CHE 622A: Introduction to Molecular Simulations

Molecular Dynamics Study of Water Diffusivity in Graphene Nanochannels

By: Abhay Gupta **(22102002) &**

Abhay Rupareliya **(22102003)**

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

Acknowledgment

We would like to thank everyone who helped facilitate the completion of the project. It provided us with a great chance to learn and improve our simulation software skills.

We express special thanks to Aindrila Indra and Mangesh Bhendale, who guide us in our projects and, despite being extraordinarily busy with their duties, took time out to guide us and our lab mates as well as all fellow colleagues.

Our deepest gratitude goes to our guide, Dr. Jayant Kumar Singh (Head of the Chemical Engineering Department) at the Indian Institute of Technology, Kanpur, for giving us useful guidelines regularly and letting us have this chance to gain the necessary exposure.

Yours sincerely,
Abhay Gupta (22102002)
Abhay Rupareliya (22102003)

Contents

1. Introduction

The nanotechnology industry has experienced significant growth in recent years as researchers have explored the use of materials at the nano-scale. Graphene is a single layer of carbon atoms arranged in a hexagonal lattice, which has gained attention due to its very surprising mechanical, electrical, and thermal properties. Diffusion occurs at the interfaces of continuous bulk water and solid membranes, governing everyday phenomena such as plants' absorption of water-soluble

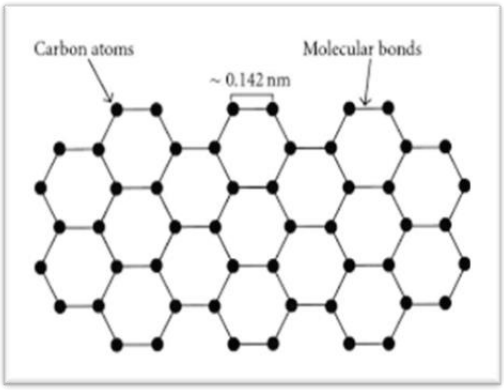

Fig.1 Atomic model of graphene sheet

nutrients, the flow of tears through ducts in the eyes, and soil wetting by raindrops. The behavior of water in such confined spaces is significant due to the importance of molecular interactions at smaller length scales, and it plays a critical role in diverse fields such as geology, material science, biology, and nanotechnology. Nano-confined fluids, defined as fluids confined in nanoscale spaces such as nano-channels, nano-tubes, and nano-pores, exist in nature and has its engineering applications such as gas separation, water filtration, and energy storage. Although nano-confined fluids are still considered fluids in essence, many forces that are usually ignored for bulk fluids dominate at the nanoscale, such as the Van der Waals force and electrostatic force. Due to these distinct characteristics, nano-confined fluids have unique mass and energy transport properties that researchers are focuses on, including transport properties such as diffusivity, thermal conductivity, viscosity, flow dynamics, and heat and mass transfer. Transport properties are important for understanding the other features. One study conducted by Sirk et al. [7] explored the thermal conductivity of water using various classical water models. They discovered that models incorporating bond stretching and angle bending, such as flexible models, predicted higher thermal conductivities than rigid models like SPC, SPC/E, and TIP3P-Ew. When water is confined in nanoscale spaces, its transport properties can

significantly differ from those of bulk water. The thermal conductivity of water confined in graphene nanochannels was recently investigated by Sun's group [13], who discovered that the thermal conductivity is both anisotropic and dependent on size. The research demonstrated that the anisotropy of thermal conductivity is due to the molecular collisions being restricted in the perpendicular direction, while the collisions are enhanced in the other directions due to water molecules being trapped in potential wells. Despite these findings, further investigations are necessary to uncover the mechanism from a thermophysical perspective, as well as to gain a deeper understanding of the transport properties of nano-confined water, including anisotropy and size-dependence.

In this paper, simulation is carried out using following software's/tools 1) VMD (Visual Molecular Dynamics) 2) LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) 3) Packmol and 4) MS Excel. VMD provides a wide range of tools for visualizing and analyzing molecular structures includes 3D rendering, interactive manipulation etc. and molecular representations that includes ball-and-stick, space-filling, and cartoon models, as well as electrostatic potential surfaces and molecular orbitals. VMD also includes tools for measuring distances, angles, and dihedral angles, as well as for creating molecular trajectories and analyzing molecular dynamics simulations. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is a software application designed for molecular dynamics simulations. It is widely used in the scientific community for simulating a wide range of systems, including solids, liquids, gases, and biomolecules. It also includes a wide range of analysis tools for post-processing simulation data, including trajectory visualization, thermodynamic analysis, and diffusion coefficient calculation. It is capable of handling large-scale simulations involving millions of atoms, making it a valuable tool for simulating complex systems in materials science, chemistry, and biology. MS Excel for the visualization and plotting the data. Molecular structure representation was conducted where water molecules are confined between two graphene sheets using VMD and Packmol and MD simulation to find diffusivity of water confined in graphene nanochannels is calculated using the Einstein equation and defining other parameters in the input file of Lammps. The nanoscale effect on the diffusivity of water confined between two parallel flat graphene sheets compared to bulk water is investigated and discussed in detail. The anisotropy and change in the behavior of diffusivity by increasing the distance between two graphene sheets are understood from the thermodynamic and experimental points of view. It is

expected that this study can improve the understanding of the diffusivity of water confined in graphene nanochannels from physical insights.

