Molecular Dynamics Simulation of Nanoconfined Water Film

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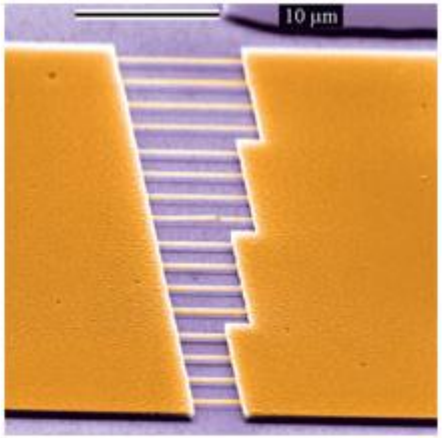
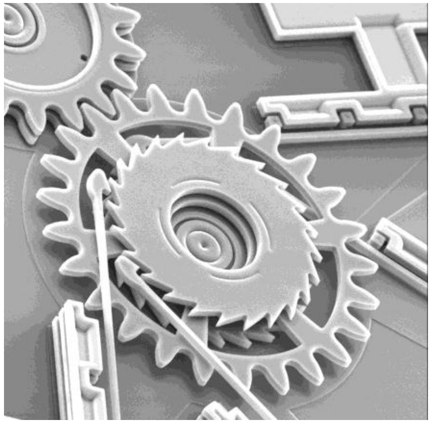
PHy466/CSE485/MSE485 **Atomic-Scale Simulation Final Project**

Motivation

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



http://www.nist.gov/cnst/nrg/nanofluidics.cfm



http://www.memx.com/

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**

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

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

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

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

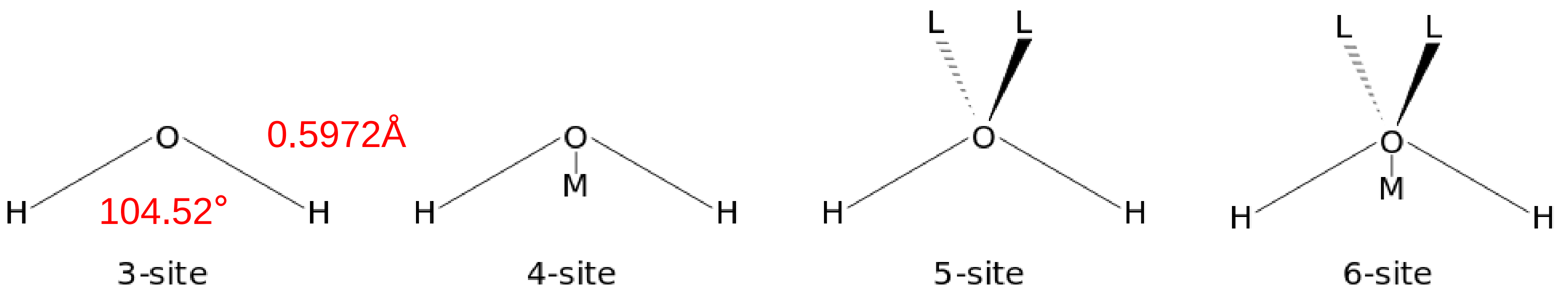
$$U_{\text{tors}} = \begin{cases} k(1 + \cos(n\psi + \phi)) & \text{if } n > 0, \\ k(\psi - \phi)^2 & \text{if } n = 0, \end{cases}$$

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

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

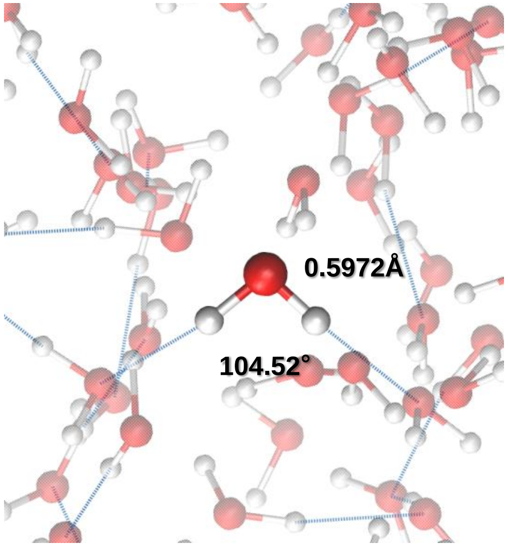
Encyclopedia of Parallel Computing, DOI10.1007/978-0-38709766-4
http://www.ks.uiuc.edu/Research/namd

Water model - TIP3P



Good:

- Computational efficiency
- Optimized with NAMD



Bad:

- Diffuse quicker than other models and real water

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

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

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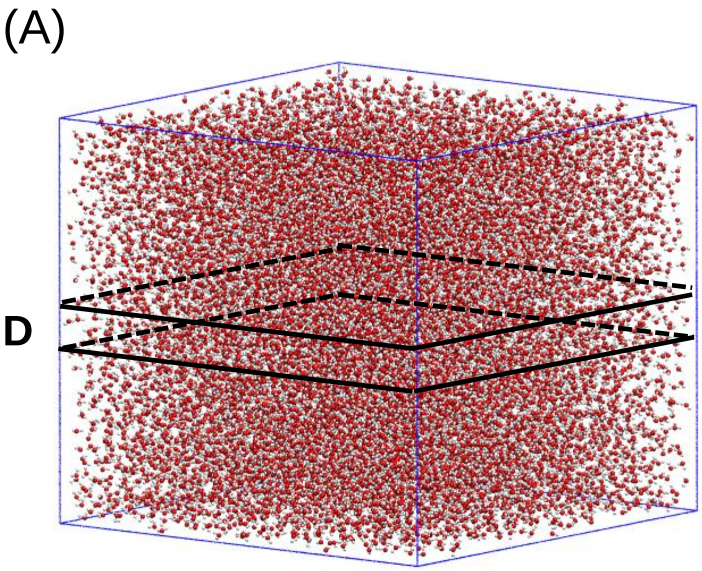
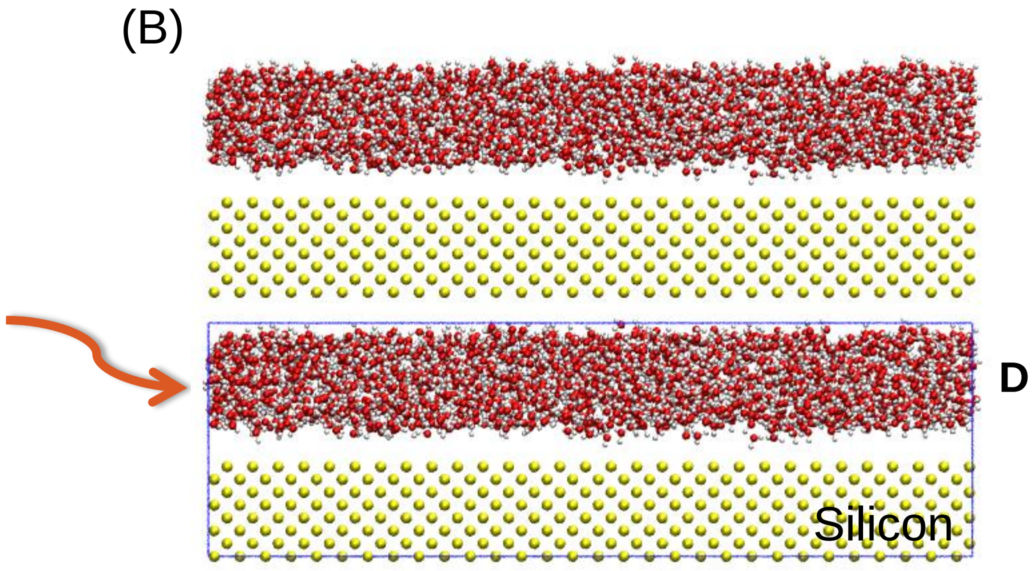
Set up the System



