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Predicting gas diffusion regime within pores of different size, shape and composition

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ABSTRACT

The ability to separate mixtures of molecules is a vital technology in a world that emits excess carbon dioxide into the atmosphere, needs purified water, desires artificial kidneys and requires hydrogen for sustainable energy alternatives. Membranes are composed of angstrom and nanometer-sized pores which may be designed to separate a gas, vapor or liquid mixture. In this paper we employ mathematical modeling, using the Lennard-Jones interactions between the gas molecule and the pore wall, to determine the gas diffusion regime occurring within pores of different size, shape and composition. This novel approach is used to predict the transport of light gases, namely, He, H_2, CO_2, O_2, N_2 and CH_4, through carbon tubes, carbon slits, silica tubes and silica slits. Minimum pore size for barrier-free transport ($d_{\min}$) and the minimum pore size for Knudsen diffusion (d_K) are calculated for each gas and a mechanism for the intermediate region is suggested in which the attractive van der Waals forces cause an accelerated entrance velocity of the gas at the pore opening. Experimental results for gas transport in carbon nanotube, carbon molecular sieving and molecular sieving silica membranes are explained well by the model. The aim of this work is to provide the guidelines for tailoring porosity in membranes and adsorbents, such that desired separations are achieved.

1. Introduction

Gas, vapor and liquid separation membranes act as sieves, allowing the desired molecules to penetrate through the membrane while blocking unwanted molecules. Membranes play an important role in removing carbon dioxide from natural gas, removing hydrogen from gas mixtures, removing toxins from the blood, removing salt from seawater as well as many other applications [1]. Typically, these membranes must be designed using a variety of inputs from experimental materials science [1] as well as methods such as Monte Carlo (MC) simulations [2], Molecular Dynamics (MD) [3,4], Positron Annihilation Lifetime Spectroscopy (PALS) [5,6], Small Angle X-ray Scattering (SAXS) [7,8] and empirical fits to experimentally determined permeability and pore size distribution (PSD) [9,10]. The present work uniquely determines specific ideal pore radii for particular gas molecules and separation mechanisms using a mathematical method that incorporates the Lennard-Jones polymer–penetrant interactions at the entrance of a pore.

Mathematical modeling in nanoscience that lends explanations to the unique physical phenomena at the nano-scale is vital for property optimization and the eventual implementation of products and processes based on nanotechnology. One particular continuum model which was originally used to successfully investigate the C_{60}-nanotube oscillator determines the van der Waals interactions between atoms of the C_{60} fullerene and the carbon nanotube (CNT) [11]. The MD simulations [12,13] of this device showed that the C_{60} fullerene is positioned at the opening of the CNT and is either repelled away from the tube or sucked inside the tube where it begins to oscillate back and forth between both openings due to the van der Waals forces at work. As expected, it is also found that if the fullerene is given an initial velocity towards the opening then the fullerene will travel through the tube and come out the other side. This latter case is closely related to gas diffusion within the pores of a membrane as previous work assigned cylindrical shaped pores as the diffusive jump pathways between cavities which each gas molecule has to jump through to successfully diffuse through the entire membrane [14]. The modeling approach used for the oscillator device delivers important information such as the minimum size of a CNT to accept a fullerene and the size of a CNT that provides the maximum suction energy, which compares well with MD simulations [11,13]. The method has since been used to successfully model nanoscale gigahertz oscillators [15], drug acceptance into CNT's for "golden bullet" drug delivery [16,17], water transport

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through CNT's [18] and other applications [19,20], and will be used in this work to determine light gas transport regimes within CNT-based, carbon molecular sieving (CMS) and molecular sieving silica (MSS) membranes.

Recently, interest has arisen in the development of CNT-based membranes [21–23]. It has been predicted by computer simulations that the molecular transport through these tubes is exceedingly fast due to the attractive van der Waals forces sucking the molecules through the tubes [24,25]. By using a mathematical method first proposed by Cox et al. [11,15], in this work we determine the optimal tube sizes necessary for gas separations. For small gas molecules there exists only one CNT that has the correct size to make separations by means of the size-sieving mechanism according to these calculations, namely a (5,5) CNT with a pore size of 3.48 Å. To date, the (5,5) CNT only exists in theory and is yet to be synthesized. Other sized CNT's are certainly capable of making separations for these small gases but they are not as efficient as the (5,5) CNT. This method can be extended for use in large molecular separations like hydrocarbons, proteins, toxins, drugs, viruses and many more, for which the recent CNT-based membranes could be expected to excel in performance [22,23].

These mathematical models and their predictions can be extended to CMS and MSS membranes by assuming that the pore geometries are cylindrical or slit shaped and their atomic configurations result in van der Waals interactions between a molecule and the pore wall in a similar manner to the interactions between a molecule and the wall of a CNT. The main features that the model predicts are minimum pore size for barrier-free transport, pore size that maximizes the suction force at the entrance and minimum pore size for Knudsen-type transport. Experimental results match the model predictions well and provide insight to the separation outcomes found in these membranes [22,26–28].

