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Florian Müller-Plathe

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Diffusion of penetrants in amorphous polymers: A molecular dynamics study

Florian Müller-Plathe

Science and Engineering Research Council, Daresbury Laboratory, Warrington WA4 4AD,
United Kingdom

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Molecular dynamics calculations are performed that simulate the diffusion of penetrant molecules through an amorphous polymer. For the polymer and the penetrant molecules, model potentials are chosen that approximate polyethylene and methane, respectively. The simulations extend over several hundred picoseconds. The results indicate that permeation proceeds by a hopping mechanism: The penetrants dwell in voids in the polymer matrix for a considerable time and perform fast jumps between neighboring voids. A potential scaling technique based on the fact that individual jump events are activated processes is presented by which the calculation of penetrant self-diffusion coefficients is speeded up.

I. INTRODUCTION

Diffusion of small molecules through polymeric materials is of technological importance in a variety of areas where polymers are acting as barriers. Different applications of polymers have different requirements on their barrier properties. The design of a polymer that is to be used in food packaging has to aim for a high barrier to certain gases such as oxygen, whereas one may aim for fast diffusion when one is removing remaining monomer molecules from a polymer sample. In some applications, i.e., gas separation or biosensors, a barrier is desired that is selective to one molecular species. In drug delivery systems, the speed by which the drug is released from a polymer matrix has to be controlled. Reliable computational predictions of diffusion coefficients for small molecules in polymers could therefore be a valuable tool in designing appropriate materials.

Most theories that describe the barrier properties of polymeric materials are based on the free-volume approach. The packing of the polymer chains leaves holes or microvoids, the so-called hole free volume, which may be occupied by the penetrant molecules. Since the chains are in constant motion the free-volume is continuously redistributed in the system, and the penetrants can move with it. According to this model, transport proceeds by a three-step mechanism: By motion of segments of the polymer chains, the so-called jumping units, a void opens up adjacent to a penetrant molecule. The penetrant performs a quick move from its original position into the new void, leaving a void of similar size behind. The latter is then filled by other polymer segments in a process similar to the first step. From this model it is expected that amorphous regions of a polymer show much higher penetrant diffusion rates than crystalline regions, since they contain more free-volume and it is redistributed more easily.

Quantitative methods for molten or glassy polymers based on the concept of free-volume have been developed.¹⁻⁹ However, these methods are not really microscopic theories of penetrant transport through polymers since they infer bulk transport properties (diffusion coeffi-

cients) from bulk properties such as molecular volume, molecular volume at $T=0$ K, thermal expansion coefficients and the like. While they have been very successful in relating diffusion coefficients to these quantities they cannot provide a detailed picture of the diffusion mechanism. The free-volume of a sample can be obtained computationally by Monte Carlo calculations.^{10,11}

Penetrant diffusion in polymers is regarded as an activated process¹² whose temperature dependence is governed by an Arrhenius-type equation

$$D = D_0 \exp(-E_A/kT), \quad (1.1)$$

where D_0 is a constant, E_A the activation energy, k the Boltzmann constant, and T the temperature. (Alternative expressions for the temperature dependence of mechanical properties of polymers have been discussed in Ref. 13.) A diffusion mechanism consistent with Eq. (1.1) is the above hopping mechanism since a molecule has to gather enough energy to cross the barrier into a neighboring void. The hopping mechanism also leads to a stochastic equation for the diffusion coefficient:⁸

$$D = \delta^2/6\tau. \quad (1.2)$$

Here δ is the mean hopping distance and τ is the average time between two hops.

In this contribution the problem of penetrant diffusion through amorphous polymers is approached by the molecular dynamics (MD) technique. Computer simulations of statistical mechanical systems (for an account, see Ref. 14) complement both analytical theories and experiment. MD simulations especially have the intriguing feature that the evolution of the system with time may be directly watched, whence they are particularly suited to the more qualitative study of diffusion mechanisms as well as to the quantitative prediction of diffusion coefficients. The molecular dynamics technique has only very recently been applied to the study of diffusion of small penetrants in bulk polymers.¹⁵ Previously, it had been quite successful in elucidating the mechanism by which oxygen molecules diffuse into their

binding site in myoglobin,¹⁶ which is a related problem since a protein core is not dissimilar to an amorphous polymer sample.

From the particle trajectories of an MD simulation the diffusion coefficient D may be obtained¹⁴ as

$$D = \langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle / 6t, \quad (1.3)$$

where $\mathbf{R}_i(t)$ and $\mathbf{R}_i(0)$ are the position of particle i at time t and time $t = 0$, respectively. The average is performed over all possible time origins, and it is denoted by angle brackets. [Note the similarity of Eqs. (1.3) and (1.2).] Alternatively, the diffusion coefficient can be determined from the particle's velocity autocorrelation function¹⁴

$$D = \frac{1}{3} \int_{-\infty}^0 \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle dt, \quad (1.4)$$

where $\mathbf{v}_i(t)$ and $\mathbf{v}_i(0)$ are the velocity vectors of particle i at times t and $t = 0$, respectively, and averaging is again performed over all time origins. Both equations hold in the limit of t being long compared to the correlation time of \mathbf{R} . In the present work, Eq. (1.3) is used.

