2. Fundamentals of Molecular Dynamics Method

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Equation of Motion

\[ m \frac{d^2 \mathbf{r}_i}{dt^2} = - \nabla \Phi(\mathbf{r}_i) \]

Pair Potential Approximation

\[ \Phi(\mathbf{r}_{ij}) = \frac{1}{2} \sum_i \sum_{j>i} \phi(r_{ij}) \]

Lennard-Jones (12-6) Potential

\[ \phi(r) = 4 \epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

Parameters for inert molecules:

<table>
<thead>
<tr>
<th>( \sigma ) [( \text{nm} )]</th>
<th>( \epsilon ) [( \text{J} )]</th>
<th>( \sigma T ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.274</td>
<td>0.50x10^{-21}</td>
</tr>
<tr>
<td>Ar</td>
<td>0.340</td>
<td>1.67x10^{-21}</td>
</tr>
<tr>
<td>Kr</td>
<td>0.365</td>
<td>2.25x10^{-21}</td>
</tr>
<tr>
<td>Xe</td>
<td>0.398</td>
<td>3.20x10^{-21}</td>
</tr>
</tbody>
</table>

Cut-Off of potential: \( r_c = 2.5 \sim 5.5 \sigma \)

\[ \phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + 8 \epsilon_c \left( r - r_c \right)^6 - 4 \epsilon_c \left( r - r_c \right)^{12} \]

Small Droplets

Only 256 molecules

864 molecules

Lennard-Jones (12-6) Potential
Non-dimensional Form for L-J System

<table>
<thead>
<tr>
<th>Property</th>
<th>Reduced Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length r*</td>
<td>( r/\sigma )</td>
</tr>
<tr>
<td>Time t*</td>
<td>( t/\tau ) = ( t(\sigma^2m/\epsilon)^{1/2} )</td>
</tr>
<tr>
<td>Temperature T*</td>
<td>( t(\epsilon/\sigma^2m)^{1/2} )</td>
</tr>
<tr>
<td>Force f*</td>
<td>( f/\sigma )</td>
</tr>
<tr>
<td>Energy ( \phi^* )</td>
<td>( \phi/\epsilon )</td>
</tr>
<tr>
<td>Pressure P*</td>
<td>( P\sigma^3/\epsilon )</td>
</tr>
<tr>
<td>Number density N*</td>
<td>( N/\sigma^3 )</td>
</tr>
<tr>
<td>Density ( \rho^* )</td>
<td>( \rho/\sigma^3 )</td>
</tr>
<tr>
<td>Surface Tension ( \gamma^* )</td>
<td>( \gamma\sigma^2/\epsilon )</td>
</tr>
</tbody>
</table>

Lennard-Jones Potential (3)

Phase Diagram

\( T \)-p

<table>
<thead>
<tr>
<th>Temperature T*</th>
<th>Pressure P*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>0.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Number density \( \rho^* = \rho\sigma^3 \)

Lennard-Jones Potential (4)

Phase Diagram

\( p-v \)

<table>
<thead>
<tr>
<th>Volume v*</th>
<th>Pressure ( p^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>20</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Lennard-Jones Potential (5)

Small Droplets

Potential for Water (BNS, ST2)

BNS potential by Ben-Naim and Stillinger (1972)

ST2 potential by Stillinger and Rahman (1974)

\( \phi_{12}(R_{12}) = 4\epsilon_{12}\left[\frac{\sigma_{12}}{R_{12}}\right]^{12} - \left(\frac{\sigma_{12}}{R_{12}}\right)^6 + S(R_{12})\sum_j \frac{q_j q_i}{4\pi\epsilon R_{ij}^3} \)

Potential for Water (SPC, SPC/E)

SPC potential by Berendsen et al. (1981)

SPC/E potential by Berendsen et al. (1987)

\( \phi_{12}(R_{12}) = 4\epsilon_{12}\left[\frac{\sigma_{12}}{R_{12}}\right]^{12} - \left(\frac{\sigma_{12}}{R_{12}}\right)^6 + \sum_j \frac{q_j q_i}{4\pi\epsilon R_{ij}^3} \)
Potential for Water (TIP4P)

\[ \phi_2(R_1, R_2) = 4e^2 \left( \frac{\sigma_{02}}{R_{12}} \right)^{12} - \frac{\sigma_{02}}{R_{12}} + \sum_{j \neq i} \frac{q_i q_j}{4\pi\varepsilon_0 R_{ij}} \]

\[ \angle \text{HOH} = 104.52^\circ \]

MCY potential by Matsuoka et al. (1976)
CC potential by Carravetta & Clementi (1984)

Potential for Water (Comparison)

