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Molecular Dynamics Simulations of Gas Diffusion through Polymer Networks

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ABSTRACT: The results of molecular dynamics simulations of simple penetrant molecule diffusion through an idealized polymer network in the rubbery regime are presented. The polymer chain model employed approximates a hard-sphere, freely jointed chain. A collection of such chains are cross-linked to form a network by tetrafunctional junctions fixed at the sites of a diamond lattice. The diffusion constant D is determined from the trajectory of the particle representing the penetrant molecule as computed in a simulation in which penetrant and network atoms are all in thermal motion. The temperature dependence of D shows Arrhenius behavior, and its dependence upon penetrant size is in qualitative accord with what is observed experimentally. The diffusion of the penetrant in the network is compared with its diffusion in the corresponding simple fluid formed by eliminating all covalent bonds. At low values of reduced density ρ or packing fraction η, it is found that diffusion in the network is slower than in the fluid. However, there is a crossover value of ρ beyond which diffusion effectively ceases in the liquid but continues at a measurable rate in the network.

1. Introduction

The diffusion of small atoms and molecules through polymeric solids has long been a subject of theoretical and experimental research. An overall survey of the field with an extensive list of references is provided by Crank and Park.[1] A more recent review of the subject, particularly as it relates to gas separation by the use of polymer membranes, is given by Stern and Frisch.[2]

Much of the theoretical work in this field falls into two categories:[2] free-volume models that focus on the statistical distribution of holes in the lattice, and molecular models that are more dynamical in character and include the nature of the interactions between penetrant and network atoms. A critical examination of one aspect of the former class of models has been given recently by Stuk,[3] while a reexamination of the Pace–Datyner[4] molecular theory has been presented recently by Kloczkowski and Mark.[5]

The extensive development in recent years of techniques for the computer simulation of polymeric systems provides a new approach to gaining insight into the nature of their behavior. It has recently been applied by Shah, Stern, and Ludovice[6] to one aspect of the diffusion process; they use Monte Carlo methods, as implemented by Suter and co-workers,[7-9] to generate atomistic models of representative static structures of a glassy polymer and from these to calculate the fractional free volume available to a penetrant molecule of specified diameter.

Here we report on the use of the method of molecular dynamics to simulate on the atomistic level the time-dependent aspects of the diffusion of a penetrant molecule in a polymer network in the rubbery state, i.e., at temperatures above T_g. As the first step in this type of simulation, we use a highly idealized network model, one that we have employed in previous molecular dynamics studies of rubber elasticity.[10] This model, which utilizes a purely repulsive interatomic potential, focuses on the roles of steric factors and thermal motion in the diffusion process. It is encouraging to find that, in spite of the idealized nature of the model, the molecular dynamics results display many of the features observed in reality, e.g., an Arrhenius temperature dependence of the diffusion constant, with a reasonable value for the activation energy, and qualitative agreement of the dependence of the diffusion constant on penetrant molecule size.

The organization of the remainder of this paper is as follows: The model of the system, consisting of a polymer network with a penetrant molecule, is described in section 2. The molecular dynamics techniques used to simulate the thermal motion of the atoms of the system are outlined in section 3; this section also describes the method used to determine the diffusion constant of the penetrant molecule from its computed trajectory through the network. Simulation results are given in section 4, while conclusions and directions for future work are contained in section 5.