Equilibrium bulk water (80A)^3

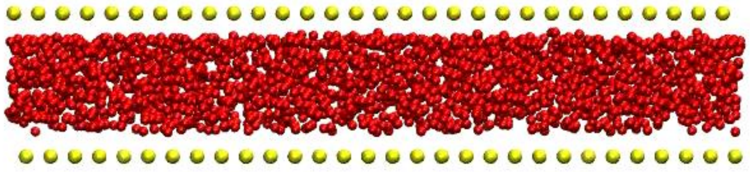


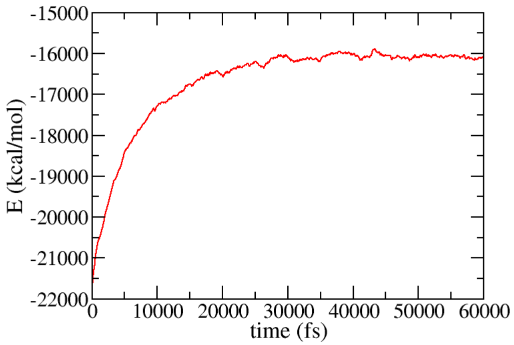
The final system size 10~50k atoms

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 bar
P_{sys} = - dU/dV

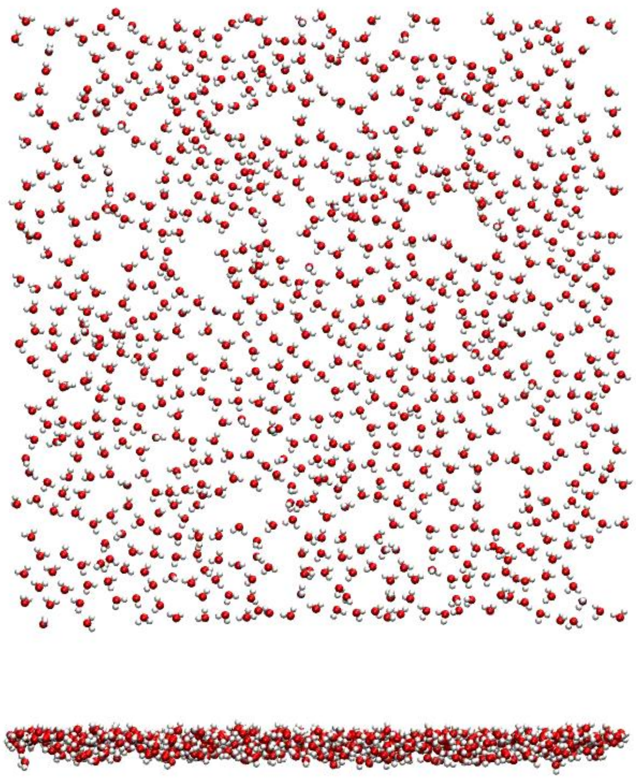


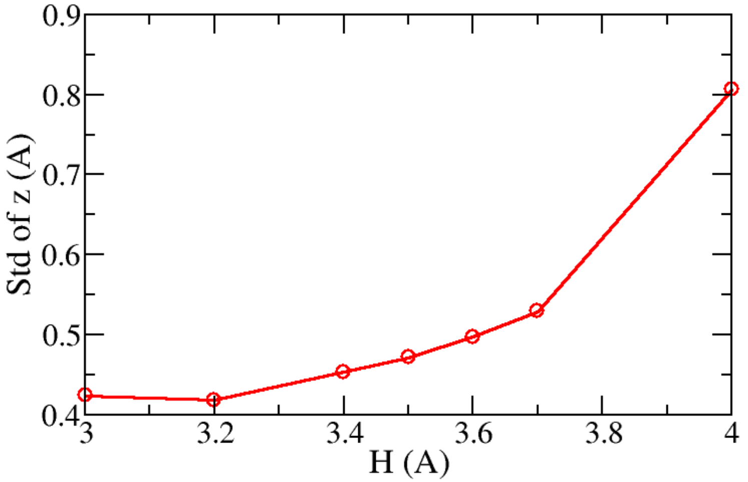


