

# Molecular Dynamics Simulation of a Nanoconfined Water Film

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## 1 Introduction

The behavior of water confined in nano-scale environment is of interest in many applications. In nano-lithography, variations in the properties of water in space could lead to changes in the expected patterning. In biological systems, like enzymes and ion channels, there are surfaces of molecules and cells everywhere. And since it is a biological system, it all takes place in water. Water is also a frequent lubricant in the study of tribology. Micro- and nano-electromechanical systems (M/NEMS) will often use water as a lubricant between moving pieces. As device sizes continue decreasing, the thickness of the lubricants may approach thicknesses on the order of the lubricant molecules.

In these nano-confined water systems, some ordering of the water molecules has been observed. If there is ordering among the water molecules in these confined areas, the behavior of the water may change from its bulk properties. In this project we will attempt to observe layers in the water and at what point the layered structure begins to vanish. In addition, we will attempt to study some dynamic properties and order parameters in these systems.

## 2 Simulation and Models

In this project, we studied the structure and dynamics of a nanoconfined water film by means of all-atom molecular dynamics (MD) simulation with periodic boundary condition. Water film systems of different thickness were studied to get a better understanding of the boundary effect.

### 2.1 Molecular Dynamics Simulation using NAMD

All MD simulation were performed using NAnoscale Molecular Dynamics (NAMD) [1], which is a parallel MD simulation code designed for computing large systems, especially biomolecular systems. In NAMD simulation, the forces between atoms are calculated using negative gradient of a scalar potential energy function, as in other MD simulations. The potential involves following terms [2]:

$$U(\vec{r}) = \sum U_{bonded}(\vec{r}) + \sum U_{nonbonded}(\vec{r}) \quad (1)$$

$$\begin{aligned}
U_{bonded} &= U_{bond} + U_{angle} + U_{torsion} \\
&= \kappa(r_{ij} - r_0)^2 + [\kappa_\theta(\theta - \theta_0)^2 + \kappa_{ub}(r_{ik} - r_{ub})^2] + U_{torsion}
\end{aligned}
\tag{2}$$

$$U_{nonbonded} = U_{LJ} + U_{Coulomb} = -E_{min} \left[ \left( \frac{R_{min}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{min}}{r_{ij}} \right)^6 \right] + \frac{C_{q_i q_j}}{\epsilon_0 r_{ij}}
\tag{3}$$

In our system, there were just water molecules and a silicon crystal, so only the first two terms in  $U_{bonded}$ , the harmonic vibration of bond length and angle in covalently bonded atom pairs, involved in the calculation. The coordinate and velocity of atoms were updated using Velocity Verlet algorithm.

## 2.2 Water Model

TIP3P water model [3] is a typical water model with three interaction sites, corresponding to the three atoms of the water molecule (see figure 1). The HOH angle is  $104.52^\circ$  and the OH distance is  $0.9572\text{\AA}$ . Each atom interacts with others as a point charge. The electrostatic interaction followed Coulomb's law and the dispersion and repulsion forces were calculated by the Lennard-Jones potential. The vibration of OH bond and the HOH angle were included in the computation.

TIP3P was used here because of its simplicity and computational efficiency. Most of all, CHARMM force field used by NAMD is parametrised with regard to TIP3P model. However, it is noteworthy that the diffusion coefficient computed from TIP3P water model is around half of the experimental value (see figure 2) and also much lower comparing to other water models [4]. We can try to use other molecule models if needed.

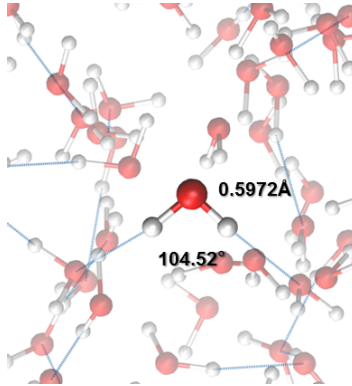


Figure 1: TIP3P water model is shown in a snapshot of bulk water.

