Diffusion of Gases in Amorphous Polymers:
The Monte Carlo Void Method Based on Molecular Dynamics;
Application to He Diffusion in Polyethylene

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Abstract
The diffusion of small molecules in polymer matrices involves time scales (microseconds [μs] to milliseCONDS [ms]) far too long for routine molecular dynamics (MD) simulations. We have formulated a new method to extract coarse-grained information from short (1-2 nanoseconds [ns]) MD simulations and use this in a mesoscale simulation to calculate diffusion constants in polymer matrices. It uses a grid to calculate the average probability of each grid point of being a void and does constrained Monte Carlo (MC) dynamics to reach much longer time regimes than possible in MD. The MC method mimics the three regimes of mean square deviation (MSD) behavior seen in MD, thus accounting for the proper mobility of the voids and the compressibility of the polymer matrix. Initial results on He diffusion in a low-density polyethylene (PE) matrix are presented. The behavior at different temperatures follows closely the trend observed from calibrating long term MD for this particular system. Details of the methodology are discussed in this paper.

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1.0 Introduction

The diffusion of gases in polymers is of major importance to the polymer industry. For example, various applications in the food industry involve impeding the diffusion of gases (such as H₂, O₂, CO₂, H₂O, and CH₄) through thin polymer films. The design of new copolymers, new monomers, or new blends to selectively impede the diffusion of some gases while allowing others (O₂ versus N₂, CO₂ versus O₂, H₂O versus O₂) underlies a number of potential applications. The design and optimization of the selectivity of polymer membranes for diffusion would be greatly facilitated if reliable predictions of diffusivity could be made rapidly in advance of synthesis and experiment. The time scale for diffusion (μs to ms) is far too long for routine applications of molecular dynamics (MD). This has made it difficult to obtain reliable diffusion data from theory. In addition, it is not easy to obtain reproducible data on gas diffusion in polymers from experiment. As a result there is little in the way of reliable predictions on how to design polymer films to achieve specific diffusion properties.

The permeability (P) of a gas through a membrane can be written as

\[ P = D S \]  

where D is the diffusion coefficient and S is the solubility. Generally only P is available experimentally, but D and S depend differently on the various design parameters. Thus, it is useful to be able to independently measure each. In this paper we will focus on D.

In the long time limit for a three-dimensional system, Einstein showed that the total distance (R) traveled in a time (t) is given by Eq. (2) (the Einstein relation)

\[ \langle R^2 \rangle = 6 D t \quad \text{as } t \to \infty \]  

where \( \langle \rangle \) designates averaging over the ensemble of starting and ending points for the given time interval t. To use theory to predict D for a gas X in a polymer, we carry out a number of MD calculations (each starting with X in various sites) for times sufficiently long that (2) is obeyed.

Some typical results are shown in Figure 1. Figure 1a shows that for He in PE a 1.5 ns run leads to a reliable D while Figure 1b shows that for O₂ in a PVC/PVDC copolymer, 1.5 ns of MD is not even close to satisfying Eq. (2). (We estimate that this latter case requires a μs time scale.) The problem with using MD to study gaseous diffusion is the time scale. It is necessary for the calculation to proceed for a time t sufficiently long that the Einstein relation (2) is valid. Even for simple gases in polymers, the relevant times are often on the order of μs or longer.
Since the MD time step is ~1 femtosecond (fs), a total time of µs requires ~1 billion steps. For a polymer of realistic molecular weight this requires very long times on even the largest supercomputer. Consequently, it is usually not practical to use MD to obtain reliable values for D.

In order to gain insight about the features of an amorphous polymer dominating the diffusional properties, we carried out MD studies of various gases diffusing through various polymers. Typical results are shown in Figure 2. Figure 2a shows the trajectories for 5 He atoms diffusing for 1.5 ns in PE. Here the atoms of the polymer are not shown. We see that there are three-dimensional regions (referred to here as felicitons) in which the gases spend significant times (∼20-70 picoseconds [ps]) separated by pseudo one-dimensional channels where they spend shorter times (∼5 to 20 ps). On the other hand, Figure 2b shows the trajectory for 5O₂ diffusing for 1.5 ns in PVC/PVDC. Here we see that each O₂ remains within a feliciton, with no channels connecting them.

