



Molecular modelling of oxygen and water permeation in polyethylene

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ABSTRACT

Monte Carlo and molecular dynamics simulations were performed to calculate solubility, S , and diffusion, D , coefficients of oxygen and water in polyethylene, and to obtain a molecular-level understanding of the diffusion mechanism. The permeation coefficient, P , was calculated from the product of S and D . The AMBER force field, which yields the correct polymer densities under the conditions studied, was used for the simulations, and it was observed that the results were not sensitive to the inclusion of atomic charges in the force field. The simulated S for oxygen and water are higher and lower than experimental data, respectively. The calculated diffusion coefficients are in good agreement with experimental data. Possible reasons for the discrepancy in the simulated and experimental solubilities, which results in discrepancies in the permeation coefficients, are discussed. The diffusion of both penetrants occurs mainly by large amplitude, infrequent jumps of the molecules through the polymer matrix.

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1. Introduction

The permeability of small penetrant molecules in polymer materials is important for many applications, e.g., fuel cells [1], gas separation [2] and packaging [3]. Polyethylene (PE) is, for example, widely used for packaging materials and its barrier properties towards penetrants such as oxygen and water is a factor that determines the shelf-life of the packaged product. It is therefore important to identify the polymer properties that affect the permeation of penetrants. This will assist in developing new polymers and polymer composites that have desired barrier properties.

Experimental studies provide valuable understanding of the macroscopic [4–9] and microscopic [10,11] properties of polymers and their transport properties. Michaels and co-workers [4,5] found that there is a slight increase in the solubility of oxygen in polyethylene between 285 and 315 K, and that a further increase in temperature results in a far larger solubility. In contrast, Compañ et al. [12] found that the largest increase in solubility occurs at temperatures lower than 315 K, and that a further increase in

temperature does not lead to a large increase in the solubility. Studies by Kurek et al. [9] yielded a decrease in solubility between 275 and 295 K, and a further increase in temperature leads to an increase in solubility. Experimental measurements of water solubility in PE or systems similar to PE are in better agreement. Schatzberg [13] obtained an increase in solubility of water in *n*-hexadecane when increasing the temperature from 298 to 315 K, and McCall et al. [6] obtained a similar increase for water in PE over a larger temperature range of 298–335 K.

Experimental studies of diffusion of oxygen in PE [8,9,12] typically show an increase in diffusion coefficient with increasing temperature. These experiments have been conducted from 277 to 335 K, and the diffusion coefficients are $\sim 10^{-8} - 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Similar results were obtained for water, where McCall et al. [6] obtained an increase in diffusion coefficient from 6×10^{-7} to $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ between 306 and 333 K.

Computational simulations complement experimental studies by allowing easy manipulation and analyses at the molecular level. Insights gained at this level are expected to assist in identifying polymers with desired barrier properties. This has stimulated the development of a variety of computational techniques to calculate solubility and diffusion in polymers. These techniques can predict properties at both the macroscopic and molecular (microscopic) levels. At the macroscopic level it is possible to calculate diffusion [14–16] and solubility coefficients [14,17,18], and at the microscopic level it is possible to analyse properties such as clustering of the penetrant molecules [19], free volume [17] and rotations of

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polymer chains [20]. The work presented here illustrates the fact that a single model can provide properties at both the macroscopic and microscopic levels.

In contrast to experiments, where the permeation coefficient is determined from

$$P = \frac{(\text{quantity of penetrant}) \times (\text{film thickness})}{(\text{area}) \times (\text{time}) \times (\text{pressure drop across film})} \quad (1)$$

it is common in simulations [21,22] to determine the solubility coefficient [23], S , and diffusion coefficient, D , separately before calculating the permeation coefficient as,

$$P = SD \quad (2)$$

Simulations are performed for a purely amorphous polymer phase, whereas experiments use polymer films with crystalline and amorphous regions. Differences between experimental and computational polymer material and measurement methods need to be taken into consideration when comparing these data, and this is discussed in the Methods section.