2. Literature Review

Molecular dynamics simulations are used to study the behavior of atoms and molecules in a system. These simulations allow researchers to observe the movement of individual molecules and predict the behavior of the system under different conditions. A number of studies have been conducted on the diffusion of water molecules between two parallel graphene sheets. In a study by Zhang et al. (2014), the authors investigated the effect of the interlayer distance and temperature on the diffusion behavior of water molecules between two parallel graphene sheets. The results showed that the water diffusivity increases with increasing temperature and also with increasing interlayer distance and in (2017), Zhang et al. investigated the effect of the graphene sheet size and functionalization on the diffusivity of water molecules. The results showed that the functionalized graphene sheets have higher water diffusivity compared to the unfunctionalized sheets. In a study by Li et al. (2019), the authors investigated the effect of the surface roughness of graphene sheets on the diffusion behavior of water molecules. The results showed that the water diffusivity decreases with increasing surface roughness due to the hindrance of water molecules by the surface roughness. In a study by Yang et al. (2020), the authors investigated the effect of the surface charge of graphene sheets on the water diffusion behavior. The results showed that the water diffusivity increases with increasing surface charge due to the attraction of water molecules towards the charged surface.

In summary, molecular dynamics simulations have been widely used to investigate the diffusivity of water molecules between two parallel graphene sheets. Previous studies have shown that various factors such as interlayer distance, temperature, sheet size, functionalization, surface roughness, and surface charge can significantly affect the diffusion behavior of water molecules. The results of these studies can provide insights into the design and optimization of graphene-based materials for various applications such as energy storage, water purification, and drug delivery.

3. Simulation Model and Methodology

In this study, a molecular structure representation was done where water molecules are confined between two graphene sheets using VMD and Packmol, as depicted in Fig. 2. The dimensions of the simulation region were fixed at L_x = 7.62 nm and L_y = 7.36 nm, while the height of the nanochannel, which is the distance between the two graphene sheets, was varied between 10 Å to 25 Å. The MD simulations were carried out in the NVT ensemble using the large-scale

atomic/molecular massively parallel simulator (LAMMPS) [8], with a Nosè-Hoover thermostat used to maintain a temperature of T = 300 K. Periodic boundary conditions were applied in the x- and y-directions, while the graphene sheets were held fixed in the z-direction throughout the simulations.

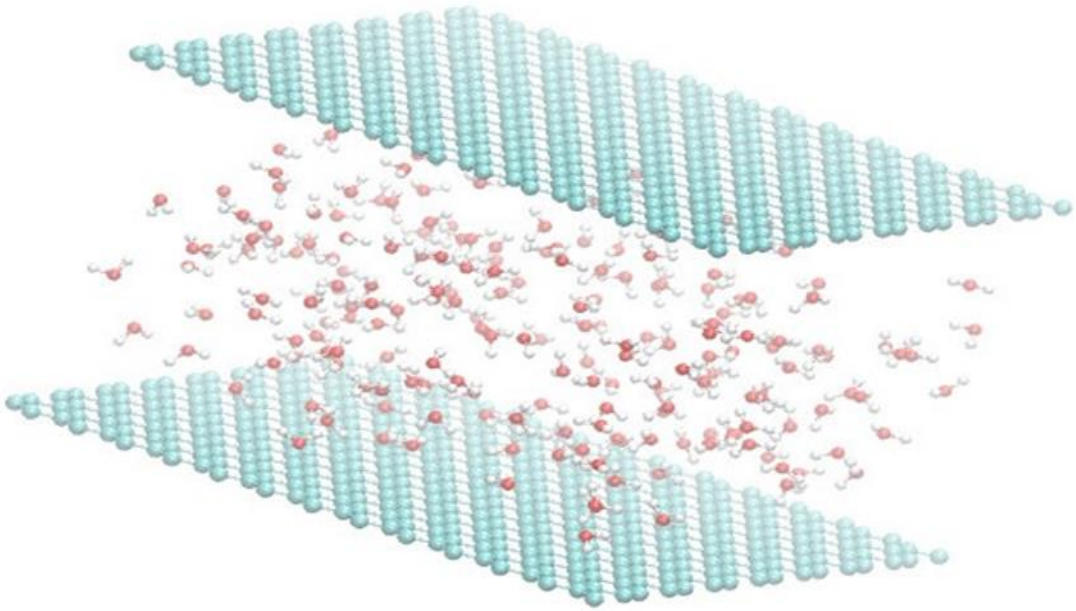

Fig. 2 Simulation system of water confined between two parallel flat graphene sheets.