The main objective of the present contribution is to explore the MD techniques necessary for the simulation of penetrant diffusion in amorphous systems and to investigate the mechanisms of penetrant diffusion at a qualitative level. The method is applied to a polymer-penetrant system resembling amorphous polyethylene and methane. A critical comparison of the quantitative results with experimental and previous theoretical information is used to establish the range of applicability of the method and to suggest future improvements.

II. COMPUTATIONAL DETAILS

A. Model

The amorphous bulk polymer is modeled as 20 linear chains of 50 interaction sites each with interaction parameters selected to approximate methyl and methylene groups. This system of amorphous pentacontane chains is used as a model for amorphous polyethylene. There are no explicit hydrogen atoms but the atomic masses and the parameters defining the van-der-Waals interactions between the carbons are chosen to mimic entire methylene (mass: 14.01565 amu) or methyl groups (mass: 15.023475 amu). Skeletal models like this have been successfully used in the past in the modeling of amorphous polyethylene (see, e.g., Refs. 17-19). In studies of ordered phases of alkane chains and polyethylene, however, more sophisticated potential functions that contain explicit hydrogen atoms seem to be essential.²⁰⁻²² The intramolecular potential function comprises harmonic bond and harmonic bond angle terms and a cosine torsional potential. Nonbonded interactions, intramolecular as well as intermolecular, are described by Lennard-Jones (LJ) 12-6 potentials. Between atoms that are separated by one or two bonds, no nonbonded potential acts; the nonbonded potential parameters for atom pairs that are separated by three bonds (third neighbors) are slightly modified. For all interactions the GROMOS force field parameters²³ have been used,

TABLE I. Potential parameters.

Bonds: $E = k_r(r - r_0)^2/2$		
r_0	0.153 nm	
k_r	336000.0 $\text{kJmol}^{-1}\text{nm}^{-2}$	
Bond angles: $E = k_\theta(\theta - \theta_0)^2/2$		
θ_0	109.5°	
k_θ	462.0 $\text{kJmol}^{-1}\text{rad}^{-2}$	
Torsions: $E = C_\phi(1 - \cos 3\phi)$		
C_ϕ	11.76 kJmol^{-1}	
Nonbonded: $E = C_{12}/r^{12} - C_6/r_6$		
$C_6/(\text{kJmol}^{-1}\text{nm}^6)$		$C_{12}/(\text{kJmol}^{-1}\text{nm}^{12})$
CH ₄ -CH ₄	1.087×10^{-3}	4.600×10^{-7}
CH ₄ -CH ₃	1.087×10^{-3}	4.600×10^{-7}
CH ₄ -CH ₂	1.087×10^{-3}	4.600×10^{-7}
CH ₃ -CH ₃	1.087×10^{-3}	4.600×10^{-7}
CH ₃ -CH ₂	2.262×10^{-3}	2.435×10^{-6}
CH ₂ -CH ₂	4.708×10^{-3}	1.289×10^{-5}
CH ₃ -CH ₂ (third neighbor)	2.513×10^{-3}	3.2455×10^{-6}
CH ₂ -CH ₂ (third neighbor)		

except for the third-neighbor interactions where the GROMOS force field favors *trans* conformations too much. These parameters are tested in a simulation of liquid n-butane where they give a *trans/gauche* ratio for the central dihedral angle of 68%/32%.²⁴ The experimental value is roughly 60%/40%.²⁵

There are 20 penetrant molecules in the system. As the CH₂ and CH₃ groups of the polyethylene chains they are described in the united atom model (mass 16.03130 amu) with a parameter set selected to mimic methane molecules. This LJ potential also acts between different methane molecules to provide a repulsion that prevents them from pooling at energetically favorable sites. The force field parameters are listed in Table I.

B. Sample preparation

Initial polyethylene chains are generated by randomly assigning to the backbone dihedral angles values of 60° (*gauche +*), 180° (*trans*), and -60° (*gauche -*) with relative statistical weights of 0.2, 0.6, and 0.2, respectively. The bond lengths and bond angles are kept fixed at their equilibrium values of 0.153 nm and 109.5°. The chains are then inserted into a cubic periodic box at random positions and in random orientations to a density of 752.8 kg/m³.