The felicitons are regions that better accommodate the diffusing particle - because this region has more available free volume or a higher compressibility. Thus, one can think of the polymer as consisting of felicitons connected by channels with the diffusing particle hopping from feliciton to feliciton through the connecting channels. We should emphasize that this feliciton/channel concept of diffusion is dynamic. At any instant there are no large voids in the polymer. However, averaged over the time scale that a particle can diffuse through a region of the polymer, there are some regions - felicitons and channels - better able to accommodate the particle than others. This framework of felicitons and channels then controls the diffusion. If insufficient channels connect the felicitons, there may not be the percolation necessary for long-range diffusion.

Numerous calculations on different gas molecules diffusing in various amorphous polymers give results such as in Figure 2. We also find that the regions occupied by the diffusing particles are defined by the dynamics of the polymer even without the particle! Thus, Figure 3 shows the dynamical void distributions in the two polymers of Figure 1 and Figure 2. Here we partitioned the unit cell into one million cells (100×100×100) and examined the voids over a period of 200 ps. Every 5 ps we examined whether a probe of 1Å radius would contact any part of the polymer. The color code in Figure 3 indicates the fraction of the times that there was a void of at least 1Å radius at that site. Here we see that the void analysis leads to an excellent match with the felicitons and channels extracted from the MD.

Given that the topology of felicitons and channels can be determined independent of the diffusing particle, we asked whether we might estimate the diffusion constants without actually considering the diffusing particle! Thus, we consider a Monte Carlo process in which a pseudo
particle migrates from one void site to an adjacent void site. Indeed, we find that such Monte Carlo Void Diffusion (MCVD) procedure lead to a diffusion trajectory very similar to the MD calculations, as shown in Figure 4.

Such MCVD calculations are many orders of magnitude faster than MD, allowing us to easily consider time scales long enough to see diffusion even in O₂/PVC-PVDC. However, to obtain the actual diffusion constant from MCVD, we must convert implicit time of a MC jump to the physical time. This is done by comparing the distance vs. MC step behavior from MCVD with the distance vs. real time behavior from MD. We find that reliable MC step to time conversion can be obtained from even short time MD. This procedure provides a practical means of predicting diffusion properties of gases in polymers. In this paper we will focus on He/PE. Subsequent papers will consider other penetrants (O₂, N₂, H₂O, CH₄, C₆H₆, etc.) as well as other polymer matrices - polypropylene, polyisobutane, polystyrene, polyvinyl chloride, polyvinylidene chloride, etc.

Section 2.0 describes the diffusion of He in PE using atomistic MD. Section 3.0 describes the void analysis procedures. Section 4.0 presents the Monte Carlo Void Diffusion method. The diffusion of He atoms in polyethylene is analyzed in Section 5.0.

2.0 Molecular Dynamics

2.1 The Amorphous Polymers

We are interested in studying the diffusion of gases in amorphous polymers. A system such as PE will often have a high percentage of crystalline lamella. In semi-crystalline polymers, the most widely accepted view² of diffusion is the electrical analog of porous media (amorphous region). According to this view, the crystalline region of the polymer is impermeable. Therefore, the effective diffusion can be derived from the diffusivity of the gas in the pure amorphous region. We consider using different approaches to equilibrate randomized conformations of polymers in order to provide the ensemble of structures mimicking amorphous polymers. We have found the following procedure to be effective and used it in the calculations reported here.

For MD calculations on amorphous polymers, we use periodic boundary conditions (PBC) so that a finite number of independent atoms can describe an infinite polymer system without surfaces. Our calculations allowed four independent chains of PE per unit cell (each with 200 carbons, a molecular weight of 2802 Dalton/chain). We started by allowing each chain to have a random conformation but with the requirement that the chain-chain interactions be reasonable.
To do this we built the initial structure using Rotational Isomeric State (RIS) theory to select the torsional distribution, assuming the trans state to be 0.8 kcal/mol more stable than gauche, for a temperature of 400K. At the end of the growth process, we used energy minimization to relax the structure removing initial bad contacts. We then carried out MD to anneal the system using the MPSim program developed at Caltech. These calculations used 8 cells of the KSR1 parallel computer. An initial MD at 500K was run for 100ps to remove bad contacts. The unit cell is a cube of volume 21835 Å³ (27.95 Å sides), leading to a final density of 0.854 gm/cc, which matches the density of the amorphous component of PE.