2. Model Description

Chain Model. The chain model employed approximates the hard-sphere, freely jointed chain. For computational and conceptual convenience the covalent potential is represented by a stiff linear spring and the hard-sphere potential is replaced by the repulsive part of the Lennard-Jones potential. That is, the covalent potential $u_c(r)$ is

$$u_c(r) = {}^1/_2\kappa(r-a)^2 \tag{1}$$

where r is the distance between adjacent atoms on a given chain, and a is the zero-force bond length. The noncovalent potential is

$$\begin{aligned} u_{nc}(r) &= 4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]+\epsilon \quad \text{for } r \leqslant r_0 \\ &= 0 \quad \text{for } r \geqslant r_0 \end{aligned} \tag{2}$$

where r denotes the distance between any nonadjacent pair of atoms on a given chain or between any pair of atoms on different chains and $r_0 = 2^{1/6}\sigma$. This restriction of the Lennard-Jones potential to the portion responsible for a repulsive force only is sometimes referred to as the Weeks–Chandler–Andersen (WCA) core potential.[11] We may think of it, qualitatively, as representing a soft-sphere potential, with σ a good measure of the sphere diameter.

Network Model. The tetrafunctional junctions of the network are taken as fixed at the sites of a diamond lattice (Figure 1). Chains with $N = 20$ bonds connect these junctions as shown, with 16 chains in the basic cell. Typically, the end-to-end distance r of chains in the network simulations has the value r/Na between 0.1 and

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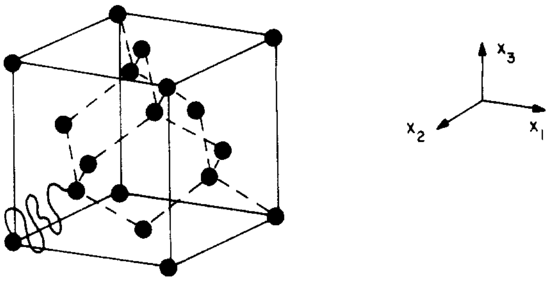

Figure 1. Basic cell of tetrafunctional network with fixed junctions located at the lattice sites of a diamond lattice. Dashed lines indicate junctions that are connected by chains; for clarity only one of the network chains, which are far from fully extended, is shown in schematic representation. Periodic boundary conditions in the x_1, x_2, and x_3 directions are employed.

0.15; ie., they are far from fully extended. Periodic boundary conditions in the x_1, x_2, and x_3 directions are employed, as is customary in molecular dynamics simulations,[12] so that atoms in the basic cubic cell interact with their images throughout space.

We define the reduced density ρ of the network as

$$\rho = n\sigma^3/v \tag{3}$$

where n/v is the number density of the network atoms. We recall that, for a hard-sphere liquid, the packing fraction η, or ratio of occupied volume to total volume, is $\eta = \pi\rho/6$.

Penetrant Molecule. A single penetrant molecule is introduced into the basic cell. It is modeled as a single particle or atom and interacts with all of the atoms of the network by means of a soft-sphere potential $u_p(r)$ that is of the same form as eq 2, but with parameters ϵ_p, σ_p, and $r_0{}^p = 2^{1/6}\sigma_p$.

The mass m_p of the penetrant and the monomer mass m of the polymer network are taken as equal, as are the parameters ϵ_p and ϵ. Thus the only distinctive feature of the penetrant explored in this study is its size, σ_p.

Model Parameters. As we have noted, we regard our chain model as an approximation to the hard-sphere, freely jointed chain. As in previous simulations of the model,[10] we use the parameter values $\kappa a^2/k_BT_0 = 202$ and $\epsilon/k_BT_0 = 0.5$, where T_0 denotes a fixed reference temperature. The first implies a change of ~7% in bond length for a bond energy of $^1/_2k_BT_0$. The second implies, at $T = T_0$, an equivalent Boltzmann hard-sphere diameter[13] of $\sigma_B = 0.93\sigma$, where σ is the parameter in eq 2. Therefore for these values of $\kappa a^2/k_BT_0$ and ϵ/k_BT_0 the model approximates the hard-sphere, freely jointed chain reasonably well; increased values of these two parameters become increasingly demanding of computer time and do not give substantially different results.