## 2.3 System setup

A thin film of water molecules was placed on the top of a solid silicon wall and forming a nanoconfined system under periodic boundary condition. In order to construct the model systems, an equilibrium bulk water was first simulated to get randomly distributed water molecules as a reference initial condition for water (see figure 3(A)). The size of bulk water was  $80\text{\AA} \times 80\text{\AA} \times 72\text{\AA}$ , whose X and Y lengths were match with the confining plate size. The crystallographic plane (100) of silicon lattice composed of 3600 atoms was built and fixed in all the following simulations (see figure 3(B)). The expansion of the plate and vibration of

	Ensemble	$T$ (°C)	$P$ (atm)	Density <sup>a</sup>	$D^b$
SPC	NPT	25	1		$3.85 \pm 0.09$
SPC/E	NPT	25	1		$2.49 \pm 0.05$
TIP3P	NPT	25	1		$5.19 \pm 0.08$
TIP4P	NPT	25	1		$3.31 \pm 0.08$
TIP3P	NVT	25	(1)	0.993 <sup>c</sup>	$5.06 \pm 0.09$
TIP4P	NVT	25	(1)	0.990 <sup>c</sup>	$3.29 \pm 0.05$
TIP5P	NVT	25	(1)	0.999 <sup>c</sup>	$2.62 \pm 0.04$
Expt. <sup>d</sup>		25	1	0.997	2.30

<sup>a</sup>Units are  $\text{g}/\text{cm}^3$ .

<sup>b</sup>Units are  $10^{-5} \text{ cm}^2/\text{s}$ .

Figure 2: Comparison between diffusion constant for water models [4].

silicon atoms were ignored to simplify the simulation. At the final step, a slice of water film with thickness  $D$  was taken from bulk water and place onto the silicon plate. A sandwiched water film is shown in figure 3(B) with a closest image cell in  $z$  direction presenting on the top of the unit cell (blue box). The final system size were  $\sim 5\text{--}15\text{k}$  atoms, depending on the slice thickness  $D$ .

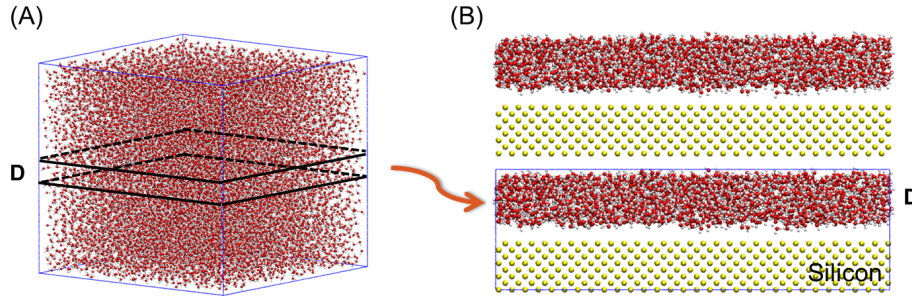


Figure 3: Illustration of system setup. The equilibrated bulk water (A) and nanoconfined water film system (B) with the unit cell (blue box) and the closest image cell in  $z$  direction.

## 2.4 Simulation

In each simulation, the system was first equilibrated in the NPT ensemble using Nosé–Hoover Langevin piston pressure control [5] for 60 ps. The temperature was set to 298 k and the pressure was 1 atm. Pressure is controlled by dynamically adjusting the size of the unit cell (here only in  $z$  dimension, X-Y is fixed) and rescaling all atomic coordinates during the simulation. To prevent the simulation crashing due to fierce volume change, which usually comes with particles moving too fast, the oscillation period and damping time scale of Langevin piston were set to 2 and 1 ps.

After equilibrium, 50 ps simulation was done in the NVE ensemble with 1 fs timestep. In order to facilitate calculation, pairlist was generated for each atom every 10 steps with a  $10 \text{ \AA}$  sphere, containing pairs of atoms for which electrostatics and Van der Waals interactions will be calculated. Atom coordinates were recorded every step.

