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Molecular Dynamics Study on the Properties of Liquid Water in Confined Nanopores: Structural, Transport, and Thermodynamic Insights

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Abstract — **This study employs molecular dynamics (MD) simulations to investigate these alterations by analyzing the structural, dynamical, and thermophysical properties of water confined within copper nanotubes using its force field parameters within the molecular level and transition. The study further examines the influence of temperature and pressure variations on the behavior of confined water, aiming to establish comprehensive trends for thermal stability, diffusion coefficients, and density gradients. The findings from this study have broad applications in designing heat transfer systems, nanoscale filtration devices, and catalytic processes, where the understanding of confined water behavior is critical. Our findings could help with designing more efficient cooling systems for various applications.**

Keywords: Molecular Dynamics, Radial Distribution Functions (RDF).

I. Introduction

Molecular Dynamics is a computational simulation technique used to study the physical moment of atoms and molecules to examine the molecular interaction and structural properties and analyze its dynamic behavior over time. The trajectories of atoms and molecules are determined by numerically solving Newton's equations of motion for a system of interacting particles; the forces between particles and their potential energies are calculated with interatomic potential or molecular dynamics force fields. [1] [2]

Water in nanopores plays an important role in MD simulations, which represent the behavior of molecules in different conditions and force fields and in various applications depending on physical and thermal properties, electrolyte behavior, atomic interaction, and phase transition [3]. Water behaves differently in nanopores due to its spatial confinement, which leads to hydration, energy storage, transport mechanisms, and various biological processes [4]

The radius and shape of the nanopore play a critical role in water behavior. For hydrophobic pores, a radius above approximately 0.55 nm can lead to a stable and liquid-filled state. Pores less than 1nm radius may lead to dewetting and can impact water permeation. The shapes with conical entrances reduce hydrodynamic hindrance. Water flowing through hydrophobic nanopores can be significantly faster than predicted by the Hagen-Poiseuille equation[5][6] The Water translational motion is restricted in the radial direction and unrestricted along the cylinder axis, which largely reflects the predictions of a model of free diffusion in a cylinder [7]

The real water further divides into different water models. The purpose of this study is to provide a physical and thermal analysis comparison between SPC/E (Extended Simple point charge) and MW (molecular model) water models of different dimensions when passing through a copper block. These two water models are widely used models that differ in structure and charge distribution.

SPC/E model is rigid and has fixed bond length 1.0A and bond angle 109.47, commonly used for bulk water applications such as interface studies, heat transfer, evaporation, and diffusion processes[8]. The SPC/E model is a widely used three-site model for MD simulations and the monte Carlo method of liquid water. It was introduced by Berendsen et al, It is an improved model of the SPC water model by incorporating self-polarization methods and thermal and dielectric properties[9] . Despite its advantages, the SPC/E model has some limitations, such as an overestimated self-diffusion coefficient and lack of explicit polarization, which limits its accuracy of the system where bonding interactions play a crucial role[10]

Whereas MW water models are used for complex systems and long-range potentials. The mW model predicts accurate properties of water such as the melting temperature, density, liquid-vapor surface tension, heat capacity, and diffusion properties[11]. Coarse-grained Molecular dynamics CGMD aims to build those complex systems for better representation of water in real values[1]. Coarse-grained models can also simulate the larger biomolecular systems, including proteins, DNA, and their complexes, by grouping multiple atoms into single Coarse-grained particles[12].

The experimental setup shows the liquid water flowing through copper nanopore. When water interacts with copper in MD simulations, its behavior depends on surface properties and interaction potentials. The copper surface, due to the absence of strong hydrogen bonding, exhibits weak adhesion. This interaction is regulated by van der Waals forces and dispersion interaction[13] Water molecules impacting on both translating and vibrating copper surfaces, explores various parameters such as surface translation velocity, vibration period and vibration and amplitude which represents the characteristics of the liquid water[14]. Understanding these interactions are crucial for several applications. The copper-copper interaction in the systems can be described using the Self-spring constant, which represents the bond stiffness in the interatomic potentials. In MD simulations, EAM potentials are widely used to model Cu-Cu interactions while the harmonic spring model is used to estimates force constants, lattice vibration, and defect interaction[15]

II. Methodology

The atomic systems are created using an open-source tool called atomsk, which converts the atomic structure in use for MD simulations. Copper blocks of different dimensions face-centered cube unit (FCC) with a Lattice parameter of 3.615 and water tubes of diameter ranging from 20 A to 40 A and 4.92 lattice parameters are created using atomsk.

