# Supplementary Information for:

# Comparing gas transport in three polymers via molecular dynamics simulation

Luke R. Anderson\*a, Quan Yangbc, Andrew M. Edigera

# Abstract

In the work MD simulation was employed to study the behavior of methane and n-butane in the bulk and interface regimes of the three polymers, PE, PMP and PDMS.

In the Supporting Information, simulation techniques and additional results are presented:

S1 PE, PMP and PDMS

S2 Penetrants

S3 Parameters of simulation

S4 Technique to compute AD of polymer chains

S5 Method to calculate cavity size distribution

S6 Determination of diffusivity, solubility coefficients K and permeability

S6.1 Three diffusion regimes and the minimal excursion ratio (MME) method

S6.2 Solubility computation

#### Nomenclature

A=geometric average of amplitudes of the oscillation of main and branch chains

ACF=accessible cavity fraction

AD=average displacement of chain units

AOA=average oscillation amplitude

CTRW=continuous time random walk

*f*=accessible cavity fraction, the fraction of cavities that are large enough to accommodate penetrants

FLE=fractional Langevin equation

MD=molecular dynamics

MSD=mean-squared displacements

PE=Polyethylene

PDMS=Polydimethylsiloxane

PMP=Poly (4-methyl-2-pentyne)

RWF=random walk on a fractal

VDW=van der Waals

## S1 PE, PMP and PDMS

Fig. 1 shows the geometry of PE, PMP and PDMS. At room temperature PMP and PE<sup>12</sup> are in a glassy state while PDMS is in a melt state. Even in glassy state, polymer chains still oscillate around the balance positions. Only at 0K, do molecules stop moving completely. Polymers even in crystalline state still have chain oscillation, though at relatively slow speed.

According to the conventional self-avoid random walk algorithm <sup>20</sup>, code was written to create the initial structure of PE, PMP and PDMS. The chains were folded when the periodic boundary condition was employed, i.e. the parts of chains beyond the box were translated to the opposite side of the simulation box, as according to periodic boundary condition, the simulation box repeats itself in all directions. This operation in fact enlarges the simulation box and the system significantly. The system

size must be large enough, otherwise relative standard deviation would be large. The system in the research is large enough to ensure the accuracy of simulation results.

Table S1 presents the free volume fractions at various temperatures obtained from MD simulations of the PDMS system based on the all-atom and mixed models. Fig. S1 shows a snapshot of the inside specifics of the simulation system of PDMS based on the all-atom model. Diffusivities of methane in 31-mers and 70-mers systems of PE, PDMS and PMP are presented in Table S2.

Table S3 shows VDW potential parameter values<sup>17,18</sup> for units of the polymer chains. For C, the size parameter (VDW diameter) should be smaller than methyl and ethyl units, whose size parameter are both 3.905 Å. The VDW energy parameter of Si is very large compared with other units. As a result, the VDW interaction between Si and gas molecules is expected to be large and would lead to high solubilities in PDMS.

**Table S1.** The free volume fractions at various temperatures obtained from MD simulations of the PDMS system ( $T_g = 150$  K) based on the all-atom and mixed models. The data in the parentheses are the corresponding standard errors.

Temperature	all-atom	mixed
145 K	0.238(0.012)	0.253(0.013)
300 K	0.305(0.014)	0.319(0.017)

**Table S2.** Diffusivities  $(D \times 10^9 m^2 / s)$  of methane in 31-mers and 70-mers systems. The data in the parentheses are the corresponding standard errors.

Polymer Items	PE	PDMS	РМР
31-mers	0.032(0.003)	0.308(0.018)	0.092(0.005)
70-mers	0.029(0.002)	0.289(0.016)	0.085(0.007)



**Fig. S1**. The snapshot of the inside of the simulation cell of PDMS based on the all-atom model (white balls: H units, light blue balls: methyl units, yellow balls: Si units, red balls: O units. Temperature: 300 K)

Unit	LJ ε(kcal/mol)	$\sigma(nm)$	
Н	0.011	0.288	
$C(sp^3)$	0.100	0.375	
$C(sp^2)$	0.105	0.379	
CH <sub>3</sub>	0.175	0.391	
$CH_2$	0.117	0.391	
Ο	0.203	0.296	
Si	0.584	0.338	

Table S3. VDW Potential parameters for units of the polymer chains <sup>12,14,17,18</sup>

 Table S4. Summary of PE, PMP and PDMS model systems (300K) studied in the work. Final cell

volume is the cell volume after NPT equilibrium run has been done to the system.