- **Run NVE for 50 ps, with Silicon fixed**

J. Chem. Phys. 101 (5), 1 September 1994

Single layer water film

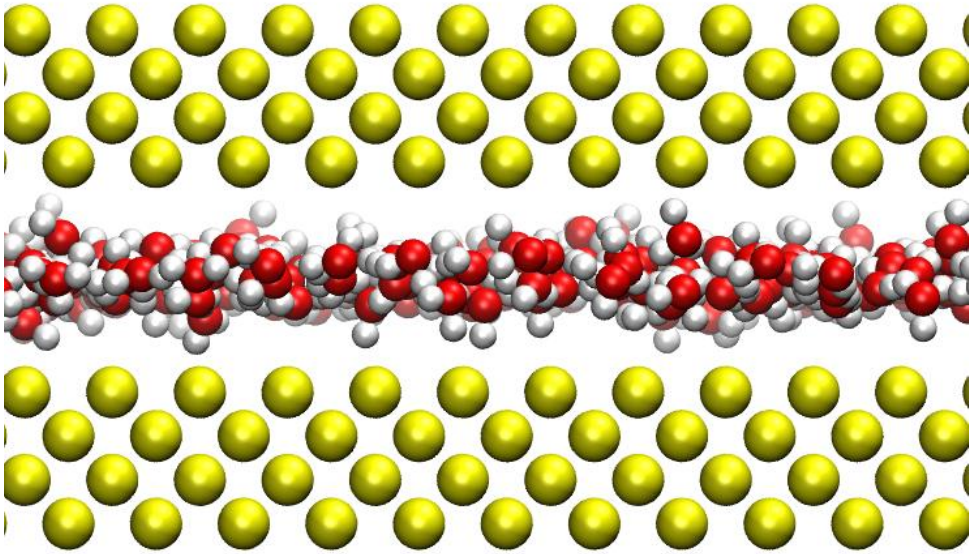


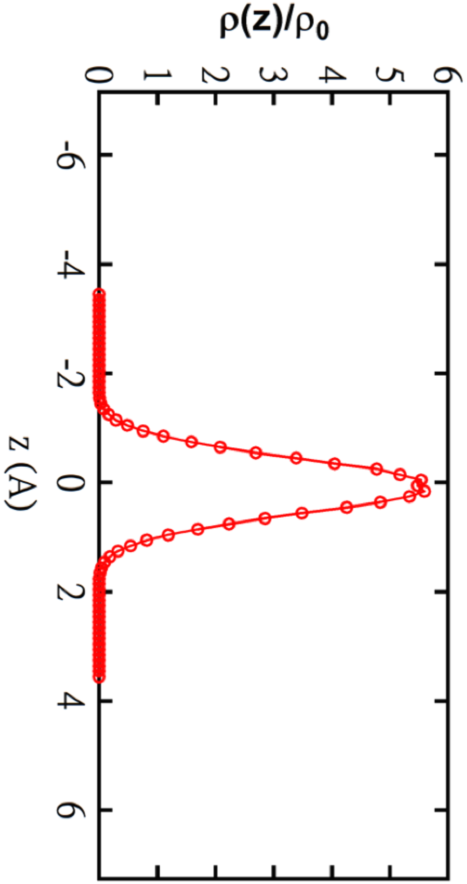


Unit thickness of layer
H ≡ 3.5 Å

Layer structure at water-Si interface

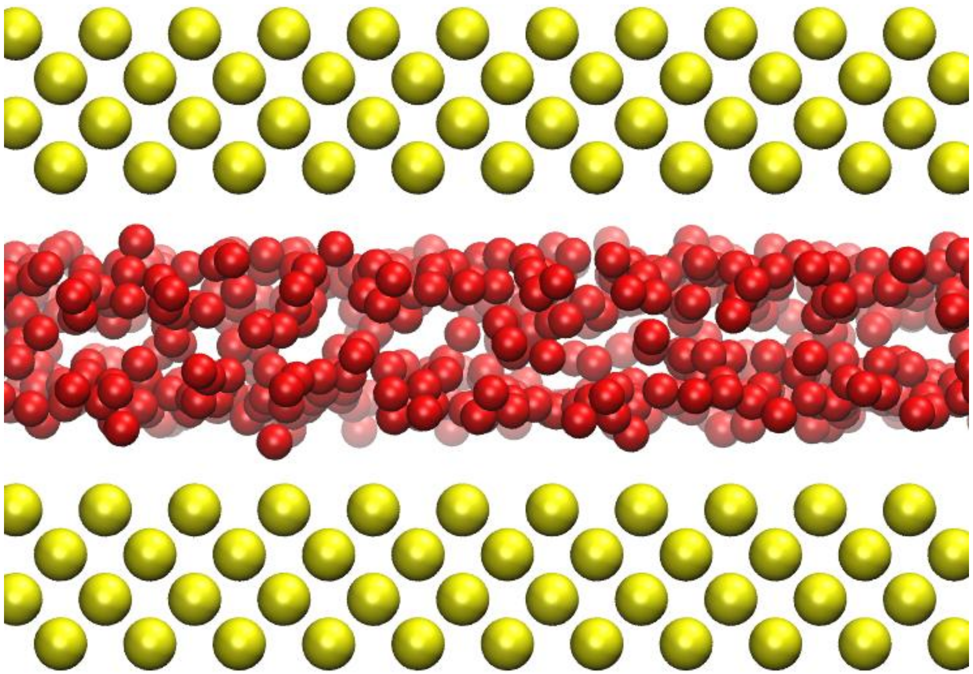
1H