Figure 5 shows a typical amorphous system built using this procedure consisting of 4 chains of PE with 100 monomers (200 backbone C atoms) per chain. For purposes of clarity, the H atoms have been removed and the various chains are color coded to follow the chain conformation and entanglements.

2.2 Placement of the He Atoms

To locate the best places to start the penetrant He atoms, we calculated the voids in the system. We divided the cell into a million cells (100×100×100 grid) and at each grid point checked for the presence of nearby polymer atoms. Here we count a microvoid at a potential grid point if there was no polymer atom whose van der Waals radius was within 1.0Å - the probe radius - of the grid point. The contiguous microvoids were collected together to form a macrovoid which is characterized by the centroid and radius of the largest single sphere that fits within the macrovoid. The program reports the centroids of these voids in descending order of size, Table 1. A probe radius of 1.0 Å leads to the voids shown in Figure 3. We then placed He atoms near centers of the voids. The simulations used 5 He atoms per unit cell, but we turned off the He-He interactions. This allows us to obtain good statistics while avoiding artifacts that might arise from the He-He interactions.

MD simulations were then carried out at various temperatures using MPSim. Since explicit H atoms are described, a time step of 1 fs was used for the MD. The trajectory of the PE chains and the He atoms was saved at 1ps intervals.

We used the MS force field (FF) for PE, which gives excellent agreement with experimental data for crystalline PE. However, the torsional potential about the C-C bond was determined from quantum chemical calculations on n-pentane. The typical calculation on 8 cells of the KSR1 leads to 50 ps of MD per day.

2.3 Analysis of the Diffusion
Figure 6 shows the track of the 5 He atoms in a 10 ns simulation. It is quite clear that the He atoms spend most of their time traversing the felicitons, occasionally hopping through a channel to an adjacent feliciton.

To calculate the mean square displacement (MSD) with time, we considered each ps step of the 10 ns trajectory to be a possible starting point. Thus,

$$R^2(\tau) = \sum_{t_o=0}^{T-\tau} \left[ R(t_o + \tau) - R(t_o) \right]^2 / \sum_{t_o=0}^{T-\tau} 1$$

where $T$ is the total time. This leads to a sampling size that decreases from $10^4$ at $\tau = 1$ ps to 1 at $\tau = 10$ ns. Thus, the value of $\langle R^2 \rangle(\tau)$ is not expected to be reliable for $\tau >> 1/2 T$. To determine whether the system is in the diffusing region where the Einstein relation (2) holds, we plot log $\langle R^2 \rangle$ vs. log $\tau$, which should have a slope of unity. Indeed, Figure 7 shows diffusive behavior for $\tau \geq 0.1$ ns averaged over all 5 He atoms. The intercept gives $6D$ which leads to $D = 1.77 \text{Å}^2/\text{ps} = 29.5 \times 10^{-6} \text{cm}^2/\text{sec}$.

The diffusion coefficient of He in LDPE ($\rho = 0.914 \text{g/cc}$) at 25°C is $6.8 \times 10^{-6} \text{cm}^2/\text{sec}$ and in HDPE ($\rho = 0.964 \text{g/cc}$) at 25°C is $3.07 \times 10^{-6} \text{cm}^2/\text{sec}$. Allowing for the difference in density, polymer length, system size and temperature, our calculated value is in the expected range.