Polymer type	Number of chains	Initial cell volume (nm <sup>3</sup> )	Final cell volume (nm <sup>3</sup> )
PE	80	128.862	118.087
PDMS	80	306.907	305.748
PMP	80	336.820	334.957



**Fig. S2**. The simulation cells of the bulk-researching (a, 6.745nm in all 3 directions) and interface-researching (b, 6.745nm, 6.745nm and 10.745nm in x, y, z directions, respectively) systems of PDMS. The cell in (b) is an extension of that in (a), in z direction by 4nm in total, 2nm in each end.



**Fig. S3**. Total potential energy of PDMS model system as a function of step number for equilibrium run in NPT ensemble. (Temperature: 300 K)

#### **S2** Penetrants

For interactions between different types of units, the Lorentz–Berthelot mixing rule is used. To simulate the transport in the bulk of polymers, 120 gas molecules were inserted to the bulk-researching simulation cell. All results of diffusivities, permeabilities are the averaged values of the 120 gas molecules inserted. To simulate the transport in the interface regime, 40 methane and 40 n-butane molecules were inserted to the vacuum portion at the two ends along *z* direction of the simulation cell.

Table S5. Lennard-Jones parameters of different penetrants

Penetrants (units)	LJ ε(kcal/mol)	LJ σ(nm)
CH4 <sup>12,18,20</sup>	0.294	0.373
CH <sub>3</sub> (C <sub>4</sub> H <sub>10</sub> ) <sup>12,18,22</sup>	0.175	0.391
$CH_2(C_4H_{10})^{12,21,23}$	0.117	0.391

#### **S3** Parameters of simulation

The DLPOLY <sup>19</sup> software system was used. Under condition of constant pressure and temperature, the Verlet algorithm <sup>19</sup> was used, in purpose of solving equations of motion with the time step of 2.5fs. To obtain a reasonable starting configuration of the simulation systems, 5000 steps of energy minimization were done, using the steepest descent algorithm. Subsequently the structure was relaxed by a 500ps MD equilibration run in the NPT ensemble. For PMP system in the glassy state, to get the system equilibrated, firstly MD equilibration run was done in NPT ensemble at higher temperature, 500K. Then temperature was decreased gradually in a step size of 50K till 300K and MD equilibration run in NPT ensemble at these temperatures were done one after one. Only after the MD equilibration run in NPT ensemble at 300K was done did we get the system ready for MD production run. If the MD equilibration run was not done in such way, but was done directly at 300K, most probably the system cannot get equilibrated, as what people observed in experiments. The weak coupling technique<sup>19</sup> was used to adjust the temperature and pressure with relaxation times of 0.1ps and 0.5ps, respectively. After the equilibration run, a production run was performed in the NVT Evans<sup>11</sup> ensemble. In this ensemble

the averaged kinetic energy  $E_{kinetic}(T)$  of molecules was held constant. The temperature was set to 300K, the pressure was set to 1 bar, the VDW potentials cut off distance was set to 1.0 nm and the electrostatic potential cut off distance was set to 1.2 nm. The electrostatic interaction was estimated using the Ewald sum algorithm<sup>11</sup>. The cut off distance of 1.2 nm for electrostatic interaction calculation is large enough to ensure the accuracy. Most other researchers<sup>9,20,22</sup> use the same or smaller cut off distance (1.0nm) for electrostatic interaction calculation. Cut off distance of 1.3nm was also used and the simulation results are in agreement with that of cut off distance of 1.2nm.

MD simulations were performed firstly to explore penetrants transport in the bulk of the polymers. To explore penetrants transport in the interface region, cell size along *z*-direction was extended by 4nm. Then energy minimization and NPT MD equilibrium run described above were done to obtain relaxed, equilibrated and energy-minimized polymer-vacuum systems. Following this, 1 ns NVT simulation was carried out to create polymer-vacuum interfaces. Finally 40 methane and 40 n-butane molecules were placed in the vacuum region and MD production in the NVT ensemble was carried out for 2 ns. Other researchers <sup>5</sup> also carried out simulations of interface-researching systems via the same technique. The gas and bulk phases are in coexistence.