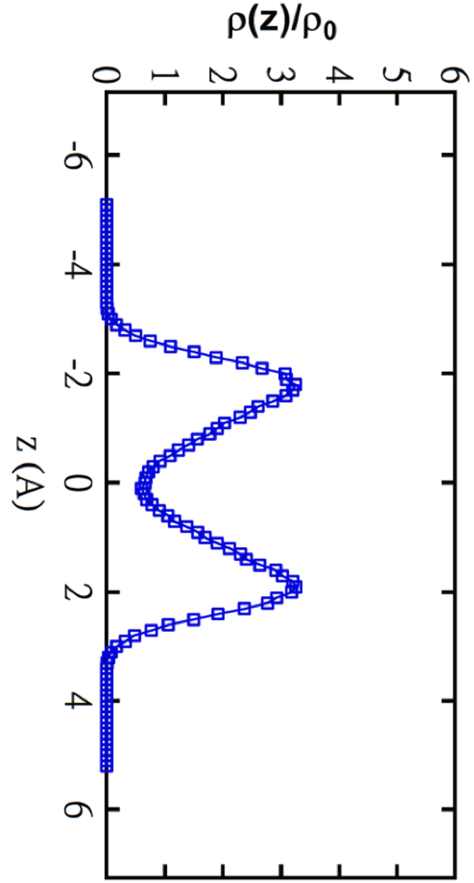




Layer structure at water-Si interface

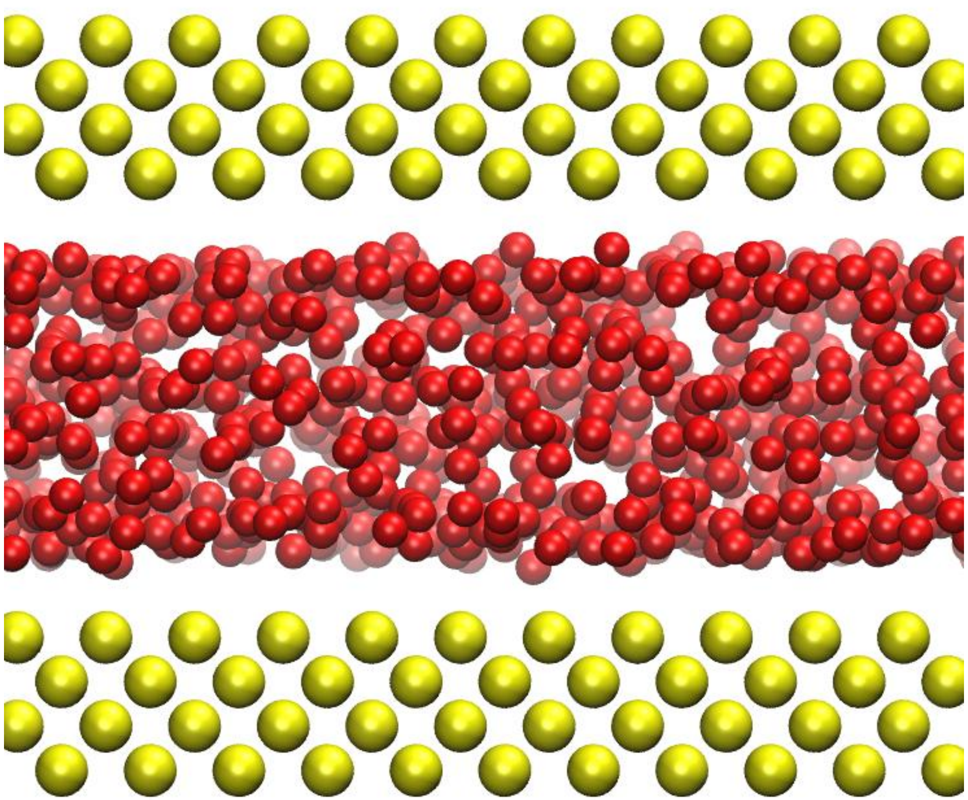
2H

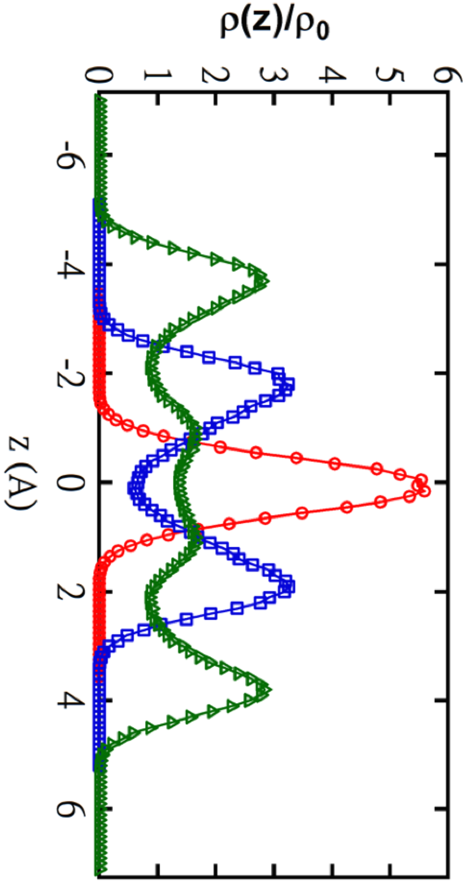




Layer structure at water-Si interface

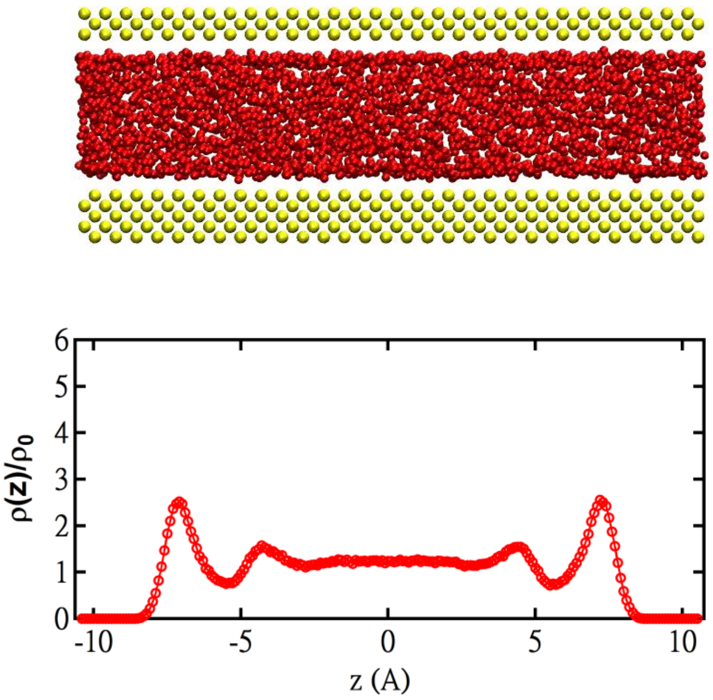
3H



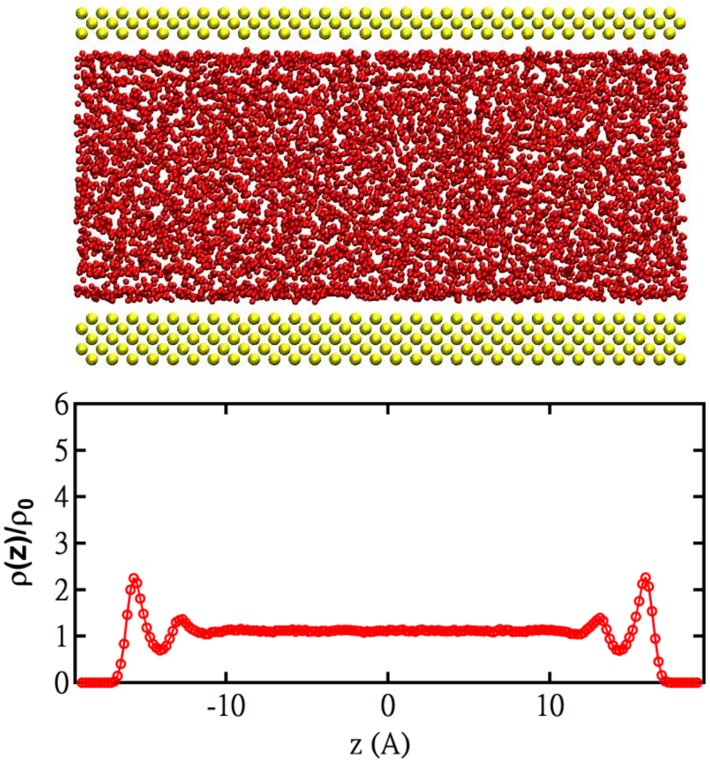


