–841

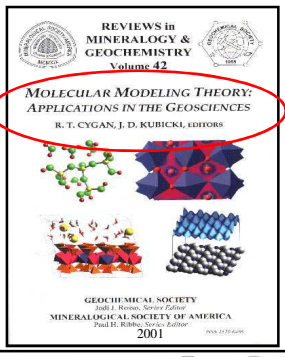
Molecular modelling of the mechanism of action of phosphonate retarders on hydrating cements

Peter V. Coveney* and William Humphries

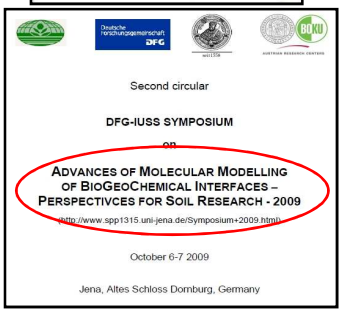
Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, UK CB3 0EL

Computational Molecular Modeling of Materials

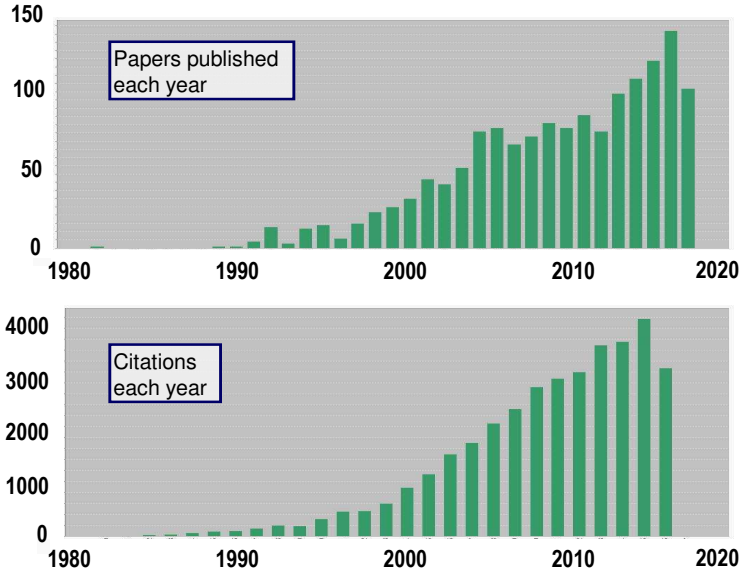


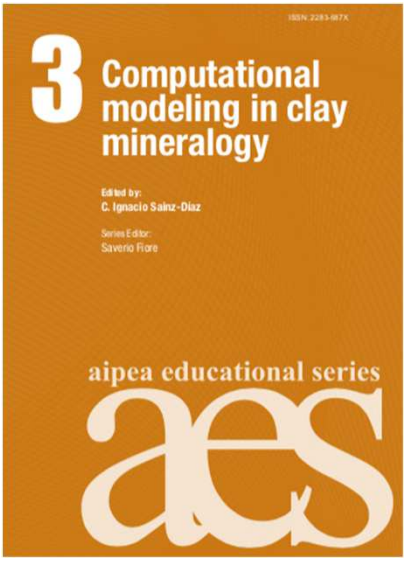


Molecular modeling can be used today as just any other technique to study the properties of complex environmentally and geochemically relevant materials, the same way all other physical and chemical methods are used (IR, Raman, NMR spectroscopies, X-ray and neutron scattering, mass spectrometry, etc.)