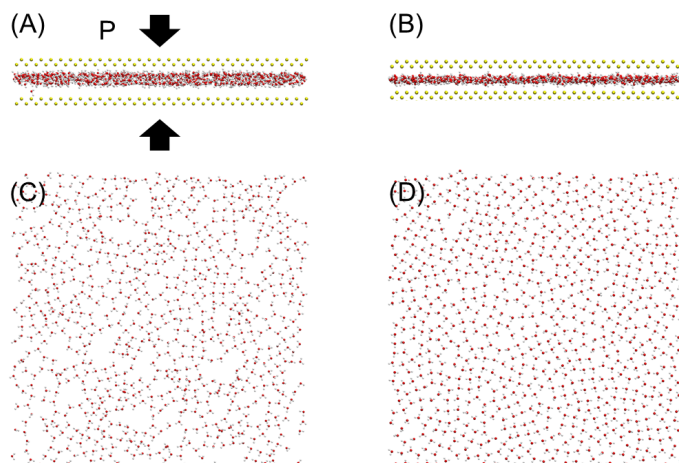


Figure 4: Single layer system reached equilibrium under constant pressure simulation. Side view before (A) and after (B) equilibrium under 1 atm, the pressure was only applied in  $z$  direction (illustrated by black arrows). The system reached its equilibrated density with smaller system. From the side view, the empty areas at initial configuration (C) were filled after equilibrium (D).

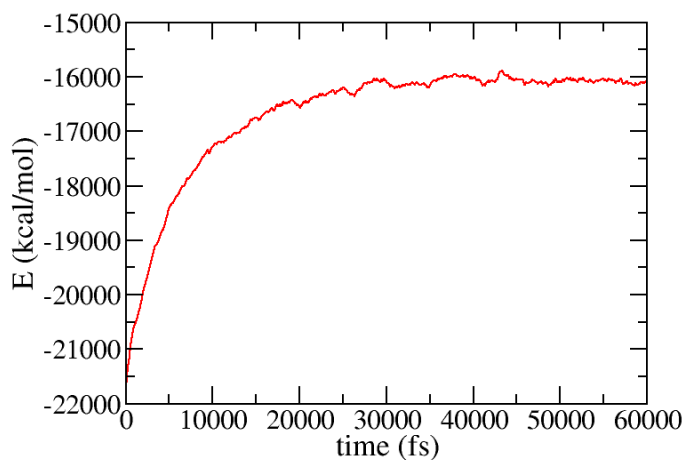


Figure 5: Energy v.s. time of the NPT simulation. The equilibrium was reached at  $\sim 30$  ps.

### 3 Results and Discussion

#### 3.1 The Layer Structure of Water Film

We first studied an extremely confined environment, whose plate separation  $D$  can barely allow the existence of single layer water molecules, i.e. water film with single atom thickness. We started from  $D = 3\text{\AA}$ , calculating the standard deviation of  $z$  position of each oxygen atom. As shown in figure 4, under the piston pressure, water molecules would rearrange to fill the empty area and lower its energy. In the system with  $D = 3\text{\AA}$ , the number of water

molecules was not enough to fill all the empty regions. When we increased the thickness to  $D = 3.4\text{\AA}$ , the standard deviation of  $z$  increased due to the saturation of water molecules in X-Y plane (see figure 6). When the system size was increased to  $D = 4\text{\AA}$ , the standard deviation of  $z$  increased largely because some of water molecules started to form a second layer. From figure 6, we defined single layer initial thickness  $H = 3.5\text{\AA}$  as an unit thickness. The sizes of other simulation systems were constructed based on this unit thickness.

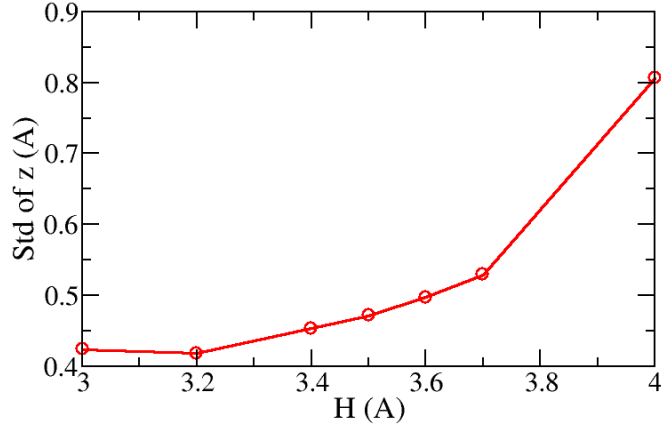


Figure 6: The standard deviation of  $z$  position of water molecules v.s. initial film thickness.