3.1. Potential Models:

In the MD simulations, the atomic interactions were simulated using the Lennard-Jones (LJ) potential model, which is commonly used in this field.

$$u_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

where u_{ij} and r_{ij} are the interaction energy and distance between particle i and j, respectively. ε_{ij} and σ_{ij} are the energy parameter and scale parameter, respectively, in the LJ potential model and the cut-off distance of LJ interactions 2.5 Å. We use TIP4P water model as it is widely used in molecular dynamics simulations for its accurate prediction of the diffusion of water at room

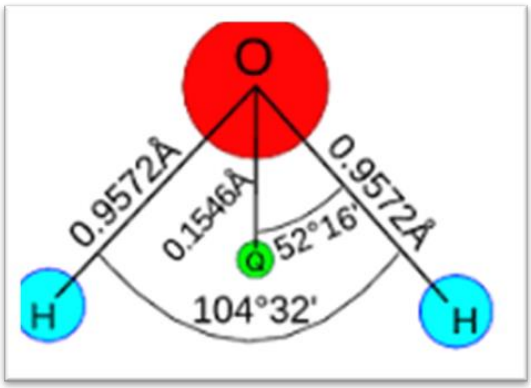

Fig. 3 Atomic model of H2O (TIP4P type)

temperature [9]. TIP4P includes an additional site that represents a partial negative charge located at the center of mass of the two hydrogen atoms as shown in the fig 3. The LJ parameters of oxygen are $\sigma_{oo} = 0.3165\, nm$ and $\varepsilon_{oo} = 0.15635\, kcal/mol$; the LJ parameters of carbon atoms are $\sigma_{cc} = 0.341\, nm$ and $\varepsilon_{cc} = 0.05541\, kcal/mol$. To determine the parameters between carbon and oxygen, we used Berthelot-Lorentz mixing rule. used to estimate the thermodynamic properties of a mixture based on the properties of its individual components. The rule is based on the assumption that the interaction energy between the molecules of two different components in a mixture is proportional to the square root of the product of their individual molar volumes.

$$\sigma_{co} = \frac{\sigma_{cc} + \sigma_{oo}}{2} \quad \& \quad \varepsilon_{co} = \sqrt{\varepsilon_{cc}\varepsilon_{oo}}$$

By using above formula, we obtain the LJ parameters between carbon and oxygen as $\sigma_{co} = 0.3273\, nm$ and $\varepsilon_{co} = 0.09341\, kcal/mol$.

3.2. Methodology and Verification:

The diffusivity can be obtained with the Einstein equation:

$$D = \lim_{t\to\infty} \frac{1}{2dNt}\left(\sum_{j=1}^{N}\left[r_j(t) - r_j(0)\right]^2\right)$$

where r_j is the position vector of the jth atom, t is the time and d is the dimensionality of the system. So, for 3-D (x-, y- and z-directions)

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

The MSD describes the average displacement of particles as a function of time, and the slope of the MSD vs. time plot provides the diffusion coefficient or diffusivity.

The mean square displacement (MSD) is defined as:

$$MSD = \lim_{t\to\infty} \frac{1}{N}\left(\sum_{j=1}^{N}\left[r_j(t) - r_j(0)\right]^2\right)$$

Therefore, the slope of the MSD determines the diffusivity. where D is the diffusion coefficient or diffusivity, and the factor of 6 arises from the fact that the particles diffuse in three dimensions. Overall, the MSD method provides a simple and intuitive way to calculate the diffusivity of particles in a system from experimental or simulation data.

In the simulation, a time step of 1 fs is used and samples are taken every 1000 fs. The first 2,500,000 steps (2.5 ns) are dedicated to relaxation and equilibration of the systems, followed by another 50,000 steps to calculate the diffusivity. Water molecules are randomly distributed at the beginning of each simulation. The diffusivity is determined by calculating the slope of the average MSD.

To validate our simulation model, we calculated the diffusivity of bulk water since there is a lack of sufficient data on the diffusivity of nano-confined water in graphene channels. The simulation was carried out at a temperature of 300 K and a density of 1 g·cm-3, using the TIP4P model, similar to the MD simulations by Zhao et al. [10] and Mashl et al. [11]. Our result of D_{bulk} = $3.08*10^{-9}$ $m^2 \cdot s^{-1}$ is almost consistent with Zhao's ($2.62*10^{-9}$ $m^2 \cdot s^{-1}$) and Mashl's ($2.67*10^{-9}$ $m^2 \cdot s^{-1}$) data, which partially validates our simulation model.

4. Results and discussion

First, water simulation is done using TIP4P model to partially validate our results. MSD vs Time plot is shown below for the bulk water molecules (i.e., production runs) and diffusivity of bulk water is calculated using slope got the average diffusivity equal to 3.9 * 10^{-9} m^2/sec.

