Applications of Charge Optimized Many Body (COMB) Potentials in Multicomponent Systems

Tao Liang¹,², Simon R. Phillpot¹ and Susan B. Sinnott¹,²

¹Department of Materials Science and Engineering, University of Florida
²Department of Materials Science and Engineering, Penn State University

Aug 6, 2015

August 2015 LAMMPS Users’ Workshop and Symposium, August 5-6, 2015 at Albuquerque, NM

tul17@psu.edu
Current COMB3 on LAMMPS is outdated
Contact me (TUL17@psu.edu) for updates
Reactive many-body empirical potentials to model materials

Historically developed for materials with specific types of chemical bonds

- SW and Tersoff potentials for Si
  - Brenner or REBO potential for C,H + O,F,S,….
  - AIREBO

- EAM potentials for metals
  - MEAM for metals and oxides
  - EAM+ES for metals and oxides

- Buckingham potentials for ionically bound materials

May 2012 issue
Modeling Multicomponent Systems

- Inherent to many applications
- Challenge for traditional empirical potentials (force fields)
- This need spurred the development of next generation potentials: charge optimized many body (COMB), ReaxFF, EAM+ES and a few others

Functional form of COMB3 potential

\[ E_T = \sum_i \left\{ E_i^{Self}(q_i) + \frac{1}{2} \sum_{j \neq i} \left[ V_{ij}^{short}(r_{ij}, q_i, q_j) + V_{ij}^{Coul}(r_{ij}, q_i, q_j) \right] \right\} + B_i(q_i) + C_i(r_{ij}, \theta_{ijk}) + E^{polar}(q_i, r_{ij}) + E^{vdW}(r_{ij}) \]

- **Self energy**: ionization energies and electron affinities; includes penalty function to capture change in self-energy due to the field from the ionic lattice
- **Short-range interactions**: reactive bond-order potential
- **Coulomb interactions**: Coulomb integral over the charge densities
- **Charge and angular correction terms**
- **Polarization**: Atomic polarizability for organic systems
- **van der Waals energy**

T. Liang et al., Materials Science and Engineering R (2013)
Current status of COMB3

- **Semiconductors**
  - Si

- **Metals**
  - Cu, Zn, Al, Zr, Ti, U, Pt, Ni, Au

- **Compounds**
  - Cu$_2$O, ZnO, UO$_2$, NO$_x$, NH$_3$, Al$_2$O$_3$, TiO$_2$, NiO
  - Ni$_3$Al, ZnCu
  - TiN, AlN, TiC, TiH$_2$, TiC

- **Carbon based systems**
  - CHO systems
  - H$_2$O and O$_2$
  - C/H/Cu/O/Zn
  - C/H/O/Ti
  - CN
  - CHON/Ti

T. Liang et al., Materials Science and Engineering R (2013)
T. Liang et al., J. Physical Chemistry A (2011)
Yu-Ting Cheng et al., Surface Science (2013)
Yangzhong Li et al., J. Physics: Condense Matter (2012)
➢ O₂ densification of porous titanium tetra-isopropoxde (TTIP) on TiO₂ surfaces

➢ Applications in electrochemical systems
Motivation

- Plasma Enhanced Chemical vapor deposition (PECVD): surface treatment, thin film growth, ion densification …
- Ti-(OC$_3$H$_7$)$_4$/TiO$_2$ commonly used in optical devices
- Details of thin film growth mechanisms not well understood

Building Porous TTIP Layer on TiO$_2$ Support

 Depositing on TiO$_2$ support
 5 eV/mole

TTIP

500 TTIPs

TiO$_2$ support (9x9x5 nm)
TiO- or O-terminated TiO$_2$ (110)
System Configuration for Densification with O$_2$

**Densification settings:**

- Incident energy 100 eV/O$_2$
- Every round has 400 O$_2$ molecules
- Performed 5 rounds of bombardment
- Ion/TTIP ratio: 4
- Thermostat at 300 K
- Relaxation time between incident beams: 0.5 ps
- Time step 0.2 fs
TTIP Desorption