LAMMPS[16] software is a powerful computational tool, a Large Scale Atomic/Molecular Massively Parallel Simulator runs based on Newtonian law of motion and classical physics. The formulas are broken down and are derived from Newton's second law[16]

The complex systems need pair potentials to describe their physical nature of matter. The Lennard-Joule potential, a simple mathematical model, describes the Van Der Waals interaction potential between two neutral atoms and molecules.

The Lennard-Joule potential is given by:

$$E_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad [1]$$

Where, $r < r_c$, r_c is the cutoff

To describe the force between charged particles, the Coulombic pairwise interaction is given by:

$$E = \frac{Cq_iq_j}{\epsilon r}$$

Where C is energy conversion constant, q_iq_j are the charges of the atoms, ϵ is the dielectric constant and $r < r_c$, r_c is the cutoff.

2.1 SPC/E setup

The simulation carries a LAMMPS code with metal units, the water tube between copper block flows SPC/E water model of -0.8476 charge of O atom and +0.4238 charge of H atoms with 1 bond and 1 angle types of harmonic bond style. SPC/E water model has the bond length of 1 Angstrom and bond angle of 109.47. A SHAKE algorithm is used to rigidify the structure and prevent energy fluctuations by constraining bond length and angles with a tolerance of 0.0001. The Lennard-Joule potential of Coulombic pairwise interacts at a cutoff distance of 12 Angstrom. It further defines the O-O and Cu-O interaction within their premised potential parameters. The water potential parameters are $\varepsilon_O = 0.00673\ eV, \sigma_O = 3.166\ A°$ and copper water interaction potential parameters are $\varepsilon_{Cu-O} = 0.00319\ eV$ and $\sigma_{Cu-O} = 2.47\ A°$

The copper and water atoms are fixed with a constant temperature of 300k. A time integration is performed with a Nose-Hoover thermostat and barostat to update position and velocity in each timestep with a damping parameter of 0.5. A spring force is applied on Copper to control its atomic motion, initial position, and avoid thermal fluctuations with a spring constant value of 10. The simulation is set up with the timestep of 1fs (femtosecond).

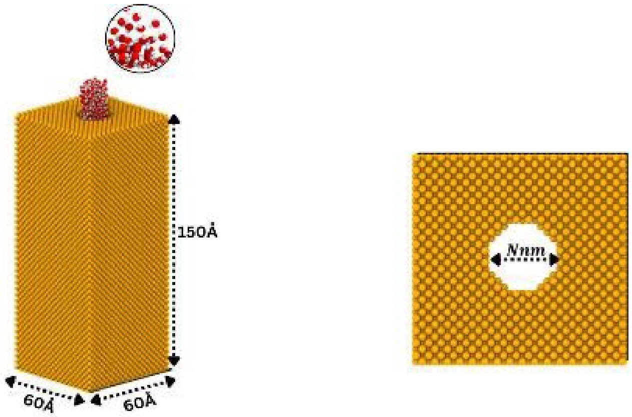

Fig. 1: Represents the SPC/E model of water passing through copper nanopore block with N diameter, N=2, 3, and 4nm