Progress of Atomistic Modeling in Clay Mineralogy





CONTENTS

FREE DOWNLOAD https://aipea.org/aes-books/

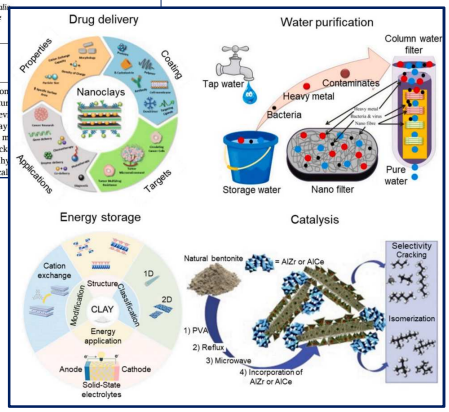
Coordination Chemistry Reviews 526 (2025) 216347
Contents lists available at ScienceDirect
Coordination Chemistry Reviews
journal homepage: www.elsevier.com/locate/ccr
ELSEVIER

Molecular modeling of clay minerals: A thirty-year journey and future perspectives

Annan Zhou [a,*], Jiapei Du [a], Ali Zaoui [b], Wassila Sekkal [b], Muhammad Sahimi [c,*]
[a] Discipline of Civil and Infrastructure Engineering, School of Engineering, Royal Melbourne Institute of Technology (RMIT), Victoria 3001, Australia
[b] Univ. Lille, IMT Nord Europe, JUNIA, Univ. Artois, ULR 4515 - LGCgE, Laboratoire de Génie Civil et géo-Environnement, F-59000 Lille, France
[c] Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089-1211, USA

ARTICLE INFO
Keywords:
Clay minerals
Molecular simulation
Nanoscale energies
Mechanical properties
Diffusion
Adsorption

ABSTRACT
The growing demand for a deeper understanding and improved utilization
need for a comprehensive review of the latest advancements and futu
modeling. This paper addresses this need by providing an in-depth rev
the past 30 years. Beginning with an introduction to classification of clay
minerals and a concise historical overview, this paper delves into the m
minerals, with detailed discussions on force fields, computational pack
nanoscale energy variation within clay minerals is described, covering hy
tion energies. The analysis is then extended to the nanoscale mechanical



Progress of Atomistic Modeling of Cement Materials

Cement and Concrete Research
Volume 102, December 2017, Pages 68-89

cemff: A force field database for cementitious materials including validations, applications and opportunities

Ratan K. Mishra [a], Aslam Kunhi Mohamed [b], David Geissbühler [b], Hegoi Manzano [c], Tariq Jamil [d], Rouzbeh Shahsavari [e], Andrey G. Kalinichev [f, k], Sandra Galmarini [g], Lei Tao [e], Hendrik Heinz [d], Roland Pellenq [h], Adri C.T. van Duin [i], Stephen C. Parker [j], Robert J. Flatt [a], Paul Bowen [b]

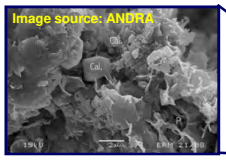
Show more

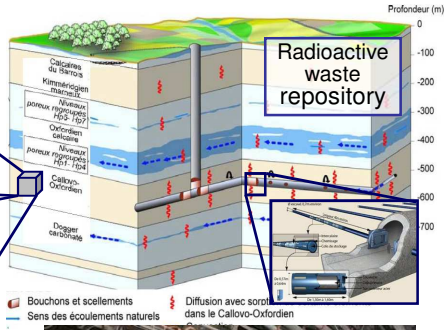
https://doi.org/10.1016/j.cemconres.2017.09.003 Get rights and content

Highlights

- Development of ***cemff*** database to improve the accuracy of atomistic simulations and guide in performance optimization of cementitious systems.
- Concepts and atomistic force field parameterizations of cementitious minerals.
- Atomistic model validations and comparison between the computed data and benchmarks (experimental or ab-initio).
- Different force fields (ClayFF, IFF, CementFF, ReaxFF and C-S-H FF) are compared. The benefits and limitations of these approaches are discussed.
- Relationships between structure, properties, and applications are discussed.