At early stage
Densification

- Density increases more than two times near the surface region.
- Densification only happens around 1.5 nm above the surface.
- No TTIP stay as TTIP.
- Wide range of molecular segments formed.
- More than 200 water molecule form.
O$_2$ densification of porous titanium tetra-isopropoxide (TTIP) on TiO$_2$ surfaces

Applications in electrochemical systems
- Recent change in O$_2$
- Reactive water potential with the variable charge
- Proton transfer
- Applying voltage in the variable charge potentials
## Water Properties (within training database)

<table>
<thead>
<tr>
<th>Properties</th>
<th>TIP4P</th>
<th>SPC/E</th>
<th>Exp.</th>
<th>COMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H_f$ (eV/mole.)</td>
<td></td>
<td></td>
<td>-2.50</td>
<td>-2.41</td>
</tr>
<tr>
<td>Charge on O, $q_O$ (e)</td>
<td>-1.04</td>
<td>-0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole moment (eÅ)</td>
<td>0.62</td>
<td>0.49</td>
<td>0.39</td>
<td>0.42</td>
</tr>
<tr>
<td>Ice $I_h$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td></td>
<td></td>
<td>4.52</td>
<td>4.55</td>
</tr>
<tr>
<td>c (Å)</td>
<td></td>
<td></td>
<td>7.36</td>
<td>7.39</td>
</tr>
<tr>
<td>O-O distance (Å)</td>
<td></td>
<td></td>
<td>2.76</td>
<td>2.78</td>
</tr>
<tr>
<td>$\Delta H_f$ (eV/mole.)</td>
<td></td>
<td></td>
<td>-3.02</td>
<td>-3.16</td>
</tr>
<tr>
<td>Charge on O, $q_O$ (e)</td>
<td>-1.04</td>
<td>-0.82</td>
<td>0.52</td>
<td>-0.87</td>
</tr>
<tr>
<td>Dipole moment (eÅ)</td>
<td>0.62</td>
<td>0.49</td>
<td>0.54</td>
<td>0.53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structures</th>
<th>Exp. or DFT</th>
<th>COMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>-2.41</td>
<td>-2.41</td>
</tr>
<tr>
<td>$\text{HO}$</td>
<td>0.38</td>
<td>0.31</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>-1.34</td>
<td>-1.72</td>
</tr>
<tr>
<td>$\text{H}_3\text{O}$</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>$\text{H}_3\text{O}_2$ (HO-H$_2$O)</td>
<td>-1.80</td>
<td>-1.80</td>
</tr>
<tr>
<td>$\text{H}_5\text{O}_2$ (H bridge 2 H$_2$O)</td>
<td>-1.45</td>
<td>3.40</td>
</tr>
</tbody>
</table>
Predicted water properties

Selected properties of water

<table>
<thead>
<tr>
<th></th>
<th>TIP4P</th>
<th>SPC/E</th>
<th>Exp</th>
<th>COMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f$ (eV/unit)</td>
<td></td>
<td></td>
<td>-2.96</td>
<td>-2.81</td>
</tr>
<tr>
<td>$\Delta H_{sol}$ (eV/unit)</td>
<td>0.99</td>
<td>1.02</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td></td>
<td></td>
<td>0.45</td>
<td>0.49</td>
</tr>
<tr>
<td>Dipole (eÅ)</td>
<td></td>
<td></td>
<td>3.9</td>
<td>2.52</td>
</tr>
<tr>
<td>Diffusion Coeff. (10$^{-5}$ cm$^2$/s)</td>
<td></td>
<td></td>
<td>2.30</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Pair distribution of water

<table>
<thead>
<tr>
<th></th>
<th>DFT+vdW</th>
<th>COMB3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O_{atop}$</td>
<td>-0.40</td>
<td>-0.49</td>
</tr>
<tr>
<td>$H_2O_{fcc/hcp}$</td>
<td>-0.28</td>
<td>-0.54</td>
</tr>
<tr>
<td>$H_2O_{dimer}$</td>
<td>-0.55</td>
<td>-0.59</td>
</tr>
<tr>
<td>$H_2O_{hexamer}$</td>
<td>-0.73</td>
<td>-0.91</td>
</tr>
</tbody>
</table>
Wetting Mechanism

1. Surface water
2. Precursor water
3. Interfacial water
4. Bulk water

No bulk water after 0.8 ns
Wetting Mechanism

\[ R_{XY}(0) \ (\text{Å}) \]

\[ y = 40.037x^{0.1833} \]

\[ R \sim t^{0.15} \]

0.2 ns

74%

66%
Wetting Mechanism

[Diagram depicting wetting mechanism with various annotations and measurements, including a scale for droplet height in Å.]

