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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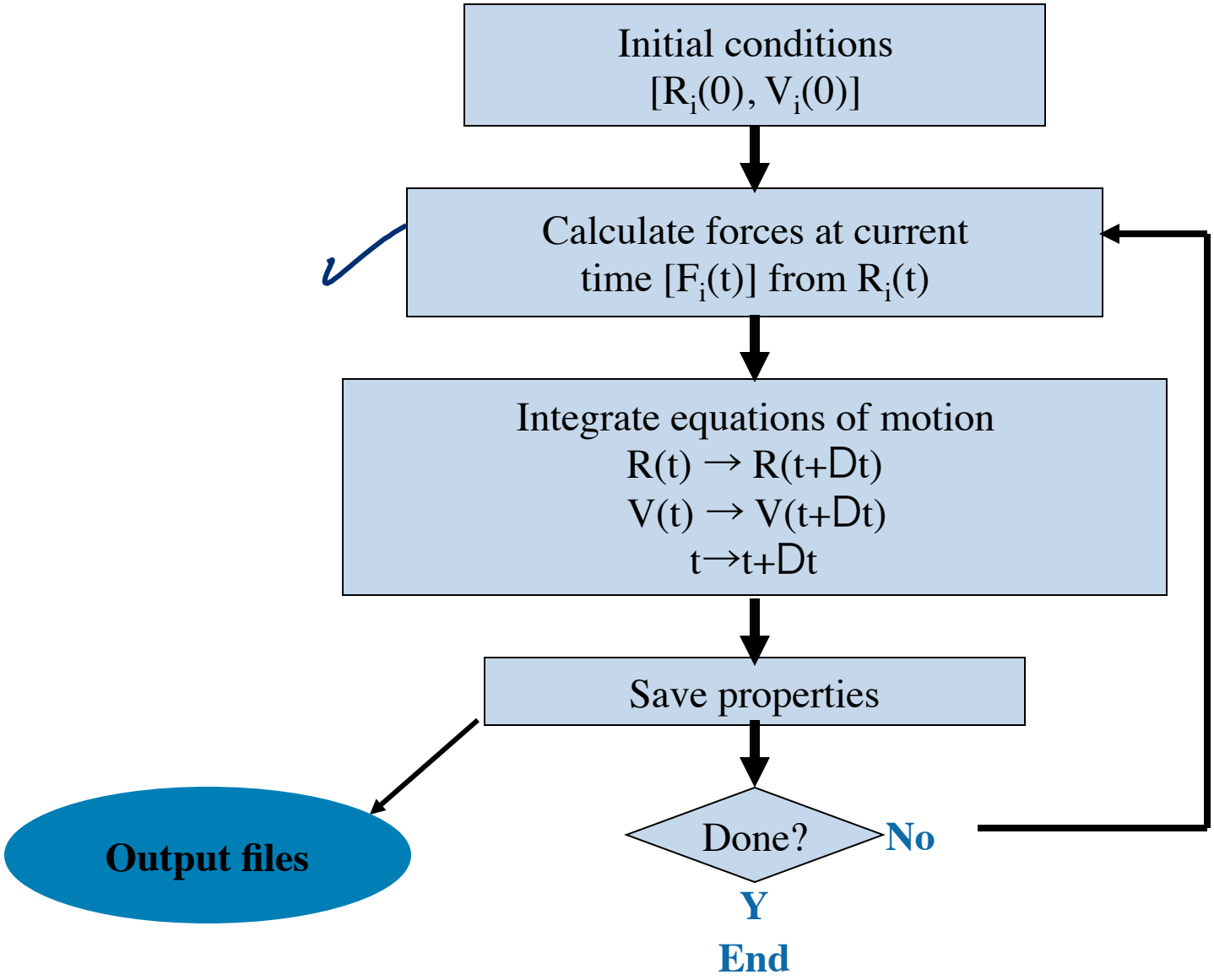
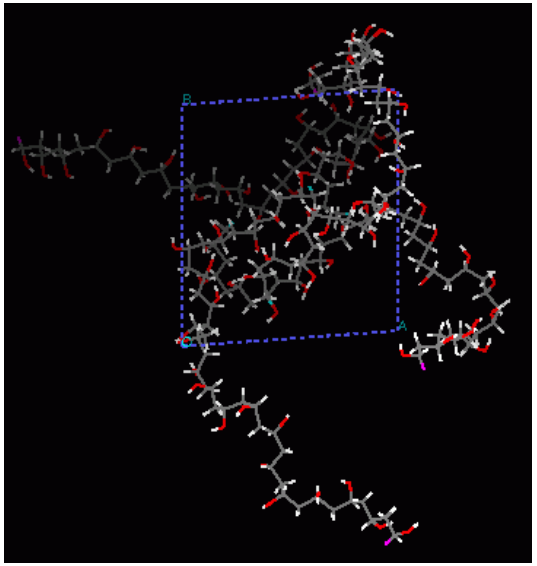
Structure of a minimalist MD code