Conversion to Physical Units. If we take the bond length $a = 1.53$ Å, the monomer mass $m = 14 \times 1.66 \times 10^{-24}$ g (as in polyethylene), and the reference temperature $T_0 = 300$ K, the above parameter values correspond to $\tau = (m/\kappa)^{1/2} = 2.54 \times 10^{-14}$ s. We use the above values of a, m, and T_0 throughout this paper to express the numerical results of the simulations in physical units.

3. Molecular Dynamics

As is customary in the computer simulation of an atomistic model by the method of molecular dynamics, Newton's equations of motion for each atom in the basic cell of the system are solved numerically using the Verlet algorithm.[12] The numerical time step employed is $\Delta t = 0.1\tau = 0.1(m/\kappa)^{1/2}$.

Preparation Period. We wish first to prepare an initial configuration in which the chains of the network are untangled and with the atoms of the system in thermal motion corresponding to thermal equilibrium at temperature T. To do this, we begin with a large cell size in which the chains are fully extended and simulate the dynamics of the system as the cell size dimensions are slowly reduced stepwise, with each step followed by a relaxation period. Simulation during the relaxation period consists of several successive blocks of time. The atomic velocities at the start of each block are chosen from a Maxwell distribution corresponding to temperature T. After the system is equilibrated at the cell size corresponding to the desired network density, the calculation is continued, with no further redefinition of the atomic velocities, for 5×10^5 additional time steps to complete the simulations. The temperature during this main calculation period is determined from the average kinetic energy over it; in general, it is found to differ from the target temperature T by less than 5%.

Calculation of Diffusion Coefficient. Consider first a collection of penetrant molecules or atoms in the network. Let $\mathbf{x}(t)$ be the position of a penetrant at time t. We compute the diffusion constant D of these atoms on the basis of the fundamental relation

$$D = \lim_{t\to\infty} \frac{1}{6} \frac{\langle(\Delta\mathbf{x}(t))^2\rangle}{t} \tag{4}$$

where

$$(\Delta\mathbf{x}(t))^2 = |\mathbf{x}(t) - \mathbf{x}(0)|^2 \tag{5}$$

and the brackets denote an ensemble average over a collection of penetrant atoms.

Initial attempts to simulate explicitly the simultaneous diffusion of a collection of penetrant atoms in the system proved difficult. Apparently, clustering of these atoms occurred in holes in the network, and they tended to follow similar trajectories. This clustering took place even in the absence of interactions between penetrant atoms and we believe it is a consequence of the fact that there are only 320 network atoms per basic cell so that more than one penetrant per cell represents a very high concentration. Since our intent is the simulation of a dilute collection of penetrant atoms, we simulate explicitly the trajectory $\mathbf{x}(t)$ of only a single atom for the time period $0 \leqslant t \leqslant t_f$ and generate from it many independent displacements $\Delta\mathbf{x}(t)$ by choosing new origins for these displacements at time intervals t_0 along it. We then compute the quantity $\langle(\Delta\mathbf{x}(t))^2\rangle$ appearing in eq 4 from the relation

$$\langle(\Delta\mathbf{x}(t))^2\rangle = \frac{1}{M}\sum_{j=0}^{M}|\mathbf{x}(t + jt_0) - \mathbf{x}(jt_0)|^2 \tag{6}$$

where[14] $M = t_f/t_0$. In practice, we used $t_f = 5 \times 10^4\tau$ and $t_0 = 50\tau$ so that $M = 1000$.

A typical plot of $\langle(\Delta\mathbf{x}(t))^2\rangle$ obtained in this way is shown in Figure 2. It is well approximated by two straight lines, with the first of larger slope in an initial period of length t_h. This first period apparently corresponds to penetrant diffusion within a hole in the network, while the second corresponds to diffusion through the network by passage from hole to hole. In support of this view, we find that t_h decreases with increase of network density and consequent decrease of hole dimensions. We compute the diffusion constant D from the slope of the line for $t > t_h$. From repetitions of the simulations for identical parameter values, we estimate the overall accuracy to be between 5 and 10%.