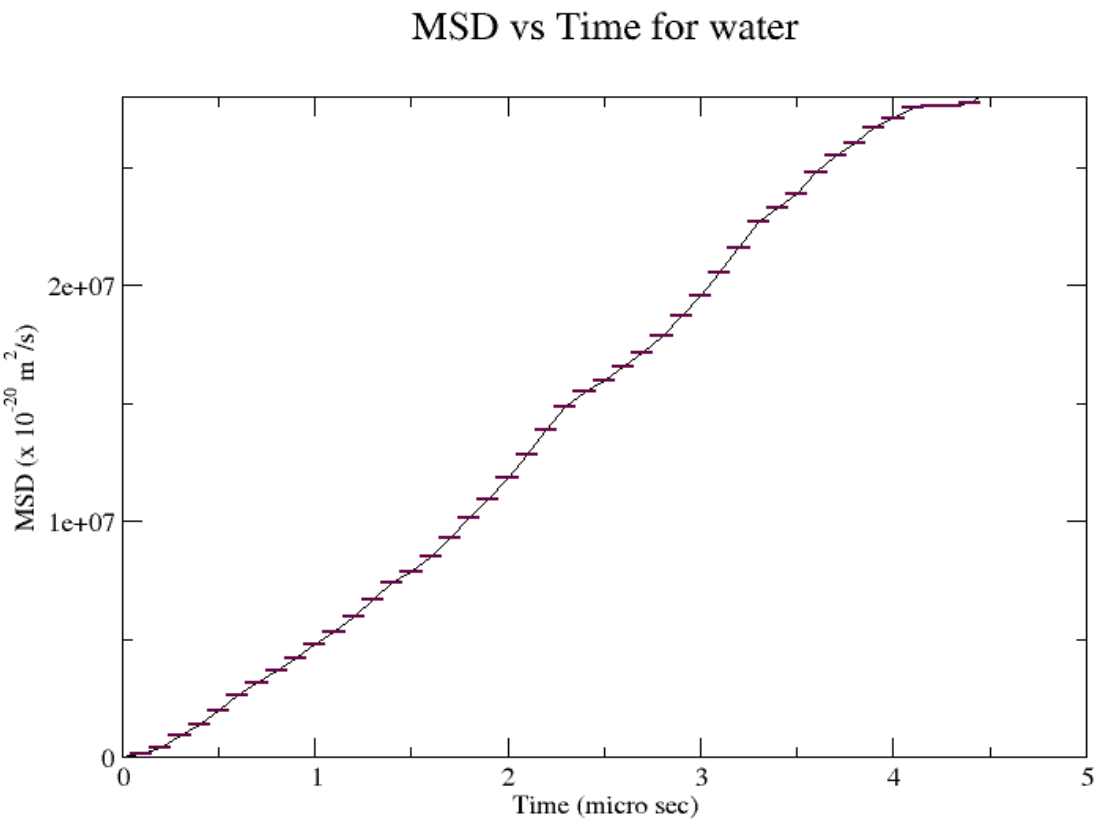

Fig.4 MSD vs Time for Bulk water

4.1. Effect of Nanochannel Height

The diffusivity of water confined in graphene nanochannels is evaluated by Four runs (shown below in four production runs) having distance varied from 10Å to 25 Å and then obtain the diffusivity varying the distance between two graphene nanochannel from 10Å to 25 Å. That shows anisotropic behavior which is strongly influenced by the channel height. When water is confined between two graphene sheets, its diffusivity can be significantly influenced by the distance between the sheets.

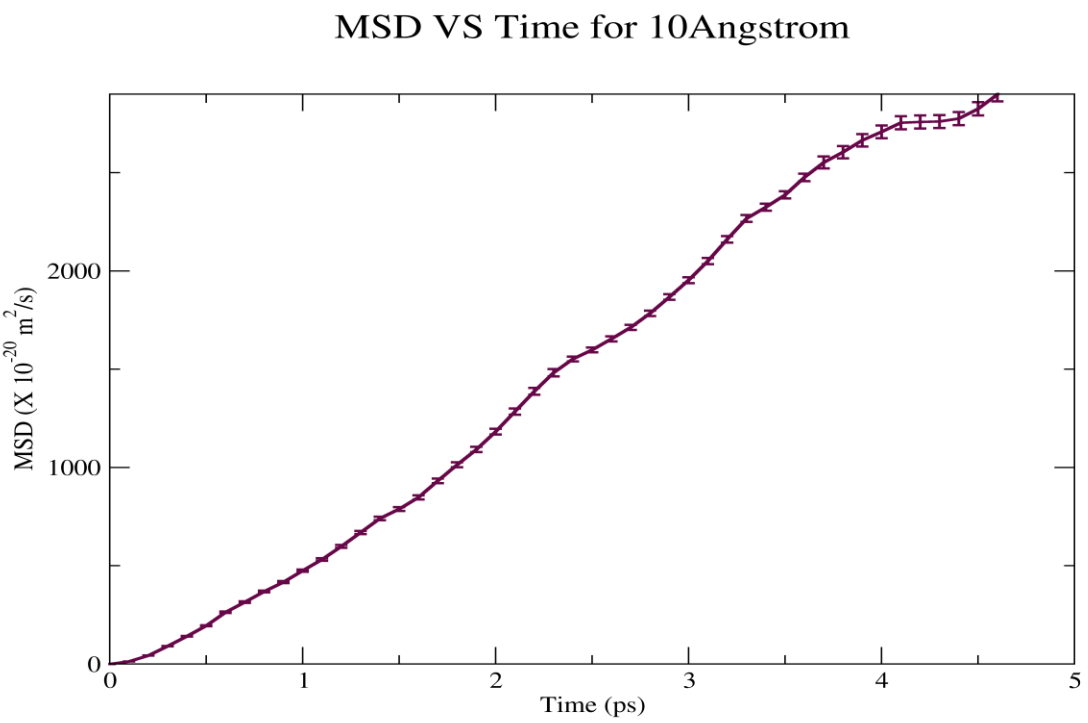

Fig. 5 MSD vs Time (water confined in a graphene nanochannel Distance between graphene sheet is 10Å)