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:

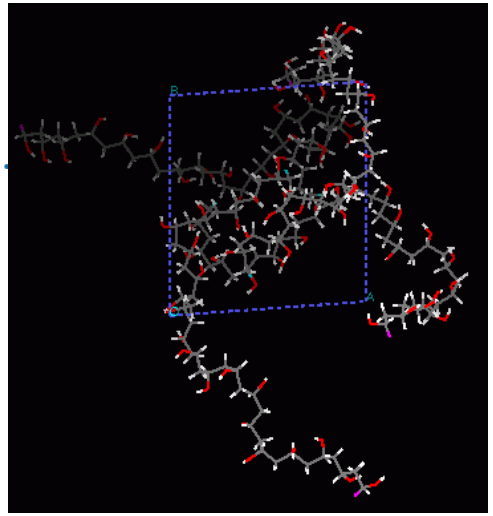


$$V\left(\left\{R_i\right\}\right) = V_{\text{cov/met}}\left(\left\{R_i\right\}\right) + V_{electr}\left(\left\{R_i\right\}\right) + V_{vdW}\left(\left\{R_i\right\}\right)$$

Parameterized to describe specific materials

- *Ab initio* data
- Experiments

Covalent interactions

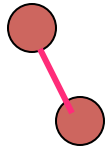


Represent the effect of chemical bonds

- 2-body, 3-body and 4-body interactions

2-body – bond stretch

- Pairs of atoms separated by a chemical bond)



$$\phi_{bond}(R) = \frac{1}{2} k_{\alpha\beta} \left(R - R^0_{\alpha\beta} \right)^2$$

~ 700 kcal/mol / Å²

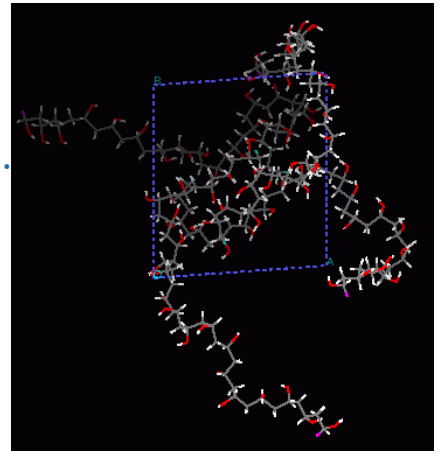
Advantages of harmonic bonds

- Stable (bonds can't be broken) and simple

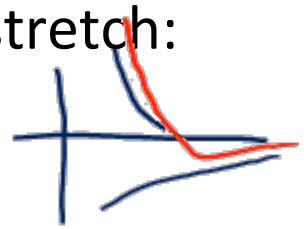
Disadvantages

- Symmetric and compression and tension (no thermal expansion)

Covalent interactions



Other functional forms for bond stretch:



Lennard-Jones (6-12)