<table>
<thead>
<tr>
<th>Potential</th>
<th>ST2</th>
<th>SPC/E</th>
<th>TIP4P</th>
<th>CC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_{OH}) [nm]</td>
<td>0.100</td>
<td>0.100</td>
<td>0.095</td>
<td>0.095</td>
</tr>
<tr>
<td>(\angle \text{HOH}) [°]</td>
<td>109.47</td>
<td>109.47</td>
<td>104.52</td>
<td>104.52</td>
</tr>
<tr>
<td>(a) [Å]</td>
<td>0.52605</td>
<td>1.0797</td>
<td>1.0772</td>
<td>N/A</td>
</tr>
<tr>
<td>(\sigma_{OO}) [nm]</td>
<td>0.08</td>
<td>0</td>
<td>0.015</td>
<td>0.024</td>
</tr>
<tr>
<td>(q_a) [C]</td>
<td>0.2357 (e)</td>
<td>0.4238 (e)</td>
<td>0.52 (e)</td>
<td>0.18559 (e)</td>
</tr>
<tr>
<td>(q_m) [C]</td>
<td>0.2357 (e)</td>
<td>0.8476 (e)</td>
<td>-1.04 (e)</td>
<td>-0.37118 (e)</td>
</tr>
<tr>
<td>Charge of electron (e = 1.60219 \times 10^{-19} \text{C})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Polarizable & Flexible

Flexible potentials

- Dang & Pettitt (1987)
- Anderson et al. (1987)

Polarizable potentials

- MCY: Niesar et al. (1990)
- SPC: Bernardo et al. (1994)

Rigid: Effective Pair Potential

- Dipole moment: Isolated water: 1.85 D
  - SPC/E: 2.351 D

Droplet of Water

\[ \phi_{ij}(R_{ij}) = \sum_{j=i}^{\infty} \frac{q_i q_j}{4\pi\varepsilon_0 R_{ij}} + a_i \exp(-b_i R_{ij}) + a_j \exp(-b_j R_{ij}) + \exp(-b_j R_{ij}) \]

Potential for Covalent System (C, Si)

Dang & Pettitt (1987)

\[ \Phi = \sum_{i<j} f_{ij}(r_{ij}) \left[ \hat{\mathbf{r}}_i \cdot \mathbf{b} \right] \mathbf{V}_{ij}(r_{ij}) \]

**Potential for Covalent System (C, Si)**

![Tersoff's Silicon](image)

**Example:** Brenner Carbon (modified)

**Integration of Newton’s Equation**

- **Verlet’s Method**
  \[
  \mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{(\Delta t)^2}{m} \mathbf{F}(t)/m,
  \]
  \[
  \mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{(\Delta t)^2}{2m} \mathbf{F}(t)/m.
  \]

- **Leap Flog Method (Modified Verlet)**
  \[
  \mathbf{v}(t + \Delta t/2) = \mathbf{v}(t) + \frac{\Delta t}{2m} \mathbf{F}(t)/m,
  \]
  \[
  \mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \Delta \mathbf{v} + \frac{\Delta t^2}{2} \mathbf{F}(t)/m.
  \]

Order of \( \Delta t \)
- 0.005 \( \tau \) for 10 fs with argon
- 0.5 fs for covalent Carbon

**Mirror Boundary**
- Simple Reflection

**Boundary Condition (Gas)**

- Mirror Boundary
- Periodic Boundary

**Boundary Condition (Periodic)**

- Potential must be Cut-Off at L/2

**Ewald sum method for Coulomb Term**

**Example**
Boundary Condition (Solid Wall)

One-Dimensional Function by Bulk Integration

$$\Phi(z) = \frac{2 \pi \rho \sigma_{INT}}{45 m} \frac{\left(\frac{\sigma_{INT}}{z} \right)^3 - \left(\frac{\sigma_{INT}}{z} \right)^2}{z}$$

Boundary Condition (Solid Wall)

One-Dimensional Function by Surface Integration

$$\Phi(z) = 4 \sqrt{3 \pi} \frac{\sigma_{INT}^2}{R_e} \left(\frac{\sigma_{INT}}{z} \right)^{10} - \left(\frac{\sigma_{INT}}{z} \right)^{2}$$

Boundary Condition (Solid Wall)

Initial Condition

$$v = \sqrt{3 k_B T_C / m}$$

Make Sure Potential is not Too Large

Temperature Control

Velocity Scaling

$$v' = v \sqrt{T/T_e}$$

Anderson method [Anderson (1980)]

Replace Velocity of Randomly Selected Molecule to Maxwell-Boltzmann Distribution

Nosé-Hoover Thermostat [Nosé (1984), Hoover (1985)]

$$m \frac{dt^2}{dt} = F - \frac{\zeta m}{\Delta t} \frac{dt}{dt}$$

$$\frac{d \zeta}{dt} = \frac{2(F_{\perp} - E_{\perp})}{Q}$$
Pressure & Stress Control

Andersen (1980)
Change Box Size as if Piston is Connected

Extension of Anderson: Change Shape of Box

Berendsen et al. (1984)
\[ \frac{dP}{dt} = \frac{(P_r - P)}{t_r} \]
\[ r = r^{\infty} \]
\[ \chi = 1 - \beta \frac{dr}{dt} (P_r - P) \]