Layer structure at water-Si interface

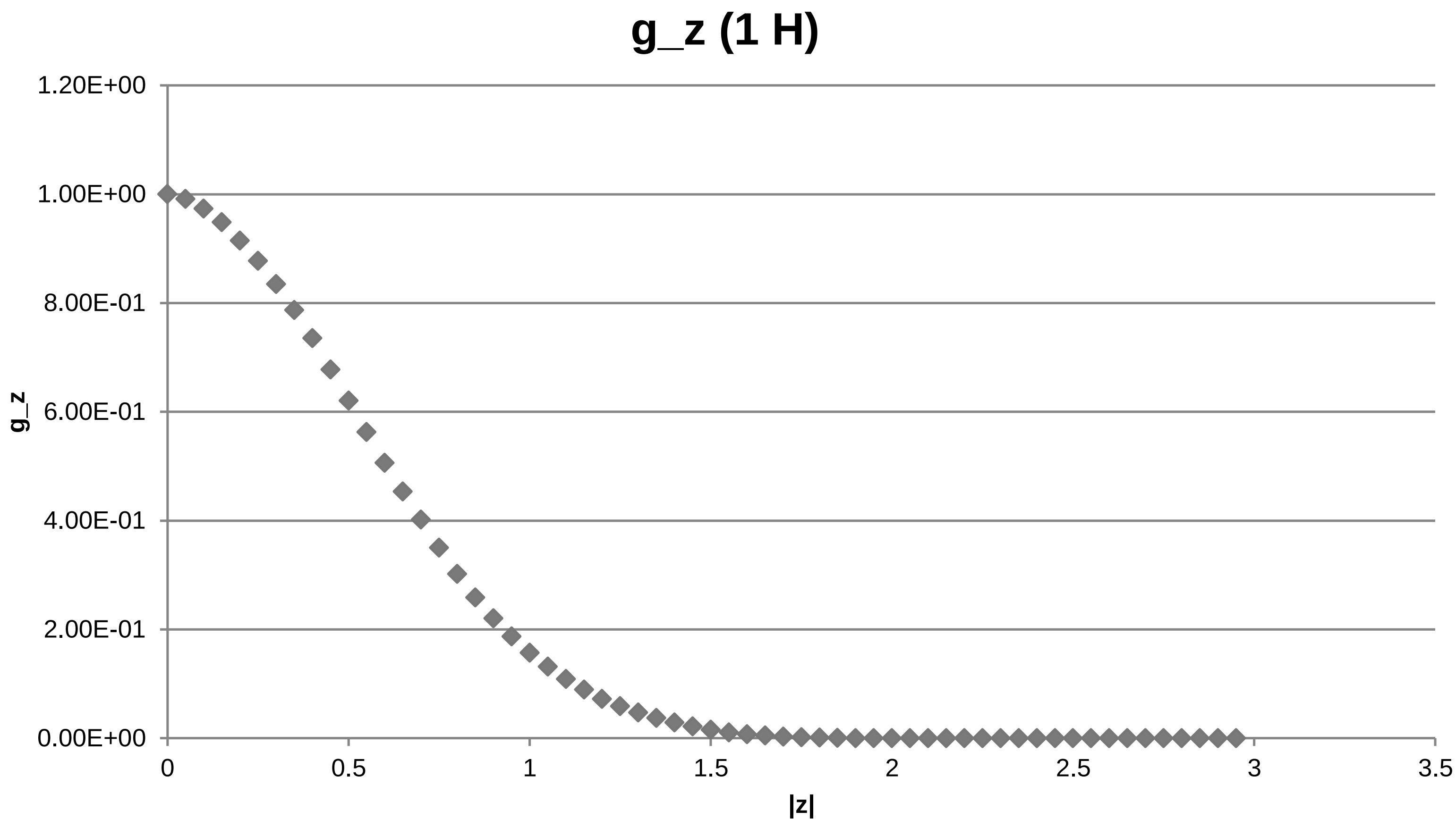
5H



10H



Pair Correlation – What can we tell about layers?



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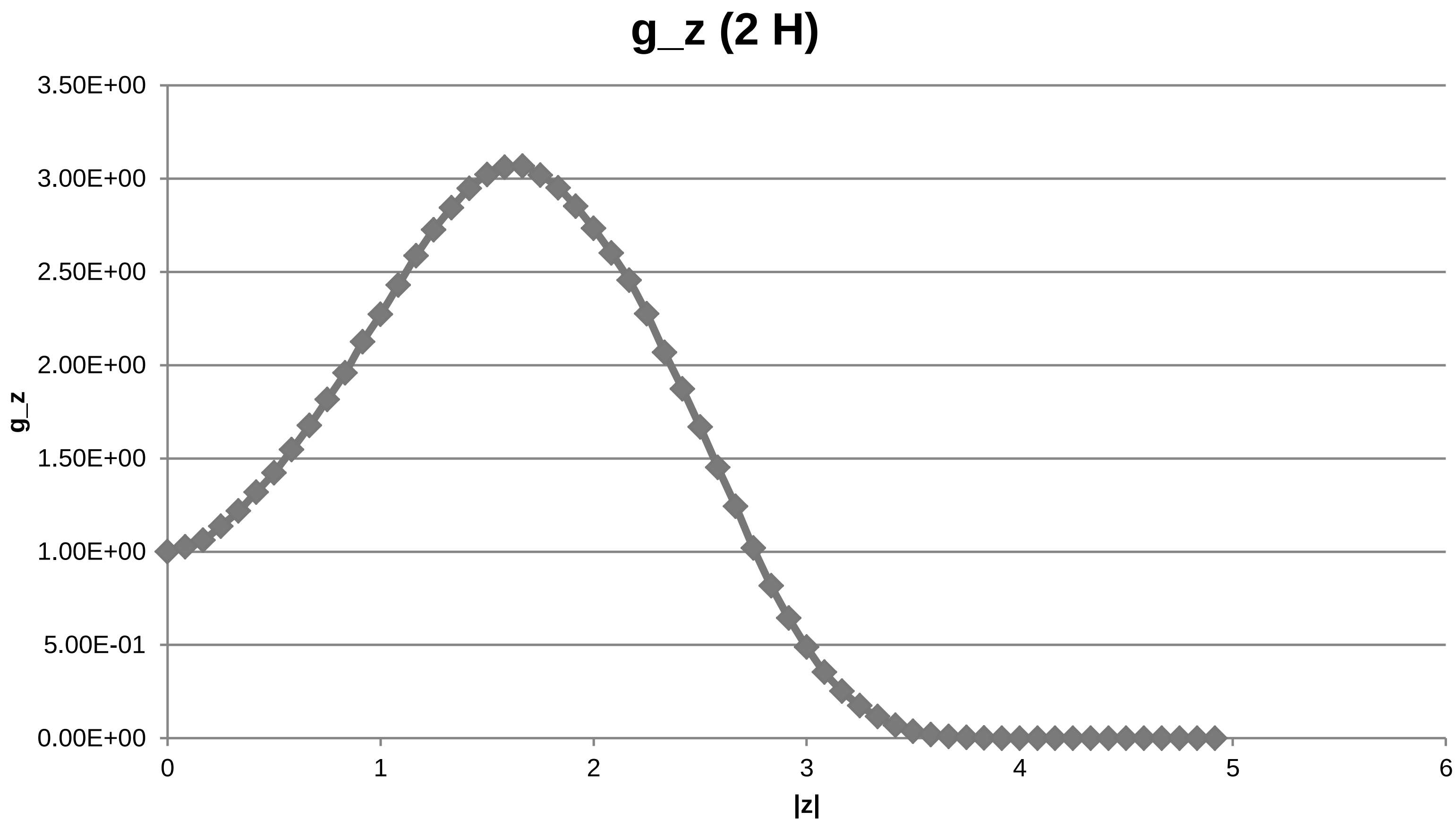

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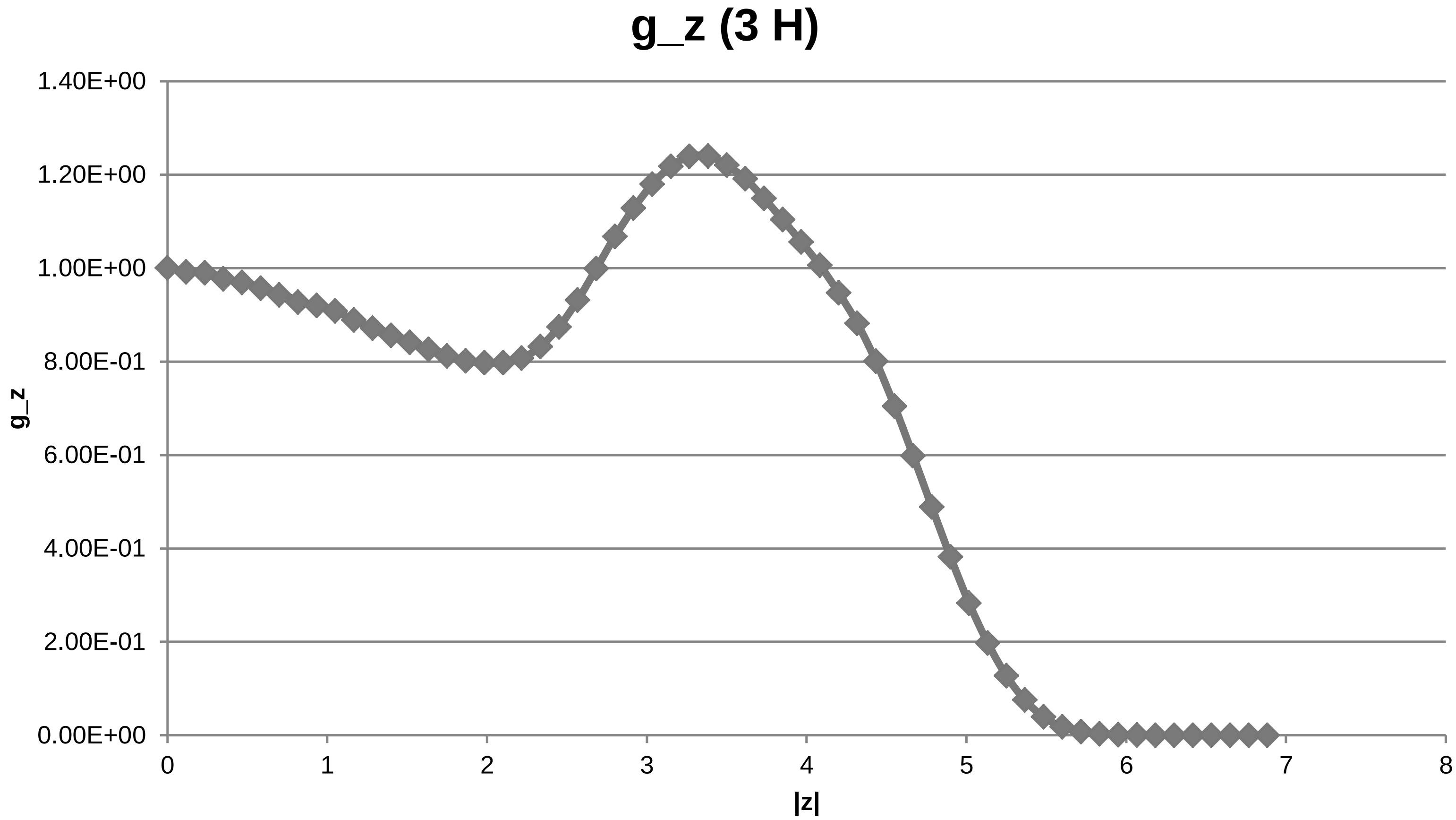

