Short Course on Molecular Dynamics Simulation

Lecture 2: Potential Energy Functions

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High Level Course Outline

1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD
MD Basics

- Process summary

  - Interaction Model
  - Initial Positions
  - Calculate Total Force on N Atoms
  - Calculate Acceleration of Each Atom
  - Calculate Velocity of Each Atom
  - Move All Atoms to New Positions
Interaction Models

\[ m \ddot{a} = F \]

\[ a = \frac{dv}{dt} \quad \dot{v} = \frac{dr}{dt} \]

\[ F = \frac{dU}{dr} \]

Interaction force is the spatial derivative of the potential energy.
Interaction Models

Potential Energy

Inter-atomic

Pair
Coulomb
EAM
Reaction

Intra-molecular

Bond
Angle
Torsion
Out of Plane
Pair Potentials

- Pair potentials – van der Waals interactions
  - Attraction
    - Act at long distances
    - Dispersive forces
    - Due to instantaneous dipoles that arise during the fluctuations in the electron cloud
  - Repulsion
    - Act at short distances
    - Exchange forces or overlap forces
    - Overlap of electron clouds such that nuclei are less well shielded by electrons
Pair Potentials

\[ U(r) \]

\[ \begin{align*}
    &\text{Repulsive} \\
    &\text{Attractive}
\end{align*} \]
Pair Potentials

- Pair potentials
  - General Form

\[
U(r) = k \varepsilon \left( \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^m \right)
\]

\[
k = \frac{n}{n-m} \left( \frac{n}{m} \right)^{m/(n-m)}
\]

Repulsive \quad Attractive

- Lennard-Jones (n=12, m=6)

\[
U_{\text{LJ}}(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)
\]

\[
F_{\text{LJ}}(r) = -\frac{dU(r)}{dr} = 24 \frac{\varepsilon}{\sigma} \left( 2 \left( \frac{\sigma}{r} \right)^{13} - \left( \frac{\sigma}{r} \right)^7 \right)
\]
Pair Potentials

\[ U(r) \quad F(r) \]

\[ \varepsilon \quad \sigma \]

\[ r \sim \sigma \]
Pair Potentials

- **Truncation**
  - The Lennard-Jones force (and similar models) decays rapidly with distance
  - Significant computation time can be saved by neglecting pair interactions beyond a cut-off

\[ U_{LJ,t}(r) = \begin{cases} 
4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) & r \leq r_c \\
0 & r > r_c 
\end{cases} \]

- Commonly, \( r_c = 2.5 \sigma \)
Pair Potentials

- Truncated and shifted
  - The potential energy vanishes at the cut off radius
  - No discontinuity → no impulsive force

\[ U_{LJ,t-s}(r) = \begin{cases} 
  U_{LJ}(r) - U_{LJ}(r_c) & r \leq r_c \\
  0 & r > r_c 
\end{cases} \]

- Shift must be taken into account in all post-processing calculations
Pair Potentials

- Typical values of LJ constants

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$\sigma$ (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>10.22</td>
<td>258</td>
</tr>
<tr>
<td>Ne</td>
<td>35.7</td>
<td>279</td>
</tr>
<tr>
<td>Ar</td>
<td>124</td>
<td>342</td>
</tr>
</tbody>
</table>

- The united atom model

$\varepsilon_{H}, \sigma_{H}$

$\varepsilon_{C}, \sigma_{C}$

$\varepsilon_{CH4} = 137$ K

$\sigma_{CH4} = 382$ pm
Pair Potentials

- Combination rules
  - Relate LJ parameters for an unlike pair (i-j) to the parameters of two like pairs (i-i and j-j)

1. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$
2. $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$
3. $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$
4. $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$
5. $\varepsilon_{ij} = \frac{2 \sigma_i^3 \sigma_j^3 \varepsilon_i \varepsilon_j}{\sigma_i^6 + \sigma_j^6}$
6. $\sigma_{ij} = \left(\frac{\sigma_i^6 + \sigma_j^6}{2}\right)^{\frac{1}{6}}$
Coulombic Interactions

- Coulombic interactions
  - Included if electrostatics between atoms are significant
  - Atomic charges $q_i$ and $q_j$

$$U_{coulomb} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$

$q_i$ and $q_j$ are the atomic charges, $r_{ij}$ is the distance between them, and $\varepsilon_0$ is the vacuum permittivity.
Coulombic Interactions

- In general, the contribution of the tail of a truncated potential is

\[ U^{\text{tail}} = \frac{N\rho}{2} \int_{r_c}^{\infty} U(r) 4\pi r^2 dr \]