#### S4 Technique to compute average displacements (AD) of polymer chains

When gas molecules are transported in polymers, they jump between cavities within the polymer chains. The positions of cavities change as polymer chains oscillate. Therefore, the cavity size distribution and the chain oscillation flexibility have significant influence on penetrants transport. Novel analysis techniques were used to analyze the polymer properties that may lead to the differences in penetrants transport. Both the average displacements of branch chains and main chains in certain time intervals were calculated. In PE, the H units compose the branch chains and C units compose the main chains.

The AD of a branch chain or main chain in certain time intervals  $\Delta t$  are computed with eqn 2.

The displacements of  $CH_4$  from the center of the simulation cell as a function of times in PMP are shown in Fig. 2(a). The AOAs of main and branch chains are calculated with eqn 2. Dividing the sum

of moving time average of units of main or branch chains by the number of units of main or branch chains gives the AOAs of main or branch chains. For PE, the main chain is the chain made of C, while the branch chain is composed of H. For PMP, the double carbon chain consists of main chain, while the other units consist of branch chains. For PDMS the main chain is composed of Si and O, while the other units consist of branch chains.

#### S5 Method to calculate cavity size distribution

Fig. 3 shows the snapshots of the inside of the bulk-researching simulation cell of PE, PMP and PDMS. It is observed that PDMS has the largest ratio of free volume. To determine the cavity size distribution, the simulation cell is divided into a cubic grid of 10<sup>6</sup> points. Fig. 3(c) shows several sample grid points. Balls with radius *r* are placed at each grid point. The distance  $\Delta_{ij}$  defined in eqn S1 is calculated with the distance,  $r_{ij}$ , from grid point *i* to polymer atom *j*. Then with distance  $\Delta_{ij}$ , the number density at point *i*,  $\rho_i$ , is calculated with eqn S2.

$$\Delta_{ij} = \gamma \left( r + \frac{\sigma_j}{2} \right) - \left| r_{ij} \right| \tag{S1}$$

$$\rho_i = \sum_{j=1}^M \theta(\Delta_{ij}) \tag{S2}$$

where  $\theta$  is the Heaviside step function  $(\theta(x) = \begin{cases} 1, x \ge 0\\ 0, x < 0 \end{cases}$ ,  $\sigma_j$  is the Lennard-Jones width of the matrix unit *j*,  $\gamma$ , being 0.8, is a parameter employed for the tune of the definition of the free volume, and the summation is performed over *M* atoms of the polymer. The sites corresponding to accessible cavity

With  $\rho_i$ , N(R > r), the number of the cavities with radius larger than *r* may be computed with eqn S3:

(cavity that is large enough to accommodate the balls) are those with  $\rho_i = 0$ .

$$N(R > r) = \sum_{i=1}^{10^6} \theta(-\rho_i)$$
(S3)

N(R > r), divided by the total number of cavities over the whole range,  $N_t = N(R > 0) = 10^6$ , will give accessible cavity fraction, f, of the ball. The number of cavities,  $N(r < R \le r + \Delta r)$ , with radius in a narrow range  $(r, r + \Delta r)$  may be obtained using the following equation:

$$N(r < R \le r + \Delta r) = N(R > r) - N(R > r + \Delta r)$$
(S4)

The number of cavities,  $N(r < R \le r + \Delta r)$ , divided by the total number of cavities over the whole range,  $N_t = N(R > 0) = 10^6$ , and the radius range width,  $\Delta r$ , will give the probability density of the cavity radius being r, p(r). That is:

$$p(r) = \frac{N(r < R \le r + \Delta r)}{N_t \cdot \Delta r}$$
(S5)

#### S6 Determination of diffusivity, solubility coefficients K and permeability

The MSD averaged on different time origins were employed to determine diffusivities with eqn 3 <sup>12,24,25</sup> when the gas molecules transport are in the Fickian diffusive regime.

According to eqn 3, diffusivities may be obtained through the least square fit of the MSD versus time for penetrants transport in the Fickian diffusive regime. The displacement of penetrants must take place in the Fickian diffusive regime <sup>9-11</sup>. To determine whether the transport is in the Fickian diffusive regime, a logarithmic plot of mean-squared displacement of gas molecules versus time was drawn.

