

Cooperative effects in the transport of small molecules through an amorphous polymer matrix

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The transport of small molecules (penetrants) through polymer materials proceeds by a hopping mechanism: A penetrant typically dwells in a cavity of the polymer for a while and then performs a quick jump into an adjacent cavity. In this article we investigate a jump event in detail. Molecular graphics is used to identify if and how the motion of the penetrant is aided by the fluctuations of the polymer matrix. We employ both traditional molecular graphics techniques to show atomic motion and surface rendering methods to display the redistribution of penetrant-accessible volume in the polymer.

Keywords: permeation of polymers, molecular-dynamics simulation, rendering of penetrant-accessible volume

INTRODUCTION

It has long been suspected^{1–3} that transport of small molecules (penetrants) through amorphous polymers proceeds by a hopping mechanism: The penetrants are quasi-stationary for longer periods of time while they are located in cavities that exist in the polymer. During these residence times they explore the cavity by oscillation and by rotational or librational motions, but do not leave it. Hence, no net penetrant flow is achieved in these periods. Exactly how long the quasi-stationary periods last depends strongly on the size of the penetrants, the details of their interactions with the polymer, the structure and flexibility of the polymer matrix, and so on. Diffusion is caused by quick leaps of penetrant molecules from one cavity to another. The time for such a jump event is much shorter than the quasi-stationary periods, typically on the order of a few picoseconds.

Molecular dynamics (MD) calculations on small-molecule permeation of amorphous polymers have recently become feasible.^{4–16} The simulations now cover a range of different polymers: polyethylene, polypropylene, poly-

dimethylsiloxane and polyisobutylene. Several studies^{5–7,9,12–14,16} were specifically aimed at the diffusion mechanism. They seem to confirm unanimously the hopping pattern described above. This shows up in the step-like shape of a penetrant's displacement curve as well as in plots of its trajectory (trace). Individual hopping events have been analyzed graphically^{5,12} to study the importance of the local free volume. In addition, the energetics of hopping events have been monitored.^{13,14}

In this contribution, we examine graphically a hopping event of an oxygen molecule dissolved in amorphous polyisobutylene ($-\text{CH}_2-\text{C}(\text{CH}_3)_2-$)_n. Polyisobutylene (PIB), which is rubbery at room temperature (copolymer with 2% isoprene: "butyl rubber"), is an interesting system because gaseous penetrants tend to diffuse through it much slower (1–2 orders of magnitude) than through any other natural or synthetic rubber.¹⁷ We analyze for the participation of polymer atoms in the jump event and for the importance of the redistribution of unoccupied volume before, during and after the jump event. We display the free volume by a surface-rendering technique borrowed from biomolecular simulations. Animation and rendering of these simulations became possible by hooking up the molecular graphics package SCARECROW written by Laaksonen¹⁸ to the molecular simulation system YASP written by Müller-Plathe.¹⁹

METHODS

Amorphous PIB samples of experimental density (913 kg·m⁻³) are generated by the rotational isomeric state method of Theodorou and Suter,²⁰ as implemented in the Polymer module of Biosym Technologies, San Diego. They consist of a single PIB chain of 80 monomers interacting with its periodic images due to the cubic periodic boundary conditions. The samples are energy-minimized, and then equilibrated for several hundred picoseconds by MD at a constant temperature of 300 K. The equations of motion are integrated by the leap-frog algorithm with a time step of 2 fs. Into these samples eight oxygen molecules are inserted. Care is taken that the oxygen molecules are more than 0.5 nm apart and that they are placed at energetically

Color Plates for this article are on pages 125–126.

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favorable sites (insertion energy less than zero). No further equilibration is necessary.

The PIB/O₂ system is run at constant 300 K for 2 ns, and the trajectory is written to the disk every 0.2 ps. We scan the O₂ trajectories for sudden jumps by inspecting each molecule's displacement from its initial position $|\mathbf{R}(t) - \mathbf{R}(0)|$. A few promising jumps are then studied by molecular graphics. All jumps have different characteristics. The one selected here we deem fairly representative. This choice is, of course, arbitrary to some extent.

Details of the force field will be given elsewhere. Let us just note that the polymer force field is very similar to the one used in earlier work on polypropylene¹¹ and polyisobutylene.^{15,16} For the methyl groups (but not for the methylene groups) we use united atoms. For O₂ we use the parameters of Fischer and Lago.²¹

For the rendering of penetrant accessible surfaces a raw three-dimensional (3D) mesh of free-volume data is generated using the algorithm by Voorintholt et al.,²² which generates the data for a probe surface at the grid points up to a specified maximum probe radius. This method is very fast and convenient if one wants to look at the molecular surfaces for several different probe radii without recalculating the mesh data. This approach can be used to study outer molecular surfaces as well as cavities and channels inside molecules.

The surface-rendering and display code is based on the NCSA isovis program.²³ The basic isovis program extracts a constant-valued (iso) surface from a regular 3D volume of scalar data using Lorensen and Cline's marching cubes algorithm.²⁴ The display program SCARECROW¹⁸ uses an improved version of isovis by Blythe²⁵ where the coherency has been utilized to reduce the number of redundant computations. The code was also restructured for additional speed-up, and the program includes the ability to compute normals at each triangle vertex by computing an approximation to the gradient at each cube corner using a central difference. This results in far superior shading (i.e., considerably less faceting) at greater computational expense.