- Coulombic force decays slower than \( r^{-3} \)
- Methods for calculating the long-range contributions
  - Ewald summation
  - Fast multipole methods
  - Particle-mesh-based methods
Coulombic Interactions

- Ewald sums
  - Assume every particle $i$ with charge $q_i$ is surrounded by a diffuse charge distribution of opposite sign
  
  - Electrostatic potential due to $i$ is exclusively due to the fraction of $q_i$ that is not screened by the cloud
  - This fraction rapidly decays to zero
Coulombic Interactions

- Contribution to the electrostatic potential due to a set of screened charges can be found by direct summation because it decays rapidly with distance.
- But we want to evaluate the contribution from \textit{point} charges, not \textit{screened} charges.
- So we correct for the screening clouds by introducing a smooth, compensating charge density.

\[
\text{point charges} = \text{(point charges + screening cloud)} + \text{compensating cloud}
\]
Coulombic Interactions

- Compensating charge distribution surrounding $i$ is a Gaussian of width $\sqrt{2/\alpha}$

$$\rho_{Gauss}(r) = -q_i (\alpha/\pi)^{3/2} \exp(-\alpha r^2)$$

- Finally

$$U_{Coulomb} = \frac{1}{2V} \sum_{k \neq 0} \frac{4\pi}{k^2} |\rho(k)|^2 \exp(-k^2/4\alpha)$$

$$- (\alpha/\pi)^{1/2} \sum_{i=1}^{N} q_i^2$$

$$+ \frac{1}{2} \sum_{i \neq j}^{N} q_i q_j \text{erfc}(\sqrt{\alpha r_{ij}})$$

$$/ r_{ij}$$
Embedded Atom Model

- Metals have ionized atom cores with a "sea" of delocalized valence electrons
Embedded Atom Model

- Model formulation

\[ E_{total} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j(i\neq j)} \phi(r_{ij}) \]

- \( \rho_i \): electron density at atom \( i \)
- \( F(\rho_i) \): embedding function
- \( \phi(r_{ij}) \): pair potential between atoms \( i \) and \( j \)
- \( f(r_{ij}) \): electron density function at atom \( i \) due to atom \( j \)

- Three look-up tables

| \( r_{ij} \) | \( f(r_{ij}) \) - electron density function |
| \( \rho_i \)  | \( F(\rho_i) \) - embedding function       |
| \( r_{ij} \)  | \( \phi(r_{ij}) \) - pair potential function |
Reactive Potentials

- Some potentials model chemical reactions
  - Bond formation
  - Bond disassociation

- Common examples
  - Tersoff
  - REBO (reactive empirical bond order)

- Models developed for
  - Silicon
  - Carbon
  - Oxygen
  - Hydrogen
Intramolecular Interactions

- For multi-atomic molecules, models describe the behavior of covalent bonds.
Intramolecular - Bond

- Bond stretching models
  - Harmonic bond model where $k$ is the “spring constant”
    \[
    U_{bond} = \frac{k}{2}(r - r_0)^2
    \]
  - What is $r_0$
    - Reference bond length – value of bond when all other terms in the force field are zero
    - Equilibrium bond length – value when other terms contribute

<table>
<thead>
<tr>
<th>Bond</th>
<th>r0 (Å)</th>
<th>K (kcal/mol/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>1.523</td>
<td>317</td>
</tr>
<tr>
<td>C=C</td>
<td>1.337</td>
<td>690</td>
</tr>
</tbody>
</table>
Intramolecular - Bond

- Bond stretching models
  - Morse bond potential where $D$ is the potential well depth, $\alpha$ is a stiffness constant, and $r_0$ is the equilibrium bond distance
  - Better handling of large displacements

\[ U_{\text{bond}} = D \left[ 1 - e^{-\alpha (r-r_0)} \right]^2 \]
Intramolecular - Angle

- Bond angle models
  - Harmonic angle model
    \[ U_{\text{angle}} = k(\theta - \theta_0)^2 \]
  - Cosine angle models
    \[ U_{\text{angle}} = k[1 + \cos(\theta)] \]

- For all of these, \( k \) is energy constant and \( \theta_0 \) is the equilibrium angle
Intramolecular - Torsion

- Torsion models (dihedrals)
  - Harmonic torsion angle
    \[ U_{\text{torsion}} = k[1 + d \cos(n\phi)] \]

ϕ is the angle between Plane 1 and Plane 2
Intramolecular – Out of Plane

- Out of plane models
  - The least common of the intramolecular potentials
  - Describes energy associated with the displacement of atoms out of their equilibrium plane
  - Relevant only to parts of molecules where atoms are known to lie in the same plane

\[ U_{oop} = kh^2 \]