# Diffusion Coefficients of Penetrant Gases in Polyisobutylene Can Be Calculated Correctly by Molecular Dynamics Simulations

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**Introduction.** The diffusion coefficient of a penetrant gas in a polymer material is an important technical property with implications in many technologies. Such diffusion coefficients are also among those quantities which can be calculated sensibly in the picosecond to nanosecond time scales accessible to classical molecular dynamics (MD) simulations. Over the last 2 years several MD studies of diffusion in amorphous polymers have appeared.[1-8]

Most of the previous studies use either model polymers or simple models of amorphous polyethylene (PE).[1-6] We are aware of only three studies of chemically more complex polymers: atactic polypropylene (PP, ref 7), poly(dimethylsiloxane) (PDMS, ref 8), and polyisobutylene (PIB, ref 5). While all studies reproduce correctly the qualitative aspects of the diffusion process (hopping of the penetrant between voids), almost all of them find diffusion coefficients which are too large by some 2 or 3 orders of magnitude. An exception to this is the work on polyethylene,[6] polypropylene,[7], and PDMS[8] where the calculated diffusion coefficients agree to within a factor of 10 or better with the experimental results. This kind of accuracy makes simulations a useful tool, since deviations between different experiments are often of the same order.

We have undertaken a series of simulations on the diffusion of $O_2$ molecuels in amorphous polyisobutylene $(-CH_2C(CH_3)_2-)_n$ in order to investigate the effect of various simulation parameters. We find that the diffusion coefficient is strongly dependent on the force field. In particular, it is found that calculated diffusion coefficients which exceed experimental values by orders of magnitude are an artifact of the isotropic united-atom approximation commonly used in polymer simulations. By introducing explicit hydrogen atoms into the model, we can reproduce experimental diffusion coefficients very closely.

**Model and Simulation Details.** We have used several amorphous polyisobutylene samples at the experimental density (913.3 kg $m^{-3}$) of single chains of 80 and 262 monomers, respectively. Starting structures of these samples were generated with the Polymer module of Biosym Technologies, San Diego, CA, which implements a modification of the rotational isomeric state (RIS) method of Theodorou and Suter.[9] These structures were energy-minimized and subjected to equilibration MD runs of 0.3- and 1-ns duration (small and large samples, respectively). Into the equilibrated structures we inserted between 4 and 27 $O_2$ molecules at sites which are energetically favorable (energy upon insertion <0) and at least 0.5 nm apart. In some cases we did further equilibration MD which, however, turned out to be unnecessary. After that we performed production runs of 2–8-ns duration. These were done at constant-volume (cubic periodic box), constant-temperature (300 K) conditions.[10] From the $O_2$ trajectories we calculated the center-of-mass mean-square displacement $\langle|R(t)-R(0)|^2\rangle$. The angle brackets imply averaging over all $O_2$ molecules and all time origins. When the regime of Einstein diffusion is reached, the mean-square displacement is linear in time. We fitted the linear domain by a straight line and calculated the diffusion coefficient $D$ from its slope

$$6D = (\mathrm{d}/\mathrm{d}t)\langle|R(t) - R(0)|^2\rangle$$

All simulations and analyses were carried out with the YASP program package.[11]

The details of our force fields will be published elsewhere. In Table I we present only the nonbonded potential energy parameters which are important in the following discussion. For the polymer we have used two different force fields. One uses united atoms to represent the methyl groups. However, hydrogens attached to backbone carbons are retained explicitly. This force field is very similar to the one used in our earlier work on PP.[7] The second force field is an all-atom force field. The nonbonded and torsional parameters are those of Suter et al.,[12] supplemented with the necessary bonded interactions of the GROMOS force field.[13] For the $O_2$ molecules we used the potentials of English and Venables[14] and Fischer and Lago.[15] The oxygen molecules of both potentials have roughly the same length. However, the Fischer and Lago oxygen is a little fatter. Also, the Lennard-Jones parameter $\epsilon$ of the Fischer and Lago model is only about 70% that of the English and Venables parameter. The English and Venables model is adjusted to reproduce the structures of solid phases of $O_2$, whereas the Fischer and Lago model is tailored to give correct excess properties in liquid mixtures of $O_2$ and inert gases. For mixed nonbonded interactions we used the Lorentz–Berthelot mixing rules.[16]

**Results and Discussion.** Diffusion coefficients of $O_2$ in polyisobutylene are listed in Table II. In our simulations we have varied the force fields for both the polymer and the oxygen molecules and the size of the periodic simulation cell.