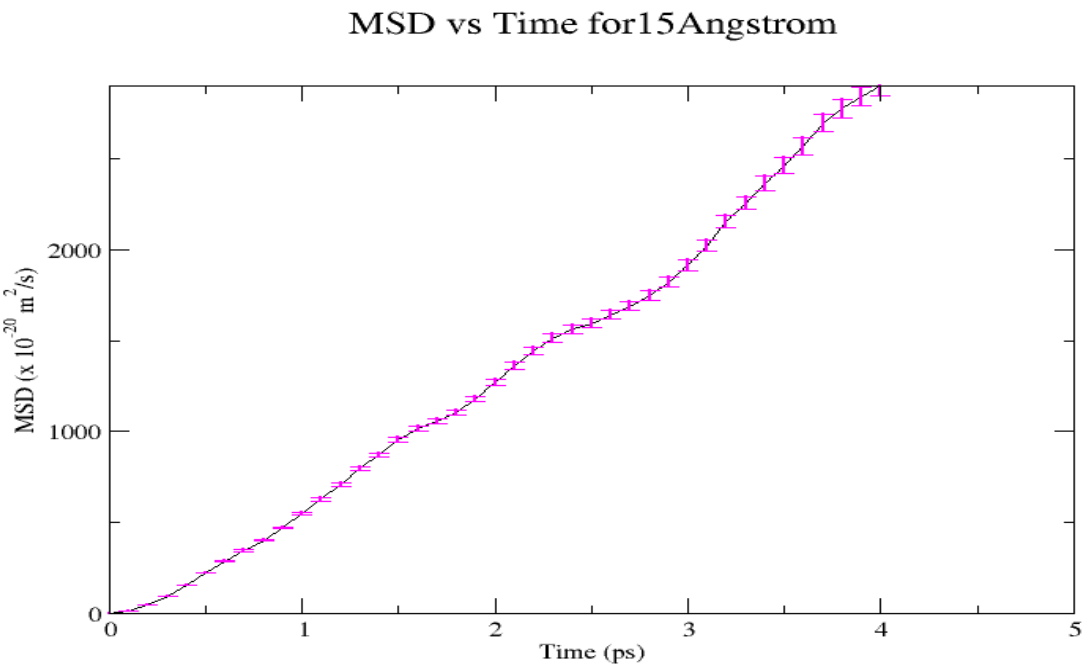

Fig. 6 MSD vs Time (water confined in a graphene nanochannel Distance between graphene sheet is 15Å)

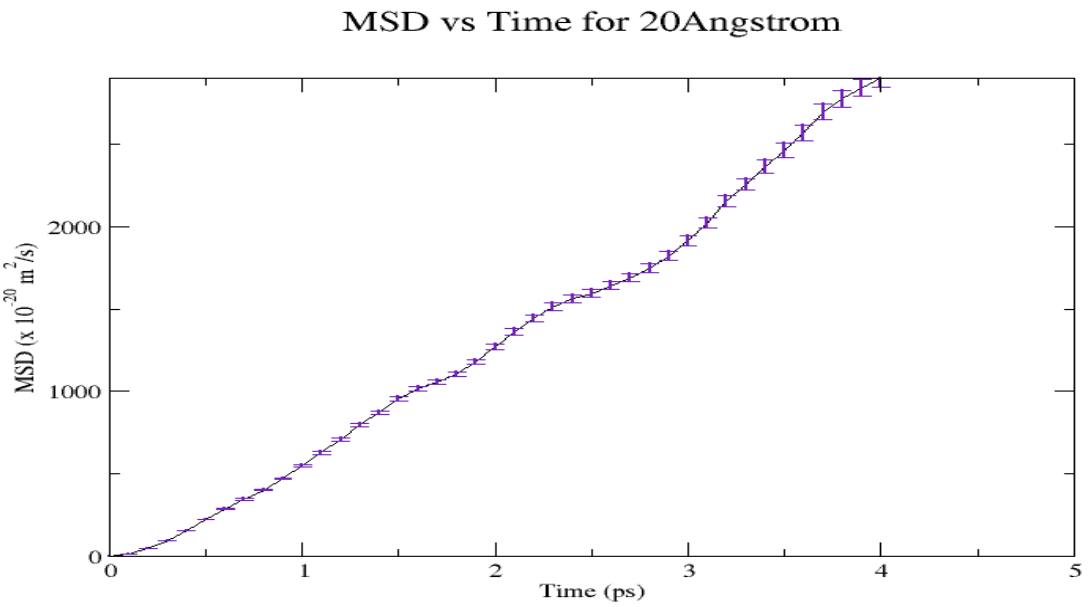

Fig. 7 MSD vs Time (water confined in a graphene nanochannel Distance between graphene sheet is 20Å)