### 3.1.1 Density Profile

The density  $\rho$  normalized by total density of the system  $\rho_0$  along  $z$  direction was calculated to show the layer structure. Figure 7 summarize the profiles for 1H, 2H, and 3H systems. Layers can be clearly distinguished from the density profile. Figure 8 are density profiles for larger systems 5H and 10H. Two apparent layers were formed at both boundary. In 10H system, the density of water at the center region was close to bulk water.

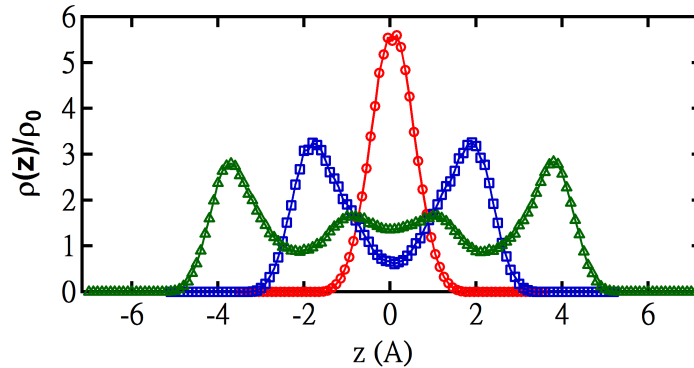


Figure 7: A summary of the normalized density profile along  $z$  direction for 1H, 2H, and 3H systems. Errors are less than the marker size.

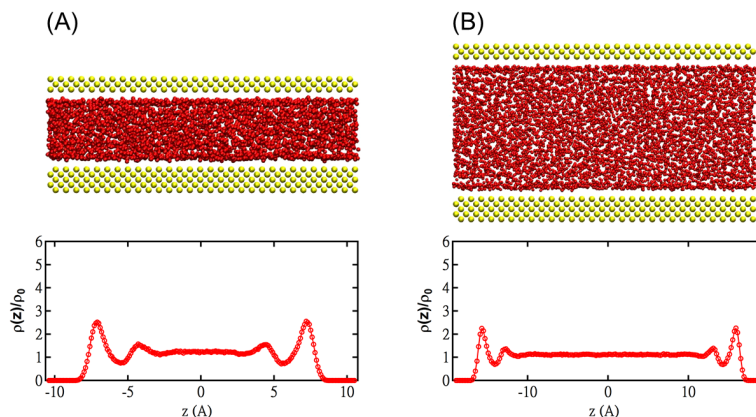


Figure 8: Density profile for two larger systems: 5H(A) and 10H(B).

### 3.1.2 Pair Correlation Function

One of the typical measurements performed in molecular dynamics is the order parameter,  $g(r)$ . Since we wanted to investigate what was happening in the  $z$  direction, we attempted to calculate the pair correlation function in just the  $z$  direction. To do this, a slice of the water would be taken (typically about the center  $z$  position). Then it would calculate the pair correlation of other particles based on their distances from particles in the center slice.

On the first attempt at calculating the pair correlation in just the  $z$  direction was naively set up. While considering the distances from a particle, this algorithm used the  $z$  positions of ALL the other particles. This does not work since there are many other particles with similar  $z$  values. In the end, after averaging over particles in the slice, the result is essentially a type of density (see figure 9 and 10). In this case, the plots are normalized at  $z = 0$ . There are peaks which can identify layers — but this did not contribute anything that the density plot does not.