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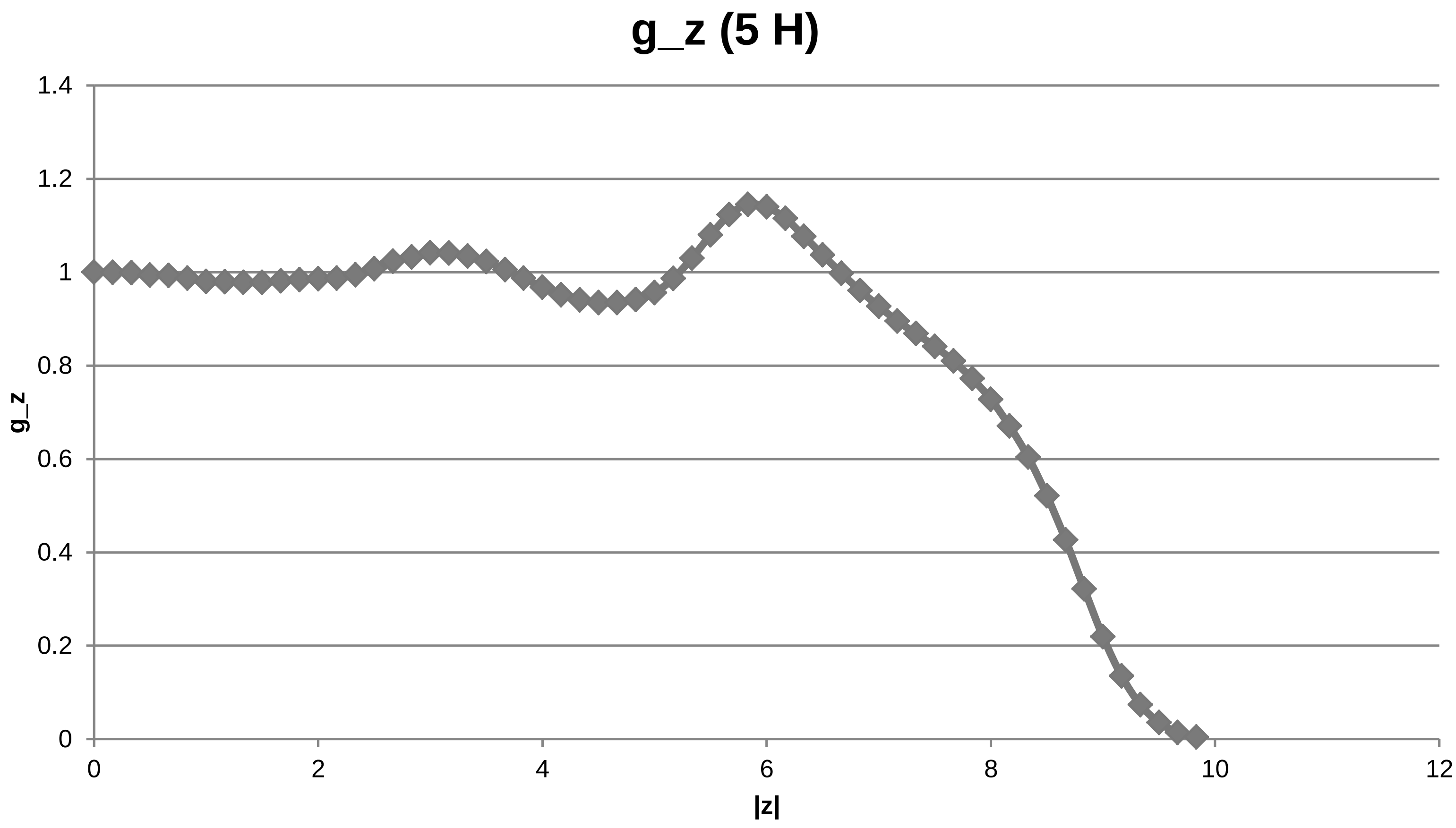