Primary Objective: Improve Molecular-Scale Understanding of the Adsorption and Transport Properties of Callovo-Oxfordian Clayey Formations





- 41% clay (illite, smectite, and interstratified I/S)
- 31% calcite
- 25% quartz and feldspar
- 3% other minerals
- ~1% organic matter

Simulating clay and cement is non-trivial

- Variable composition, low symmetry, complex crystal structures
- Incompletely and poorly characterized, occur as very fine-grained material
- **Availability of empirical force-fields for realistic molecular modeling**

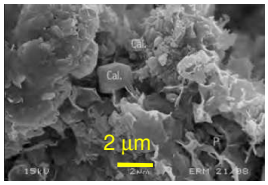
MD Modeling of Clay-Water and Related Interfaces

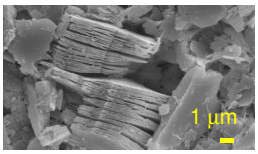
Objectives

- Use statistical mechanics to develop quantitative molecular-level understanding of substrate-water interfaces:
  - Structure and dynamics of aqueous interfacial species
  - Hydration, adsorption, H-bonding, diffusion, intercalation
  - Atomistic mechanisms of interfacial ionic sorption and transport

Non-trivial problems

- Complex crystal structures, low symmetry, variable composition
- Incompletely and poorly characterized, occur as very fine-grained material
- Large unit cells, stacking disorder
- Layered structures with significant electrostatic fields
- Availability of empirical force-field parameters for realistic molecular modeling



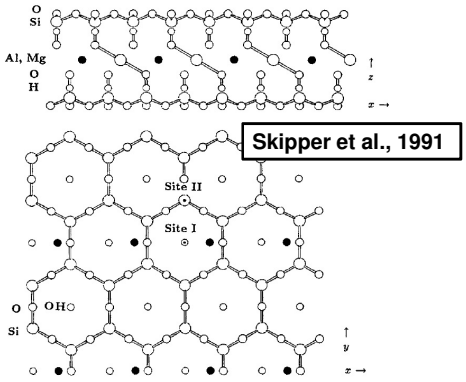


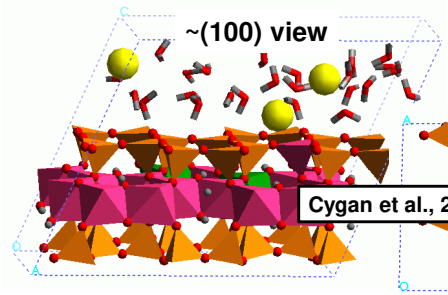
Atomistic Simulation of Complex Clays

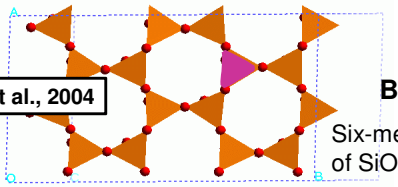
Wyoming Montmorillonite

$Na_3(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$

- No refined structures
- Cryptocrystalline
- Stacking disorder
- Complex compositions
- Site disorder







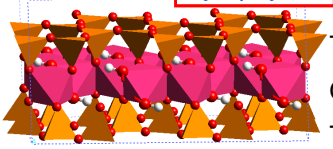
Basal view

Six-member rings of SiO_4 tetrahedra

Structure and Composition of Complex Clays

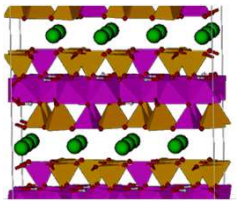
$Si_4Al_2O_{10}(OH)_2$
No substitutions
Non-swelling

Pyrophyllite



Illite (muscovite)

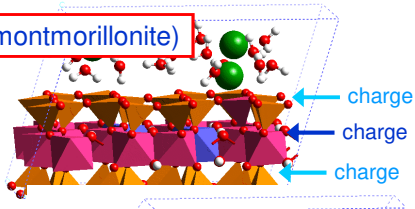
$K\ (Si_3Al)Al_2O_{10}(OH)_2$
Many substitutions
Many interlayer ions
1.0*e* charge per $O_{10}(OH)_2$
Non-swelling



Smectite (montmorillonite)