We cannot expect the polymer sample to relax to equilibrium during the time of our simulation of a few nanoseconds. Therefore, polymer starting structures have to be prepared that are already close to an equilibrium conformation. In order to investigate the influence of different RIS starting structures on the diffusion coefficient, we have performed simulations using four different starting structures, denoted as samples 1–4 in Table II. It can be seen that the calculated diffusion coefficients are scattered between $2.5 \times 10^{-6}$ and $7.3 \times 10^{-6}$ $cm^2$ $s^{-1}$, the average being $4.9 \times 10^{-6}$ $cm^2$ $s^{-1}$ with a standard deviation of $2.2 \times 10^{-6}$ $cm^2$ $s^{-1}$. This indicates that we can obtain relatively accurate results already using very small samples (a box size of 2 nm is just about compatible with the customary 0.9-nm cutoff for the nonbonded interactions) and few of them. Since an accuracy of a factor 3 is well within what is required for the method to be predictive, this finding is very encouraging.

However, in absolute values the calculated diffusion coefficients are 2 orders of magnitude larger than the experimentally measured diffusion coefficient.[17] Our results are of a magnitude similar to that of the MD result of Boyd and Pant[5] of $6.2 \times 10^{-6}$ $cm^2$ $s^{-1}$ for methane in PIB. Boyd and Pant use a united-atom description for both the methyl and the methylene groups in PIB. However, they use a completely different method to generate amorphous starting structures (reptation Monte Carlo). The agreement between our result and theirs is

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**Table I**
**Lennard-Jones Potential Energy Parameters for Nonbonded Interactions**

| force field | atom | $\epsilon$/(kJ mol$^{-1}$) | $\sigma$/nm | $O_2$ bond length/nm | ref |
|---|---|---|---|---|---|
| E&V | O | 0.5122 | 0.295 | 0.121 | 14 |
| F&L | O | 0.3630 | 0.3090 | 0.10166 | 15 |
| united $CH_3$ | H | 0.3149 | 0.2316 | | 7 |
| | C | 0.3471 | 0.3207 | | |
| | $CH_3$ | 0.5730 | 0.3564 | | |
| all atom | H | 0.3180 | 0.2318 | | 12 |
| | C | 0.3519 | 0.3207 | | |

**Table II**
**Diffusion Coefficients of $O_2$ in Amorphous Polyisobutylene**

| PIB sample | cubic box size/nm | simulation time[a]/ns | PIB force field | $N_{O_2}$ | $O_2$ force field[b] | $D$[c]/$10^{-6}$ cm$^2$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 2.0131 | 0.3/2.0 | united $CH_3$ | 8 | F&L | 7.35 (1) |
| 2 | 2.0131 | 0.3/2.0 | united $CH_3$ | 8 | F&L | 6.94 (4) |
| 3 | 2.0131 | 0.3/2.0 | united $CH_3$ | 8 | F&L | 2.50 (1) |
| 4 | 2.0131 | 0.3/2.0 | united $CH_3$ | 8 | F&L | 2.841 (2) |
| 4 | 2.0131 | 0.3/2.0 | united $CH_3$ | 8 | E&V | 8.155 (8) |
| 4 | 2.0131 | 0.3/2.0 | united $CH_3$ | 4 | E&V | 5.381 (2) |
| 5 | 2.993 | 1.0/8.0 | united $CH_3$ | 27 | E&V | 6.240 (2) |
| 4 | 2.0131 | 0.3/8.0 | all atom | 8 | F&L | 0.169 (1) |
| expt[d] | | | | | | 0.081 |

[a] Time for equilibration and production, respectively. [b] F&L, Fischer and Lago;[15] E&V, English and Venables.[14] [c] Indicated in parentheses are the standard deviations of $D$ as calculated from the least-squares fits. These are not error bars on $D$. [d] van Amerongen.[17]

another indication that the particulars of the amorphous starting structure cannot have a very big influence on the diffusion coefficient. Minor effects can, however, not be ruled out since they could be compensated by other simulation parameters (e.g., differences in the force field, much shorter simulation lengths in ref 5).

For one of the small samples (no. 4) we have calculated the diffusion coefficient using both oxygen force fields. In the force fields there are two competing effects: The English and Venables $O_2$ is slightly slimmer. Hence, it should be able to slip through the narrows more easily and diffuse faster. On the other hand, the Lennard-Jones $\epsilon$ of the English and Venables $O_2$ is larger. Because both the attractive and the repulsive part of the potential scale with $\epsilon$, this increases the energy gap between $O_2$ in a cavity and $O_2$ at a transition state. Since diffusion is an activated process, the English and Venables oxygen should diffuse slower.[4] We found that diffusion of the English and Venables $O_2$ proceeds somewhat faster. This means that the diffusion rate is more sensitive to the size of the penetrant than to its interaction energy. However, we see also that the diffusion coefficient is relatively insensitive to the penetrant model. This has two implications: In general, we can expect accurate diffusion coefficients if we use any reasonable penetrant model. (Short-time dynamic properties of the oxygen molecules in PIB, on the other hand, can be considerably affected by the oxygen model.[18]) In this particular case, possible deficiencies in the oxygen model do not sufficiently explain the discrepancy between calculated and experimental data, and we probably would have to use a completely unphysical oxygen model if we wanted to force the calculated diffusion coefficient down to the experimental value in this way.

