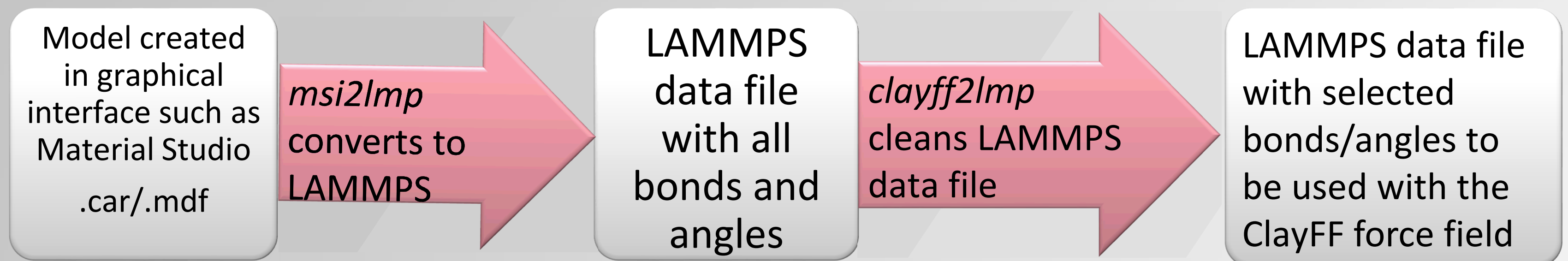


# Development of Pre-processing Scripts for Molecular Simulations of Clay Minerals

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The Python script *clayff2Imp* was created to convert a molecular model generated from a graphical user interface such as Material Studio into a format compatible with the LAMMPS molecular dynamics software package.<sup>1</sup> The script has been tested on minerals and mineral phases of geochemical interest based on the ClayFF set of atomic interaction parameters (force field). The final outputted LAMMPS data file contains newly developed parameters for angle bending terms specific to hydroxyl groups in mineral phases.<sup>2</sup>



