Molecular Dynamics Simulation of Nanoconfined Water Film

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PHy466/CSE485/MSE485 Atomic-Scale Simulation Final Project
Motivation

• Investigating behavior of water confined between surfaces in nano-scale environment is important for:
  • Biological systems (ex: ion channel)
  • Nanoelectromechanical systems (NEMS)
  • Nanolithography
  • Tribology

MD simulation by NAMD

- **NAMD** (NAnoscale Molecular Dynamics) is a parallel molecular dynamics code designed for high-performance simulation of large biomolecular systems.
- **Velocity Verlet.**
- **CHARMM force field**

\[
\vec{F}(\vec{r}) = -\nabla U(\vec{r}),
\]

\[U(\vec{r}) = \sum U_{\text{bonded}}(\vec{r}) + \sum U_{\text{nonbonded}}(\vec{r}),\]

\[
U_{\text{bond}} = k(r_{ij} - r_0)^2,
\]

\[
U_{\text{angle}} = k_\phi(\theta - \theta_0)^2 + k_{ub}(r_{ik} - r_{ub})^2,
\]

\[
U_{\text{tors}} = \begin{cases} 
  k(1 + \cos(n\psi + \phi)) & \text{if } n > 0, \\
  k(\psi - \phi)^2 & \text{if } n = 0,
\end{cases}
\]

\[
U_{\text{LJ}} = (-E_{\text{min}}) \left[ \left( \frac{R_{\text{min}}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{\text{min}}}{r_{ij}} \right)^{6} \right],
\]

\[
U_{\text{elec}} = \epsilon_{14} \frac{q_i q_j}{\epsilon_0 r_{ij}},
\]

Encyclopedia of Parallel Computing, DOI 10.1007/978-0-38709766-4
http://www.ks.uiuc.edu/Research/namd
Water model - TIP3P

Good:
- Computational efficiency
- Optimized with NAMD

Bad:
- Diffuse quicker than other models and real water

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>$T$ (°C)</th>
<th>$P$ (atm)</th>
<th>Density$^a$</th>
<th>$D^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC</td>
<td>25</td>
<td>1</td>
<td>3.85±0.09</td>
<td></td>
</tr>
<tr>
<td>SPC/E</td>
<td>25</td>
<td>1</td>
<td>2.49±0.05</td>
<td></td>
</tr>
<tr>
<td>TIP3P</td>
<td>25</td>
<td>1</td>
<td>5.19±0.08</td>
<td></td>
</tr>
<tr>
<td>TIP4P</td>
<td>25</td>
<td>1</td>
<td>3.31±0.08</td>
<td></td>
</tr>
<tr>
<td>TIP3P</td>
<td>25</td>
<td>(1)</td>
<td>0.993$^c$</td>
<td>5.06±0.09</td>
</tr>
<tr>
<td>TIP4P</td>
<td>25</td>
<td>(1)</td>
<td>0.990$^c$</td>
<td>3.29±0.05</td>
</tr>
<tr>
<td>TIP5P</td>
<td>25</td>
<td>(1)</td>
<td>0.999$^c$</td>
<td>2.62±0.04</td>
</tr>
<tr>
<td>Expt.$^d$</td>
<td>25</td>
<td>1</td>
<td>0.997</td>
<td>2.30</td>
</tr>
</tbody>
</table>

$^a$Units are g/cm$^3$.
$^b$Units are $10^{-5}$ cm$^2$/s.

Set up the System

(A) Equilibrium bulk water \((80\text{A})^3\)

(B) The final system size 10~50k atoms
Simulation setup

- 1 fs timestep
- Pairlist 10 Å, update every 10 steps
- Run NPT for 60 ps at 298 K to reach equilibrium
  - Nosé-Hoover Langevin piston pressure control
  - System size fluctuate in z

\[ P_0 = 1 \text{ bar} \]
\[ P_{\text{sys}} = -\frac{dU}{dV} \]

- Run NVE for 50 ps, with Silicon fixed
Single layer water film

Unit thickness of layer
\[ H \equiv 3.5 \text{ Å} \]
Layer structure at water-Si interface

1H
Layer structure at water-Si interface

2H
Layer structure at water-Si interface

3H
Layer structure at water-Si interface

5H

10H

$\rho(z)/\rho_0$

$z (\text{Å})$

$\rho(z)/\rho_0$

$z (\text{Å})$
Pair Correlation – What can we tell about layers?

\( g_z (1 \text{ H}) \)
Pair Correlation – What can we tell about layers?

$g_z (2 \text{ H})$

$g_z$

$|z|$

0.00E+00 5.00E-01 1.00E+00 1.50E+00 2.00E+00 2.50E+00 3.00E+00 3.50E+00

0 1 2 3 4 5 6

0.00E+00 5.00E-01 1.00E+00 1.50E+00 2.00E+00 2.50E+00 3.00E+00 3.50E+00

0 1 2 3 4 5 6
Pair Correlation – What can we tell about layers?

\( g_z (3 \text{ H}) \)
Pair Correlation – What can we tell about layers?

\[g_z (5 \text{ H})\]
Pair Correlation – What can we tell about layers?

$g_z (10 \ H)$
Pair Correlation – What can we tell about layers?

$g_z (15 \, H)$

![Graph showing the correlation function $g_z$ for $15 \, H$. The graph plots $|z|$ on the x-axis and $g_z$ on the y-axis, with values ranging from 0 to 1.2.]
Pair Correlation – What can we tell about layers?
Translational Diffusion

\[ D = \frac{1}{6Nt} \left\langle \sum_{j=1}^{N} \left[ r_j(t) - r_j(0) \right]^2 \right\rangle \]

For 5H (17.5 Å) Gap : \( D_{\text{edge}}/D_{\text{mid}} \sim 0.71 \)

For 10H Gap (52.5 Å) : \( D_{\text{edge}}/D_{\text{mid}} \sim 0.52 \)
Summary

• In the nanoconfined environment, water molecules tend to form 2-3 layers at the interface. Each layer is around 3-4 Å.

• Water dynamics at the boundary layer is more retarded, the diffusion coefficient is even half of that in the center.

In the future:
• Rotational diffusion/ Exchange rate between layers
• Imply Load/Shear force. Will it enhance the layer structure?

Thank you! Questions?
## Appendix

<table>
<thead>
<tr>
<th>System &amp; Location</th>
<th>Diffusion Coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Water</td>
<td>4.2E-5</td>
</tr>
<tr>
<td>Entire 1H</td>
<td>4.3E-5</td>
</tr>
<tr>
<td>Top Edge, 5H</td>
<td>4.3E-5</td>
</tr>
<tr>
<td>Center, 5H</td>
<td>4.0E-5</td>
</tr>
<tr>
<td>Bottom Edge, 5H</td>
<td>4.0E-5</td>
</tr>
<tr>
<td>Top Edge, 10H</td>
<td>1.1E-3</td>
</tr>
<tr>
<td>Center, 10H</td>
<td>1.2E-3</td>
</tr>
<tr>
<td>Bottom Edge, 10H</td>
<td>1.1E-3</td>
</tr>
</tbody>
</table>