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Microscopic Diffusion Mechanism of CO_2 in a Glassy Amorphous Polymer Matrix

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1. Introduction

Transport properties of gases and small molecular weight penetrants inside polymers are of great importance in separation processes related to a wide range of chemical, environmental and biomedical applications. Molecular simulation serves as a valuable predictive tool that effectively maps out the relations between the constitution and the properties of a material and aids the design of new membranes with controlled permeability properties. Studying the microscopic diffusion mechanism of a penetrant inside a glassy polymer appears to be very challenging, as diffusivity is too slow to be predicted by conventional molecular simulation techniques, such as molecular dynamics (MD). In this work, a systematic methodology is developed to study the microscopic diffusion mechanism and predict the diffusivity of CO_2, in a full-atom representation, within a glassy poly(amide imide) (PAI) of complex repeat unit constitution using multidimensional transition state theory implemented in Cartesian coordinates.

2. Methodology and Results

Transition State Theory [1] describes diffusion as a succession of infrequent jumps between clusters of accessible volume in the polymer matrix. During each jump the system is required to overcome an energy barrier in the multidimensional configuration space of the polymer-penetrant system. Neighboring minima that are separated by energy barriers less than k_BT belong to the same macrostate. Geometric analysis [2] of the accessible volume of the polymer provides an initial estimate of the sorption sites and the saddle points through which the diffusion pathway passes. Transition state theory is applied to all possible transitions detected by geometric analysis. Transition states are calculated by gradually increasing the number of degrees of freedom, including polymer atoms in the vicinity of the penetrant. The diffusion pathways are determined using Fukui's intrinsic reaction coordinate. The diffusivity is calculated via a kinetic Monte Carlo (KMC) scheme, having first obtained the sorption probabilities within each macrostate and the macrostate-to-macrostate transition rate constants. The network, in which the KMC simulation is conducted, is dictated by the atomistically calculated transition pathways.

The microscopic diffusion mechanism along the elementary jumps is investigated. The energy barriers decrease rapidly, reaching an asymptotic limit as the dimensionality of the transition state theory calculation increases. The rate constants appear widely distributed, with the majority of transitions being characterized by rate constants of 10^{-1}-10^{2} μs^{-1}. The calculated diffusion coefficient (0.25×10^{-8} cm^2s^{-1}) is in good agreement

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with the experimental value (0.81×10^{-8} cm^2s^{-1})[3]. Detailed study of the diffusion mechanism during the elementary jumps reveals that there is a concerted motion of the polymer atoms allowing the penetrant to pass from one sorption state to another. Changes in the orientation of the CO_2 along the pathway are also of great importance in realizing the jump. Fig. 1 displays the potential energy profile along an elementary jump, with the activation energy of the transition (~8 kcal mol^{-1}) being within the experimental range of activation energies for diffusion in glassy polymers. Fig. 2(a) depicts changes in the orientation of CO_2 along the transition path relative to its orientation at the transition state, while fig. 2(b) illustrates the correlation of CO_2 orientation with the projection of the reaction coordinate path in 3-dimensional space during the elementary jump.

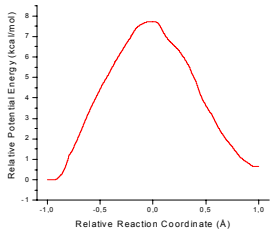

Fig 1: Potential energy of the CO_2-PAI system along a transition path. The reaction coordinate has been normalized, so that zero corresponds to the transition state, while -1 and 1 correspond to the initial and the final states, respectively.

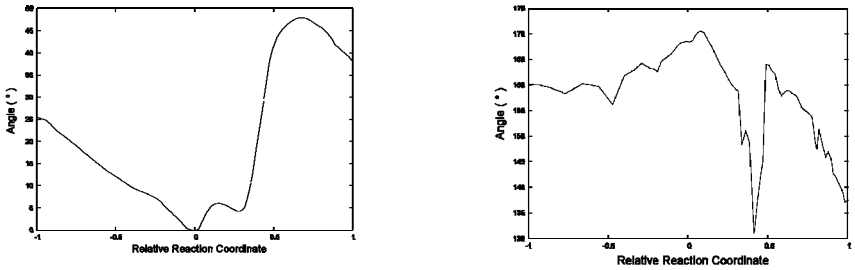

Fig 2: (a) Orientation angle of CO_2 vector along the transition path relative to its orientation at the transition state and (b) angle between CO_2 vector and tangent to the projection of the reaction path on the 3-dimensional space of center of mass coordinates.

3. Conclusion

A systematic methodology has been developed for the prediction of diffusivity of a non-spherical penetrant within a glassy polymer. The implementation of the method has led to a wealth of microscopic information about the diffusion mechanism of CO_2 within the glassy polymer.

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