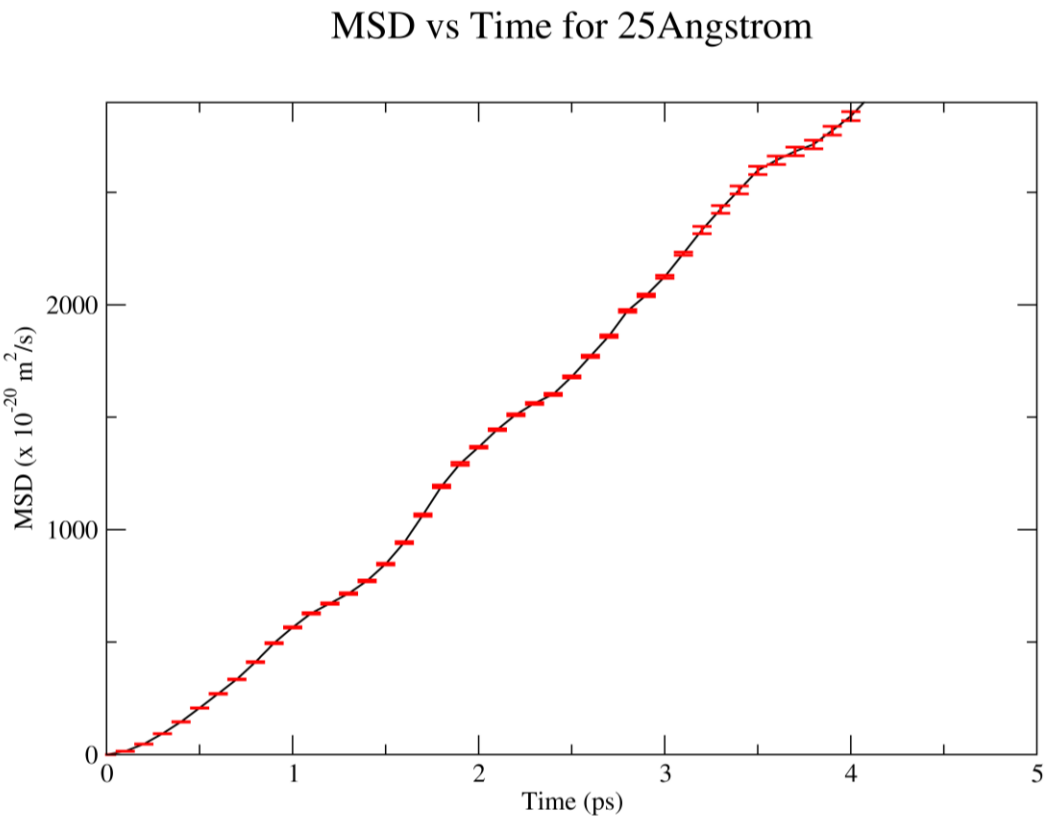

Fig. 8 MSD vs Time (water confined in a graphene nanochannel Distance between graphene sheet is 25Å)

Specifically, as the distance between the graphene sheets increases, the diffusivity of water molecules can increase as shown in the fig. 9. This is due to several factors:

a) Reduced confinement: As the distance between the graphene sheets increases, the confinement of water molecules between the sheets decreases. This reduced confinement leads to less interaction between the water molecules and the graphene sheets, allowing the water molecules to move more freely and with less hindrance.

b) Enhanced water structure: The confinement of water between graphene sheets can lead to changes in the structure of water molecules, including increased hydrogen bonding between water molecules. However, as the distance between the graphene sheets increases, this confinement effect weakens, leading to a more bulk-like water structure with increased diffusivity.

c) Reduced attractive interactions: At close distances between graphene sheets, water molecules can experience attractive forces due to van der Waals interactions with the graphene sheets. These forces can slow down the diffusion of water molecules between the sheets. As the distance between the graphene sheets increases, these attractive forces decrease, allowing water molecules to diffuse more freely.

After a certain distance between the two graphene sheets, the diffusivity of water molecules confined between the sheets becomes nearly equal to that of bulk water. This distance is often referred to as the "bulk-like" regime, and it typically occurs when the distance between the graphene sheets is greater than several nanometers as observed in the fig. 7 diffusivity is approaching towards bilk water diffusivity.

In the bulk-like regime, the confined water molecules are less affected by the presence of the graphene sheets and can move more freely, similar to bulk water. The water molecules in this regime have a more bulk-like structure and are less ordered compared to water molecules confined within smaller distances.

Overall, the diffusivity of water molecules confined between two graphene sheets is influenced by a complex interplay between confinement, water structure, and interactions with the graphene sheets. While the diffusivity generally increases with increasing distance between the graphene

sheets, the relationship is not necessarily linear and can depend on a variety of factors, including the size and shape of the graphene sheets and the presence of other solutes or ions in the water.