Graph showing the distribution of MSD XY and MSD W across different regions (Bulk, Surface, Interface, PF).
Reaction Energies $\Delta G$ of Steps in Electrochemical Reactions

\[ \text{CO}_2 + 2 \text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{CO}^* + \text{H}_2\text{O} \]

\[ \Delta G_{\text{CO}^*} (U) = G_{\text{CO}^*} - G_* - G_{\text{CO}_2(\text{g})} + G_{\text{H}_2\text{O}(\text{aq})} - G_{\text{H}_2(\text{g})} + 2 \text{eU} \]

**Kinetics dictate the activity and selectivity with the CO$_2$ ER pathway**

## CO$_2$ Reduction on Cu and 1ML Cu/ZnO

The calculated reaction energies with added entropic terms at 0V vs. RHE

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Surface</th>
<th>DFT (eV)</th>
<th>COMB (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$^<em>$ + H$^+$ + e$^-$ → COH$^</em>$</td>
<td>Cu (111)</td>
<td>1.31</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>1ML Cu/ZnO</td>
<td>0.83</td>
<td>0.85</td>
</tr>
<tr>
<td>CO$^<em>$ + H$^+$ + e$^-$ → CHO$^</em>$</td>
<td>Cu (111)</td>
<td>0.96</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>1ML Cu/ZnO</td>
<td>-0.14</td>
<td>-0.22</td>
</tr>
</tbody>
</table>

T. Liang and et al., CAT. Comm., 52 (2014)
Applying Potential in COMB3

At ES equilibrium:

- Electronegativity \( \chi_i = \frac{\partial U}{\partial q_i} \)

\[ \bar{\chi} = \frac{1}{N} \sum_i \chi_i \]

At ES non-equilibrium:

- Electronegativity is biased by V

\[ \frac{\partial U_{cathode}}{\partial q_i} - \frac{\partial U_{anode}}{\partial q_i} = V \]

EOM \[ m_q \ddot{q}_i = \bar{\chi} - \chi_i + v \dot{q}_i \]

\[ E: m_q \ddot{q}_i = \bar{\chi} - \chi_i + v \dot{q}_i \]

C: \[ m_q \ddot{q}_i = \bar{\chi} + \frac{N_C}{N_A + N_C} V - \chi_i + v \dot{q}_i \]

A: \[ m_q \ddot{q}_i = \bar{\chi} - \frac{N_A}{N_A + N_C} V - \chi_i + v \dot{q}_i \]
E-COMB Results

\[ \rho_q(z) \]

\[ \frac{\rho(O)}{\rho(0)} \]
E-COMB Results

\[
\frac{\rho(0)}{\bar{\rho}(0)}
\]

For 0V and 2.5V, the ratio of the density at the origin to the averaged density is plotted over time. The graph shows a decrease in the ratio as time increases, with a more pronounced decrease for 2.5V compared to 0V.

\[
P(z) = \left\langle \frac{1}{N(z)} \sum_{i=1}^{N} \left( 3\mu^2_{z,i} - 1 \right) \right\rangle
\]

The order parameter, \(P(z)\), is calculated as the average of the expression \(3\mu^2_{z,i} - 1\) over all particles at a given z-coordinate, normalized by the number of particles at that z-coordinate.
Proton transfer

H₃O  H₅O₂

OH distance = 1.2 Å

OH distance = 0.96 Å
Hydrogen bond = 1.78 Å

Proton transfer
Barrier ~ 0.2 eV
COMB ~ 1.5 eV

Ongoing applications

• CDC materials
• Electrochemical simulations with applied potentials
• TiC₂, Ti₂C₃ 2D MXene materials
• Proton transfer in electrochemical systems and MXene materials