From Atoms to Materials: Predictive Theory and Simulations

Week 3: Dynamics of Atoms – Classical Mechanics and MD Simulations
Lecture 3.2: Interatomic Potentials for Molecular Materials: Covalent Interactions

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Structure of a minimalist MD code

Initial conditions
\([R_i(0), V_i(0)]\]

Calculate forces at current time \([F_i(t)]\) from \(R_i(t)\)

Integrate equations of motion
\(R(t) \rightarrow R(t+\Delta t)\)
\(V(t) \rightarrow V(t+\Delta t)\)
\(t \rightarrow t+\Delta t\)

Save properties

Done?

Output files

Y

End

No
How can we compute interatomic potential?

- **Ab initio electronic structure methods**
  - Density Functional Theory, Hartree-Fock
  - Quantum Monte Carlo
  - Very accurate but computationally intensive (applicable to small systems – 100s-1000s atoms)

- Interatomic potentials:

\[
V \left( \{ R_i \} \right) = V_{\text{cov/met}} \left( \{ R_i \} \right) + V_{\text{electr}} \left( \{ R_i \} \right) + V_{\text{vdW}} \left( \{ R_i \} \right)
\]

*Parameterized* to describe specific materials
- **Ab initio** data
- Experiments
Covalent interactions

Represent the effect of chemical bonds
• 2-body, 3-body and 4-body interactions

2-body – bond stretch
• Pairs of atoms separated by a chemical bond

\[ \phi_{\text{bond}}(R) = \frac{1}{2} k_{\alpha\beta} (R - R_{\alpha\beta}^0)^2 \]

Advantages of harmonic bonds
• Stable (bonds can’t be broken) and simple

Disadvantages
• Symmetric and compression and tension (no thermal expansion)
Covalent interactions

Other functional forms for bond stretch:

**Lennard-Jones (6-12)**

\[ \phi_{LJ}(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right] \]

**Exponential-6**

\[ \phi_{\text{exp-6}}(R) = \varepsilon \left[ e^{-\gamma R} - AR^{-6} \right] \]

**Morse**

\[ \phi_{\text{Morse}}(r) = \varepsilon \left[ \exp\left( \gamma \left( 1 - \frac{R}{R_0} \right) \right) - 2 \exp\left( \frac{\gamma}{2} \left( 1 - \frac{R}{R_0} \right) \right) \right] \]
Covalent interactions: 3-body

Angle bending:

\[ \phi_{\text{angle}}(\theta) = \begin{cases} 
\frac{1}{2} k_{ijk} \left( \theta - \theta_{ijk}^0 \right)^2 \\
\frac{1}{2} \sin^2 \theta_{ijk}^0 \left[ \cos \theta - \cos \theta_{ijk}^0 \right]^2
\end{cases} \]
Covalent interactions: 4 body

Torsion bending (dihedral angles)

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

Ethane (staggered)

**sp\(^3\) hybridization**
- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
  - Rotating around C-C bond breaks the PI bond

Ethylene (planar)

**sp\(^2\) hybridization**
- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
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Ethylene (planar)

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

**sp\(^3\) hybridization**
- Equilibrium at 60°, 180°, & 300°
- Maxima at: 0°, 120°, & 240°
- Low torsional barrier
  - Dominated by vdw between H
Hybrid orbitals and torsional potentials
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

• Reactive force fields (like ReaxFF and REBO) describe interactions purely in terms of atomic positions and allow for atoms to change coordination and environment
Force fields for molecular simulations