Initial bad contacts between different chains (or different parts of the same chain) are relieved by 1000 steps of steepest-descent energy minimization using the full potential described in subsection A. The minimization is not fully converged. The structure is, however, relaxed enough as not to cause any numerical problems to the subsequent MD calculations. In order to optimize the sample further, the system is subjected to a series of MD calculations of 20

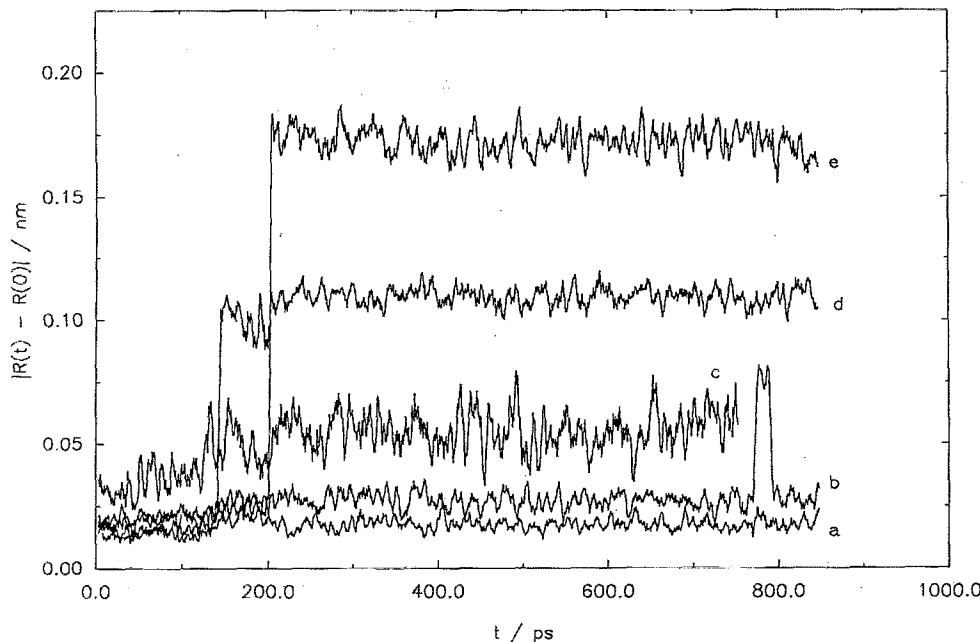


FIG. 1. Displacement of several CH_4 molecules from their initial positions. In this simulation the full interaction potential between the CH_4 and polyethylene is used. The noise in the original data is smoothed by displaying 10-point rolling averages in order to facilitate distinction between different curves.

ps duration during each of which the imposed temperature is linearly decreased from an initial 2300 K to 300 K. This facilitates some local rearrangements of the chains. After five of these so-called simulated-annealing cycles, further cycles do not lead to a significant decrease of the potential energy.

The polyethylene system is then equilibrated for 250 ps at 300 K. Into this system the CH_4 molecules are inserted at random positions, and the structure is again energy minimized. It is then equilibrated for another 100 ps at the desired temperature before sampling commences. The mass concentration of CH_4 in the sample corresponds to 2.2%.

The task of generating polymer samples that are low in energy and yet truly amorphous is a difficult one. The approach described here is a rather simplistic one and probably not the ultimate solution to the problem. The initial chain conformations are generated as though the chains were *in vacuo*. No interactions between different chains or periodic images of the same chain are taken into account at this stage. The energy minimization and equilibration MD can correct for these deficiencies only in part because the relaxation times of polymeric systems are typically of the order of milliseconds to seconds, so that complete equilibration cannot be accomplished in a few hundred picoseconds. As one result, the average pressure in the system is rather high (in the range of GPa). However, over the entire simulation there are no significant drifts in the pressure after the equilibration runs.

C. Simulations

The MD calculations are performed using the leap-frog algorithm and a timestep of 2 fs. The temperature T is kept constant at 300 K by the loose-coupling velocity-scaling algorithm of Berendsen *et al.*²⁶ The main purpose of using a constant-temperature rather than a constant-

energy scheme is to counter numerical errors, arising, e.g., from cutting off the nonbonded interaction at some finite distance, which could creep into these very long simulations. At each time step the velocities are rescaled by a factor λ_T

$$\lambda_T = [1 + (\Delta t/\tau)(T_{\text{ref}}/T - 1)]^{1/2}, \quad (2.1)$$

where T_{ref} is the desired temperature, Δt is the length of the time step, and τ is a constant which describes the coupling of the system to an external heat bath. In the present simulations a relatively large τ of 1 ps is used so that the coupling to the temperature bath is fairly loose.

The runs usually extend over several hundred picoseconds. Coordinate frames are written to a trajectory file every 0.5 ps. All simulations are performed using the sequential and parallel versions of the YASP package²⁷ on a multiprocessor Hewlett-Packard/Apollo DN10000 workstation. A simulation of 200 ps duration (100 000 time steps) typically takes 90 h cpu time on a single processor. For detailed performance figures, see Ref. 27.