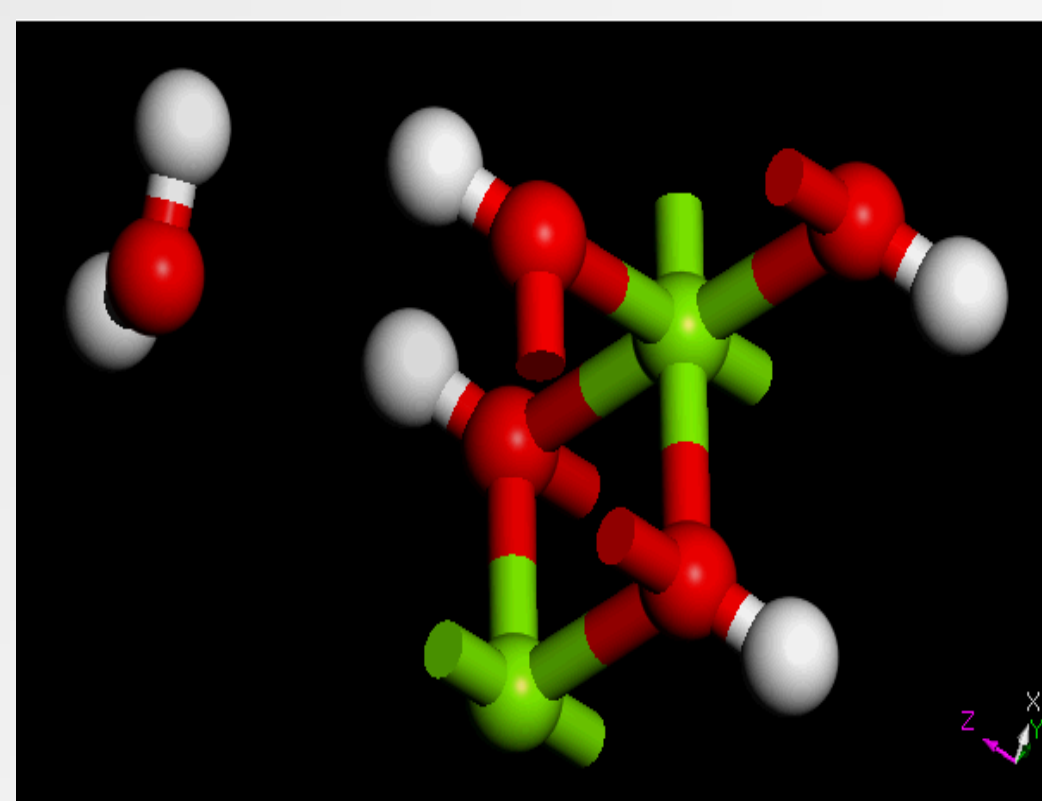
## Code Functionality

The energy expression in ClayFF (see  $E_{total}$  below) is based primarily on nonbonded interactions. The Python script *clayff2Imp* removes unwanted bonded energy terms from LAMMPS data files created from the *msi2Imp* utility code. Specifically, *clayff2Imp* removes bonded energy terms from the ClayFF based models of minerals so that only hydroxyl O-H bonds and M-O-H angles remain. Here, M stands in for any metal atom mineral bonded to an O-H group. (Si, Al, Mg, Ca, Fe, Li).

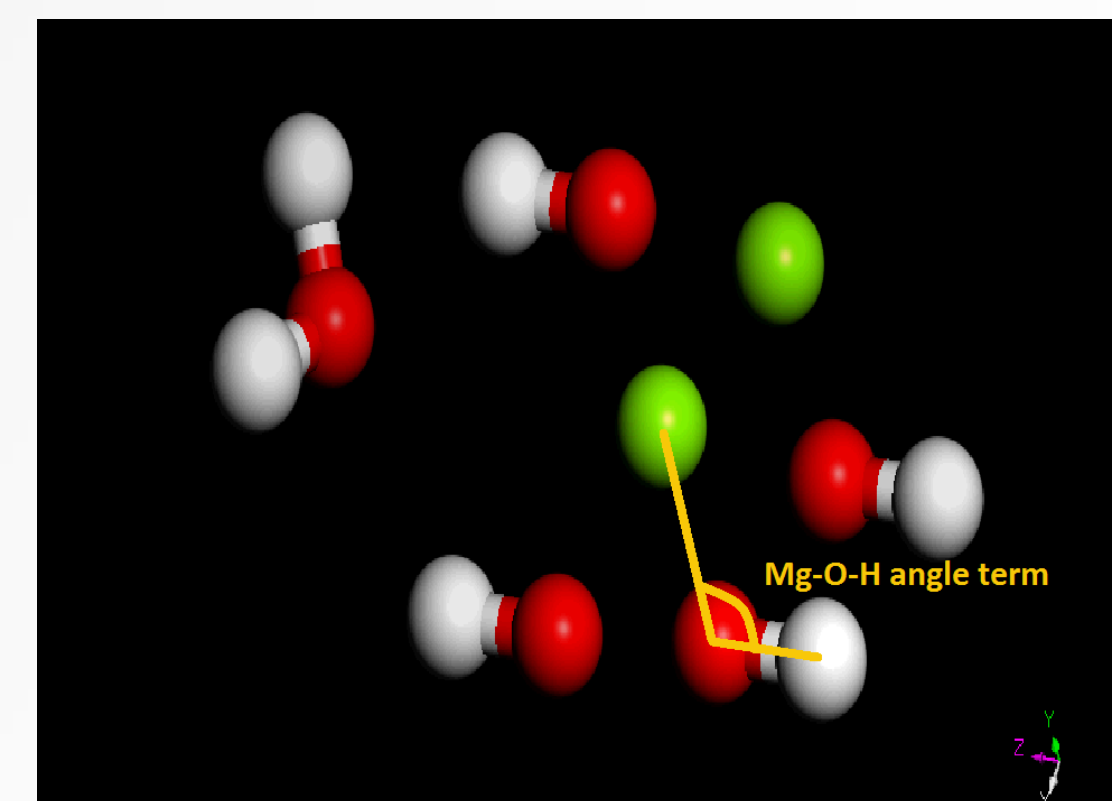
## Relevance

Removing unwanted bonds, angles and dihedrals from the LAMMPS data file produced by *msi2Imp* maintains the nonbonded features of ClayFF while adding newly developed parameters for M-O-H angle bending (see equation for  $E_{total}$  below). The functionality enabled by *clayff2Imp* allows for accurate molecular simulations of mineral edges that are dominated by hydroxyl groups. These mineral edges were difficult or impossible to model using the previous version of ClayFF, yet they control much of the mineral growth, dissolution, and adsorption properties.

