PARTICLE SELF-DIFFUSION AND DENSITY DISTRIBUTION WITHIN A SLIT PORE

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Summary

Molecular dynamics simulations were performed on a system containing either one or two types of particles confined within a slit pore geometry. Particle "A" had a greater Lennard-Jones repulsion from the pore walls while particle "B" had a greater Lennard-Jones attraction to the wall. The goal was to understand particle self-diffusion, particle number density distribution in the pore, and the effect on these properties when mixing the two particle types with different particle-particle Lennard-Jones interactions. It was found that the diffusion coefficient and particle density distribution is quite sensitive to the presence of other molecular species and its respective interaction potential. These results have implications toward molecular design to enhance transport properties of particles in confinement.

I. BACKGROUND

The transport property of fluids confined in pores is important and stimulates much research and applications in fields like biology and materials science. A noteworthy example is the Carbon nanotube, which could be used as an industry membrane,[1] a proton storage device,[2] and drug-delivery devices.[3] When developing these applications, it is important to understand how the molecular species used interacts with both one another and the pore walls.

In this report the diffusion and density profile of particles confined within a slit pore geometry is studied. More specifically these properties are first examined for isolated particles and subsequently for mixed systems containing two particle types with varied particle-particle Lennard-Jones (LJ) interactions. The two hypothetical particle types used are denoted "A" and "B". The two particle differ in how they interact with the pore wall. Particle "A" has a larger LJ repulsion from the pore walls while particle "B" has a larger LJ attraction to the wall. This is interesting as one could imagine a pore wall having a specific affinity for a particular molecular

species over another. The dimensionless LJ potential used has the form:

$$U_{ij} = 4(C(r_{ij})^{-12} + D(r_{ij})^{-6}) \tag{1}$$

For this study, the "A - wall" LJ interaction uses $C = 4$ and $D = 1$ while the "B - wall" LJ interaction uses $C = 1$ and $D = 2$. The particles "A - A" and particles "B - B" LJ interactions use $C = 1$ and $D = 1$. These coefficients are held fixed throughout the study. It is the hope that although this model is quite elementary that some generalizable information about transport can be elucidated.

II. SIMULATION METHODS

Molecular dynamics simulations were performed in the NVE ensemble initialized at T* = 7.988. The total number of free particles was fixed at 150 and a step size of 0.0005 was employed to preserve energy conservation. A two atomic-layer thick wall consisting of 400 atoms total was constrained to an FCC lattice with a 1 unit lattice spacing. Minimum image distance was employed in the x and y coordinates for the system. A box length of 10 units was used. All interaction potentials were cut and shifted at half of the box length. The particles were initialized on a lattice for convenience within the confinement of the walls and their energy was subsequently minimized via the conjugant gradient method. Two equilibration periods consisting of 50,000 md steps each were used. The Anderson thermostat[4] using "massive collisions" was employed during the equilibration period to help reach the desired starting temperature. The production period was 500,000 md steps. Data was collected every 1000 md steps for a total of 500 data points. This was done to ensure independent sampling. Three trials were performed and averaged over for the calculation of the diffusion coefficient and the particle density distribution. The density profile of particles confined within the slit pore was determined via histograms.

III. RESULTS AND INTERPRETATION

Four scenarios were studied to better understand particle self-diffusion, particle number density distribution, and the property changes upon mixing particle types while changing particle-particle LJ interaction potentials. These are:

Case 1) Particle "A" isolated

Case 2) Particle "B" isolated

Case 3) Particle "A" and "B" 50:50 mixture with greater "A - B" attraction ($C = 1$ and $D = 4$)

Case 4) Particle "A" and "B" 50:50 mixture with greater "A - B" repulsion ($C = 4$ and $D = 1$)

Case 1

In case 1 a MD simulation of 150 particles of type "A" was performed. These particles have a large short-range repulsion from the pore wall. Figure 1A) shows the density distribution of particle "A" within the slit pore $g(z)$ and Figure 1B) displays a snapshot of the simulation. The

particle distribution in the pore is relatively uniform except for slight bias towards the pore walls. The diffusion coefficient D_A is reported as 0.665 ± 0.429.

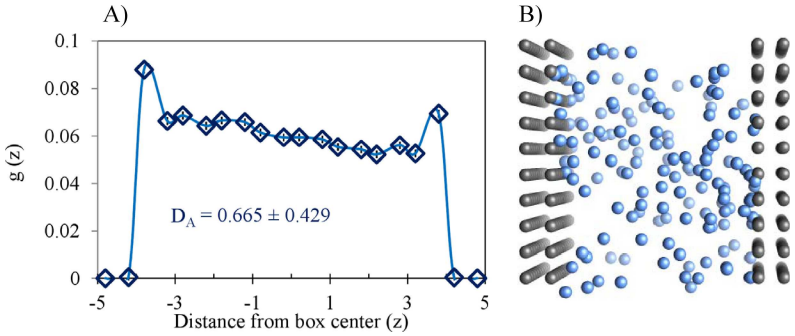

FIG. 1. A) The density profile of particle A inside the slit pore at equilibrium. B) A snapshot of the simulation.