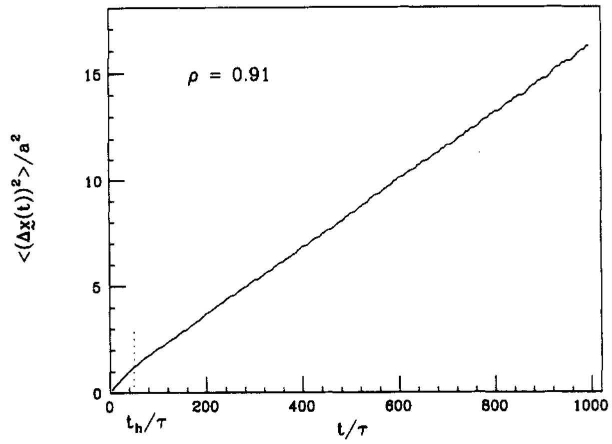

Figure 2. Typical plot of $\langle(\Delta x(t))^2\rangle$, eq 6, as determined from computer simulation at temperature T_0. a is chain bond length, eq 1; $\tau = (m/\kappa)^{1/2}$; and ρ is reduced density, eq 3. Diffusion constant D computed by means of eq 4 from slope of line for $t \geqslant t_h$. See end of section 2 for fixed parameter values and conversion to physical units.

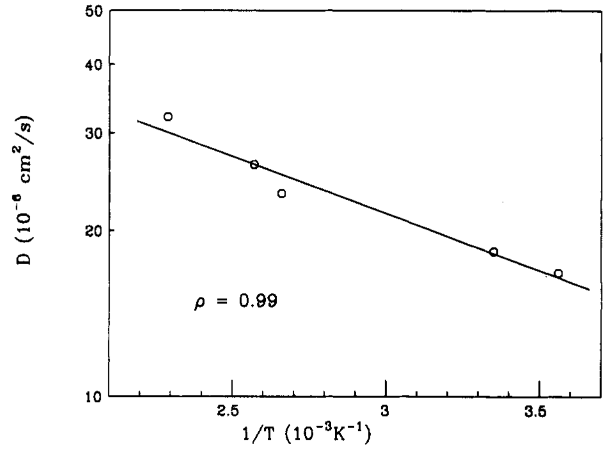

Figure 3. Arrhenius plot of penetrant diffusion constant D as determined from computer simulation; $\sigma = \sigma_p = a$.

4. Simulation Results

Temperature Dependence. A set of simulations were performed to determine the effect of temperature variation on the diffusion rate in a given penetrant atom-network system. In addition to the parameter values previously listed as common to all of these simulations, these simulations employed $\sigma/a = \sigma_p/a = 1$ and a reduced density $\rho = 0.99$.

The results for the diffusion constant D are shown in Figure 3. It is seen that diffusion in this model is in reasonable agreement with an Arrhenius relation. A least-squares straight-line fit in an Arrhenius plot yields an activation energy, $E_b = 0.94$ kcal/mol. This simulation result is in reasonable agreement with the range of activation energies (1-20 kcal/mol) observed in real systems.[1]

Density Dependence. In the next sequence of simulations, the fixed parameter values were $\sigma/a = \sigma_p/a = T/T_0 = 1$, with the network reduced density ρ varied by change of the basic cell dimensions.

As expected, an increase in the network density results in a decrease in penetrant atom mobility. This is illustrated in Figure 4 in which are shown portions of the penetrant atom trajectory for two different network densities.