Researchers use permeabilities to make comparisons among transport properties of gas molecules. eqn S6 is used to calculate permeabilities as follows <sup>21,23-29</sup>.

$$P = S \cdot D = K \cdot \frac{C_0}{p_0} \cdot D \tag{S6}$$

where S and P are solubilities and permeabilities of gas molecules, respectively;  $p_0$  is the standard pressure of 1bar;  $C_0$  is the gas concentration under ideal standard conditions; K is the solubility coefficient and D is diffusivity. K can be calculated as

$$K = \int_{-\infty}^{+\infty} d(\Delta E_k) \rho(\Delta E_k) e^{-\Delta E_k / RT}$$
(S7)

where  $\Delta E_k$  is the difference of potential due to the insertions of gas molecules and  $\rho(\Delta E_k)$  is the probability density of the difference of potential being  $\Delta E_k$ . The integration yields the average of  $e^{-\Delta E_k/RT}$ . The discretization of it can be done as Widom <sup>15,21,30</sup>.

We used the Widom insertion method  $^{15,31}$  to calculate the solubility coefficients *K*. It is assumed that the insertion of particles into the system is random. If *N* times of insertions are performed and *N* is large enough, then the solubility coefficient can be computed with eqn S8.

$$K = \frac{\sum_{k=1}^{N} e^{-\Delta E_k / RT}}{N}$$
(S8)

Both full random (unbiased) Widom insertion method and biased Widom insertion method, whose insertions are biased by the free volume, were employed.

If  $P_1$  and  $P_2$  are the permeabilities of gas molecules of two types, 1 and 2, the selectivity of gas molecule 1 over 2 should be calculated using the following equation:

$$Sel = \frac{P_1}{P_2}$$
(S9)

## S6.1 Three diffusion regimes and the minimal excursion ratio (MME) method<sup>37-43</sup>

Penetrant transport has different characteristics in different time intervals  $^{37-38}$ . Over short time intervals, the mean-squared displacements (MSDs) follow a power law of  $t^2$  and the ballistic regime of penetrant transport is observed. At intermediate time intervals, anomalous diffusion is observed and the MSDs obey a power law of  $t^{0.5}$ . Over long time intervals, when penetrants enter the Fickian diffusive zone, the MSDs are linear in time.

Rrandom walk on a fractal (RWF) and fractional Langevin equation (FLE) are models applied to describe anomalous diffusion. The RWF model, not homogeneous in space, characterizes geometric

constraints effects in complex geometries and RWF processes are non-Gaussian, while FLE processes are Gaussian <sup>37,38,44-46</sup>

To explore how the anomalous diffusion behavior of penetrants in the polymers was caused, it is essential to test whether the transport dynamics of the penetrants follow the RWF or the FLE models. We used the techniques given by Meroz and Sokolov.<sup>47,48</sup> The minimal excursion ratio (MME) method was used to determine if a process is non-Gaussian or Gaussian:

$$MME = \frac{\langle [\underline{R}(t_0 + \Delta t) - \underline{R}(t_0)]^4 \rangle_{t_0}}{\langle [\underline{R}(t_0 + \Delta t) - \underline{R}(t_0)]^2 \rangle_{t_0}^2}$$
(S10)

where  $\underline{R}(t)$  is the position of gas molecules at  $t_1 < ... >$  denotes a moving time average and the sub-index  $t_0$  indicates the average it taken with respect to  $t_0$ .

#### S6.2 Solubility computation

#### S6.2.1 Unbiased Widom insertion method

*N* insertions were performed at random positions in a snapshot of the polymers. If the penetrants do not have spherical symmetry, the insertions were done with random molecular orientations. The change in the total potential energy,  $\Delta E_k$ , upon insertion and the Boltzmann factor were calculated. These factors were then averaged to obtain the solubility coefficients *K* according to eqn S8.

For a snapshot of the polymers, an initial insertion position is chosen randomly anywhere within the snapshot. When a penetrant is inserted, the initial neighbor list and long-range electrostatic energies are computed. The electrostatic interactions are estimated using the Ewald sum algorithm<sup>11</sup>. The short-range VDW terms in the energy are also calculated, to give  $\Delta E_k$ . Two parameters, *m* and *d*, are defined. *m* is the number of insertions for each initial position and *d* is the diameter of the sphere where an insertions are performed. For the next *m*-1 insertions, the gas molecule is shifted randomly about its initial position within a sphere of diameter *d* and a further random rotation is applied if the penetrants are not spherically symmetric. The *d* value is small. The neighbor list and long-range electrostatic

energies can be assumed to remain unchanged and short-range VDW terms in the energy are computed to obtain  $\Delta E_k$  at each step. The radii of neighbor list for VDW interaction and electrostatic interaction calculation are 10Å and 12 Å, respectively.