Figure 7 shows that the Einstein relation (2) is satisfied above times of $\sim 100$ ps, corresponding to diffusion length of $\sqrt{\langle R^2 \rangle} \sim 13\text{Å}$ (indicated by the line with long dashes). The shorter time scale region is asymptotic to the short dashed line where $\langle R^2 \rangle$ is proportional to $t^{1/2}$. The analysis in Figure 7 used trajectory data that was saved only at 1ps intervals during the 10 ns MD run. Consequently, this does not allow an analysis of the early time behavior below $\sim 5$ ps. To examine the early region, we ran the MD for 95 ps and saved the trajectory every fs. This leads to Figure 8a. Up to $\langle R^2 \rangle = 0.25 \text{Å}^2$ and times up to $\sim 0.03$ ps, the distance increases rapidly with time ($\langle R^2 \rangle \propto t^2$ or $R = vt$ where $v \approx 506 \text{Å/ps}$ is the velocity). This is the *ballistic regime*, before the particle hits a wall. From $\langle R^2 \rangle \sim 4\text{Å}$ to $12\text{Å}$ and time from $\sim 0.25$ ps to $\sim 4$ ps, the trajectory fits the $\langle R^2 \rangle \propto t^{1/2}$ line quite well. This is the *anomalous diffusion region*, corresponding to intra-feliciton motion. During this time the motion is primarily within felicitons, suggesting an average feliciton size of 12Å diameters. We find such an anomalous diffusion region (where $\langle R^2 \rangle \propto t^{1/2}$) for diffusion in all amorphous polymers.

### 3.0 Void Analysis
As discussed in the Introduction, our MD studies of diffusion always show well-defined feliciton regions separated by channels in which the gas particle spends considerable time. We can define void analysis procedures that lead to the same regions in space that the gas particle samples during diffusion.

The question is what size to use for the probe radius in defining the void region. In Figure 9 we show the void analysis for various sized probes from 0.1 to 1.2Å. This analysis can be compared to the diffusion trajectory in Figure 2a, which has the same orientation. We see that probe radius of 0.9Å leads to a definition of the felicitons that matches the dynamics trajectory well. By running MD for 500 ps (the first 300 ps to adequately equilibrate the system and then 200 ps for sampling), we extract snapshots at 5 ps intervals to give 40 snapshots spread over 200 ps. Then we calculate whether there is a void larger than the probe radius at each of the 1,000,000 grid points. Each grid point is then weighted by the fraction of the 40 snapshots that it is a void. This weight embodies atomistic information about the polymer matrix like compressibility, porosity, and dynamical behavior.

### 4.0 The Monte Carlo Void Diffusion (MCVD) Model

Given the void probability grid from Figure 3 we will consider a random walk in which a particle on a grid point moves to an adjacent grid point. We assume the probability to be proportional to the void weight - 1 if always a void to 0 if never a void. Figure 10 shows a MD trajectory within a void at 1 fs resolution. In order for a random walk process to mimic this, we include a bias in the jump probability with an angular dependence based on the last previous step direction. We find that a simple cosine term, of the angle between the last step and the next possible jump direction, leads to a smooth linear trajectory within a feliciton with the particle changing direction mostly on reaching the edge of the feliciton. This mimics the MD trajectory as indicated in Figure 8b.

A second issue concerns which neighboring points are allowed for the jump. Simple choices are

a) only the 6 nearest neighbor points (forward, backward, up, down, right, left),
b) the 18 points also including next nearest neighbors, or
c) the 26 points also including third nearest neighbors.

We chose case c since it efficiently spans the solid angle choices, allowing channels in diagonal direction to be found. Thus, starting at point $G(l_x, l_y, l_z)$ with the previous point at $P(l'_x, l'_y, l'_z)$ (where $|l_i - l'_i| = 0.1$ but at least one is nonzero), we then calculate the probability as
\[ G(I^x, I^y, I^z) = W(I^x, I^y, I^z) \left[ q \cos(I^\tau - I^\omega) \cdot (I^\omega - I^\tau) + (1 - q) \right] \]

where \( q \) can have values from 0 to 1 (we use \( q = 1/2 \)).