In order to eliminate the finite-size effects, we have also constructed a much larger polymer sample (3 instead of 2 nm; sample 5) and used a corresponding number of $O_2$ molecules (27 instead of 8). We find a diffusion coefficient which is very similar to the ones for the smaller polymer samples. We conclude that finite-size effects play no role in predicting diffusion coefficients by MD, at least not on this small scale. Much larger length scales, on the other hand, are not accessible to MD simulations. It appears to be safe to use the small box sizes for the calculation of diffusion coefficients.

In the approximation of Henry's law we can estimate from the experimental solubility of $O_2$ in PIB[17] the oxygen partial pressure corresponding to our system. It amounts to some 300 atm. We therefore wanted to check how this high pressure affects the diffusion coefficients. Unfortunately, the simulation of a system with an oxygen pressure of 1 atm is completely unfeasible. As a compromise, we have repeated the calculation using sample 4, but with only four oxygens. This halves the oxygen pressure but still gives reasonably good statistics. We have found a diffusion coefficient which is smaller than that for the higher oxygen pressure. However, the effect seems to be small, and it cannot be made responsible for the disagreement between calculation and experiment. These results are consistent with high-temperature, high-pressure measurements of the diffusion coefficients of methane in PIB.[19] There it had been found that over methane pressure ranges between 0 and 200 atm the methane diffusion coefficient does not change by more than a factor of 2. For oxygen one would expect an even smaller effect since in polyolefins oxygen is not as good a plasticizer as methane.

Finally, we have studied the influence of the united-atom approximation, again using PIB sample 4. From Table II it is obvious that this approximation has by far the most dramatic effect of all the parameters investigated. Upon changing to the all-atom force field the diffusion coefficient drops to $0.169 \times 10^{-6}$ cm$^2$ s$^{-1}$. This is very close to the experimental value of $0.081 \times 10^{-6}$ cm$^2$ s$^{-1}$.

United-atom models of the type given in Table I are frequently used in molecular simulation. In most cases this has little effect on calculated properties. So we may speculate why the united-atom approximation produces so large an artifact in the present case and why this did not show up in our earlier calculations on PP and PDMS.[6,7] The most probable reason is a packing argument. Even though the united-atom model produces the same space filling as the all-atom model (after all the radii of the united atoms have been adjusted to do just that), the geometry of the holes between the polymer atoms is different. Small spheres, closely packed, leave smaller interstitial sites than large spheres, and it is the space left by the polymer atoms where diffusion takes place. While the sizes of the cavities where the oxygen atoms spend most of their time are probably similar in both cases, the united-atom description introduces wider channels between adjacent cavities. This leads to more jump events and increases the diffusion rate artificially.

The packing argument also explains why we have not noted an effect of the united-atom approximation in our earlier calculations. Both atactic PP and PDMS have diffusion coefficients much larger than that of PIB. This is mainly due to much looser structures and lower atom densities. In these cases, the geometry of the channels is much less influenced by the particular shape of a methyl group. However, reexamining our previous results, we find a small feature (at the time not understood, see ref 7) which can be explained as an artifact caused by the united-atom model: In both series of calculations we found that the larger the penetrant is, the closer to experiment the calculated diffusion coefficients are. For PP,[7] $H_2$ diffusion coefficients are overestimated by a factor of 7.6, $O_2$ diffusion coefficients are overestimated by a factor of 3, and methane diffusion coefficients are correct. Similarly,

in the PDMS[8] system the He diffusion coefficients are overestimated by 1.8, whereas methane diffusion coefficients agree perfectly with experiment. The penetrant molecule acts as a probe for the size and shape of cavities in the polymer. If the probe size is small, the probe will be more sensitive to small details in the cavity geometry. On the other hand, if the probe is of the same size as a whole methyl group (which methane is) and a methyl group as a whole has to get out of the way to let it pass, the detailed shape of the methyl group matters less.

In contrast, most other MD studies of penetrant diffusion in polymers were performed on polyethylene[1-5] which experimentally has penetrant diffusion coefficients substantially lower than atactic PP or PDMS. These studies used isotropic united-atom models, and the calculated diffusion coefficients exceeded corresponding experimental results by 2–3 orders of magnitude. We suspect that the united-atom approximation might be the culprit for this.

It should be noted, however, that very recently Pant and Boyd[6] obtained very good agreement between calculated and experimental diffusion coefficients of methane in PE using the modified united-atom model of Toxvaerd.[20] This so-called anisotropic united-atom model uses off-center Lennard-Jones potentials for the nonbonded interactions. The interaction sites thus no longer have a spherical symmetry, but some eccentricity is introduced into the description of the methylene groups. In the present contribution, the eccentricity of methyl and methylene groups is provided for by the use of explicit hydrogen atoms. It is, therefore, no surprise that both the all-atom force field and the anisotropic united-atom force field improve upon the customary isotropic united-atom force fields.

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