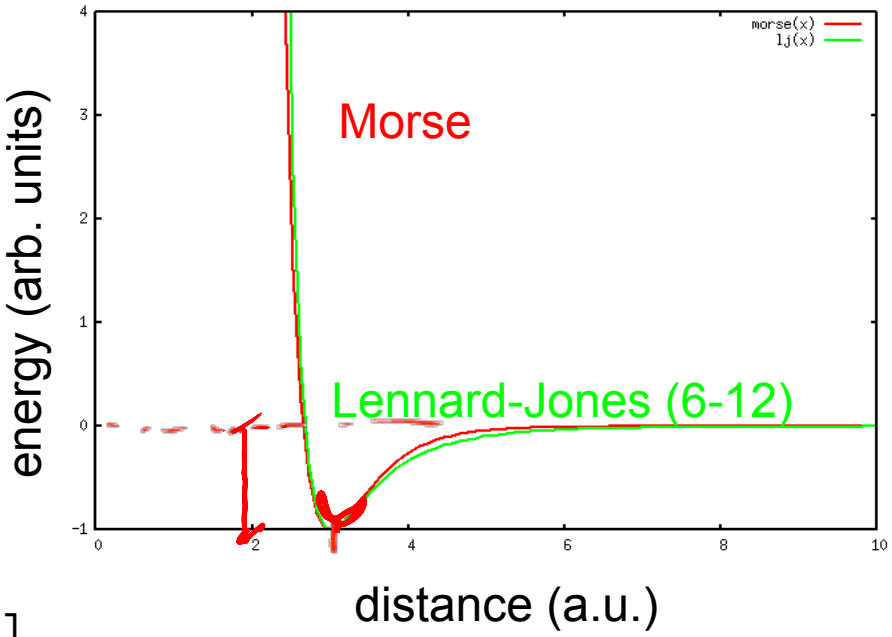
$$\phi_{LJ}(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

Exponential-6

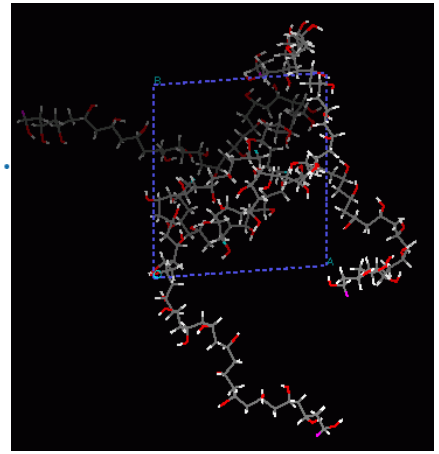
$$\phi_{\exp-6}(R) = \varepsilon\left[e^{-\gamma R} - AR^{-6}\right]$$

Morse

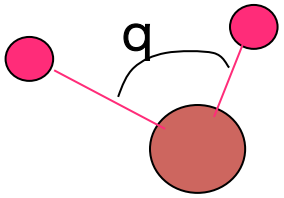
$$\phi_{Morse}(r) = \varepsilon\left[\exp\left(\gamma\left(1-\frac{R}{R_0}\right)\right) - 2\exp\left(\frac{\gamma}{2}\left(1-\frac{R}{R_0}\right)\right)\right]$$