5.0 Results: He/PE

Our model system was 4 chains of PE, each with 200C, MW=2802 Dalton, in a PBC box. Figure 7 shows the MD diffusion of 5 He atoms for 10 ns. This can be compared with the MCVD results in Figure 4, which parallels the MD simulation quite closely. The MD analysis showed three distinct regimes of diffusion

- early \textit{ballistic} regime where the penetrant fills up the voids very rapidly
- middle \textit{anomalous} regime where the penetrant occasionally finds channels to adjacent voids, but is still quite directional
- late \textit{Fickian} regime where the jumps between voids are isotropic in nature

This behavior can be better seen in Figure 8A from MD and Figure 8B from MCVD. It is particularly gratifying to note that the anomalous regime and the Fickian regime exhibit similar time dependence in both simulations.

The last problem concerns converting the MCVD step to an actual time. There are 3 possibilities for doing this

1. If MD for sufficiently long times is available, then one can obtain the diffusion constant from the Fickian regime of the MSD plot. By matching this diffusion constant to that from MCVD gives the conversion from MC step to actual time. This is equivalent to matching the intercepts of the Fickian regimes.

2. One can match the crossover point from the anomalous regime to the Fickian regime.

3. One can match the intercepts of the anomalous regime from MD and MCVD.

The problem with the first method is that if MD can be done long enough to get a reliable diffusion constant, then there is not much need for a faster method. In most cases, it is not practical to do the MD for sufficiently long times. If there is a clean crossover from MD and MCVD, then one can also use the second method. The third method is the easiest to access from the MD simulations since on the ps to ns time scale, most polymer systems show the anomalous behavior. For He/PE we have sufficiently long dynamics to use all 3 methods and we show in Table 2 the MD to MCVD time constant for all 3 cases. We see that while the diffusion constant changes by a factor of 15 between the temperature extremes (1.77 @ 400K \( \rightarrow \) 0.12 @ 200K) the time conversion factor remains relatively constant within a factor of 2. The time conversion is most reliable by matching the slopes of the Fickian regime, but as noted above, this time domain
will not be readily accessible for most cases of interest, where either the system will be too large for sufficiently long dynamics, or it will be too rigid for showing much diffusion within the MD run. The crossover point is difficult to define unless a clear Fickian regime can be observed. The cleanest operational procedure is to use the slopes of the anomalous regime, which is easily accessed from doing short (~ 500 ps) dynamics. As the last column in Table 2 shows, the ratio of the time conversion from this regime to the Fickian regime is relatively constant. Under ideal circumstances, it would have been exactly the same at all temperatures. For the purposes of extracting an order of magnitude diffusion constant, and more importantly understanding the physical parameters controlling diffusion, it is sufficiently accurate to determine the conversion factor from the anomalous regime. Consequently we use the third method which leads to a time conversion of 3.6fs/MCVD step.

6.0 The Discussion of Voids
6.1 Free Volume Concepts

Given the behavior of the penetrant molecule in the polymer matrix from MD, can we model this by the mobility and dynamics of the voids itself? The free volume approaches essentially treat diffusion as the redistribution of space unoccupied by the polymer matrix. An alternative approach called the Transition State Theory (TST) is to treat the process as a sequence of activated hopping between adjacent sorption sites. While Suter and co-workers were successful in simulating the diffusion of helium in glassy polycarbonate and melt polyisobutylene, the method failed for hydrogen and larger penetrants, primarily due to the rigidity of the imposed polymer network. They did MD to extract amplitude of short time vibrational motion, but the atoms essentially were fixed in space with small amplitude motions about their mean positions. Greenfield and Theodorou analyzed the geometric properties of the sorption sites and their connectivities as a prelude to a more atomistically correct input to the TST model. They observed that free volume rapidly rearranged in the melt, while they were much more rigid in the glass with occasional channel openings in between them. Our idea is based on the fact that if one can do MD for times longer than the characteristic times for void fluctuations, whether they be redistributions in the melt, or thermal fluctuations in the glassy state, then one can extract this information averaged over many static snapshots of the system and use this information to coarsen the model. The simplest way to measure fluctuations is to measure all the voids and average them. Figure 11a shows the voids in the PE as a function of MD time at 1ns intervals. Each distinct void is color coded for clarity. At 400K, in the melt the voids are redistributed rapidly and carry the penetrant molecule with it. At the lower temperature
of 150K, similar analysis shows that the voids do not redistribute as rapidly but show fluctuations about their mean position, Figure 11b.