2.2 MW setup

MW water models are often known for long-range interaction potentials commonly used in CGMD. MW model represents water molecules as a single particle capturing all its physical and thermal properties. In this simulation setup, the mW water model used hybrid pair potentials, which includes Lennard-Joule potential and Stillinger-Weber (SW) potential with a cutoff distance of 12. The SW potential simulates the material when distinguishing three-body angles and creates an interaction between them to form a tetrahedral order. SW potentials ensure mW model water has similar properties to real water. The Stillinger-Weber potential is given by:

$$E = \sum_{i}\sum_{j>i} \emptyset_2(r_{ij}) + \sum_{i}\sum_{j\neq i}\sum_{k>j} \emptyset_3(r_{ij}, r_{ik}, \theta_{ijk}) \quad [1]$$

$\emptyset_2$ defines the two-body term (attraction and repulsion) and $\emptyset_3$ defines the three-body term. whereas,

$$\emptyset_2(r_{ij}) = A_{ij}\epsilon_{ij}\left[B_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right]\exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right) \quad [1]$$

$$\emptyset_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ij}\epsilon_{ijk}[cos\theta_{ijk} - cos\theta_{0ijk}]^2 \exp\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)\exp\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}}\right) \quad [1]$$

The script further includes the pair potential parameters of Copper and water are $\varepsilon_{Cu-O} = 0.00319eV$ and $\sigma_{Cu-O} = 2.47\ A°$ and fixes the temperature at 300 k using a Nose-Hoover thermostat and barostat. The copper is fixed with a spring force to maintain the stable initial potion and fixed motion.

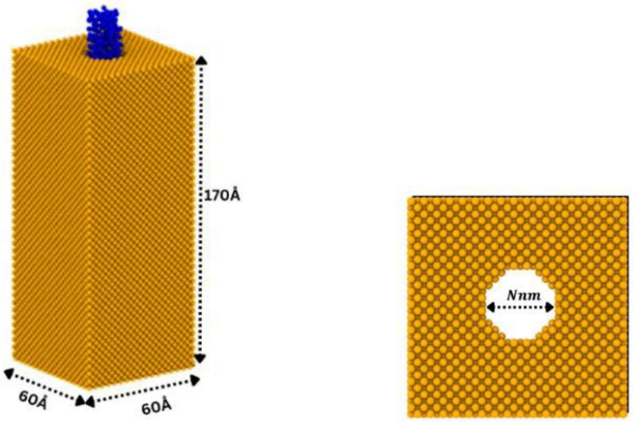

Fig. 2: Represents the mW model of water passing through copper block nanopore with N diameter, N=2, 3, and 4nm

III. Results and discussion

Radial distribution function

The Radial Pair Distribution Function (RDF) describes how particle density varies with a distance from a reference particle in a system. It is widely used in molecular dynamics to analyze structural properties by indicating how atoms are arranged to understand the atomic order and interactions. The expression is given by:

$$g(r) = \frac{n(r)}{\rho 4\pi r^2 \Delta r}$$

Whereas, $g(r)$ is the RDF function, $n(r)$ is the number of particles found in the spherical region with the radius r, ρ is density and $4\pi r^2\Delta r$ is the volume the sphere formed with the distance of Δr.

Below, we represent the RDF graphs comparing the two water models. The RDF was calculated using the Radial distribution function tool in VMD by defining a confined region from the water molecules with a cutoff distance of 40Å. This tool selects a reference particle and calculates its density based on its volume and distance.

3.1 mW model water

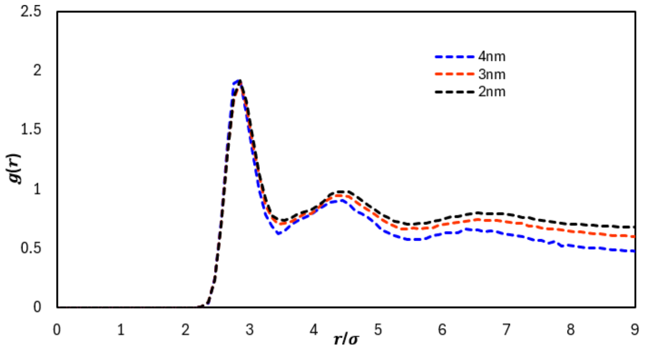

Fig. 3: This graph represents the calculation of water using the mW model with different diameters.