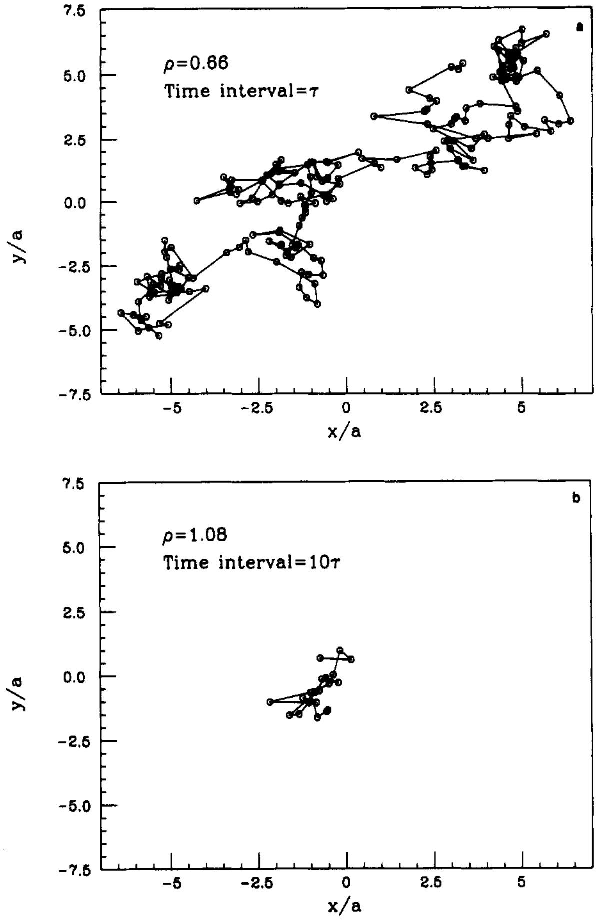

Figure 4. Typical trajectories of penetrant atom projected onto x-y plane. (a) Reduced density $\rho = 0.66$; time interval between points is $\tau = (m/\kappa)^{1/2}$. (b) Reduced density $\rho = 1.08$; time interval between points is 10τ. Total elapsed time is 200τ, the same for both trajectories.

The penetrant diffusion constant as a function of network density is shown in Figure 5. For comparison, simulations on the same system but with all of the covalent bonds eliminated (i.e., κ in eq 1 set equal to zero) were also performed; these simulations lead to the diffusion constant of the penetrant atom in the corresponding unbonded fluid.

In the lower range of reduced density, the diffusion in the network is lower than in the corresponding fluid; this is in accord with intuition since it is expected that the atomic mobility in the network is less than in the fluid due to the restraints imposed by the covalent bonds and the fixed junctions. However, at higher values of reduced density a surprising crossover occurs (Figure 5). For $\rho \gtrsim 1.15$, or $\eta \geqslant 0.60$, diffusion in the liquid effectively ceases while it continues at a low but measurable rate in the network at $\rho = 1.24$ or $\eta = 0.65$. It thus appears that at high values of reduced density (or, equivalently, at high packing fractions) the covalent bonds serve to maintain network atom mobility beyond what is possible in the liquid and this, in turn, permits penetrant atom diffusion to continue.

To further test the importance of network atom mobility in enabling penetrant atom diffusion, the simulations for $\rho = 0.67$ and 0.84 ($\eta = 0.35$ and 0.44) were repeated with the network atoms fixed at an arbitrary instant ("frozen network"). The simulations showed that the diffusion of the penetrant effectively ceased in the frozen network at $\eta = 0.44$ and decreased by 2 orders of magnitude compared to the mobile network at $\eta = 0.35$.

Dependence on Penetrant Atom Size. In this series of simulations, the fixed parameters are $\sigma/a = T/T_0 = 1$ and $\rho = 1.08$. The size of the penetrant atom is varied in the range $0.8 \leqslant \sigma_p/a \leqslant 1.3$. The results are shown in Figure 6a. For comparison, experimental results[15] for the diffusion