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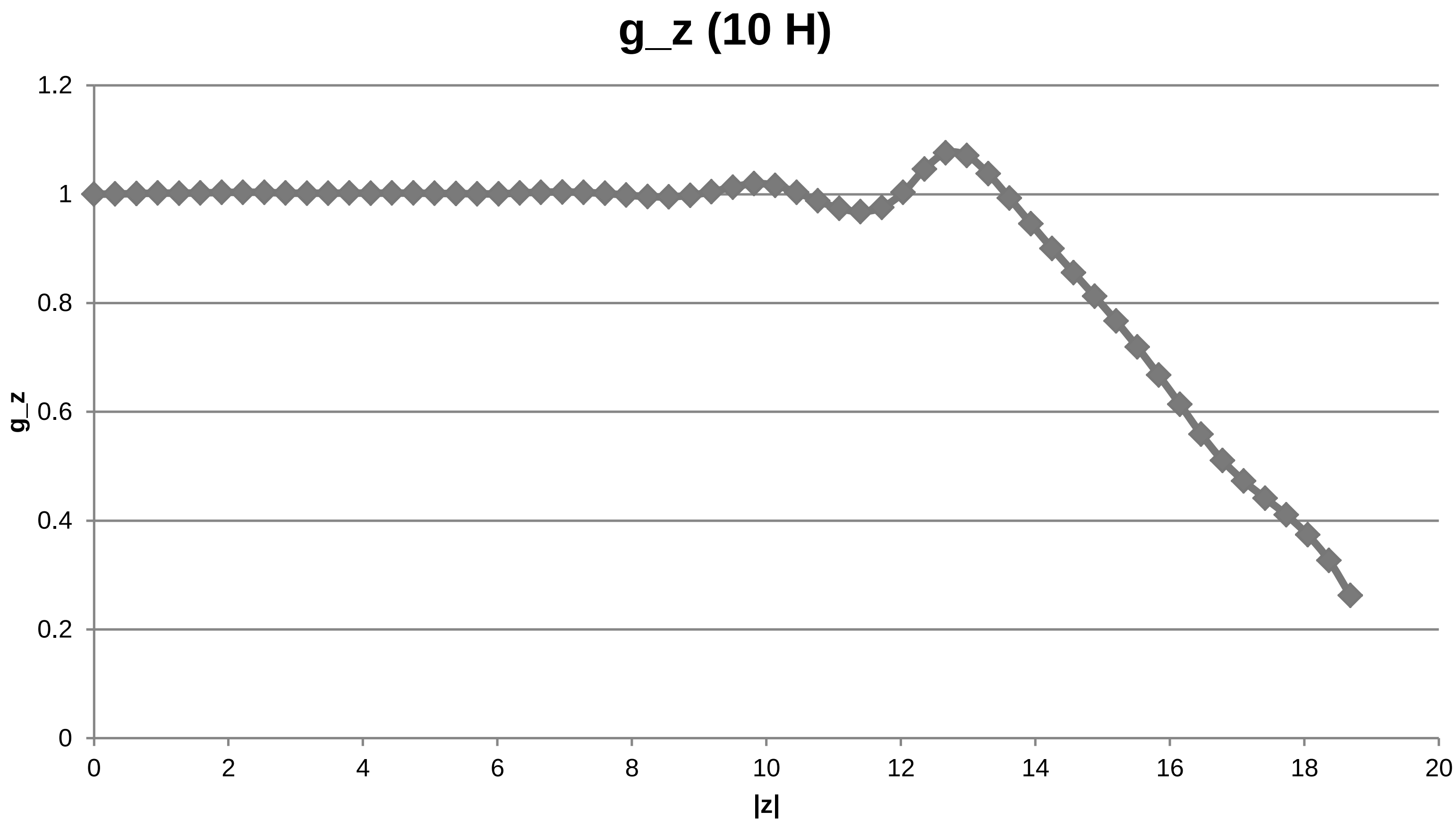

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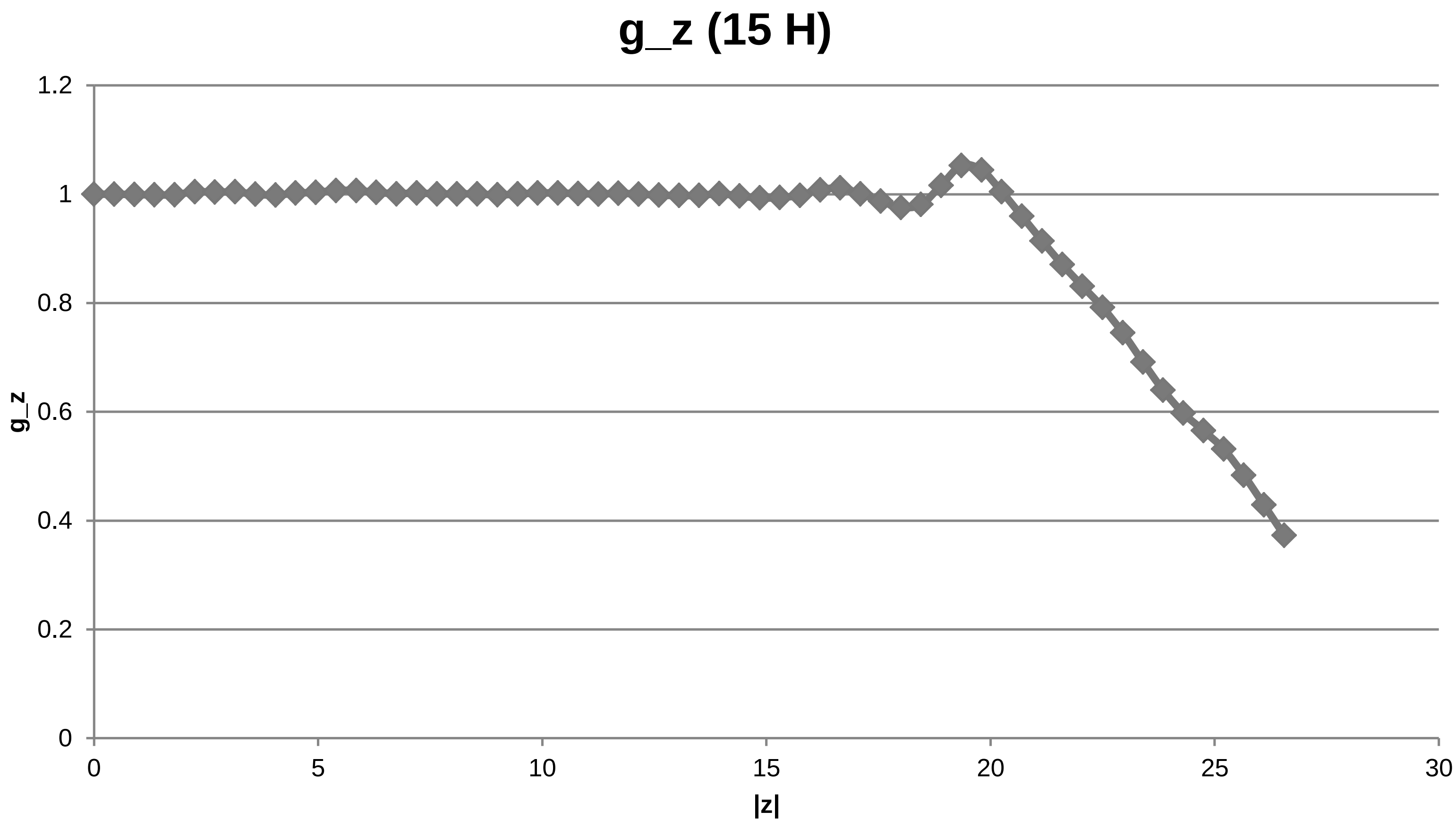