Case 2

In case 2 a MD simulation of 150 particles of type "B" was performed. These particles have an attraction to the pore walls. As seen in Figure 2A) the particle B density distribution is peaked near the pore walls due to this attraction. This can be visualized from Figure 2B). The diffusion coefficient D_B is reported as 1.594 ± 0.009, which is significantly faster than for case 1. Visually it appears that the particles move more quickly near the pore walls.

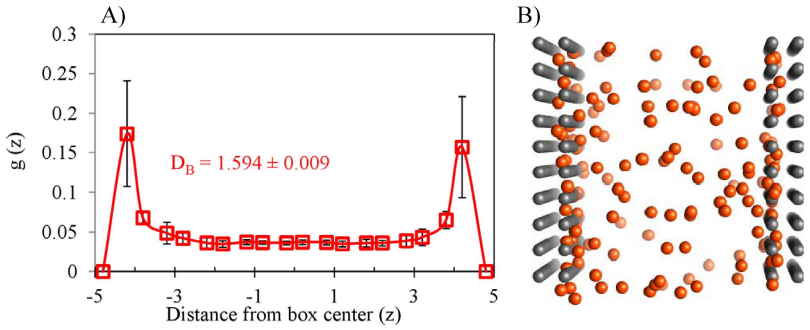

FIG. 2. A) The density profile of particle B inside the slit pore at equilibrium. B) A snapshot of the simulation shows a larger fraction of particles near the wall.

Case 3

In case 3 a MD simulation of 75 particles of type "A" and 75 particles of type "B" was performed. In Figure 3A) it is seen that, when the mixed particles have a dominate attraction to each other, the density profile for the two particles follow a similar trend. A snapshot of this distribution is shown in Figure 3B). The diffusion coefficients have both increased from the isolated cases. Also in this scenario $D_A > D_B$ but in the isolated cases (case 1 and case 2) it was determined that $D_A < D_B$. This transport property appears to be quite sensitive to the presence of other molecular species.

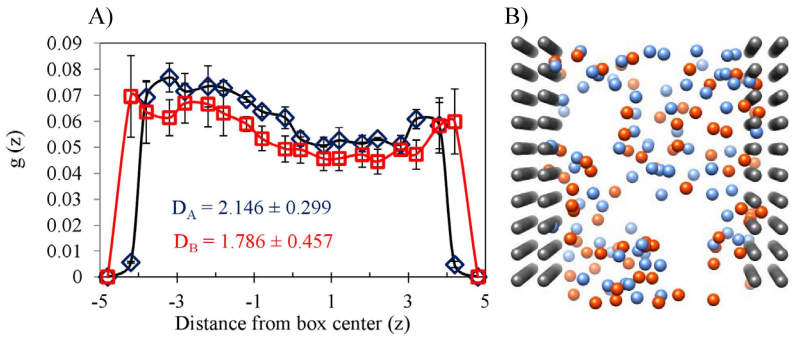

FIG. 3. A) The density profile of particle "A" and "B" with strong LJ attraction inside the slit pore at equilibrium. B) A snapshot of the simulation.

Case 4

In case 4 a MD simulation of 75 particles of type "A" and 75 particles of type "B" was performed. Here the two particles have a large short-ranged repulsion with each other. The density profile is displayed in Figure 4A). The particle distributions for the two types are quite distinct from one other, contrary to case 3. The characteristic bimodal behavior seen in case 2 for particle "B" was present in this simulation. Particle "A" has severe depletion at the wall boundaries due to its repulsion from both particles of type "B" and the pore wall. The particle distribution and their diffusion coefficients can be greatly altered by varying their interactions. This implies the possibility to use molecular design to enhance transport properties of particles in confinement.

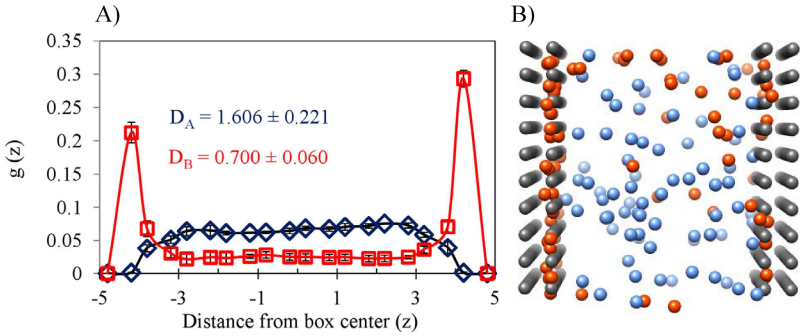

FIG. 4. A) The density profile of particle "A" and "B" with strong LJ repulsion inside the slit pore at equilibrium. B) A snapshot of the simulation.

REFERENCES

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