6.2 Probe Radii

At 0.0Å probe radius the free volume consists mainly of one big percolative void, whereas at larger probe radii isolated voids begin to emerge. If the probe size is too large, then there are very few voids, which stay isolated with no channel openings and closings. Obviously, there is an ideal probe size for extracting the void information and it has to be related to the percolation properties of the system. Takeuchi showed that if one measures the free volume as a function of the decreasing probe size, then at approximately the probe size that leads to 5.5% free volume, the system shows percolative channels. Greenfield and Theodorou reached similar conclusions. We have analyzed the free volume as a function of probe radii, which is shown in Figure 12a. As expected, the free volume is a smoothly decreasing function of increasing probe size. 5.5% free volume occurs at approximately 0.75Å probe radius. In addition to analyzing a static snapshot, we have also analyzed a collection of snapshots from the MD and can measure what fraction of them are percolative at a specific probe radius, which is shown in Figure 12b. The change from all snapshots being percolative to none being percolative is quite sharp, between 0.6 and 1.0 Å. Another view of this is shown in Figure 12c where the fraction of percolative snapshots is plotted against the free volume available in them. Corroborating the results of Takeuchi, we find that at above 5.5% free volume, 50% of the snapshots show percolative channels.

6.3 Percolation

We have two ways of analyzing percolation. One method is to start in the largest cavity and perform the grid walk algorithm, marking each visited point and counting transitions across the unit cell boundary. If we visit a marked point a second time after a transition across a cell boundary that implies a percolative channel exists. If percolation does not happen within a large number of steps, typically 10M, we assume that the probability of a percolative channel existing is quite small. There can be very narrow channels of percolation, but these will be insignificant in the diffusion process. Now we start the percolation analysis in another cavity until all major cavities are analyzed. This algorithm is simple and very fast for porous systems with well-defined percolative channels provided the initial placement is in the right cavity. If repeated starts are required in many cavities then this method slows down substantially. It is also non-deterministic since random grid walk is performed and the maximum number of steps is also arbitrary and can affect the outcome. Although this determinism is physically insignificant as
discussed above, we have devised a second algorithm, which is deterministic with a well-defined termination. In this recursive algorithm, similar to finding a path in a labyrinth, we explore all neighbors that have not been marked as visited. If the algorithm gets stuck then it recurses back to the previous branch point and takes a different branch. If all branches from the last branch point is marked visited, then the recursion steps further back to the earlier branch point. If this leads to the initial starting point, then a new starting point is chosen from among the points that have not been marked. Using the number of unmarked points as a metric, it is easy to show that this algorithm will terminate after a fixed number of steps. This number of steps might be quite large for porous systems with large free volume. Both algorithms produce track files, which can be visualized to show the actual trajectory of the probe.

Percolative channels are one criterion by which to select the probe radius of our voids. However, as the preceding analysis shows, below a particular probe radius, most of the snapshots will show percolation. At very small probe radius, the whole polymer will be percolative and a MC dynamics will treat this essentially as one infinite cavity and only ballistic behavior will be observed. On the opposite end, with too large a probe radius, there will be no percolation at all. Since we want to include dynamical effects, such as the compressibility of the polymer, and more importantly, channel openings and closings, in our void data, percolation is not a sufficient criterion for choosing the probe size. A probe radius (say 1.3Å) may not show percolation in a static snapshot but the conjoint set of many snapshots might show percolation at this large probe radius. After several initial trials, we selected a second criterion to adopt the probe radius. Our coarsened physical model must reflect the atomistic behavior of the MD. The coarsening of the model is at the level of selecting voids and their mobility and compressibility. In the MSD plot, this is reflected in the anomalous regime, where the gas molecule finds occasional channel openings and closings between adjacent voids. The MSD from MC should mimic the MD behavior in terms of the slope of the anomalous region. This gives a narrow range of penetrant size where this physical relationship holds. For the cases reported here, 0.9Å was the probe radius chosen for mimicking the behavior of He atoms in PE.

