ME 517: Micro- and Nanoscale Processes

Lecture 28: Molecular Dynamics - I

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Molecular Interaction Forces: Lennard-Jones 6-12 Potential

\[ V_{ij}(r) = 4\varepsilon \left[ c_{ij} \left( \frac{r}{\sigma} \right)^{-12} - d_{ij} \left( \frac{r}{\sigma} \right)^{-6} \right] \]

\[ F_{ij}(r) = -\frac{\partial V_{ij}}{\partial r} = \frac{48\varepsilon}{\sigma} \left[ c_{ij} \left( \frac{r}{\sigma} \right)^{-13} - \frac{d_{ij}}{2} \left( \frac{r}{\sigma} \right)^{-7} \right] \]

- \( V_{ij} \) = potential energy between two molecules \( i \) and \( j \)
- \( F_{ij} \) = force between two molecules \( i \) and \( j \)
- \( c_{ij} \) and \( d_{ij} \) are parameters for chosen molecules
- \( \varepsilon, \sigma \) are characteristic energy and length scales respectively
- \( r \) is the separation distance
- \( r \approx 10\sigma \) for a gas
- \( r \approx 1 \) for a liquid

Micro/Nanoscale Physical Processes
# Lennard Jones Constants

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \varepsilon/K ) (K)</th>
<th>( \sigma ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>97</td>
<td>0.362</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>91.5</td>
<td>0.368</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>190</td>
<td>0.400</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>113</td>
<td>0.343</td>
</tr>
<tr>
<td>Ar</td>
<td>124</td>
<td>0.342</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phases</th>
<th>Intermolecular Forces</th>
<th>Ratio of Thermal Vibration Amplitude Compared to ( \sigma )</th>
<th>Approach Needed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Strong</td>
<td>« 1</td>
<td>Quantum</td>
</tr>
<tr>
<td>Liquid</td>
<td>Moderate</td>
<td>~ 1</td>
<td>Quantum/classical</td>
</tr>
<tr>
<td>Gas</td>
<td>Weak</td>
<td>» 1</td>
<td>Classical</td>
</tr>
</tbody>
</table>
Molecular Dynamics Governing Equations

\[ m \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j \neq i} \frac{\partial V_{ij}}{\partial \mathbf{r}_i} - \frac{m}{\tau} \frac{d\mathbf{r}_i}{dt} + \eta_i \]

- Where \( \mathbf{r}_i \) is the position vector, \( V_{ij} \) is the potential energy between any two molecules, \( \tau \) is characteristic time scale, \( m \) is atomic mass.
- Last two terms on RHS couple the particle dynamics with thermodynamics
  - Velocity term governs heat exchange with reservoir
  - \( \eta_i \) term is a Gaussian stochastic force with variance \( \frac{2mk_b}{\tau} \)
- For liquid argon, \( \tau = 2.2^{-12} \) sec
- Evolve the position of every molecule forward in time using Newton’s 2nd Law

Numbers Formidable!
Shifted Lennard-Jones Potential

\[ V_{ij}(r) = 4\varepsilon \left[ c_{ij} \left( \frac{r}{\sigma} \right)^{12} - d_{ij} \left( \frac{r}{\sigma} \right)^{6} - \left( c_{ij} \left( \frac{r_c}{\sigma} \right)^{12} - d_{ij} \left( \frac{r_c}{\sigma} \right)^{6} \right) \right] \]

- \( r_c \) is cut-off radius, typically \( 2.2\sigma < r_c < 2.5\sigma \)
Lennard-Jones Potential

- Works reasonably well for electrically neutral, polarizable, spherical molecules.
- Dynamics for immiscible liquids ($d_{12} = d_{21}$)
  - $d_{12} = 0$ implies pure short-range repulsion
  - $d_{12} = 1$ implies symmetric interaction
  - $d_{12} > 1$ implies enhanced attraction
- Dynamics of wall boundaries can be simulated with same L-J approach but different constants.
- Complicated molecules require complicated potentials, e.g. polymer chains can have a potential between all monomers plus a strongly attractive potential when all monomers in neighboring molecules line up.
Temporal Evolution

- Equations of motions can be integrated forward in time by typical predictor-corrector scheme
  - typical time step size $\Delta t = 0.005 \tau$
  - for liquid Ar, $\Delta t = 1.1 \times 10^{-14}$ sec
- Another commonly used discretization called Verlet integration rule is

$$\mathbf{r}^{n+1} = 2\mathbf{r}^n - \mathbf{r}^{n-1} + \Delta t^2 \mathbf{a}(t) + O(\Delta t^4)$$
Imposing External Forces

• Most flows driven by some external force
  – e.g. vibrating wall, pressure gradient, body force

• Need some way to couple in those forces

• Eulerian velocity computed as time average of $N_i$ molecules according to

\[ \mathbf{v}(x) = \frac{1}{N_i} \left< \sum_j \frac{d\mathbf{x}_j}{dt} \right> \]

\[ \tau(x) = \frac{1}{V_i} \left< \sum_j \left[ \frac{d\mathbf{x}_j}{dt} - \mathbf{v}(x) \right] \left[ \frac{d\mathbf{x}_j}{dt} - \mathbf{v}(x) \right] + \sum_{j<i} \mathbf{r}_{ij} \mathbf{f}_{ij} \right> \]
Computational Complexity

• Have to sum over all pairs of molecules so order $N^2$
• Cut-off distance reduces computational complexity somewhat
• Pairs of interacting molecules stored in Verlet list
  – For each molecule $a=1,2,\ldots,N$ create a list of neighbors that are within a distance $r_c+r_s$ where $r_c$ is the cut-off distance and $r_s$ is called a skin thickness
  – $r_s$ is chosen such that in a time interval of $S\sim 20 \Delta t$, no molecules from outside the skin enter the interaction range of molecule $a$
• Computational intensity reduced somewhat to (order $N$) + $S^{-1}$ (order $N^2$)
MD/Continuum Approach

- Occasionally desirable to combine MD and Continuum approach (e.g. N-S)
  - For example external flow over a body

Karniadakis and Beskok, 2002

Micro/Nanoscale Physical Processes
MD: Water Flow between Graphite Sheets

- ETH-Zurich simulated flows in and around CNTs and graphite sheets (Nanotech 2003)
- Exploring validity of no-slip assumption
- www.fisica.uniud.it/~ercolessi/md/; www.icos.ethz.ch

Slip lengths of 14-63 nm → No-slip violated
Flow Around CNTs (ETHZ)
Flow Around CNTs (ETHZ)

- Flow agrees quite well with continuum theory
- Slip length less than a single molecular diameter
- Considerable variations in fluid density near CNT