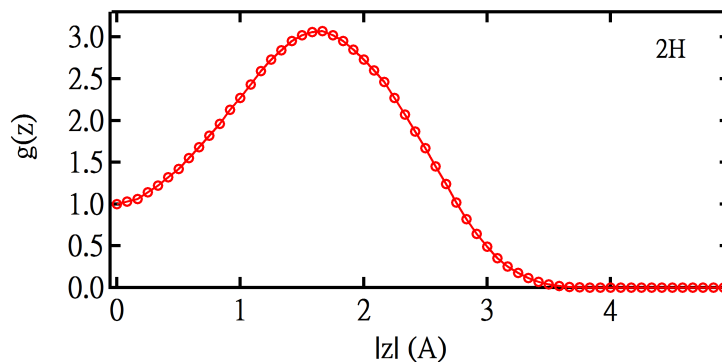
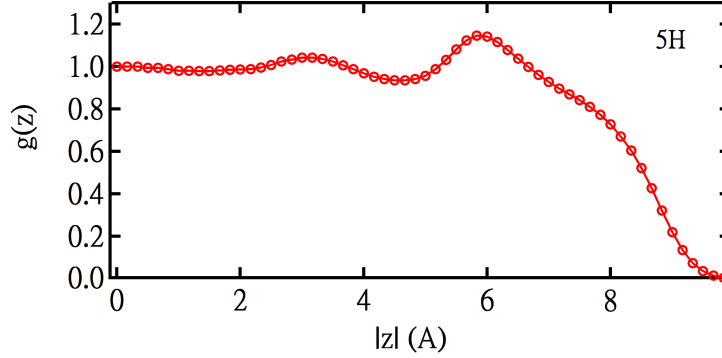


Figure 9:  $g(z)$  v.s.  $|z|$  in 2H system.

The next attempt to calculate the pair correlation in the  $z$  direction tried to ensure that it was not just another pseudo-density. Again, a slice of water about the center plane is selected. Then, a region of space in  $x$  and  $y$  would be defined. Using a circular region about

Figure 10:  $g(z)$  v.s.  $|z|$  in 5H system.

the particle, it would be extended in the  $\pm z$  directions making a cylinder. Choosing the right radius in the X-Y plane should allow for a more standard pair correlation function that is zero until the first nearest neighbor. This algorithm is in development, no results were able to be obtained at this time.

### 3.2 Water Dynamics in a Confined Environment

The other observable we wished to see was the self-diffusion coefficient of the water. In particular, how the diffusion coefficient from edges and center of the nanoconfined systems compare. The diffusion coefficient was calculated for bulk water, the 1H system, and edge and center values for the 5H and 10H systems. For the 5H and 10H systems, the domain was evenly divided into 3 sections — the bottom edge, center, and the top edge.

The diffusion coefficient for a section of the water is done by finding particles that primarily exist within one slice for most of the simulation. Then the diffusion coefficient is calculated by the Einstein expression

$$D = \frac{1}{6Nt} \left\langle \sum_{i=0}^N [r_i(t) - r_i(0)]^2 \right\rangle, \quad (4)$$

System & Location	Diffusion Coefficient (cm <sup>2</sup> /s)
Bulk Water	4.2E-5
Entire 1H	4.3E-5
Top Edge, 5H	4.3E-5
Center, 5H	4.0E-5
Bottom Edge, 5H	4.0E-5
Top Edge, 10H	1.1E-3
Center, 10H	1.2E-3
Bottom Edge, 10H	1.1E-3

Figure 11: A summary of calculated diffusion coefficient from different systems and locations.

For the above results, there is no clear trend in the diffusion coefficient for different system thicknesses. Nor is there a trend depending on whether or not it is measured in the center or in a layered region in the edges. In addition, the values for the 10H system are about 25

times larger than the values for the rest of the observed systems. The diffusion coefficient for our water model has been found to typically be about  $5E-5$  cm<sup>2</sup>/s. So our calculation of the diffusion coefficient is about 15–20% smaller than the typical value.

## 4 Conclusion

In this project, we have attempted to gather information about nanoconfined water. In this case, water of varying thicknesses confined by two Si sheets was simulated. Using density profiles, we are able to identify the layered structure. As the thickness of confined water increases, the density in the middle approaches the bulk water density because of reducing boundary effect. The layering effects was confined to the outer regions for the thicker systems of 5H and 10H. Unfortunately incorrect assumptions were made in the attempted calculation of a directional order parameter,  $g(z)$ . In the first attempt it became a type of pseudo-density. A re-tooling of the directional order parameter was developed, but not be able to be implemented. To start looking into dynamical properties of the system, we measured the self-diffusion coefficient of the water. There was little variation for system type or location until the 10H system. With the value of the diffusion coefficient being comparatively abnormally large, this is a prime system for future detailed investigation. In summary, layered features tend to manifest near the edges with increasing thicknesses and a large change in the diffusion coefficient has been observed for a certain case.

## References

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