Molecular Simulation, Vol. 30 (10), 30 August 2004, pp. 661–667

Taylor & Francis
Taylor & Francis Group

Atomistic Simulations of Rare Gas Transport through Breathable Single-wall Nanotubes with Constrictions and Knees

M.W. ROTH* and J. MESENTSEVA

Department of Physics, University of Northern Iowa, Cedar Falls, IA 50614, USA

(Received July 2003; In final form April 2004)

We present the results of molecular dynamics (MD) computer simulations of rare gas diffusion through breathable nanotubes with pentagon–heptagon pair defects resulting in constrictions and knees. Diffusion involves interrupted high speed "choppy" motion with intermittent reversal in velocity direction. Single atoms exhibit a spiral-like path, in contrast to atoms traveling in groups. Considerable resistance to flow appears to reside in the upstream section of the nanotube where density gradients are small, prior to the constriction. Subsequently, considerable density gradients are present and speeds increase, becoming greatest at the tube exit. For the nanotubes examined, Kr and Xe diffusion was too hindered to provide reliable results. Diffusion of He through the nanotubes with knees occurs in a single-file fashion nearly along the center of the tube and the knee has no detectable effect on the diffusion kinetics. Transport diffusion coefficients are in the order of 10^{-4}–10^{-2} cm^2/s.

Keywords: Nanotube diffusion; Molecular dynamics; Rare gases; Permeation; Transport diffusivity

INTRODUCTION

Since their discovery in the early 1990s [1–3] nanotubes have been found to vary considerably in structure and dimension. As a result, arrays of carbon nanotubes present interesting and diverse environments in which to study equilibrium and non-equilibrium atomic and molecular processes. In particular, gradient-driven diffusion of various species through membranes is of considerable scientific and technological importance because of applications in gas separation and storage, in sorbent design and also in catalysis. There have been relatively few studies of atomic and molecular diffusion through various types of carbon nanotubes.

Tuzun and coworkers employ an MD technique to study the dynamics of He, Ar and C_{60} fluid flow through single wall nanotubes (SWNTs) [4,5]. They model flexible nanotubes with bond stretching and bending potentials, and all non-bonded interactions with Lennard–Jones (LJ) potentials. They find that incorporating the dynamic aspect of the nanotube is important because fluid–wall collisions slow the fluid down much more quickly in time than in a rigid tube. In addition, diffusing species with smaller mass flow more easily through the tubes. However, the fluid slowing depends on simulated time but not the length of the nanotube utilized. Overall, fluid flow through nanotubes is still poorly understood, and there is evidence that nanosystems could exhibit novel laminar/turbulent flow transitions with possible practical implications [6].

Not surprisingly, some of the first gas diffusion studies involve hydrocarbons. Düren and coworkers [7] use Dual Control Volume Grand Canonical Molecular Dynamics (DCV-GCMD) techniques [8] to calculate transport diffusion properties of CH_4/CF_4 mixtures in rigid nanotubes with three wall layers. Composition-dependent transport properties are calculated for driving pressure gradients four orders of magnitude larger than in corresponding real systems, but the calculated transport diffusivities are independent of the driving gradient. Mao and coworkers [9–11] model diffusion

*Corresponding author. Tel.: +1-319-273-7336. Fax: +1-319-273-7136. E-mail: rothm@uni.edu

ISSN 0892-7022 print/ISSN 1029-0435 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/08927020410001722276