III. RESULTS AND DISCUSSION

A. Qualitative description of the diffusion mechanism

A convenient measure for the transport of a molecule i during a simulation is its displacement from its initial position $\Delta_i(t)$

$$\Delta_i(t) = |\mathbf{R}_i(t) - \mathbf{R}_i(0)|. \quad (3.1)$$

The displacement of several methane molecules is displayed in Fig. 1 as a function of time. The fluctuations in the original data are somewhat smoothed by taking 10-point running averages in order to avoid overlapping of different curves. This figure illustrates some of the more common motion patterns for molecules solvated in polymers. Most curves show a typical hopping pattern. For

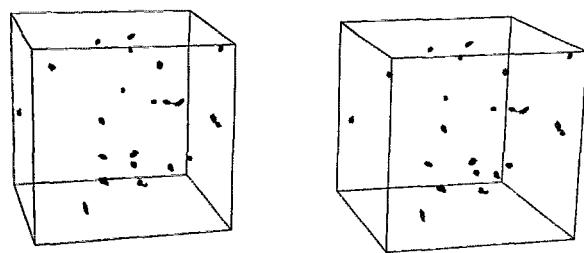


FIG. 2. Stereoscopic representation (cross-eyed) of the trajectories of all 20 CH_4 molecules during a 825 ps simulation using the full interaction potential between the CH_4 molecules and polyethylene.

longer periods of time the methane molecules stay oscillating in certain voids. The amplitudes of their oscillations vary according to the sizes of the voids. No net motion of a molecule is associated with these positional fluctuations. The molecules from time to time perform quick leaps into a neighboring void such as molecules b, c, and e in Fig. 1. The jumping distance is typically less than a molecular diameter in the present simulation. In some cases, like molecules c, d, and e, the leap leads to a permanent—on the time scale of this simulation—transition into the other void. Molecule b, however, only briefly explores a neighboring void before returning to its original position.

The trajectories of all 20 methane molecules are shown in Fig. 2 in a stereoscopic projection. Most methane molecules stay in their original places throughout the whole of the simulation. This behavior corresponds to curve a in Fig. 1. However, some of the trajectories clearly show jumps.

The difference between the motion of the methane and the polymer chains is illustrated in Fig. 3, where the mean-square displacement of CH_4 is compared to the mean-

square displacement of a central methylene group in the polymer CH_2 group number 24. Averaging is performed over all methane molecules and all of these CH_2 groups, respectively, and over all possible time origins. This leads to an increase of statistical fluctuations toward the end of both curves. Whereas the methylene groups essentially remain in their original places the methane molecules show diffusive behavior already on this short time scale.

As can be seen from Figs. 1 and 2 there are relatively few jump events in the time of the current simulation (825 ps), and hence little diffusion. Molecular dynamics simulations for this sort of system and time scale tend to be computationally relatively expensive. A way of increasing the number of jumps and the diffusion rate is suggested by Eq. (1.1). Assuming that the jump rate depends on the activation energy for crossing barriers between voids, reduction of the barrier height should lead to faster diffusion. It is further assumed, that the height of the energy barrier is proportional to the strength of the interaction potential between the methane molecules and the polyethylene chains:

$$E_A \propto C_{12}/R^{12} - C_6/R^6. \quad (3.2)$$

This assumption is reasonable since at the top of a barrier between two voids a methane molecule will be very close to some surrounding polymer segment. Because of the large inverse powers in the Lennard-Jones force law this interaction will then dominate the energetics of the methane molecule.

Hence, scaling the methane-polyethylene interaction potential by a factor λ leads to a similar scaling of the activation energy for barrier crossing, or equivalently by virtue of Eq. (1.1), to a scaling of the effective temperature for this process by $1/\lambda$. The polymer-penetrant system in