RESULTS AND DISCUSSION

The jump event is displayed in two series of stills in Color Plates 1 and 2. Color Plate 1 uses the traditional plumber's-nightmare or licorice representation. The polymer carbon atoms are grey; the hydrogens are omitted for clarity. Oxygen molecules are colored green, except one which is highlighted in red. It is this red one whose jump is being studied here. Note that a periodic box is shown here: Atoms at the upper edge are connected to periodic images of atoms at the lower edge and so on. This sometimes leads to polymer atoms which appear to be orphaned (unconnected) in the display.

During the time series shown the red oxygen molecule performs a jump from a position in the upper right quadrant (Color Plate 1a, 0 ps) of the frame into the lower right corner (Color Plate 1i, 12 ps). During the first five picoseconds (not shown) the molecule briefly explores a location in the upper left quadrant but returns quickly to its initial position (Color Plate 1b, 5 ps). During the next 3 picoseconds (Color Plates 1c–e, 6–8 ps) it slowly drifts downward, approaching the transition state between the 2

cavities. The transition state is reached in Color Plate 1f (9 ps). The molecule emerges from the transition state with a high kinetic energy. This can be noted in Color Plate 1g (10 ps): in the picosecond between Color Plates 1f and 1g the molecule has achieved a displacement which is comparable to that between Color Plates 1b and 1f, which took 4 ps. In the last two figures of this series (Color Plates 1h and 1i) the oxygen settles in its new cavity. There it will stay for at least the next 25 ps, which is as far as we monitor its movements. In Color Plates 1c–f one notes that the oxygen undergoes substantial tumbling while approaching the transition state. This is consistent with our analysis of the rotational kinetic energy of jumping molecules,^{13,14} which showed that rotation (or libration) persists during the transition. Also, the length of the jump event proper, roughly 5 ps (Color Plates 1c–h), corresponds to the window of approximately 4 ps around the jump event during which the total kinetic energy of the oxygen is significantly above its average kinetic temperature of 300 K. This window is smaller, more like 1.5 ps, for hydrogen molecules.

While the traditional graphical representation of the jump event is very useful for picturing details of the oxygen motion, it is difficult to extract the role of the surrounding polymer. It is seen to be mobile, though not as mobile as the oxygen, but not much more can be said. We therefore present the same time series in a different representation (Color Plate 2) where the oxygen molecules appear as before, whereas all polymer atoms now are omitted. Instead, we show the accessible volume. This contains all positions where the center of an oxygen atom can be placed without causing an overlap of the oxygen with any of the polymer atoms. Note that the accessible volume is different from the free volume often used in polymer science, which just denotes the fraction of space outside any polymer atom.

In Color Plate 2 the pieces of accessible volume appear in grey. They correspond to cavities in polyisobutylene which are large enough to hold an oxygen atom. Since we have to cut our pseudo-infinite periodic system at some level in the display (this happens to be the boundary of the periodic box), we also cut through some of the cavities. Hence, some cavities nearer to the observer show their inside, the side on which an oxygen could be, rather than their outside, the side toward the polymer. To mark this difference we color the inside surface of the cavity purple. Actually, this is done by recalculating the probe surface with a slightly different probe radius and displaying both surfaces in different colors.

Comparing first the start and the end of the series (Color Plates 2a and 2i, 0 ps and 12 ps), one notes a strong similarity in the distribution of the accessible volume. One may conclude that the polymer chains have more or less the same positions before and after the jump. It can also be seen that both before and after the jump there is no connection—no channel—between the two cavities.

In between, however, connections between the two cavities come and go by means of fluctuations in the polymer. In Color Plate 2b (5 ps) there is some connection which disappears again in the following frame. In Color Plate 2d (7 ps) there is a situation in which the oxygen is almost at the transition state and ready to jump but there is no path open to the lower cavity. The channel then forms which can be seen in Color Plates 2e and 2f (8 ps and 9 ps). In Color Plate 2g (10 ps) the oxygen has already traversed most of the chan-

nel. In the last two frames (Color Plates 2h and 2i, 11 ps and 12 ps) the oxygen settles into the new cavity while the channel closes behind it.

This three-phase pattern—channel opens, penetrant jumps, channel closes—has been found for other penetrants in other amorphous polymers as well: oxygen in polyethylene⁵ and methane in polydimethylsiloxane.¹² It appears therefore that this mechanism, also called the Red Sea mechanism, is quite general.

From inspection of this, as well as of other time series,^{5,12} it would appear that the rate-determining process is the formation of the channel, and that once the channel exists the penetrant can slip through it without any effort. From our studies of the energetics of hopping events,^{13,14} however, we know that during and immediately before and after the hop the penetrants have translational kinetic energies substantially higher than what would correspond to the average temperature of the simulation. In the case of oxygen we found an increase by 200–300 K. It seems, therefore, that the activation of a hop involves more than the opening of the channel, and that the oxygen has to acquire extra kinetic energy to pass through it.

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