$$\begin{aligned}
 E_{total} = & \sum_{nonbond} \left( \epsilon \left[ \left( \frac{R_{minij}}{r_{ij}} \right)^{12} - \left( \frac{R_{minij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\epsilon r_{ij}} \right) \\
 & + \sum_{bonded} (K(r - r_0)^2) + \sum_{angle} K(\theta - \theta_0)^2 \\
 & + \sum_{dihedral} K[1 + d\cos(n\phi)] \\
 & + \sum_{improper} K[1 + d\cos(n\phi)]
 \end{aligned}$$



**Before:** Brucite Water System with all angles and bonds.



**After:** Brucite Water System with excess bonds removed leaving only Mg-O-H angles.

Energy equation ( $E_{total}$ ) for molecular system using ClayFF.

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## msi2lmp

*msi2lmp* is used to translate models created in the graphical interface Material Studio into LAMMPS format so that LAMMPS calculations can be done on the molecular model. However, the data file created from *msi2lmp* contains many more bonded energy terms than the ClayFF force field needs. With *clayff2lmp*, a mineral model created from a graphical interface such as Material Studio will be translated into to a LAMMPS data file ready to be applied to the ClayFF force field without hand editing a data file.

LAMMPS data file. msi2lmp v3.9.7 / 24 Oct 2015 / CGCM for kaol\_edge\_1wl\_bonds

```
315 atoms
337 bonds
653 angles
1275 dihedrals
61 impropers
```

```
7 atom types
7 bond types
16 angle types
20 dihedral types
3 improper types
```