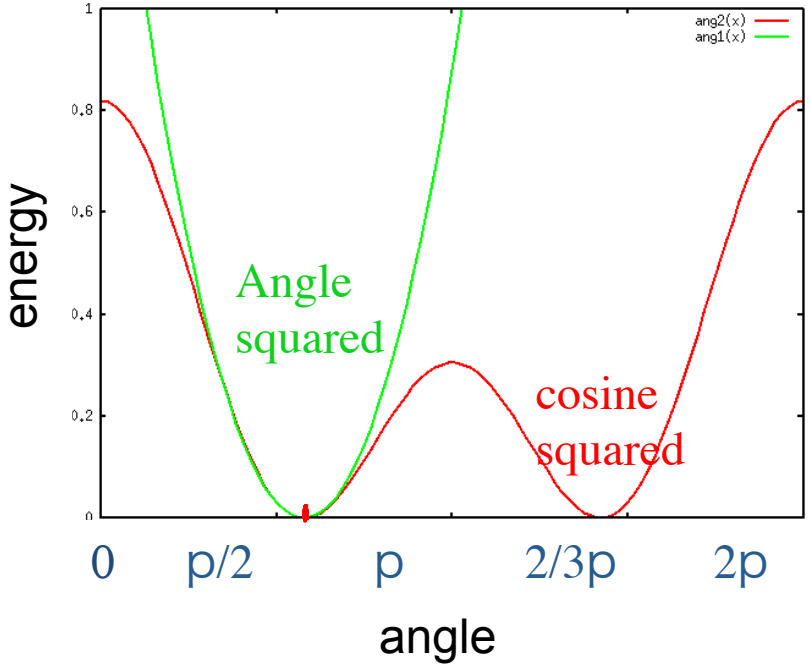


Covalent interactions: 3-body



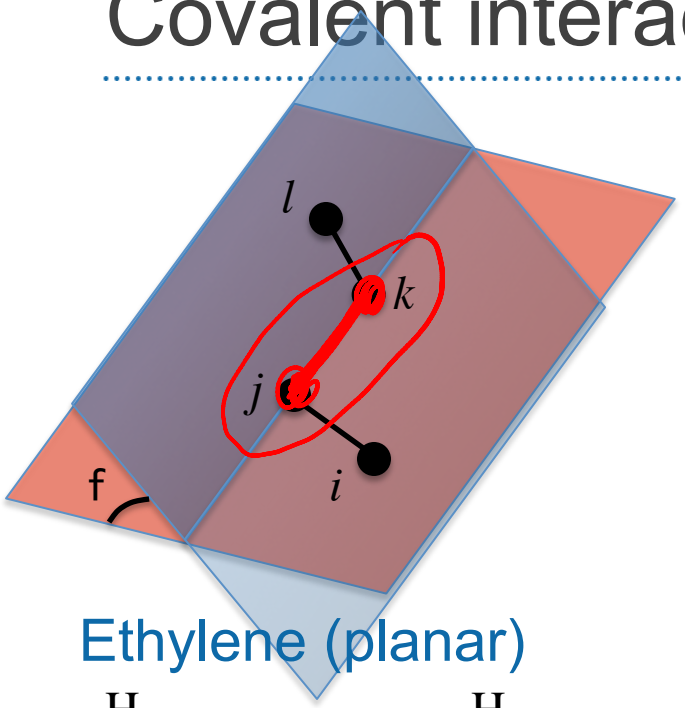
Angle bending:





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

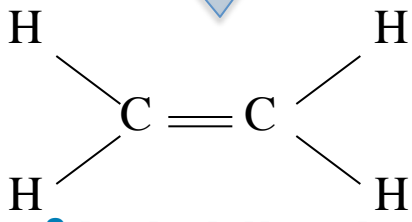
Covalent interactions: 4 body



Torsion bending (dihedral angles)

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

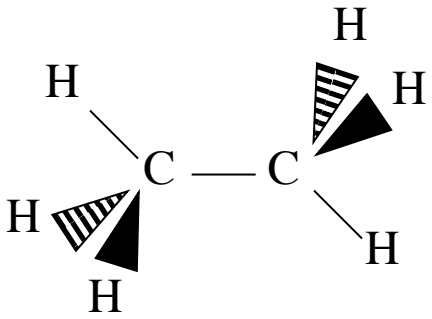
Ethylene (planar)



sp² hybridization

- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
  - Rotating around C-C bond breaks the PI bond

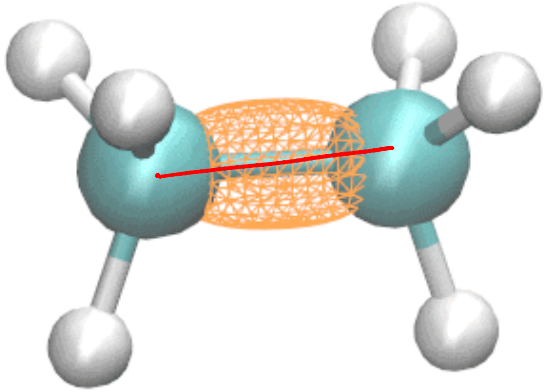
Ethane (staggered)