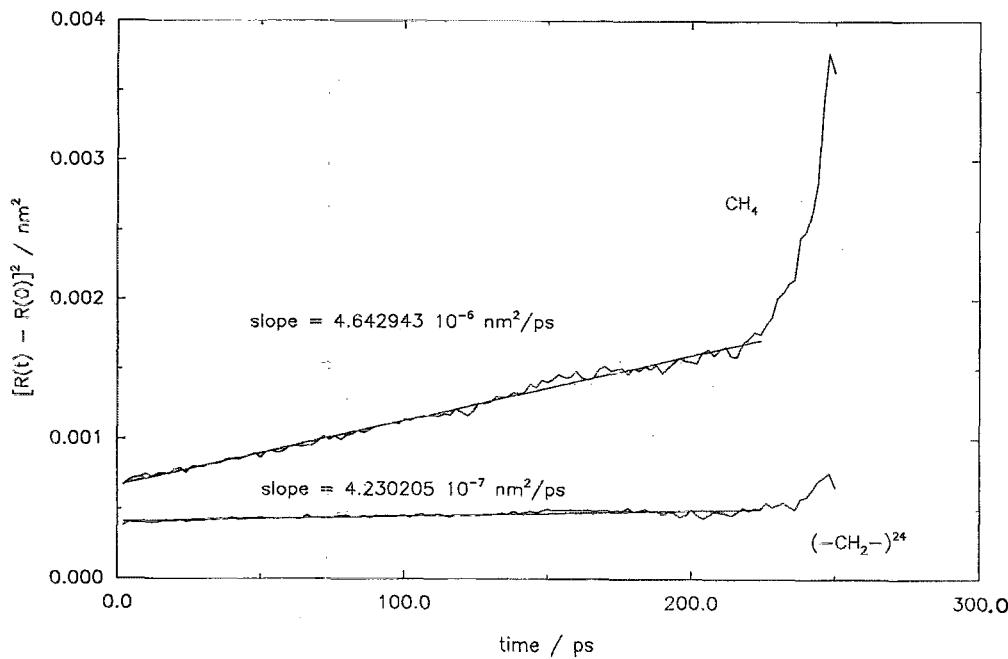


FIG. 3. Comparison of the mean-square displacement, averaged over molecules and time origins, of penetrant methane molecules (upper curve) and central methylene groups of the polyethylene chains (lower curve). The full interaction potential between CH_4 and polyethylene is used.

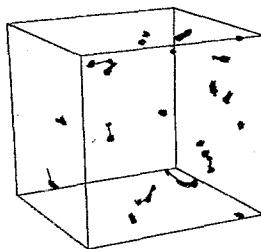


FIG. 4. Stereoscopic representation (cross-eyed) of the trajectories of all 20 CH_4 molecules. The methane-polyethylene interaction potential is scaled down by a factor of $\lambda = 0.1$.

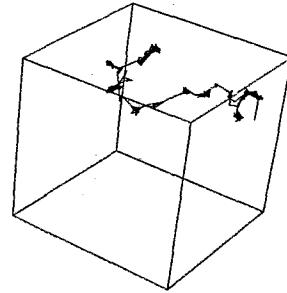
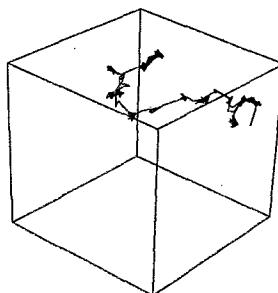
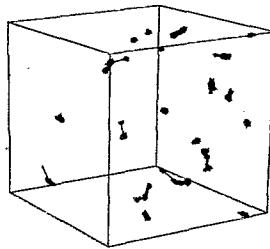


FIG. 5. Stereoscopic representation (cross-eyed) of the trajectory of a single CH_4 molecule. The methane-polyethylene interaction potential is scaled down by a factor of $\lambda = 0.01$.

this model is quite interesting: the motion of the polymer chains corresponds to a temperature T while the penetrants effectively move at an effective temperature T/λ . This decoupling should work as long as there are many more polymer interaction sites than penetrant interaction sites, so that the polymer motion is dominated by the polymer-polymer interaction rather than the polymer-penetrant interaction. Increasing selectively the effective temperature for the penetrants by scaling their interaction potential is to be preferred over performing the simulation at a higher temperature for the whole system. If the polymer chains are kept at a higher temperature as well this will change their motions and almost certainly the diffusion mechanism. Ultimately, the polymer should, of course, also change its structural properties, e.g., melt. Since the scaling approach to a first approximation only influences the penetrant motion whilst the polymer motion is largely unperturbed, it may be expected that the scaling approach allows the use of a higher effective temperature than a global increase of the temperature without changing the diffusion mechanism.

Figures 4 and 5 display the methane trajectories from simulations employing a methane-polyethylene interaction reduced by a factor of $\lambda = 0.1$ and $\lambda = 0.01$, respectively. As can be seen the number of hops increases substantially with decreasing λ . Nonetheless, the motion pattern is unchanged. The molecules dwell in a cavity for a while before they jump into a neighboring void. From inspection of these figures and displacement plots similar to Fig. 1 it may be concluded that at a qualitative level reducing the methane-polyethylene potential does not change the diffusion mechanism and merely leads to an increased diffusion rate.

B. Diffusion coefficients

In the preceding section it has been demonstrated how the diffusion increases with a decreasing barrier height in a qualitative picture. With all the above caveats it can be assumed that the barrier height can be controlled by scaling the interaction potential between penetrant and polymer. It has also been shown that reducing the barrier height leads to a larger number of jumps. In this way, not only the diffusion rate increases but also the statistics on the jump events is improved. In other words, the MD simulations can be shorter for the same statistical accuracy.

Since the accurate prediction of penetrant diffusion coefficients in real materials requires a large amount of computer time performing the simulations with a reduced potential appears to be very attractive. However, the diffusion coefficients obtained in this way have to be related to the diffusion coefficients obtained with the full realistic interaction potential.

