Simulation of Diffusion of Small-Molecule Penetrants in Polymers

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Molecular dynamics (MD) has proven to be a useful tool in elucidating the structure and properties of polymeric liquids and glasses.[1] One of the important applications has been in the study of the diffusion of small molecules through amorphous polymers.[2–8] Among the effects studied have been the influence of the polymer chain length,[5] the free volume and its distribution,[7,8] the size of the penetrant,[2] the mechanism of penetrant jump motions,[4] the density,[5,8] and the comparative effect of the packing efficiency in different polymers.[8] Although the results of these studies have been of great value, one of the important goals of the simulations has been elusive. That is, the ability to predict reasonably quantitative values for diffusion coefficients, D, for the penetrants would be of great practical importance. However, the absolute values of D and the associated activation energies for their temperature dependence from the MD simulations have been in poor agreement with experiment. The calculated values of D both in our own work and the other cited studies have been between 10 and 100 times higher than experimental values. The calculated activation energies have been only one-fourth of the experimental values (~10 vs ~45 kJ/mol experimentally). The purpose of the present paper is to present a resolution of the problem and to report calculated diffusion coefficients in agreement with experiment.

A number of details of the MD methodology such as time step, nonbonded truncation radius, precise values chosen for intramolecular force constants, and polymer chain length appear to have been eliminated as major sources of the discrepancy. In fact, the only variable that appears to be capable of influencing the calculated values of D to the degree necessary is the density.[8] In all the studies quoted, polyethylene (PE) has been used as a reference polymer. All these works have used very similar potentials for the nonbonded interaction between "united-atom", contracted-hydrogen methylene beads. It is thus important to carefully investigate whether the densities used in the simulations are appropriate to the nonbonded potential employed. This can be accomplished by generating P–V–T data by simulation for the potential used and checking the pressures at the volumes employed in the diffusion simulations.

The pressure is "measured" in simulations, via the virial theorem, through the relation[9]

$$PV = Nk_{\mathrm{B}}T - (1/3)\langle \sum_i \sum_{j>i} \mathbf{r}_{ij}\cdot\mathbf{F}_{ij} \rangle \qquad (1)$$

where $\mathbf{F}_{ij}$ is the force on center i due to j and $\mathbf{r}_{ij}$ is the vector from i to j, N is the number of centers in a system of volume V, and T is the temperature. It is extremely important to carry out the summation to very large distances. In doing this we have evaluated it explicitly to 9 Å, the truncation distance of the nonbonded functions in the simulations. Beyond this distance a truncation correction based on uniform density is employed

$$(PV)_{\mathrm{trunc}} = -(2/3)\pi N\rho \int_{r_{\max}}^{\infty} r^3 \frac{\mathrm{d}v(r)}{\mathrm{d}r}\,\mathrm{d}r \qquad (2)$$

where $v(r)$ is the nonbonded interaction potential. This latter contribution is a large correction to the explicit summation.

For the volume chosen for the simulations, the pressure should be near zero (i.e., 1 atm). The densities used previously in our case were equal to the experimental ones for PE. We have found that, for the methylene nonbonded potentials previously used,[8] the measured pressures at this density are actually highly negative; see Table I. This implies that the structure or packing seen by the diffusant is considerably too open to be realistic and that a zero-pressure structure is much more dense. We have already seen that more dense structures do lead to much slower diffusion.[8] It is thus important to investigate the effect on diffusion of using a potential that gives densities (at 1 atm) close to experimental ones. In this connection it is of interest to make some comments concerning the methylene group united-atom (UA) nonbonded potential. The ones used in all the above studies are close to a potential found to give good densities at 1 atm in MD and Monte Carlo (MC) simulations on short-chain alkanes.[10] However, it has recently been found that this potential gives densities that are systematically too low as the alkane chain length increases.[11] Although not tested in ref 11 at the temperatures, densities, and chain lengths appropriate to the present diffusion conditons, this effect is in at least qualitative agreement with the results found here with respect to pressure and density and reported in Table I, item 1. Further, it was found in ref 11 that the agreement of simulation densities with experimental values is much better and more independent of chain length when a modified potential that is no longer centered on the carbon atom position but displaced outward on the bisector of the chain valence angle is employed. We have found this "anisotropic united-atom" or "AUA" potential to give densities at zero pressure much closer to experiment than the previously utilized UA potential. We also find that the diffusion constants found from simulations at fixed volume corresponding to zero pressure (1 atm) utilizing the AUA methylene potential are in good agreement with experiment.