In the work the electrostatic interactions between an inserted penetrant molecule and polymer units do not need to be computed due to each particle composing the penetrant molecule having a charge of zero. To calculate  $\Delta E_k$ , no relaxation of the polymer system is allowed after the penetrant insertion. The exact configuration of the polymer system before the penetrant insertion should be maintained, otherwise the calculation results for  $\Delta E_k$  would be wrong.

A new initial position is then chosen randomly in the snapshot. The process is repeated until N insertions in total have been performed. The parameters m and d were set to 10 and 0.10nm, respectively. With respect to calculation results, to obtain solubilities within a standard error of 5%,  $N = 10^7$  insertions are required for all 250 snapshots from each of 20 independent configurations generated with the code developed according to self-avoid random walk algorithm.

#### S6.2.2 Biased Widom insertion method

As the contribution of insertions in zones already occupied by atoms is a negligible amount to the solubility, biased Widom insertions are performed only in place where there is free volume. A distribution map of the free volume is determined for a given snapshot first. Then insertions are performed at random positions (and orientations if applicable) within such regions. Finally the total solubility is computed after accounting for the bias that has been incurred.

The distribution map of the free volume is determined with the method presented in section S5, with H atoms placed in each grid point, instead of balls. H atoms have the smallest Lennard-Jones widths among all the units. As a result, eqn S1 becomes:

$$\Delta_{ij} = \gamma \left( \frac{\sigma_H + \sigma_j}{2} \right) - \left| r_{ij} \right| \tag{S11}$$

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where  $\sigma_{H}$  is the Lennard-Jones widths of H atom. The free-volume sites are those with  $\rho_{i}$  of eqn S2 being 0.

If 50 insertions are performed for each grid point that is defined as free volume, for a fractional free volume of 0.5%, this corresponds to  $2.5 \times 10^5$  insertions in total, 40 times fewer than that in the random Widom insertion method. Although it takes time to generate a free-volume distribution map, this is required only once per snapshot, as it is independent of the type of penetrants being inserted and ultimately the calculation speed is increased nearly by a factor of 40.

The bias introduced by performing insertions only in regions of free volume is accounted for by multiplying the solubility coefficients K by the probability of insertion in free volume, that is, the fractional free volume. For simulations performed in NVT ensembles, the probability is equal to the ratio of the number of free-volume sites to the number of total grid points,  $10^6$ .

#### S6.2.3 Determination of parameters for solubility calculation

Fig. S4(a) shows the relative standard error (standard error as a percentage of its average solubility coefficients) in the solubility coefficients of methane in PMP as a function of the number of starting configurations (p) and the number of snapshots for each configuration (s) for the unbiased Widom insertion method. Increasing p contributes the most rapid reduction in the relative standard error. Nevertheless, this has to be balanced against computational cost because equilibrating an independent configuration requires a 3ns simulation, whereas generating an additional snapshot takes only 20ps. Balancing these considerations while minimizing the relative standard error in solubility coefficients give the choice of p=20 and s=250, 250 snapshots for each of 20 independent configurations generated with the code developed according to self-avoid random walk algorithm.

# S6.2.4 Determination of the number of insertions needed

Fig. S4(b) presents the relative standard error in solubility of methane in PMP as a function of the number of insertions. For all the insertion tests, the number of independent initial configuration, p, is set to 20 and the number of snapshots for each, s, is set to 250.

According to Fig. S4(b), for unbiased Widom insertion method,  $10^7$  insertions are enough to ensure a relative standard error less than 5%, while for biased Widom insertion method,  $2.5 \times 10^5$  insertions are enough to ensure the same error.



Fig. S4. (a) The relative standard error (standard error as a percentage of its average solubility coefficients) in the solubility coefficients of methane in PMP as a function of p and s for the unbiased Widom insertion method; (b) the relative standard error in the solubility coefficients of methane in PMP as a function of the number of insertions. (Temperature: 300 K)



**Fig. S5.** Density profile of PE (a), PMP (b) and PDMS (c) along *z*-direction. (Temperature: 300 K)







**Fig. S6.** The snapshots of the gas-PE system (a), gas-PMP system (b) and gas-PDMS system (c) after the penetrants are put in the vacuum portion and the simulation production run has been done for 2ns (yellow molecule: methane, purple molecule: n-butane). (Temperature: 300 K)