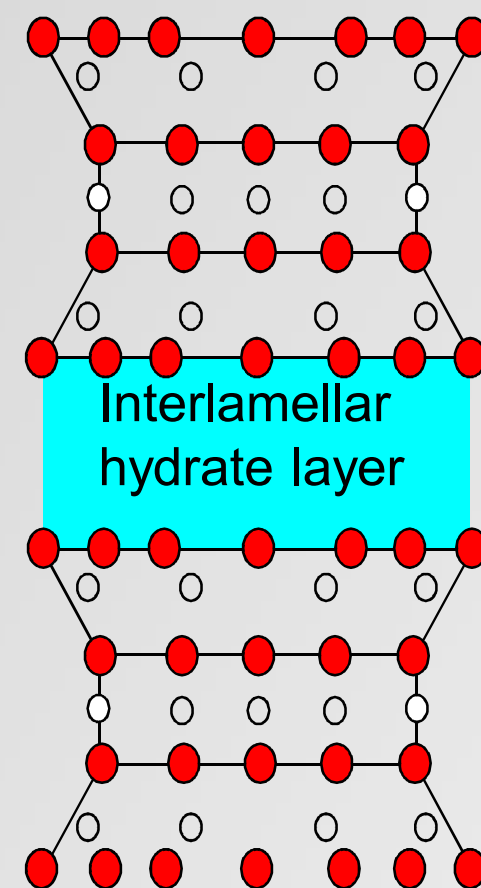
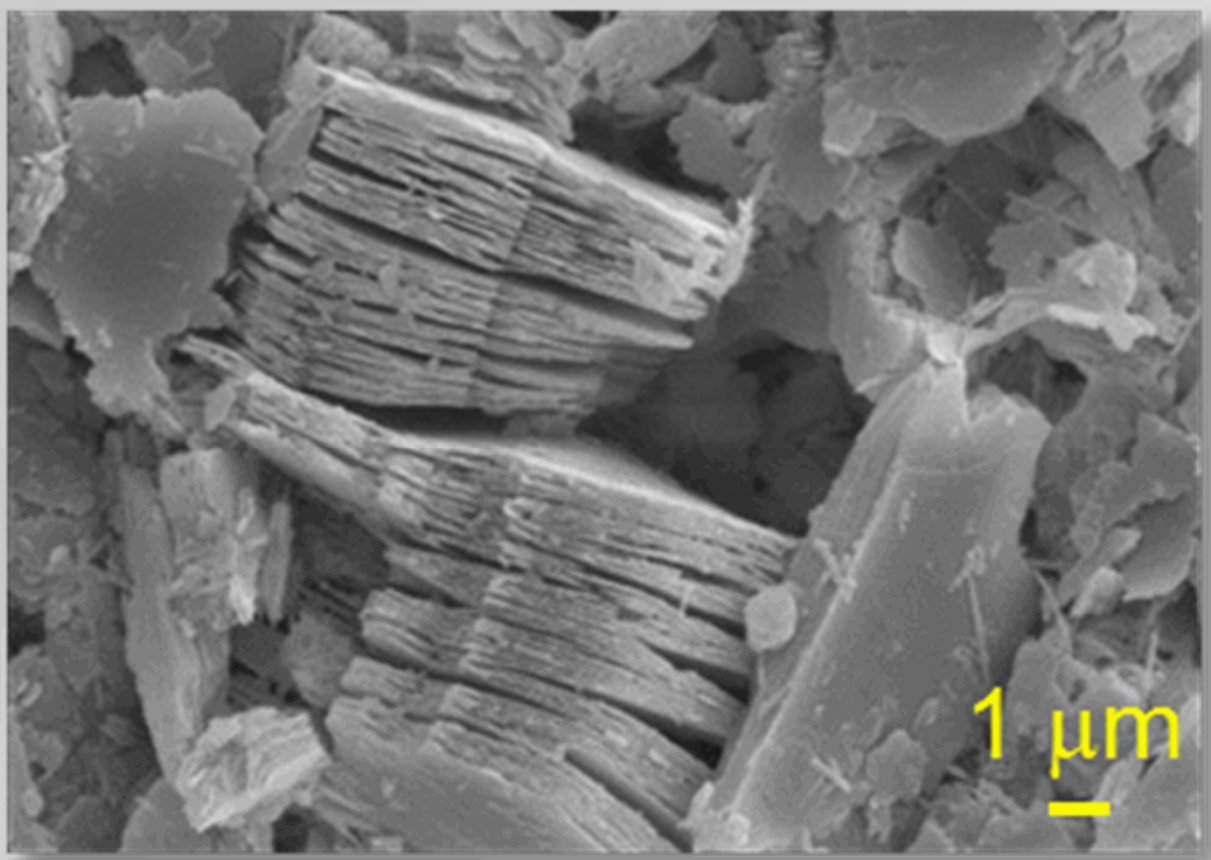
Portion of a LAMMPS data file for a mineral system produced by *msi2lmp*. Note the unwanted bond terms.

LAMMPS data file. msi2lmp v3.9.7 / 24 Oct 2015 / CGCM for kaol\_edge\_1wl\_bonds

```
315 atoms
130 bonds
39 angles
0 dihedrals
0 impropers
```

```
7 atom types
2 bond types
1 angle types
```

Portion of a LAMMPS data file for a mineral system after unwanted bonded terms were removed by *clayff2lmp*.



Left: Micrograph image of Kaolinite clay edge.  
Right: Molecular model of a layered mineral.

## Molecular Modeling and Clays

Clays are heterogeneous, unstructured and molecularly complex so uncertainties arise when using experimental methods to study the adsorption of other atoms, ions and molecules at clay surfaces.

Molecular modeling provides an atomic-level description of these systems that can aid in the interpretation of experimental results.

## ClayFF Force Field

The ClayFF force field was created to simulate mineral systems and their interfaces.<sup>3</sup> ClayFF uses primarily nonbonded interactions so that it can not only successfully model energy transfer between the fluid and the mineral but also minimize the number of parameters.

$$E_{total} = E_{nonbond} + E_{bond}$$

In the ClayFF force field,  $E_{bond}$  only applies to hydroxyl groups and water whereas  $E_{nonbond}$  applies to all atoms.

$$E_{nonbond} = \sum_i \sum_j \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} + \frac{q_i q_j}{\epsilon r_{ij}}$$

## References

[1] [lammps.sandia.gov](http://lammps.sandia.gov) [2] Zeitler et al., *J. Phys. Chem. C* **2014**, *118*, 7946 [3] Cygan, Liang, and Kalinichev. *J. Phys. Chem. B* **2004**, *108*, 1255.