The work presented here extends previous calculations of polymer transport properties by determining S , D and P for gas phase oxygen and liquid water in PE. Although it is possible to determine S using a variety of methods, including grand canonical Monte Carlo [24] (GCMC) and Henry's law method [21], the results presented below are obtained from the Gibbs ensemble Monte Carlo method [25,26] (GEMC). This method was selected since the long term aim of this research is to perform a systematic study of transport properties over a variety of polymers, including hydrophobic and hydrophilic systems, where a large range of penetrant concentration will be studied. In addition, whereas the chemical potential is required GCMC simulations, a pressure is used as input in the GEMC technique. This simplifies comparison with experimental data, as well as the transfer of input parameters to the (NpT) molecular dynamics (MD) calculations. S and D are therefore determined for the same system at the same conditions, which allows for the correct calculation of P . The pressure studied in this work is 1 atm and the temperatures are 278, 288, 298 and 308 K. These conditions are relevant, for example, to the packaging industry and mimic and range from refrigerator to hot room temperatures.

2. Methods

2.1. Force field

The AMBER (Assisted Model Building with Energy Refinement) [27], DREIDING [28], OPLS-AA (Optimized Potentials for Liquid Simulations – All Atom) [29] and CHARMM (Chemistry at HARvard Macromolecular Mechanics) [30] force fields have been successfully used to study polymeric systems [21,31–33]. These models were therefore considered for the present study, and their validity were tested for the PE system studied here. The tests focused on the polymer density (although other properties such as melting and glass transition temperatures are also important), since this is expected to be a critical property for the permeation of molecules through the polymer. For example, if the force field yields a density that is too low, then there will be more free volume that can be occupied by the penetrant, hence increasing S and perhaps D (and hence P).

The initial density simulations were performed using n -octane (which has a similar structure to PE) since these systems require far less computational time to equilibrate. One of the force fields that gave the proper density for n -octane (AMBER) was then used to

calculate the density of PE which, as discussed below, was also in agreement with experiment. This force field was therefore used in the MC and MD simulations to determine S and D , respectively.

A second reason for choosing the AMBER force field is that one can include atomic charges [27] using, for example, the restrained electrostatic potential (RESP) method [34]. This was done using n -dodecane as a model of PE, and the R.E.D. code [35] (RESP and ESP charge Derive) in conjunction with Gamess-US [36]. As discussed below, this method yielded very small atomic charges, which is reasonable since n -dodecane (and PE) molecules do not contain highly electronegative groups.

An alternative to the computationally demanding RESP charge calculations is the AM1-BCC [37,38] scheme which is designed to mimic the RESP charges but is based on bond charge corrected semi-empirical AM1 Mulliken charges instead of Hartree-Fock charge density. This method was also examined, and the AM1 charges were calculated using Mopac [39] for 20 different structures of n -octane. The final atomic charge was obtained by averaging over all 20 structures and ensuring neutrality of each methylene unit. These charges, which are shown in Fig. 1, are larger than the charges obtained from the RESP method and were therefore included in the AMBER force field to test their effect (*i.e.*, simulations were performed with and without atomic charges to ascertain their importance).

The force field of Fischer and Lago [40] was used for the oxygen molecules, and the modified TIP3P force field [41] was used for the water molecules. The modified TIP3P force field includes Lennard-Jones terms for the hydrogen atoms which improves the simulation results, especially when Ewald summation methods are used [42].

2.2. Polymer structures

Although it is, in principle, possible to obtain S and D from single, long simulations, the long-time dynamics of the polymer chains makes this an extremely resource intensive approach. An alternative is to simulate an ensemble of trajectories, where each trajectory is performed using a polymer matrix that is significantly different from the matrices used in the other trajectories, but that is still representative of the polymer structure at the given temperature and pressure.

The initial PE matrices were created by randomly inserting six PE chains of 200 carbon atoms each in a cubic simulation box with 45 Å sides. Previous studies [43] have shown that this number of chains is sufficiently large, and that the chains are sufficiently long, to provide converged results for PE. These structures were constructed using the GCMC method with a chemical potential that was sufficiently large to induce the six PE chains into the box while at the same time avoiding large atomic overlaps.

The box was then compressed until the sides were 30 Å, which corresponds to a PE density of approximately 1 kg/L. This is far larger than the experimental value of ≈ 0.855 kg/L [44] for

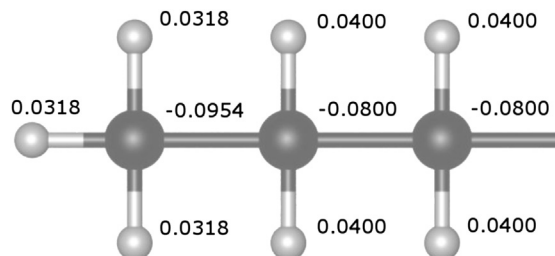


Fig. 1. The AM1-BCC charges for terminal CH_3 and interior CH_2 units of PE.

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