In the above graph, the x axis represents the radial distance (r/σ) and y axis represents the RDF function, a probability of finding a particle at distance r. the first peak at 2.85σ which points at 1.98 $g(r)$ corresponds to the nearest shell where the probability of finding the atoms is maximum and also indicates strong hydrogen bond interactions taking place. The highest degree of ordering is found in this peak. The smallest nanopore 2nm experience the sharper peak indicates stronger structure and well effected due to its confinement. The second peak at $4.55\ \sigma$ reflects the intermediate range order as very few atoms are found at this region. The larger systems of 3nm and 4nm nanopores experience the smoother curves decreasing to 1 $g(r)$ is less affected due to its confinement. Also, the third peak at 6.05 represents the same confinement experienced at second peak, indicating the bulk like behavior. The 4nm system equilibrates to the larges distance, indicating the long-range behaviors and impacts more natural fluctuation of the atom to its finite size. This concludes that 3nm and 4nm nanopores closely represent the bulk water behavior and weak confined. Whereas the 2nm nanopore exhibits strong confinement, rigid, and good structural behavior due to its enhance hydrogen bonding but not fully encourage for long range behaviors.

3.2 SPC/E water model:

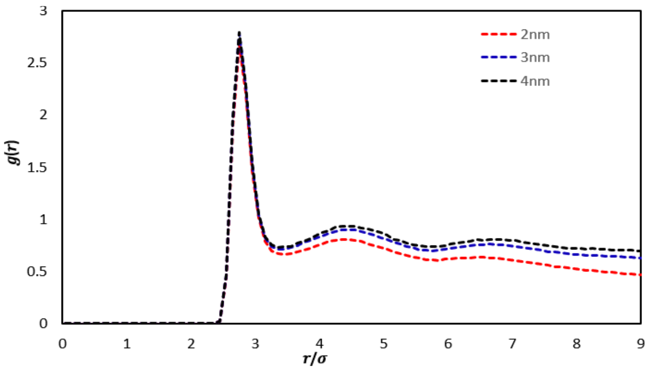

Fig. 4: This graph represents the calculation of water using the SPC/E model with different diameters.

The above graph represents the RDF graph differentiating the behavior of SPC/E model water in confined nanopore. The x-axis and y-axis represents the radial distance and RDF probability of finding molecules at a distance r respectively. The sharp first peak is observed at 2.75 σ and points at 2.78 $g(r)$ correspond the finding of number of molecules in this region is maximum. The sharp peak indicates the nearest O-O bonding distance in SPC/E model. All the nanopores with sharper peaks indicates the stronger molecular structure due to their confinement. The second peak at 4.5 and third peak at 6 becomes slightly smooth for the larger nanopores, leads to reduction in confinement indicating only fewer atoms are found in these regions. The 3nm and 4nm nanopores equilibrates for longer run representing the long range interactions and experience the characteristics of bulk water and its affects. The 2nm nanopore has the strong confinement effects which reduces the long range interaction and do not exhibit the bulk water behavior. This is useful in understanding the hydration effects in biological systems and membrane filtration.

IV. Conclusion

This study concludes that size of the nanopore plays a vital role in its confinement and alters hydrogen bond networks and how O-O interaction distance influences the transport properties and phase transitions. It also concludes that nanopores greater than 4nm in size experience the bulk water behavior and further suitable for long range interactions. Whereas the smaller nanopores (2nm or less) indicates the strong confinement due to its strong structuring and bond formation, but the impacts restrain long range correlations.

The mW model at 1.98 $g(r)$ and SPC/E model with 2.73 Indicates the mW model finds its density before the SPC/E model indicating strong local structure and confinement due to its tetrahedral potential. The SPC/E experienced the broader peak due to its electrostatic interactions

These findings applicable for understanding membrane based technologies, biological transport and moreover crucial for understanding the behavior of water in confined nanopores.

V. References

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