6.4 Length of MD for Calibration of MCVD

The final questions that need to be answered about the spatial grid is how long should the MD run be and how frequently does one need to take snapshots of the system for the purpose of extracting void information. In a polymer, bonds and angles constitute stiff degrees of fluctuations because typically the well depth for a bond is about 70-180 kcal/mol. While a similar well depth cannot be described for an angle, the force constant (or curvature at the bottom of the well) for an angle is 70kcal/mol (force constants for bonds are about 700-1000 kcal/mol).
In contrast, the torsional potentials are relatively shallow with barriers being on the order of 5-10 kcal/mol and van der Waals and hydrogen bonds also constitute softer degrees of freedom. In the case of PE, the barrier between trans and gauche conformers for the model n-butane is about 4.02 kcal/mol. Consequently, in MD, the fluctuations are significantly smaller in the bonds and angles than in the dihedrals. This is graphically shown in Figure 13, where for 1 chain of PE, for a 200ps MD run the fluctuations in selected bonds and angles are shown along with the fluctuations of all the dihedrals along this chain. While the bond fluctuates between 1.50-1.56Å and the angle fluctuates between 102-115° there are quite a few dihedrals that undergo frequent flips between gauche+ (60°), trans (180°) and gauche- (300°) conformations.

The plot in Figure 13 shows two specific dihedrals, one of which stays constant at gauche+ while the other undergoes rapid flips. While the behavior of each dihedral is dependent on a number of factors, on the average, the overall motion of chains is due to rotations of dihedrals. Rearrangement of these dihedrals is the primary cause of the void mobility because these entail motions of large segments of the polymer chain. The dihedral motion constitutes the characteristic time/frequency of the system under study. In the case of PE, we observe dihedral flips on the average of 1/10ps. This indicates that one needs to do MD for sufficiently long time to cover many such dihedral flips and we have found 200ps sufficient to sample the dynamical motion of PE. For a polymer with a more constrained dihedral motion, like polyenes, the characteristic time will be different. For this paper, we have run longer MD to also inspect the longer-term diffusive behavior from MD, but in general this will not be necessary.

The issue of how many snapshots are needed to average the properties is still an open question. Channel openings and closings have characteristic times of 10ps from Takeuchi MD simulations even though he had to run 1ns MD to observe this. In our work, we have found that 40 snapshots, at 5ps intervals are optimum for our void extraction procedure. If too many snapshots are averaged, then for the melt, almost all of the space will likely be a void at some instant in time. Too few snapshots will not span the dynamical nature of the polymer matrix adequately. However, this question is not settled and we are continuing to investigate it.

7.0 Discussion

The replacement of MD on gases diffusing through a real polymer with MCVD on particles migrating through negating voids (obtained from the MD) corresponds to a coarse gaining of the gas-phase system. In this process the details in the atomistic description of the voids is replaced by the void probability distribution. This is analogous to going from the quantum mechanical wavefunction and its detailed information on electrons and nucleus to the
more averaged molecular mechanics FF comprising of balls and strings. In the case of diffusion, we are going from the atomistic MD to a procedure based on the mesoscopic length and time scale by averaging the voids and their mobility information. The anomalous regime in the MD is precisely this time and length scale, and thus it is reasonable to match the slopes for this regime.

To be useful the MD to MCVD time conversion should be the same for different temperatures. In order to check, we carried out MD on PE at various temperatures from 400-200K in steps of 50K. Table 3 lists the diffusion constants we get from the slope of the Fickian part of the msd plot. We then performed MCVD on the set of voids derived from the MD at various temperatures. Using the time conversion factor reported above (derived at 400K), we then derived the MCVD diffusion constants over the full range of temperatures for the MD simulations. The normalized diffusion constants from both MD and MCVD are plotted in Figure 14. The agreement between the MD and MCVD values is within 33%.

Thus, MCVD affords a remarkably simple method to convert short time (ns) MD trajectories to a mesoscopic simulation (µsec) using only the voids to simulate small molecule diffusion in a polymer matrix. This should be useful above and below the glass transition temperature Tg.

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Figure Captions

Figure 1. (a) MSD from 1.5 ns MD of 5 He atoms in PE; (b) MSD from 1.5 ns of MD of 5 O₂ molecules in a PVC/PVDC copolymer.