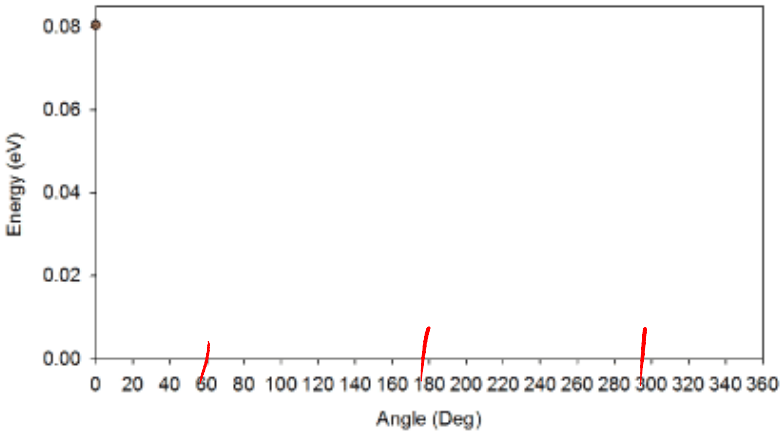


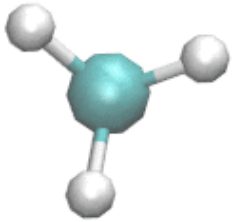
sp³ hybridization

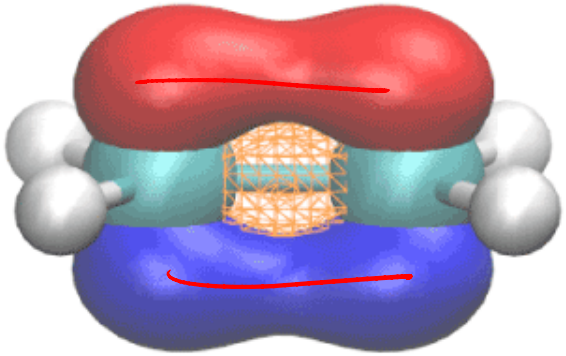
- Equilibrium at 60°, 180°, & 300°
- Maxima at: 0°, 120°, & 240°
- Low torsional barrier
  - Dominated by vdW between H

Hybrid orbitals and torsional potentials

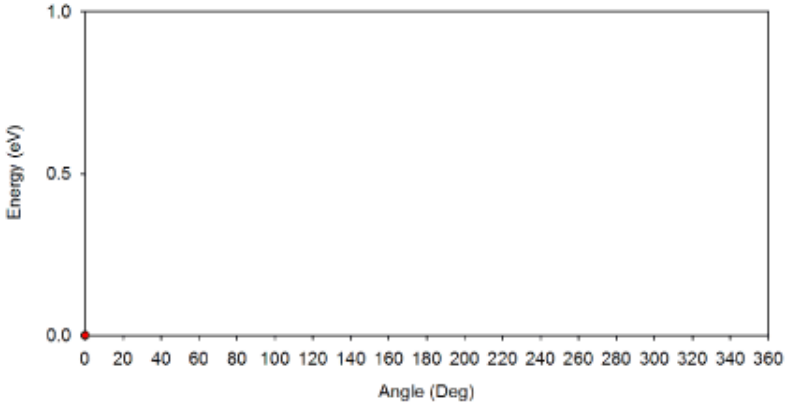








Bond Length=1.33 Ang



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

CHARMM: Brooks, Bruccoleri, Olafson, States, Swaminathan, and Karplus. J. Comput. Chem., **4**, 187 (1983).

DREIDING: Mayo, Olafson, and Goddard, III, J. Chem. Phys. 94, 8897 (1990).

AMBER: Cornell, Cieplak, Bayly, Gould, Merz, Ferguson, Spellmeyer, Fox, Caldwell, and Kollman. J. Am. Chem. Soc., **117**, 5179 (1995).

COMPASS: H. Sun, J. Phys. Chem. B, **102**, 7338–7364 (1998)

OPLS: G. A. Kaminski, R. A. Friesner, J. Tirado-Rives, and W. L. Jorgensen J. Phys. Chem. B **105** 6474-6487 (2001).