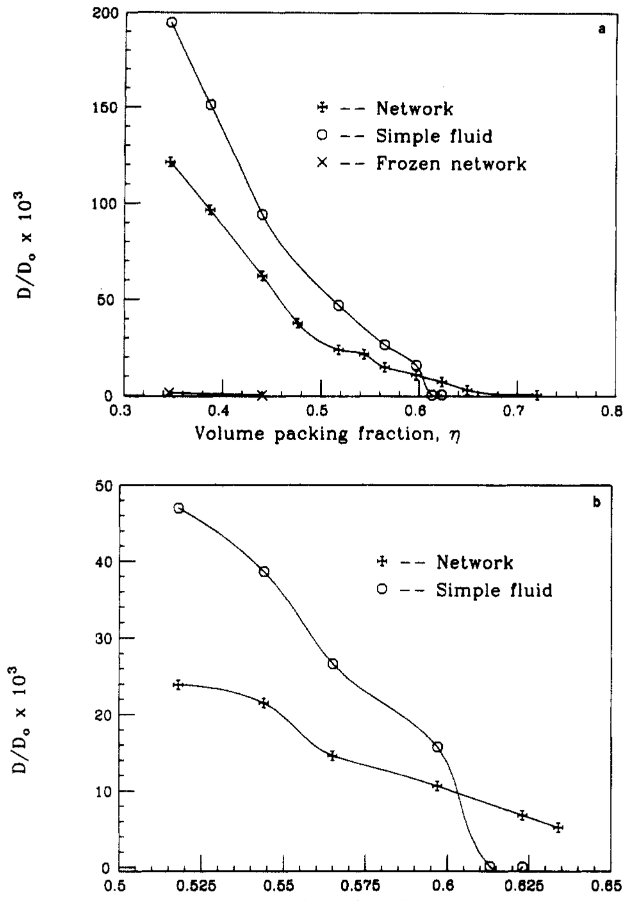

Figure 5. (a) Dependence of penetrant diffusion on network packing fraction $\eta = \pi\rho/6$, where η is ratio of volume occupied by network atoms to total volume. $D_0 = \sigma_p(k_BT_0/m)^{1/2}$. $\sigma/a = \sigma_p/a = T/T_0 = 1$. Simple fluid is obtained from network by eliminating all covalent bonds. Diffusion data for frozen network obtained by keeping atoms of network fixed while penetrant atom retains thermal motion. (b) Expansion of crossover region for diffusion in network and in corresponding simple fluid.

constant of various molecules in natural rubber are shown in Figure 6b; the qualitative similarity of the simulation to the experimental results is apparent.

5. Conclusions

This work represents the first step in the study of penetrant atom diffusion through polymer networks in the rubbery regime by the method of molecular dynamics. The initial results reported here are encouraging. Although idealized models for the system were employed, a number of features of the process observed in experiment were reproduced qualitatively by the simulations. In particular the temperature dependence of the diffusion constant showed Arrhenius behavior with a reasonable value for the activation energy, and the dependence of the diffusion constant on penetrant atom size is of the same form as observed experimentally.

In addition these simulations provided two specific insights into the process:

(i) They demonstrated the importance of the mobility of the network atoms to the diffusion process. In the rubbery state, i.e., above the glass transition temperature of the network, the network atoms are highly mobile and their thermal motion has large amplitude. When, in the simulation, the thermal motion of the network atoms is completely prevented (frozen network), it is found that the diffusion of the penetrant atoms is greatly reduced and effectively ceases in densely packed networks. Apparently, once the penetrant atom becomes trapped in a hole in the network, thermal motion of the network is required to permit its escape.