The relation that links the diffusion coefficient calculated with the full interaction potential D to the diffusion coefficient D_λ calculated with an interaction potential scaled by λ follows from Eq. (1.1) for constant T and the assumption (3.2):

$$D_\lambda = D \exp(-\lambda E_A^*/kT). \quad (3.3)$$

Equation (3.3) assumes that over the range of λ the effective activation energy E_A^* is constant, in other words that the diffusion mechanism does not change. One purpose of this section is to establish the range of λ where this assumption is valid.

From the particle trajectories the mean-square displacements $|\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2$ of all penetrant molecules i are calculated at certain time intervals (typically every 0.5 ps). These are then averaged over all methane molecules and all possible time origins in order to improve the statistical accuracy. As an example, Fig. 6 shows such an averaged mean-square displacement versus time. The graph clearly shows the onset of large fluctuations at about 670 ps due to the decreasing number of time steps over which averaging is performed. At very short times (< 1 ps) the mean-square displacement is not linear in time but quadratic. This is due to the fact that at those time scales the penetrant only moves within its current void. These oscillations are essentially unhindered so that the penetrant's path corresponds more to a free flight than diffusive motion. Although Fig. 6 does not resolve the quadratic regime its presence manifests itself in the fact that the linear regime is shifted slightly upward. The linear domain between 1 ps and 670 ps is least-squares fitted by a line, whose slope is proportional to the diffusion coefficient.

The diffusion coefficients D_λ for different values of the potential scaling parameters λ are listed in Table II. In general, the same starting configuration is used for all values of λ . The only exception is the table entry for $\lambda = 0.2$

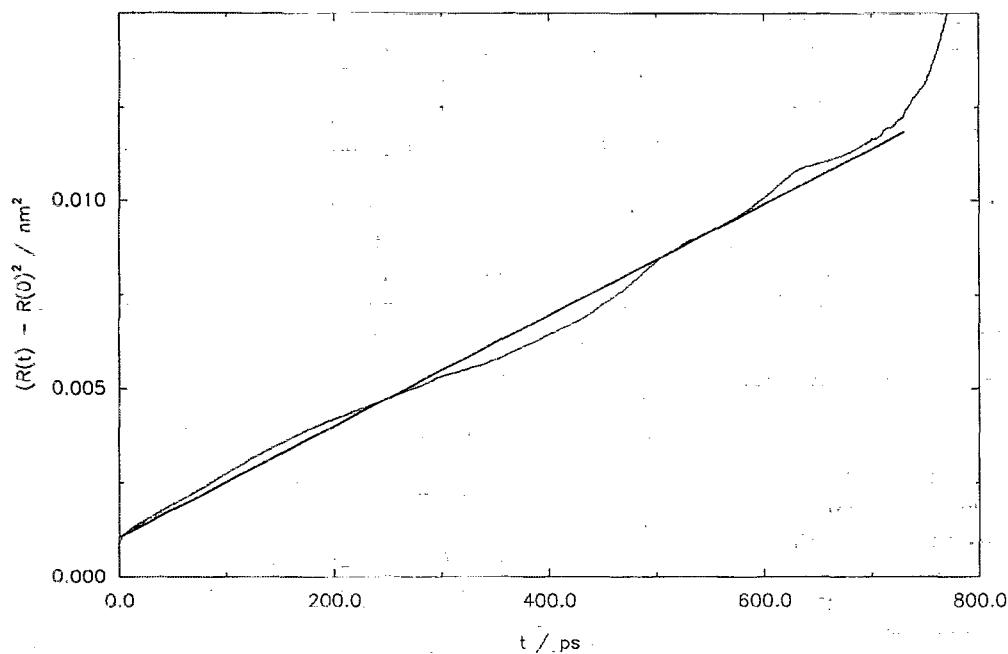


FIG. 6. Mean-square displacement of penetrant methane molecules for a reduced methane-polyethylene interaction potential ($\lambda = 0.5$). The values are averaged over all 20 methane molecules as well as over all possible time origins, which accounts for the smaller fluctuation at small times. The thick line represents a linear least-squares fit to the data in the region indicated.

where a second simulation is performed in which the penetrants are inserted at other locations. This simulation is referred to as sample II in Table II. The two values at $\lambda = 0.2$ give an indication, although not a quantitative measure, of the scatter of the results due to different starting geometries.

Provided the assumptions leading to Eq. (3.3) are correct, plotting $\ln D_\lambda$ versus λ should give a straight line. Figure 7 shows the points listed in Table II. It shows that the portion between $\lambda = 0.1$ and $\lambda = 1.0$ reasonably follows Eq. (3.3), whereas below $\lambda = 0.1$ the equation clearly breaks down. This means that below $\lambda = 0.1$ the underlying assumptions are no longer valid: The activation energy

may not be treated as a constant and there are probably changes in the diffusion mechanism as well, although these differences do not show up at the qualitative level (cf. Sec. III A).