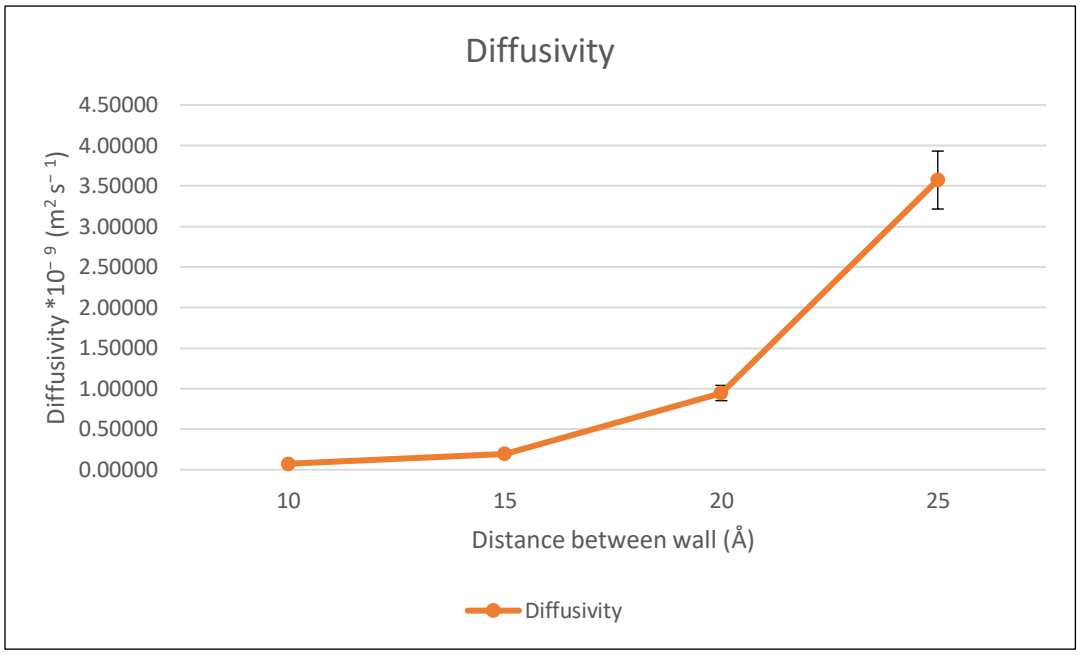

Fig. 9 Diffusivity variation as we increase distance between two flat graphene sheets.

4.2. Anisotropy

Anisotropy of water diffusivity refers to the variation in the rate of diffusion of water molecules in different directions. Water molecules in confined environments such as porous media or biological tissues tend to exhibit anisotropic diffusion due to the presence of geometrical features and interactions with the surrounding environment.

In general, water diffusivity is a measure of how quickly water molecules move through a particular medium. Anisotropic diffusion means that the diffusion coefficient is different in different directions, which can be quantified using various techniques such as diffusion tensor imaging (DTI). The fig. 10 depicts the changes in MSD over time in the x-, y-, and z-directions for a channel with a height of 10Å. The MSD in the x- and y-directions showed slight differences but were notably higher than the MSD in the z-direction. Applying the Einstein equation, the slope of MSD determines the diffusivity, leading to the conclusion that the diffusivity in the x- and y-directions were greater than in the z-direction. Therefore, the diffusivity of confined water in graphene nanochannels was found to be anisotropic in longitudinal and perpendicular

directions. A previous study [1] has attributed the anisotropic diffusivity in nanochannels to the presence of boundary walls that limit the mobility of fluid molecules in the z-direction. However, the reduced mobility in the perpendicular direction is also caused by the interactions between

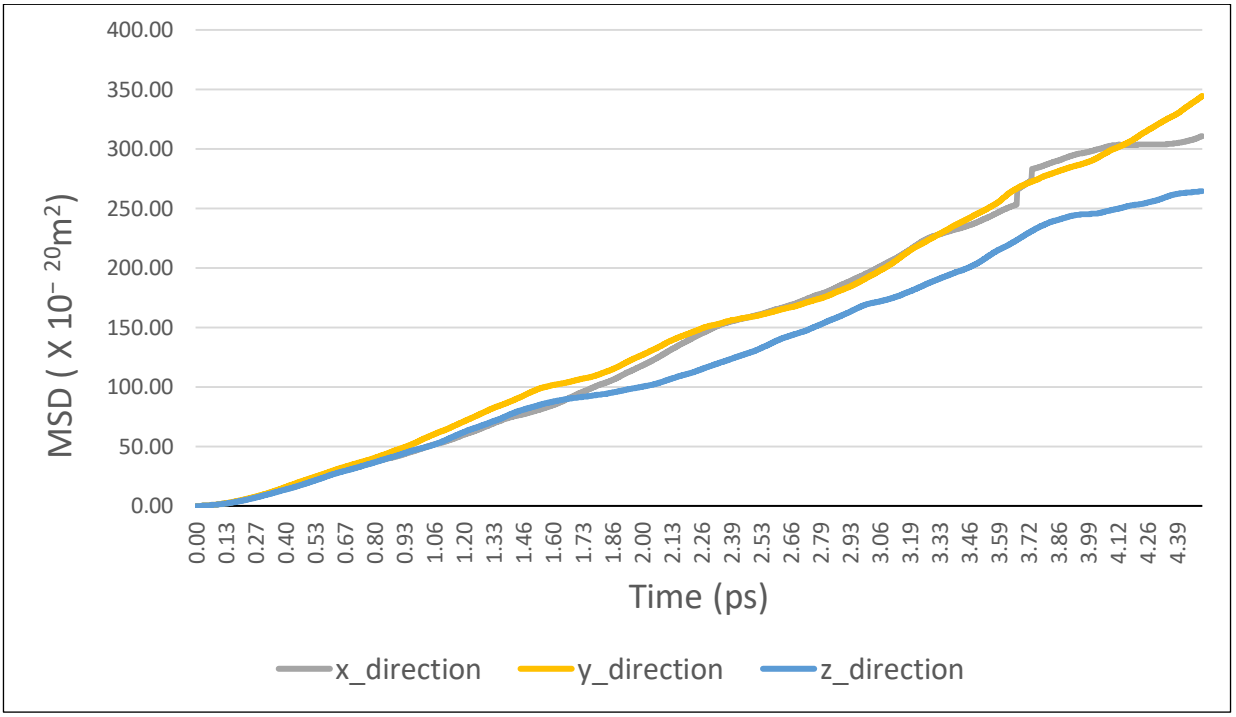

Fig.10 Diffusivities of confined water in the x-, y- and z- directions for the channel height of 10Å

