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Bimodal Diffusion of Binary Lennard Jones Mixtures in Atomically Detailed Single-Walled Carbon Nanotubes

Qu Chen[1], Joshua D. Moore[2], Ying-Chun Liu[1,2], Thomas R. Roussel[2], Qi Wang[1] and Keith E. Gubbins[2]

[1]Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China
[2]Department of Chemical and Biomolecular Engineering and Center for High Performance Simulation (CHiPS), North Carolina State University, Raleigh, NC, USA 27695-7905
Email: quchen@zju.edu.cn

Several diffusion mechanisms are possible in small cylindrical pores, including ballistic motion, Fickian diffusion and single-file diffusion (SFD). Mon and Percus have reported that pure hard sphere fluids exhibit a crossover from single-file to Fickian diffusion in cylindrical tubes with hard walls with a narrow pore radius [1]. In applications of binary mixtures diffusing in cylindrical pores, each component of the mixture may crossover from Fickian to SFD in a different pore diameter, giving rise to bimodal diffusion. Recently, Ball et al. have demonstrated bimodal diffusion for hard disks diffusing in structureless cylindrical pores with hard walls [2]. We investigated systems of rigid and flexible (6,6), (7,7), (8,8), (9,9) and (10,10) armchair carbon nanotubes, solvated with binary mixtures of Lennard-Jones (LJ) fluids (Ar/Kr, Ar/Ne and Ar/Xe). A range of effects are examined including the use of continuous potentials and an atomically detailed wall, the size ratio of the two components in the mixture, the mixture concentration, and the nanotube diameter. The influence of these variables on the individual crossover diameters of each component is analyzed in terms of the Fickian diffusion coefficient, the single-file mobility and the mutual diffusion coefficient of the mixture. Microcanonical (NVE) and canonical (NVT) production runs are compared. The canonical (NVT) production runs utilize a Langevin thermostat which mimicks fluid-wall momentum exchange through the inclusion of random damping of the fluid velocities. We find that significantly smaller system sizes can be used with the Langevin thermostat, especially for single-file fluids which have dramatic long range correlations of the velocities [3]. The crossover diameter occurs in (6,6) for Ne, (7,7) for Ar and Kr, and (8,8) for Xe. In the (7,7) nanotube for the Ar/Ne mixture and the (8,8) nanotube for the Ar/Xe mixture, the larger of the two components in each binary mixture diffuses in single-file while the smaller of the two components diffuses by a Fickian mechanism. This computational study might be further applied extensively in gas separation and provide insights for diffusion limited gas catalysis in porous media.

References

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