Development of Reactive Potentials for Molecular Dynamics Simulations

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Mentors: Scott Grutzik, Normand Modine, Mark Wilson

Computational Materials and Data Science (1864)
Component Science and Mechanics (1556)
Motivation: Materials Modeling with Chemical Accuracy

ReaxFF: Permeation of AO and $O_2$ gas in MoS$_2$ solid lubricant

ReaxFF: Impact of water in fracture of silica glass

Images courtesy of Mark Wilson

- Reactive potentials are at the scientific cutting edge for atomistic modeling
- Lack of physical connections between atoms
- Charge equilibration- partial charges
- Estimates of bond orders – allows for modeling of chemical reactions
Material performance is often observed and quantified at the continuum scale. However, the mechanisms start at the finest scales: electronic, chemical, microstructural, etc.

Challenges with atomistic MD modeling:
- Length and time scales
- Rates at typically *fast*

Benefits in atomistic MD modeling:
- Chemical specificity and microstructural content typically unavailable to other scales
- Non-bonded reactive potentials offer the ability to explore chemistry
What are Reactive Potentials?

Incorporate physics not typically accounted for in classical MD

- As a consequence are more computationally expensive

- ReaxFF treats bond order as a continuous function of interatomic distance

- **BOND ORDER** is the number of covalent bonds between two atoms

![Diagram showing bond orders](image)
General Goals of the Project

**Challenge:** As a user of reactive potentials, we are often limited by the available elemental constituents within a given potential

**Goal:** Develop the framework necessary to modify, create, and expand either existing or novel reactive potentials

**Specific:** Add BaSiO glasses potential

**Approach:** Utilize Dakota as an optimization engine to run multiple, small MD simulations designed to extract a single quantity of interest

Adri C T van Duin, npj Computational Materials, (2015)
Why BaSiO Glasses?

- Brittle materials are used throughout the stockpile. Examples include all headers, electronic connectors, and strong links.
- Challenge: Make 30 year lifespan reliability predictions for components containing brittle materials. This requires predictive modeling.

Glass to metal seals

Glass-ceramics

Images courtesy of Kevin Strong and Steve Dai
The Training Data

C-C triple bond
Bond order = 3

C-C double bond
Bond order = 2

H₃C

C-C single bond
Bond order = 1

C-O partial double bond
Bond order = 1.5

Energy (Kcal/mol)

Radius (Ang)

DFT data
What is a parameterization?

$$E_{\text{System}} = E_{\text{bond}} + E_{\text{lp}} + E_{\overline{\text{over}}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{C2} + E_{\text{trip}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{H-bond}} + E_{\text{vdW}} + E_{\text{coulomb}}$$

- **Parameterization** is a way of expressing a model as a function of some number of independent parameters.
- Currently only looking at parameters related to atoms and bonds.
- 60+ parameters per element, not including the cross interactions.
- It’s complicated!
- The parameters incorporate physics.

$$E_{\text{bond}} = -D_e z^{\sigma_{B0}} \exp \left[ p_{\text{del}} \times \left( 1 - B_{02} \right) \right]$$

$$E_{\text{lp}} = \frac{p_{\text{ip2}} \times \Delta_{\text{ip}}}{1 + \exp \left[ -75 \times \Delta_{\text{ip}} \right]}$$

$$E_{\overline{\text{over}}} = \frac{\sum_{\text{bonds}} \frac{D_{01}^2 + D_{12}^2}{\Delta_{\text{ipcor}}^2 + \Delta_{\text{val}}} \times \Delta_{\text{ipcor}}^{-1}}{1 + \exp \left[ \frac{D_{01}^2 + D_{12}^2}{\Delta_{\text{ipcor}}^2 + \Delta_{\text{val}}} \right]}$$

$$E_{\text{under}} = \frac{1}{1 + \exp \left[ -p_{\text{under}} \times \Delta_{\text{ipcor}}^{-1} \right]} \times f_0(B_{01}, \Delta_i)$$

$$E_{\text{trip}} = p_{\text{trip1}} \times \exp \left[ -p_{\text{trip2}} \times \left( B_{02} - 2.5 \right) \right] \times \exp \left[ -p_{\text{trip3}} \times \left( \sum_{\text{neighbors}(i)} B_{0k} - B_{0j} \right) \right] \times \exp \left[ -p_{\text{trip4}} \times \left( \sum_{\text{neighbors}(i)} B_{0k} - B_{0j} \right) \right] \times \frac{1}{1 + 25 \times \exp \left[ p_{\text{trip5}} \times \left( \Delta_i + \Delta_j \right) \right]}$$

$$E_{\text{tors}} = f_{10}(B_{01}, B_{02}, B_{03}) \times \sin \theta_{ij} \times \sin \theta_{jk} \times \left( \frac{1}{2} V_1 \times \left( 1 + \cos \omega_{ijk} \right) + \frac{1}{2} V_2 \times \exp \left[ p_{\text{tor1}}(B_{01}^2 - 1) + f_{11}(\Delta_i, \Delta_j) \right] \times (1 - 2 \cos \omega_{ijk}) + \frac{1}{2} V_3 \times (1 + \cos \omega_{ijk}) \right)$$

$$E_{\text{conj}} = f_{12}(B_{01}, B_{02}, B_{03}) \times p_{\text{coa1}} \times \left( 1 + (\cos \omega_{ijk} - 1) \right) \times \sin \theta_{ij} \times \sin \theta_{jk}$$