Figure 2. (a) trajectories for 1.5 ns MD of 5 He atoms in PE corresponding to the MSD of Figure 1a; (b) trajectories for 1.5 ns of MD of 5 O₂ molecules in a PVC/PVDC copolymer corresponding to the MSD of Figure 1b.

Figure 3. The dynamical void distributions in the two polymers of Figures 1 and 2. The unit cell is partitioned into one million cells (100×100×100) and at intervals of 5 ps in the MD trajectory, a probe of 1Å radius is used to analyze the polymer structure. The color code indicates the fraction of the times that there was a void at that site.

Figure 4. Monte Carlo Void Diffusion (MCVD) trajectory for He in PE.

Figure 5. Typical amorphous system used in this work, consisting of 4 chains of PE with 100 monomers (200 backbone C atoms) per chain. For purposes of clarity, the H atoms have been removed and the various chains are color coded to follow the chain conformation and entanglements.

Figure 6. Track of 5 He atoms in PE for a 10 ns MD.

Figure 7. MSD from 10 ns MD for 5 He atoms in PE.

Figure 8. (a) MSD from 95 ps of MD of 5 He atoms in PE with trajectories saved at each 1 fs interval; this plot clearly shows the three different regimes of behavior – early ballistic, middle anomalous, late Fickian (b) MSD from MCVD at finer resolution, showing three regimes similar to the MSD from MD.

Figure 9. Void analysis of 4 chain PE for various probe sizes ranging from 0.1 to 1.2Å.

Figure 10. MD trajectory of a single He atom in PE showing smooth behavior of the particle within a feliciton.

Figure 11. (a) Voids in PE at several time steps in the 400K MD showing rapid redistribution of the voids in the melt; (b) Same as in (a), but at 150K, below the $T_g = 220K$ showing slow redistribution in the glassy state.

Figure 12. (a) Free volume as a function of probe radii; (b) fraction of percolative snapshots as a function of probe radius; (c) fraction of percolative snapshots as a function of free volume.

Figure 13. Fluctuations in two bonds, two angles, all torsions for 1 chain and two selected torsions of PE from a 200ps MD run. The bond fluctuates between 1.50-1.56 Å and the angle fluctuates between 102-115°.

Figure 14. Normalized diffusion constants plotted against inverse temperature from MD and MCVD.
Table 1. Void analysis.

<table>
<thead>
<tr>
<th>#</th>
<th>Size</th>
<th>Area</th>
<th>Asphericity</th>
<th>Radius of gyration</th>
<th>Centroid</th>
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<td></td>
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Table 2. Time conversion from different regimes.

<table>
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<tr>
<th>Temperature</th>
<th>Diffusion Constant(a)</th>
<th>Time conversion (fs/MCVD step)</th>
<th>Ratio</th>
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\(a\)In units of Å\(^2\)/ps – the He atom displacements were recorded at each 1 ps interval from the saved trajectory.

Table 3. Diffusion constants for He in PE from MD and MCVD. The diffusion constants are obtained from the slopes of the Fickian regime of the respective MSD plots and have different units.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Molecular Dynamics</th>
<th>Monte Carlo Void Dynamics</th>
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<tbody>
<tr>
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<tr>
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<td>0.12</td>
<td>0.07</td>
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</table>

6. Using the Amorphous Builder Module in Cerius2 from Molecular Simulations Inc. (San Diego, Calif.).
10. This gives a sorption density higher than experiment. The actual solubility of He in PE is $0.054 \times 10^{-6}$ (cm$^3$/cm$^3$) which converts to $3.18 \times 10^{-8}$ molecules in our simulation volume of 21835 Å$^3$.
11. Karasawa, N.; Dasgupta, S.; and Goddard III, W. A. *J. Phys. Chem.* 1991, 95, 2260. The MSXX FF is used for accurate intrachain vibrations and not required for these applications. Thus, we used the MS FF but avoid the more complete description of the torsions.
14. Polymer Handbook, Wiley
19. This is the original Takeuchi paper that Seiichi had. I have lost my copy and need the reference once more from SK.