Dioctahedral Smectites

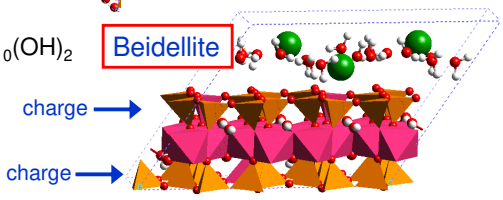
$Na_3(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$
Some tetrahedral Al sub
Mostly octahedral Mg sub
Swelling



0.375*e* charge per $O_{10}(OH)_2$

Beidellite

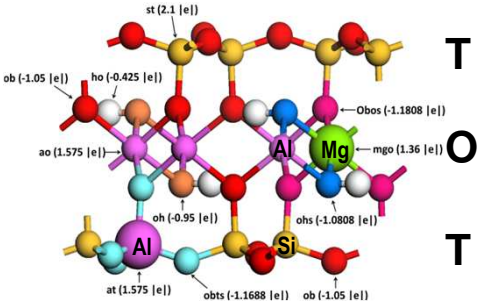
$Na_3(Si_{29}Al_3)Al_{16}O_{80}(OH)_{16}\cdot nH_2O$
Mostly tetrahedral Al sub
Swelling



ClayFF Construction and Parametrization

1. **No explicit bonds – quasi-ionic**
2. **LJ parameters for all oxygen atoms are assumed to be equal to Ow for SPC water**

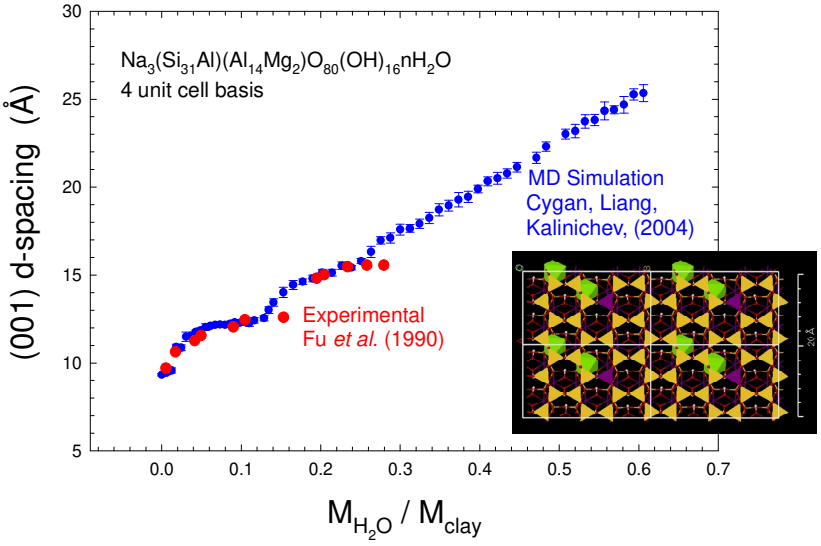
Both assumptions are great simplifications of reality, but they seem to work quite well



- Accurate determinations of partial charges are required to represent charge distributions of interlayer and external surfaces where electrostatic forces control sorption and transport processes
- Atomic charges derived from DFT calculations for cluster and periodic models of ***simple oxide and hydroxide phases*** (brucite, gibbsite, kaolinite, quartz…)
- Allows for ***charge delocalization*** among coordinating oxygens for substitutions