On the other hand it is quite surprising for what a large range of λ Eq. (3.3) holds considering that a polymer-penetrant interaction potential reduced by a factor of 10 corresponds to a "diffusion temperature" of 3000 K. The data points between $\lambda = 0.1$ and $\lambda = 1.0$ are fitted to a line which also is indicated in Fig. 7 (regression coefficient $\rho = -0.93$). From its slope the effective activation energy E_A^∞ for the diffusion process is estimated to be 4.0 ± 0.9 kJ/mol.

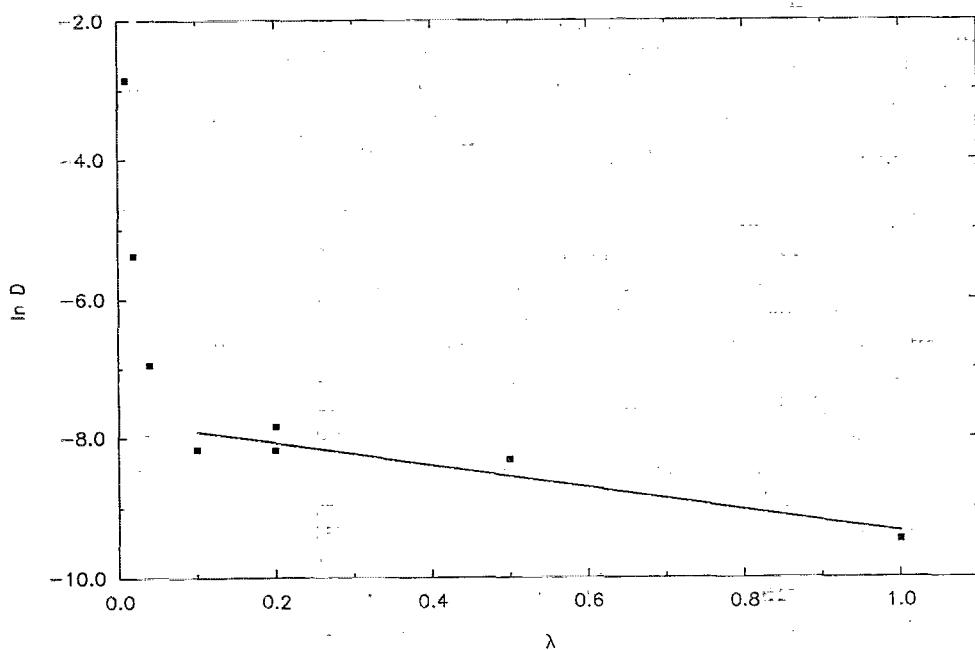


FIG. 7. Graphical representation of the data points of Table II. The straight line is at least-squares fit to the points between $\lambda = 0.1$ and $\lambda = 1.0$.

TABLE II. Diffusion coefficients (in cm^2/s) for methane in polyethylene for different values of the methane-polyethylene interaction scaling parameter λ .

λ	D_λ	$\ln D_\lambda$	Remarks
0.01	5.75×10^{-2}	-2.86	
0.02	4.62×10^{-3}	-5.38	
0.04	9.68×10^{-4}	-6.94	
0.1	2.83×10^{-4}	-8.17	
0.2	2.82×10^{-4}	-8.17	sample I
0.2	3.95×10^{-4}	-7.84	sample II
0.5	3.19×10^{-4}	-8.05	
1.0	7.74×10^{-5}	-9.47	

It should be pointed out here that the effective activation energy E_A^* reported is calculated from a variation of the scaling parameter λ , not the overall system temperature, which accounts for increased mobility of the penetrant molecules but not of the polymer subunits. It may be expected that the dependence of the diffusion coefficient on λ is weaker than its dependence on the system temperature since the latter incorporates effects from rearrangement of the polymer as well. Hence, the effective activation energy observed here is smaller than the true activation energy for the diffusion process. Indeed, in Ref. 15 the true activation energy for a related polymer-penetrant model has been calculated to be 6.4 kJ/mol under constant-volume conditions. Due to the presence of crystalline domains that inhibit diffusion the experimental apparent activation energy of polyethylene is substantially larger.^{12,28}

The present polyethylene model has been chosen to investigate the applicability of MD methods to the problem of penetrant diffusion in amorphous polymers and to study the microscopic events underlying the diffusion process. The model is quite simple and can therefore not be expected to reproduce experimental results quantitatively. With this in mind it is, however, useful to look at the numerical results of this study in a wider framework in order to discuss possible improvements to the model.