Simulations of diffusion of methane in PE using the AUA potential were carried out at fixed volumes corresponding to zero pressure at a number of temperatures. These volumes were established via constant P (=0) simulations carried out prior to the diffusion runs. The PE was a single chain with 768 methylene units per periodic box but without ends.[5] One methane molecule per periodic box was employed. With one exception, the intramolecular potentials were those previously employed.[8] The carbon–carbon bond stretching constant was decreased by a factor of 4. This was done to increase the integration time step by a factor of 2 and thus decrease computer time. The change had no noticeable effect on diffusion results. The UA methane potential is the one previously used.[8] The AUA potential for CH_2 is a 6–12 potential with $\epsilon = 0.67$ kJ/mol, $r_{\min} = 3.959$ Å, and centered 0.37 Å outward from the carbon on the valence angle bisector.[12] The forces are transferred to the carbon centers via constraints as described in ref 11. Self-diffusion constants for methane were obtained from one-sixth of the slope of the averaged R^2 progress of the diffusant; see Figure 1. An Arrhenius plot of the constants from several tempera-

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Table I
Calculated and Experimental Diffusion Constants (at 300 K) for Methane in Polyethylene

	density, g/cm^3	pressure, atm	diffusion constant D, 10^{-9} m^2/s	activation energy for D, kJ/mol
1. Calculated from United-Atom CH_2 Potential at Experimental PE Density[a]				
infinite chain	0.855	−1640	0.7	
C_{24} alkane	0.855	−350	1.2	10.5
2. Calculated from Anisotropic United-Atom (AUA) CH_2 Potential, Infinite Chain				
	0.872[b]	0	0.049	53
3. Experimental Diffusion Constants[c]				
	0.855	0 (1 atm)	0.060[d]	45.6
			0.045[e]	43.5
			0.030[f]	49.0

[a] Density is for amorphous fraction.[15] [b] Density found in a separate constant P (=0) simulation, diffusion simulation carried out at this constant density. Density values found at other temperatures are 0.865 (320 K), 0.862 (330 K), 0.853 (350 K). [c] Diffusion coefficients are estimates for the amorphous fraction derived from measured values for semicrystalline PE[13,14] and a correction for crystallinity (see text). [d] From measurements on 45% crystalline BPE from ref 13. [e] From measurements on 78% crystalline LPE from ref 13. [f] From measurements on 46% crystalline BPE from ref 14.

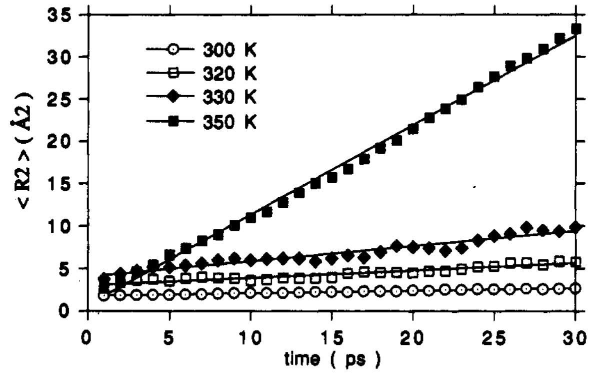

Figure 1. Diffusion of methane in amorphous polyethylene. R^2 smoothed over 30-ps intervals from 200-ps trajectories vs time, at the temperatures indicated. AUA methylene bead potential.

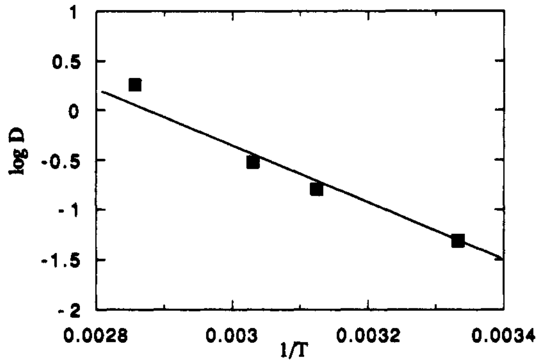

Figure 2. Arrhenius plot of diffusion coefficients, in units of 10^{-9} m^2/s, for methane in polyethylene.

tures is given in Figure 2.

The experimental values of D shown in Table I are derived from experimental values on semicrystalline PE.[13,14] The experimental density of amorphous PE at room temperature is extrapolated from the melt.[15] Since penetrant diffusion is thought to proceed nearly exclusively through the amorphous phase, it is necessary to make a correction for the presence of the crystalline fraction. The local structure in PE is of lamellar organization and, by analogy with previous work,[16] an upper bound estimate of the effective diffusion constant of the isotropic composite material is $D = (2D_H + D_V)/3$ where $D_H = v_1D_1 + v_2D_2$, $1/D_V = v_1/D_1 + v_2/D_2$, and in turn D_1 and D_2 are the diffusion coefficients of the amorphous and crystalline phases, respectively, and v_1 and v_2 are their volume fractions. For $D_2 = 0$ and solving for D_1, this leads to the following lower bound estimate for the diffusion coefficient for the amorphous phase, D_1, in terms of the experimental one $D_{\mathrm{exptl}} = D$ and the volume fraction of amorphous material v_1 as

$$D_1 = 3D_{\mathrm{exptl}}/2v_1 \qquad (3)$$

It may be concluded from the results in Table I that the calculated AUA diffusion constant at 300 K and the activation energy near this temperature are in agreement with experiment. No doubt the nonbonded potential needs to be further investigated and improved in terms of generating good P–V–T results. However, the source of the poor quantitative results for diffusion coefficients previously obtained seems to be attributable to an insufficiently realistic nonbonded potential for the polymer–polymer bead interactions.

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