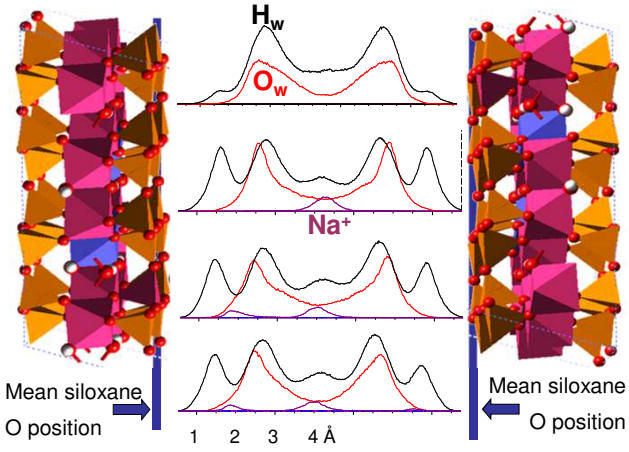
ClayFF: Cygan, Liang, Kalinichev, *J.Phys.Chem. B*, **108** 1255-1266 (2004)
Cygan, Greathouse, Kalinichev, *J.Phys.Chem. C*, **125** 17573-17589 (2021)

Swelling of Smectite (Montmorillonite)



Association of Metal Cations with Clay Surfaces

Two-Layer Clay Hydrates



Pyrophyllite
Zero

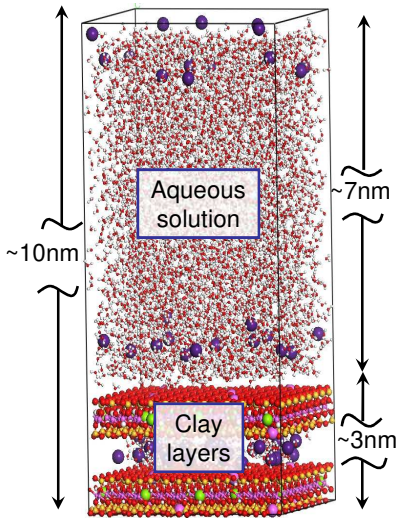
Montmorillonite
Oct

Wyoming
Montmorillonite
~Oct

Beidellite
Tet

Location of substitution sites in the clay structure can strongly influence the distribution and mobility of adsorbed ions and H_2O molecules

MD Modeling of Clay-Solution Interfaces



Classical Newtonian dynamics

- N_{tot} ~ 3,000 – 10,000 atoms
- N_{H2O} ~ 0 – 1,000 molecules
- *ClayFF* force field (Cygan et al., 2004)
- $a \times b \times c$ ~ $3 \times 3 \times 10$ nm^3
- Periodic boundary conditions
- *NVT*- or *NPT*-ensemble *T*=300K; *P* =1 bar
- *t* ~ 200 - 1,000 ps
- Δt = 0.5-1.0 fs

Solution structure:

- ✓ Atomic density profiles (⊥)
- ✓ Atomic density surface distributions (| |)
- ✓ Topology of the interfacial H-bond network

Dynamics:

- ✓ Diffusion coefficients (longer time scale)
- ✓ Spectra of vibrational and rotational dynamics (shorter time scale)

Homework problems

(Your everyday life experience and reasonable knowledge of high school / undergraduate college science should be sufficient to answer these questions)

- What are the most abundant chemical element: a) in the Universe?; b) on Earth?
- Name as many different kinds of energy as you can.
- Give an estimate of pressure and temperature at the 2 km depth on the ocean floor. Explain your estimate.
- The solubility of CO_2:
  - increases or decreases with increasing pressure at room temperature? (give an example)
  - increases or decreases with increasing *T* at atmospheric pressure? (give an example)
- Under different conditions, water can exist in at least three different states: solid (ice), liquid water, and water vapor. Can you think of a set of conditions at which all these three states can coexist simultaneously? If yes, at what temperature and pressure this can happen? What other materials show such behavior?
- Describe in principle (in a few sentences, without great detail) how a car engine works.
- Describe in principle (in a few sentences, without great detail) how a refrigerator works.
- What is common and what is different in the working principles of a car engine and a refrigerator?
- Why clays are important materials for nuclear waste disposal applications?
- Name other minerals / materials important in the context of geological disposal of radioactive waste? Explain your choices.
- What is "white" hydrogen? "Blue" hydrogen? "Green" hydrogen? What other "colors" of hydrogen are there and what do they mean?