**Molecular Dynamics simulations**

**Introduction**
- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

**Part 1: the theory behind molecular dynamics**
- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

**Part 2: total energy and force calculations**
- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

**Part 3: advanced techniques, mesodynamics, verification and validation**
- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom
- Before you perform production runs

- Tutorial to perform MD simulations using the nanoMATERIALS simulation tool at the nanoHUB
- Homework exercises
**Molecular materials**

\[ V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) + V_{\text{elec}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\}) \]

Interaction between atoms separated by chemical bonds

**Bond stretch:**

\[ \phi_{\text{bond}}(r) = \frac{1}{2} k_{ij} (r - r_{ij}^0)^2 \]

\[ \text{Morse, } L - J \]

**Angle bending:**

\[ \phi_{\text{angle}}(\theta) = \begin{cases} 
\frac{1}{2} k_{ijk} (\theta - \theta_{ijk}^0)^2 \\
\frac{1}{2} \frac{k_{ijk}}{\sin^2 \theta_{ijk}^0} \left[ \cos \theta - \cos \theta_{ijk}^0 \right]^2
\end{cases} \]
Covalent interactions

Torsion bending (dihedral angles)

\[
\phi_{torsions}(\varphi) = k_{ijkl}\left[1 - \cos(n_{jk}(\varphi - \varphi_{jk}^0))\right]
\]

Ethylene (planar)

\[
\begin{align*}
\text{H} & \quad \text{C} = \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\]

**sp\(^2\) hybridization**
- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
  - Rotating around C-C bond breaks the PI bond

Ethane (staggered)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} = \text{C} \\
\text{H} & \quad \text{H}
\end{align*}
\]

**sp\(^3\) hybridization**
- Equilibrium at 60°, 180°, & 300°
- Maxima at: 0°, 120°, & 240°
- Low torsional barrier
  - Dominated by vdW between H
Atom types in molecular force fields

- Element alone is not enough to determine the interactions
  - E.g.: sp3 carbon and sp2 carbon behave differently

- In traditional molecular force fields the user specifies *force field types* to establish the character of the atom
  - Force field types & connectivities need to be determined prior to MD simulation
  - FF types and connectivities are kept fixed during run

Widely used force fields for molecular simulations:


**Reactive force fields**

**Features:**
- Interactions should depend only on element and environment
  - No force field types
  - Partial charges should depend on environment
- No pre-determined connectivites
  - Bonds should be determined based on geometry
  - Bonds can be broken and formed

\[ V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) + V_{\text{elect}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\}) \]
Reactive force fields: covalent interactions

- Bond stretch, angle, & torsion terms depend on bond orders involved
  - E.g. distinguish between sp\(^2\) and sp\(^3\) carbon
- As a bond order goes to zero all terms involving also tend to zero
  - Bond orders are pre-factors for all covalent terms
- Over-coordination penalty
  - Limit the number of bonds an atom can make

van Duin & Goddard, Caltech
Reactive force fields: electrostatics

Partial atomic charges should be allowed to change as chemical reactions occur.

Charge equilibration enables the calculation of partial charges based on atomic positions:

\[ V_{elec} = \sum_{i<j} q_i q_j J(r_{ij}) + \sum_i \left( \chi_i q_i + \frac{1}{2} H_i q_i^2 \right) \]

**Interactions**
(shielded Coulomb)

**Atomic terms**
(electron affinity and ionization potential)

Reactive force fields: key developments

• Reactive Empirical Bond Order (REBO):

• AI-REBO:

• ReaxFF:
EAM potentials: parameterization

- Fit parameters based on experimental data
  - Lattice parameter, elastic constants, vacancy & surface energy
- Use of \textit{ab initio} data enables the incorporation of more information

EAM potential for Tantalum

\textbf{Strachan et al. MSMSE (2004)}
EAM potentials: parameterization

- Large deformations
  - Shear transformation in the twinning mode (ideal strength)

\[
a = \frac{1}{2}[-111] + s[-1-11] \\
b = \frac{1}{2}[1-11] + s[-1-11] \\
c = \frac{1}{2}[11-1]
\]

<table>
<thead>
<tr>
<th>vol</th>
<th>qEAM FF</th>
<th>DFT-GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (eV)</td>
<td>(\tau) (GPa)</td>
</tr>
<tr>
<td>18.36</td>
<td>0.188</td>
<td>7.14</td>
</tr>
<tr>
<td>17.618</td>
<td>0.2</td>
<td>8</td>
</tr>
<tr>
<td>15.144</td>
<td>0.26</td>
<td>12.05</td>
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<tr>
<td>10.91</td>
<td>0.43</td>
<td>28.2</td>
</tr>
</tbody>
</table>

DFT-data from:

- Vacancy and surface formation energies
EAM potentials: validation & application

Thermal expansion

Experiment

qEAM FF

linear thermal expansion

From isothermal and isobaric MD runs
EAM potentials: validation and application

2-phase MD simulation

Melting at ambient pressure
- Simulation: 3150±50 K (4%)
- Experiment: 3290±50 K

Strachan et al. MSMSE (2004)
Reactive force fields: parameterization

ReaxFF (Adri van Duin and Bill Goddard @ Caltech)

**Bond breaking**

- H\textsubscript{3}C-NH\textsubscript{2} dissociation

**Angle bending**

- H\textsubscript{2}N-O-NH\textsubscript{2} angle

**Torsion bending**

- H\textsubscript{2}C=NH torsion angle

- Bond breaking curves for all bonds
- Angle and torsion bending
- Gas phase reactions
- Crystalline data
- 100s chemical reactions
- 1000s equilibrium structures
Reactive force fields: parameterization

ReaxFF (Adri van Duin and Bill Goddard @ Caltech)

• Unimolecular decomposition pathways of RDX
• QM vs. ReaxFF

**Reactive force fields: applications**

<table>
<thead>
<tr>
<th>Shock decomposition</th>
<th>32 RDX molecules on 32 RDX molecules</th>
</tr>
</thead>
</table>


**Thermal decomposition**

Constant temperature & density

Interatomic potentials: summary

• Ab initio electronic structure calculations
  • Very accurate but computationally intensive

• Parameterize “first principled-based interatomic potentials”
  • Equations of state for various crystals, elastic constants
  • Chemical reactions
  • Defect structure and energies

• Enable predictive simulations
  • Validate approach for well characterize materials
  • Use it to predict the behavior of new materials or devices