Freeman [29] provides a theoretical basis for the upper-bound relationship empirically determined by Robeson [30] between selectivity and permeability for a range of polymers and gases. This theoretical basis was established using the Lennard-Jones parameters in terms of the kinetic diameter σ and well depth ε. The diffusion of a gas is dependent on its kinetic diameter while its solubility mainly depends on the condensability of the gas and consequently dependent on the well depth for gas–gas interactions. It is noted by Freeman [29] that gas–polymer interactions are also an important factor but the dependence was not determined. The present study shows the importance of gas–pore wall interactions in molecular-scale gas separations occurring in a variety of membranes. Gas–pore wall interactions have been used before to identify different pore size regimes for adsorption established by Everett and Powl [31] and later modified to determine separation scenarios by de Lange et al. [32]. These studies only consider the interaction forces normal to the pore wall and therefore do not consider interactions in the axial direction which we show are important for the determination of transport through pores.

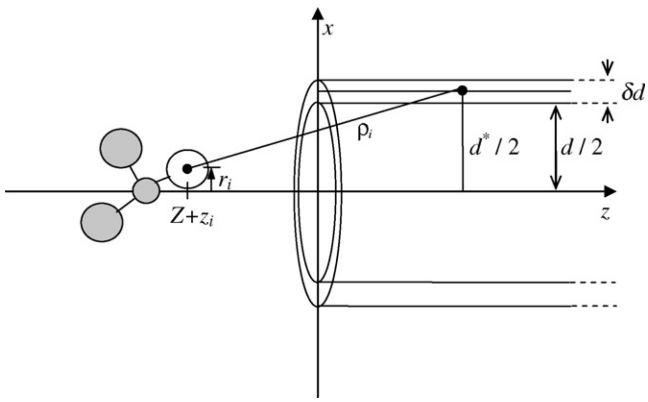

Fig. 1. Geometry of molecule entering a pore channel. Experimental pore diameter d is equivalent to the theoretical pore diameter d^* minus the electron cloud thickness δd of the wall atoms, i.e. $d = d^* - \delta d$.

The following section is an outline of the mathematical details used to investigate the kinetics of a gas molecule entering a pore. Consequently, the results are compared with experimental data for gas flow rates in CNT-based, CMS and MSS membranes in Section 3. The diffusion regimes within different pore sizes calculated from the model agree well with the observed flow rates available in the literature. The limited available experimental data prevents the completion of a full testing of the model; however, the model predicts that certain pore systems may be designed to take full advantage of the gas–pore wall interactions to improve separation performance. As the ability to tailor the porosity of membranes develops, results such as these will guide the materials designer.

2. Mathematical formulation

The entrance of a pore can be at the surface of the membrane or at a transition region from a larger section within the membrane. The rate of diffusion is believed to be controlled at these pore openings where the gas molecule experiences either an energy barrier or a suction energy, decreasing or increasing the rate of diffusion, respectively [33,34]. In a system of long symmetrical pores, like that of a CNT-based membrane, the suction energy can be converted to kinetic energy causing an accelerated velocity which continues through the frictionless environment until the end of the tube, where an identical opposing suction force reduces the velocity back to the gas' original velocity before entering the tube. This newly proposed diffusion mechanism we will term "suction diffusion". In systems with pores of short length this accelerated velocity is of little advantage and the rate of diffusion is dominated by effects such as surface adsorption, number of transitions, tortuosity and connectivity, etc. Here the van der Waals interactions between the gas and the pore wall are integrated throughout the transition state at the opening of the pore resulting in the work done by the van der Waals forces. Assuming that the amount of energy is converted to kinetic energy this work done can be understood in terms of kinetic energy, in which a negative kinetic energy means an energy barrier for the gas molecule while a positive kinetic energy means an acceptance energy (or suction energy).

As a molecule approaches a pore opening each atom in the gas molecule will interact with every atom making up the pore wall through van der Waals forces. If the pore opening is too small then the attractive van der Waals forces will not be strong enough to suck the molecule inside and so the molecule will need to have a certain amount of kinetic energy to enter the pore. Therefore, by calculating the total work done by the forces between each gas molecule and the pore wall a minimum pore size for transport (d_{min}), and an optimal pore size (d_{opt}) which provides a maximum suction energy, and a minimum pore size for Knudsen transport (d_{K}) can be determined. By assuming an even distribution of atoms on the pore wall a hybrid discrete-continuum formulation [35] is employed, such that the total interaction potential energy is given by

$$\mathrm{PE} = \sum_i \eta \int v(\rho_i)\,\mathrm{d}S,$$

where $v(\rho_i)$ is the potential function for atom i of the gas molecule interacting with a surface element $\mathrm{d}S$ on the pore wall at a distance of ρ_i away as shown in Fig. 1, and η is the mean atomic surface density of the atoms on the pore wall, which in this case is assumed