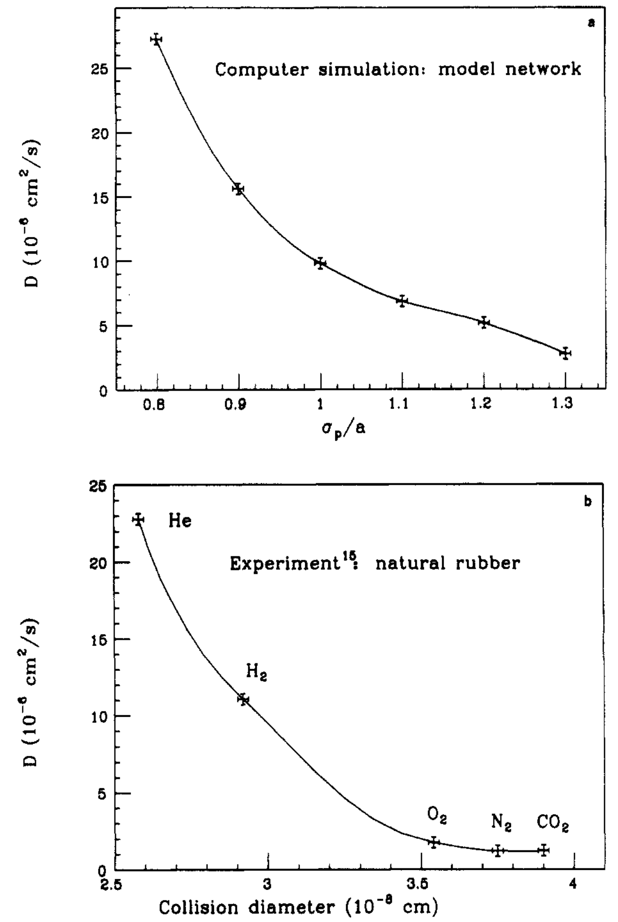

Figure 6. Dependence of D on penetrant size. (a) Results from computer simulation; $\sigma/a = T/T_0 = 1$, $\rho = 1.08$. (b) Experimental results (Barrer[15]) for diffusion of various penetrants in natural rubber at $T = 300$ K. Collision diameters taken from DiBenedetto.[16]

(ii) The second observation concerns the comparison of diffusion through a network with diffusion through the corresponding simple fluid model created by eliminating all of the covalent bonds of the network model. At lower values of the reduced density ρ of the network, it is found that diffusion through the network is slower than through the corresponding fluid. This result appears to be in accord with physical intuition since the covalent bonds and the nodes of the network should decrease the mobility of the network atoms. Counterintuitive behavior, however, is observed at higher values of ρ or packing fraction η. There is a crossover value of η beyond which diffusion in the fluid decreases sharply and effectively ceases, while penetrant atom diffusion in the network continues. The following mechanism is conjectured by us for this crossover: At very high densities or packing fractions the opportunities for thermal motion of network atoms are very limited. The motion that becomes possible due to the creation of adjacent holes takes place on the part of only a few network atoms at a time and is not well coordinated along the chain; this limited motion is accompanied therefore by strains in the covalent bond structure. This strain, in turn, aids further motion on the part of the network atoms. An alternate mechanism for the crossover suggested by the reviewers is the presence of a broader distribution of hole size in the network as compared to the corresponding simple fluid; since the network atoms are tightly packed along the chains, room remains for larger holes in the network than in the corresponding fluid at a given packing fraction. It may be possible to test the roles of these different mechanisms in future simulations.

The model studied in this paper utilized only the repulsive portion of the Lennard-Jones potential, a potential frequently referred to as the Weeks–Chandler–Andersen (WCA) core potential.[11] The fact that the model yields behavior qualitatively similar to that observed in real systems supports the view that steric considerations are dominant in the diffusion process in these systems. Work on diffusion in simple fluids shows that adding the attractive tail to the WCA potential has a small but not negligible effect;[17] this question should be studied as well for impurity atom diffusion through networks.

Other aspects of this problem that could be studied by the techniques presented here include the effect of cross-link density, the effect of chain flexibility, and the effect of junction fluctuation. It appears to be an approach whose utility and range of applicability are bound to increase as computer capabilities grow.

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(18) **Added in proof**: For another recent study of small-molecule diffusion in rubbery polymers by molecular dynamics see: Takeuchi, H.; Okazaki, K. *J. Chem. Phys.* **1990**, *92*, 5643.