carbon atoms in the graphene walls and water molecules. These interactions can be explained through thermodynamic insights, as the van der Waals forces that primarily govern the interactions between graphene and water molecules are a function of the position in the z-direction. Due to the symmetric structure of the graphene walls, the interaction energy between graphene and water molecules could result in a symmetric distribution profile in the perpendicular direction, resulting in the appearance of two potential wells near the graphene walls. The trapped water molecules within these potential wells will have limited mobility in the z-direction, leading to a lower diffusivity. However, the interaction exerted on water molecules in the xy-plane is balanced due to the symmetric structure of the graphene walls. This deduction is due to the density profile along the z-direction and the higher number density of water near the graphene walls [12]. Thus, the mobility in the xy-plane is barely restricted and the water molecules could freely move in the xy-plane.

5. Applications

This work was aimed to investigate the behavior, structure and dynamical properties of water confined between two parallel and flat graphene sheets at different interwall distances. Study of these systems has become an important area of research with potential applications such as development new mesoscale device.

a) Water filtration membrane:

Graphene membrane has ability to remove salt and other impurity from sea water and decrease the hardness of water and create efficient water filtration membrane.

b) Energy storage device:

Due to high surface area and capacitance of water confined between graphene sheets is used to create energy storage device such as super capacitor which has higher energy densities then traditional batteries.

c) Sensors:

Sometimes graphene sheets could be used to create highly sensitive sensors for detecting chemical, gases and other substance.

d) Biomedical device:

Graphene oxide nanochannels could be functionalize with specific molecules to target cancer cells or other diesis tissue so it's useful tool for drug delivery and medical imagining.

In materials science, anisotropic diffusion plays an important role in the transport properties of porous materials, such as membranes, catalysts, and adsorbents. Understanding and controlling the anisotropy of diffusion can be crucial for optimizing the performance of these materials in applications such as water purification, gas separation, and drug delivery. Overall, the confinement of water in graphene nanochannels opens up new possibilities for the development of advanced technologies in various fields.

6. Conclusion

The diffusivity of water confined in graphene nanochannels was analyzed using MD simulations and the Einstein equation. This study aimed to identify the unique characteristics of confined water in comparison to bulk water. The results showed that the diffusivity in the z-direction was lower than that in the x- and y-directions, indicating that nano-confined water had anisotropic diffusivity. To explain the mechanisms behind this anisotropic diffusivity, Lagrangian dynamics was employed to analyze the displacement of water molecules within the confined region. It was found that interactions between water molecules and carbon atoms in the graphene walls trapped many water molecules in potential wells near the walls, thereby limiting the mobility of water molecules in the z-direction. Additionally, the channel height had a significant impact on diffusivity. Specifically, the perpendicular diffusivity D_z increased with increasing channel height, approaching the parallel diffusivity (D_z and D_{xy}). This phenomenon was due to a decreasing proportion of trapped water molecules in the potential wells. As the height of the nanochannels increased, a smaller proportion of water molecules were trapped, allowing most of the water molecules to move freely with normal molecular mobility. These findings contribute to the academic study of mass and energy transport in nano-confined fluids.

7. References

[1] F. Sofos, T. Karakasidis, A. Liakopoulos, Int. J. Heat. Mass. Transf. 52, 735 (2009).

[2] Y. Liu, Q. Wang, T. Wu, L. Zhang, J. Chem. Phys. 123, 234701 (2005).

[3] C. Sun, B. Wen, B. Bai, Chem. Eng. Sci. 138, 616 (2015).

[4] D. Cohen-Tanugi, J.C. Grossman, Nano Lett. 12, 3602 (2012).

[5] C. Sun, M.S.H. Boutilier, H. Au, P. Poesio, B. Bai, R. Karnik, N.G. Hadjiconstantinou, Langmuir 30, 675 (2014).

[6] A.P. Straub, N.Y. Yip, S. Lin, J. Lee, M. Elimelech, Nat Energy 1, 16090 (2016).

[7] T.W. Sirk, S. Moore, E.F. Brown, J. Chem. Phys. 138, 064505 (2013).

[8] S. Plimpton, J. Comput. Phys. 117, 1 (1995).

[9] D. van der Spoel, P.J. van Maaren, H.J.C. Berendsen, J. Chem. Phys. 108, 10220 (1998).

[10] M. Zhao, X. Yang, X. Yang, Acta Phys. -Chim. Sin. 31, 1489 (2015).

[11] R.J. Mashl, S. Joseph, N.R. Aluru, E. Jakobsson, Nano Lett. 3, 589 (2003).

[12] Giancarlo Cicero, Jeffrey C. Grossman, Eric Schwegler, Francois Gygi, and Giulia Galli, J. Am. Chem. Soc. 2008, 130, 6, 1871–1878.

[13] Z. Zhao, C. Sun, R. Zhou, Int. J. Heat. Mass. Transf. 152, 119502 (2020).