$$E_{\text{H-bond}} = p_{\text{hb1}} \times \left[ 1 - \exp \left( p_{\text{hb2}} \times B_{0XH} \right) \right] \times \exp \left[ p_{\text{hb3}} \times \left( \frac{\tau_{\text{hx}}}{\tau_{\text{hh}}} + \tau_{\text{ht}} - 2 \right) \right] \times \sin \left( \theta_{XHZ} / 2 \right)$$

$$E_{\text{vdW}} = T ap \times D_{ij} \times \left\{ \alpha_{ij} \times \left( 1 - f_{13}(r_{ij}) / r_{\text{vdW}} \right) - 2 \times \exp \left[ \frac{1}{2} \times (f_{13}(r_{ij}) / r_{\text{vdW}}) \right] \right\}$$

$$E_{\text{coulomb}} = T ap \times C \times \frac{q_i \times q_j}{\left( r_{ij}^3 + (1 / \gamma_{ij})^3 \right)^{1 / 3}}$$
Optimization Scheme

Optimization Engine
- Sample parameter space
- Identify best representation of training data

Simulation
- Performs LAMMPS
- Unique force field parameterization
- Variety of modules: NEB, elastic properties, etc.
- Designed to obtain comparison to training data

Python scripting
- File management
- Creation of force field based upon parameters provided by OE
- Extract QoI from MD result
- Perform comparison to training data

Training data set
*Considered to be the “truth”*
Originating from DFT
Originating from experiment

- Utilize Dakota and a genetic algorithm as an optimization engine to run multiple, small MD simulations to extract QoI
- Strong connection between training data, simulation module, and scripting
What is a Genetic Algorithm?

• **A genetic algorithm or GA** is an optimization technique that is inspired by the process of natural selection.

```plaintext
- Selection
- Reproduce
- Mutate
- Check fitness
- New population
```

1. **Selection**: Choose the best individuals from the current population based on their fitness.
2. **Reproduction**: The best individuals are used to create offspring for the next generation.
3. **Mutation**: Randomly alter some of the genetic material to introduce new variations.
4. **Check fitness**: Evaluate the fitness of the new population.
5. **New population**: The best individuals from the previous steps form the new population.

This cycle is repeated until a satisfactory solution is found or a predefined number of generations have been completed.
Why so Complicated?

• You might say, “This sounds complicated. There are easier ways. Why would you want to do it this way?”

• Provides the opportunity to fit for a range of training data, not just DFT. **ANY** quantity of interest that we can extract from an MD simulation, we can train our parameterization for it.

• Pitfall: method is agnostic to analytical forms of potential energy interactions. We must be cognizant of the physical meaning of each parameter.
Results

rms = 5.094

• Not fitting the well
• Fitting parameters one by one
• Looking into how order and parameter fit pairings effect our results
Validation of the Approach

- Wrote a postprocessor that builds histograms of parameters swept by the GA
- GA isn’t getting stuck in local minima
- Parameter fitness curves vary wildly depending on order of fitted parameters
Planned Experimental Validation

- Challenge: find a QoI that would varies enough with concentration of Ba

- Possibilities: Constant of thermal expansion (CTE), Density as a function of concentration

- Experiment: Either physically or computationally, steadily increase temperature and measure volume at regular intervals

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**TABLE 6.46**

Thermal Expansion Coefficients of $\text{Rb}_2\text{O-BaO-SiO}_2$ Glasses

<table>
<thead>
<tr>
<th>Composition (mole %)</th>
<th>$\alpha \times 10^7 \text{ (C}^{-1}\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Rb}_2\text{O}$</td>
<td>$\text{BaO}$</td>
</tr>
<tr>
<td>13.1</td>
<td>5.3</td>
</tr>
<tr>
<td>19.3</td>
<td>5.8</td>
</tr>
<tr>
<td>9.4</td>
<td>17.3</td>
</tr>
<tr>
<td>21.2</td>
<td>12.9</td>
</tr>
<tr>
<td>15.6</td>
<td>19.2</td>
</tr>
<tr>
<td>10.3</td>
<td>25.3</td>
</tr>
</tbody>
</table>

*Data from Simpson (1959, 1961).*

*Handbook of Glass Properties, Narottam P. Bansal and Robert H. Doremus 1986*
Accomplishments this Summer

• Familiarized ourselves with Dakota and Lammps documentation
• Researched functional form of ReaxFF reactive Potentials
• Initialized and de-bugged python based Dakota-Lammps interface
• Began fitting Atom, Bond, and Off-diagonal parameter terms
• Wrote a script that will strip DFT/VASP data for fitting simulations
• Wrote post-processing scripts for validation and informing future fits
Future Directions

• Angle / torsions / condensed phase

• How complicated is the next data set? 82,000 DFT simulations!!! No one does that; it was a heroic simulation effort that Normand achieved while on vacation.

• Experimental validation of our parameterization: a BaSiO glass. CTE (coefficient of thermal expansion)

• Quantify the uncertainty in an MD result for a given parameterization

• Goal for time remaining: Fit crystal BaO and compare large radii behavior

• Stretch goal: add Barium to the ReaxFF reactive potential for SiO with confidence
Acknowledgements

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Thank you for listening
Comments? Questions? Concerns?