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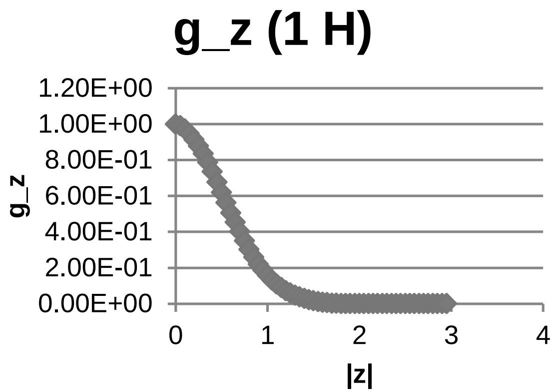
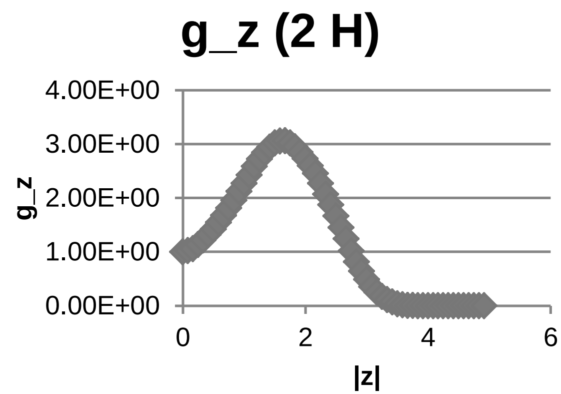
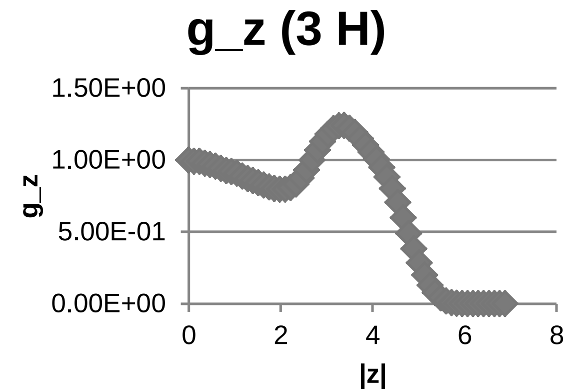
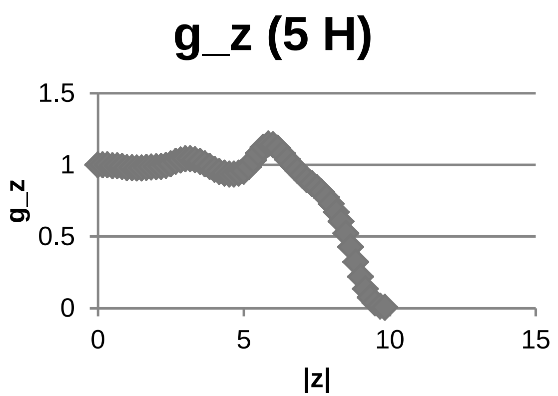
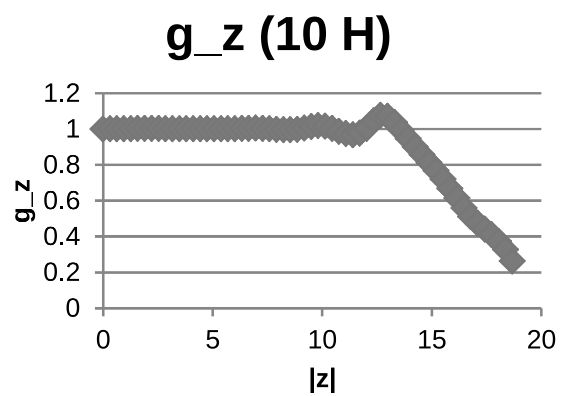
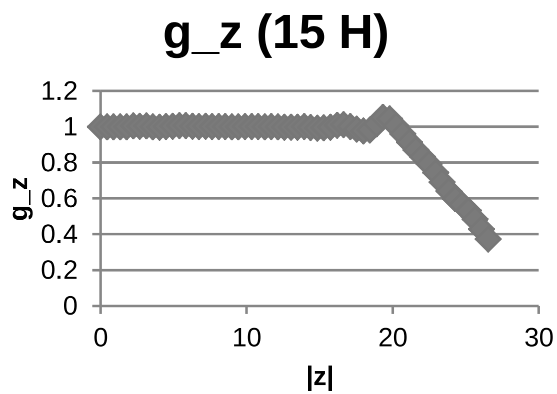












Translational Diffusion

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

For 5H (17.5 Å) Gap : D_edge/D_mid ~ 0.71

For 10H Gap (52.5 Å) : D_edge/D_mid ~ 0.52

Summary

- In the nanoconfined environment, waters 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.

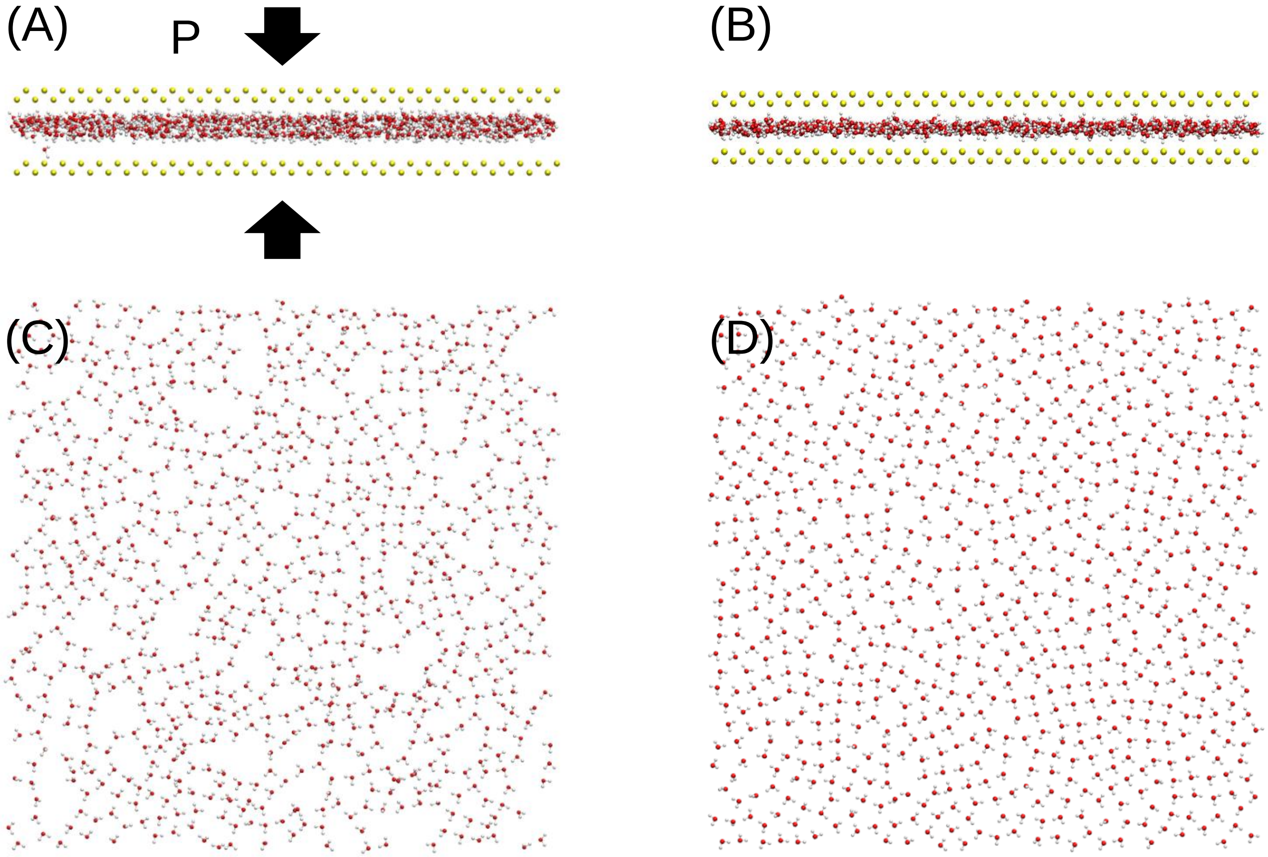
In the future:

- Rotational diffusion/ Exchange rate between layers
- Imply Load/Shear force. Will it enhance the layer structure?

Thank you! Questions?

Appendix

System & Location	Diffusion Coefficient (cm^2/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


(A)
P
(B)
(C)
(D)