The diffusion coefficient for CH_4 in amorphous polyethylene at 300 K predicted in this work is $7.74 \times 10^{-5} \text{ cm}^2/\text{s}$. This is in stark contrast to the accepted literature value for low-density polyethylene of $0.193 \times 10^{-6} \text{ cm}^2/\text{s}$.^{12,28} It is, however, difficult to compare these numbers directly because real polyethylene is not entirely amorphous but contains a significant amount of crystalline material from which some reduction of the diffusion coefficient is to be expected. It has been pointed out^{15,29} that the diffusion of small molecules in truly amorphous polymers above their glass transition temperature (oxygen in silicone rubber, in that case) is much faster, and the diffusion coefficients are in the order of $10^{-5} \text{ cm}^2/\text{s}$ at room temperature. It is also interesting to note that the coefficients for the diffusion of methane in melts of polyethylene (413.2–461.5 K) are between 1.4×10^{-5} and $5.5 \times 10^{-5} \text{ cm}^2/\text{s}$ depending on the temperature and the density of the melt.³⁰ In the melt there are no crystallites and part of the increase in diffusion speed must certainly be attributed to this fact, although the higher temperature per

se accounts for a large amount of the speed-up. The value of this work is also very close to the simulation result of Ref. 15 where a diffusion coefficient of $4.04 \times 10^{-5} \text{ cm}^2/\text{s}$ is reported for $T = 304 \text{ K}$. The remaining difference between the two simulation results is explained by the choice of the model (the penetrant molecule of this work is smaller in diameter) and the difference in density.

Some of the approximations in the computational model are expected to affect the value of the calculated diffusion coefficients. Besides possible inadequacies of the force field, the main candidates are the low density, the finite chain length, the way of generating the initial polymer configurations and the constant-volume conditions under which the simulation is performed. At the time scale of the simulation reported here ($< 1 \text{ ns}$) the $\text{C}_{50}\text{H}_{102}$ chains do not show any motion except dihedral angle flips. Therefore, their dynamical behavior can be assumed to be too similar to that of infinite polyethylene chains as to cause substantial discrepancies. In fact, recent simulational predictions of diffusion in both quasi-infinite polyethylene and a polyethylene model of only 20 methylene units per chain differ only slightly.³¹ Constant-volume and constant-pressure values of the diffusion coefficient have been compared in Ref. 15. Although their temperature dependence is different due to free-volume effects their absolute magnitude is rather similar in the studied temperature region. The choice of the starting configuration for the polymer-penetrant system certainly has an influence on the calculated diffusion coefficient as is hinted by the two entries for $\lambda = 0.2$ in Table II. It is well possible that the amorphous configurations generated by the prescriptions of Sec. II B are "too amorphous," in other words that in the amorphous parts of a polyethylene sample the chains are more ordered than in the initial configurations of the present work.

None of these possible deficiencies in the model on its own can explain a deviation as large as that found between the present computed and the experimental diffusion coefficient. However, all the approximations of the present model should lead to too large a diffusion coefficient so that the individual errors should rather accumulate than cancel. Work is in progress to establish the influence of the individual approximations on the diffusion coefficients.

IV. SUMMARY AND CONCLUSIONS

This article examines the diffusion of CH_4 penetrant molecules through an amorphous sample of pentacontane which is chosen as a model for polyethylene. Qualitatively, the diffusion proceeds by a hopping mechanism, i. e., the methane molecules orbit for longer periods of time around certain positions and perform quick jumps between these positions. This qualitative motion pattern remains unchanged when the magnitude of the potential acting between the methane molecules and the polyethylene chains is selectively reduced. There are just more jumps per unit of time.

The diffusion coefficients calculated by MD simulations with a varying methane-polyethylene interaction potential exhibit an Arrhenius-like scaling behavior [Eq.

(3.3)] over a rather large range. Simulations with a reduced interaction potential take less simulation time and hence considerable less computer time than simulations employing the full potential. From the diffusion coefficients obtained with a reduced potential the diffusion coefficients corresponding to the full potential can then be estimated using the scaling relation. Hence, the scaling relation provides a way to a more economical computational determination of penetrant diffusion coefficients also for larger and more complex polymeric systems with a realistic description of the forces.

The diffusion coefficient for the methane in amorphous polyethylene calculated in this work agrees well with the value from a previous simulation¹⁵ in spite of differences in the model potentials used. However, the calculated diffusion coefficient is substantially larger than the experimental value for CH₄ in polyethylene. A consideration of possible deficiencies in the model suggests that while none of them is likely to produce so large a deviation the errors could add up. However, polyethylene at room temperature is also partially crystalline which is ignored in the present model. Crystallinity, in general, reduces the diffusion coefficient significantly.¹² On the other hand, the calculated diffusion coefficient is quite typical for the diffusion of small penetrants in genuinely amorphous polymers at room temperature as well as molten polyethylene. Hence, it may be concluded that in the case of polyethylene microcrystallites have a noticeable effect on the experimentally observed penetrant diffusion rates.

Since the original submission of this article the hopping mechanism of penetrant diffusion has been confirmed by an independent molecular simulation study.³²

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