Supporting Information for Analysis of Time-Varying, Stochastic Gas Transport through Graphene Membranes

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Simulation procedures

The positive simulations were generated with the three pore model and a set of parameters to give data sets qualitatively similar to the experimental data sets. At each time step, each pore in the "low" permeance state had a probability of randomly switching to the "high" permeance state, and each pore in its high permeance state had a distinct probably of randomly switching to its low permeance state. Once the pores are given a chance of switching states, the output permeance value is a sum of the low permeance states, plus the difference between the high and low permeance states for any pores in the high states; these equations are summarized in Table 1 of the main text. The probabilities for switching states, and the permeance difference between the high and low states are given in Table S1. The sum of the low states in these simulations was 0.109 $x10^{-23}$ mol s^{-1} Pa^{-1}. This process was repeated for each time point to generate data that adheres to the three pore model. Once the data at each point was generated, the permeance value of each point was averaged with its four nearest neighbors, both two before and after the point, to emulate the smoothing that results from fitting in the experimental data; a small amount of random normal noise, standard deviation 0.002 $x10^{-23}$ mol s^{-1} Pa^{-1}, was also added to each smoothed data point. The purpose of these simulations was to determine the how well a data set of limited size would conform to the relations of the three pore model.

Pore	Probability of switching to "high" permeance state at time step	Probability of switching to "low" permeance state at time step	Permeance difference between "high" and "low" states (10^{-23} mol s^{-1} Pa^{-1})
a	0.13296	0.01911	0.0829
b	0.06575	0.10354	0.1814
c	0.01191	0.08037	0.4042

Table S1. Simulation parameters for positive simulations following the three pore model.

Data sets from negative simulations were generated in a very similar manner as with the positive simulations. In these simulations, the system was given a probability to leave its current state at a given time step, and then could enter any of the other seven states. The relative probabilities and permeance values for the eight states were all distinct, and their averages were given by Table S2. When in use, the relative probabilities were renormalized to a sum of one. For the probability of entering the state, and the permeance value of the state, the parameters between simulation runs were varied by a multiplier centered at one with normal random deviation with standard deviations of 0.11 and 0.03 respectively. The probabilities of leaving a state were varied from state to state and across simulation runs according to equation (S1), where M was a constant corresponding to the average probability of leaving the state and r was a normal random number centered about zero with a standard deviation of 4.

$$\text{probability of leaving state} = \frac{2}{(1+r+M)} \qquad \text{(S1)}$$

At each time point, the current state's probability of leaving determined the random chance of leaving that state and transitioning to a new one; if leaving the state, the probabilities for entering the other seven states were renormalized to a sum of 1 and one state was randomly chosen,

weighted by the probabilities, for the new time point. This procedure was repeated for each time point in simulated data set. Parameters were randomized as described above between simulated data sets. Data points were smoothed with averaging and a small amount of random noise was added in the same manner as described above for positive simulations. The parameters for negative simulations were randomly varied because the purpose of negative simulations was to determine the likelihood that a data set of limited size that was not generated as a three pore system could be fit well to the constraints and modeling of a three pore system.

State	Average relative probability of entering state upon leaving another	Average probability of leaving state at time step	Permeance value of state (10^{-23} mol s^{-1} Pa^{-1})
1	0.3	0.0952	0.1000
2	0.25	0.1111	0.2143
3	0.2	0.1429	0.3286
4	0.15	0.1818	0.4429
5	0.09	0.1333	0.5571
6	0.05	0.1000	0.6714
7	0.08	0.1538	0.7857
8	0.05	0.1818	0.9000

Table S2. Average simulation parameters for randomized parameters in negative simulations having eight states unconstrained by the relations defining the three pore model. The relative probabilities of the entering a state were renormalized to a sum of one when used in simulations.

Additional Simulation Results

In addition to the simulations described in the main text to match the length and noise in the experimental data, we also performed simulations with the same parameters but with a much greater number of simulated data points, 7000 instead of 700, and without added smoothing.

Increasing the number of data points averages out the stochastic nature of the fluctuations and makes the observed values more consistent with the ideal relations defined in the main text. These simulations served to confirm that the "positive" simulations fit to the three pore model and that "negative" simulations are not accurately fit by the model by removing the other factors, small data sets and smoothing. Figure S1 gives the distribution of SSE_P, defined by equation (31) of the main text, for these simulations; it is consistent with expectations, in that the positive simulations can be fit near perfectly (sum squared error near zero), and the distinction between the positive and negative sets is much clearer.

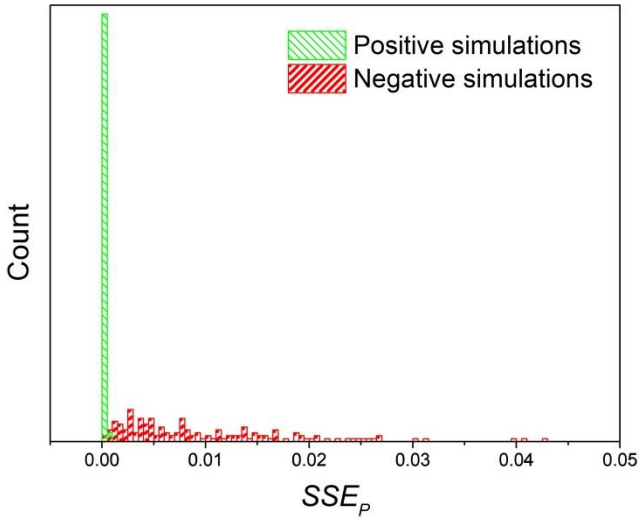

Figure S1. Histogram of the sum squared errors (SSE_P) when fitting fraction of time spent to three pore model for unsmoothed, 7000-point simulations. Positive simulations are generated by a mock three pore system; negative simulations are generated with randomized parameters for eight states unconstrained by three pore relations.