Single-Pore Model: a Simplified Diffusion Simulation

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A Monte Carlo simulation of Knudsen diffusion in a porous solid is conducted with the single-pore model (SPM). It is intended to be the simplest model possible, while still accounting for measurable pore geometries and topologies and the effects of network structures. Nominal diffusion parameters calculated with this first-generation SPM compare favorably with more complex models that have been published.

Background

A common method of simulating gas diffusion through porous solids is to shoot test molecules through a computer-generated pore structure and measure their maximum penetration depth. Evans et al. (1980) demonstrated this technique for Knudsen diffusion through a random assembly of spheres which has the appearance of a real porous structure, albeit with convex surfaces only. The process is much like a complex pinball game except that the reflections from a solid surface are randomly directed and no energy is lost in the collision.

In the past decade, many researchers have applied the same technique to increasingly complex porous structures. Abbasi et al. (1983) extended the above simulation to ordinary diffusion. Nakano and Evans (1983) constructed a simulated Swiss cheese solid where the pores are all concave. Nakano et al. (1987) compared diffusion in single long pores whose walls were straight (capillary) or necked in a convex (cannonball) or concave (Swiss cheese) fashion. Burganos and Sotirchos (1988) studied diffusion in randomly overlapping cylindrical capillaries and later (1989) added overlapping spherical cavities to the structure. Melkote and Jensen (1989) essentially inverted this structure to represent fibrous media, where the capillaries are solid and diffusion occurs in the interfiber space. Most of these studies were for Knudsen diffusion; ordinary diffusion adds some complexity to the model and certainly increases the execution time due to the increased number of steps.

These models predicted effective diffusivities and other diffusion parameters for real solids. Of course, the agreement will be best when the simulated and real solid's physical parameters match. These parameters could include: porosity, pore-size distribution, throat-size distribution, pore shape, and connectivity. More than one size distribution can occur even for bimodal solids.

The ultimate goal would be to predict effective diffusivity from pore structure measurements of real solids without having to conduct actual diffusion experiments (which are by no means simple nor is their interpretation straightforward). An obvious problem is that the sophistication of the models exceeds the ability of pore characterization techniques to supply meaningful parameters. For instance, the meaning of pore size distributions from mercury porosimetry has been an active area of research for some time (Conner et al., 1986). We are not aware of any routine techniques to measure connectivity or pore shape. Even the deceptively simple question of what constitutes a pore is still being discussed (Melkote and Jensen, 1989).

Simulations using arrays of interconnected pores have shown the importance of network effects. Therefore, most computer simulations involve two major steps: the construction of a complex porous solid composed of interconnected voids and then repeated tests of molecules allowed to traverse the solid. One can imagine that the simulations require a fair amount of computer memory and execution time and the routines are complex. However, the difference in effective diffusivity at constant porosity calculated by some models is small (Nakano and Evans, 1983) and probably within the accuracy of the physical parameters needed as inputs. Could a simpler, rather than more complex, model be developed which still accounts for network effects?

The model presented here is called the single-pore model. It utilizes what may be the ultimate in periodic boundary conditions: only one pore is created at a time and a new pore is generated whenever a test molecule passes out through its boundaries. This has several major programming and modeling advantages which, along with limitations, will be discussed subsequently.

The first-generation SPM will be modified and tested for other geometries and topologies in future work.

Single-Pore Model

Most pore spaces consist of relatively large cavities (pores) interconnected by smaller constrictions (throats). The pore space can be approximated by the cubic network of pores and throats as was done by Conner et al. (1986) in demonstrating

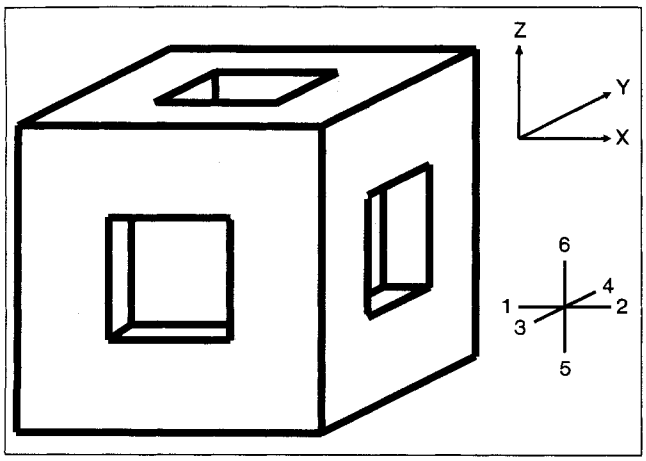

Figure 1. SPM unit cell.

The spatial orientation and the throat numbering system are shown on right.

the network effects occurring during mercury porosimetry. Using a cubic network implies two important assumptions: the average connectivity is six and the throats are oriented in the X, Y, and Z directions only. How limiting and inflexible are these restrictions?

The first generation SPM void is shown in Figure 1. The entire structure is called the cell and is of unit length. The void consists of a square pore with six square throats. The combined volume of the pore and throats is the porosity. This allows construction of any porosity, while pore and throat sizes are obtained by scaling the cell length. Note that the flat surfaces are intermediate between the usual concave or convex surfaces used in previous models.

These could be stacked in a three-dimensional array as would be more typical in pore-structure modeling. A novel feature of the SPM is that only one cell at a time is considered. Once a traversing molecule passes through any of the planes bounding the cell, a new cell is created at that position and the old one is discarded. There should be no impact on the calculated effective diffusivity whether or not memory of the void structure is retained.

The porous solid is assumed to be a semi-infinite slab with the diffusing molecule traveling from the entry face at $X=0$ to some maximum depth before it eventually turns around and exits the entry face. The molecule is allowed to visit as many voids in the Y and Z directions as required. Only the maximum penetration depth in the X direction needs to be saved to calculate the effective diffusivity.

Knudsen Diffusion Simulation

The simulation of Knudsen diffusion within the SPM starts by randomly choosing a pore size and six throat sizes around mean values that will yield the desired porosity. The input parameters are the porosity, throat-to-pore size ratio (these fix the pore and throat sizes), and the standard deviation of the size distributions. Conveniently, these parameters can all be measured with mercury porosimetry (Conner et al., 1986). Parameters that are more difficult to measure, such as pore shape and connectivity, are implicit and can be adjusted only by varying the geometry and topology of the model.

A molecule is randomly placed in throat #1 at the $X = 0$ face. It is then randomly assigned polar and azimuthal angles (within limits defined by the face from which it originates) and travels until it intersects a solid wall or an opening. If within a throat, two openings exist: the external opening at the cell boundary and an internal opening accessing the pore. Within the pore there are six openings accessing the six throats. If the molecule intersects an opening, it continues into the new void space with the same direction angles. If it intersects a solid wall, new direction angles are chosen away from the wall. If an intersected opening happens to be at the cell boundary, a new cell is created and the old one is discarded.

The polar and azimuthal direction angles are both randomly chosen from a uniform distribution. Other researchers sometimes use a cosine probability distribution for the azimuthal angle which is appropriate for smooth surfaces rather than rough surfaces; it is a matter of assumption and probably does not impact the calculation of effective diffusivity significantly. Depending on the face of origin, the angles are bounded by the restriction that the molecule not pass through the wall. The rectangular coordinates of the next intersection are given by:

$$X = C\sin\Phi\cos\Theta \tag{1}$$

$$Y = C\sin\Phi\sin\Theta \tag{2}$$

$$Z = C\cos\Phi \tag{3}$$

Only the faces of the one SPM void need be tested for intersection with this model.

The simulation only remembers the depth of penetration in the X direction. Actually, other data such as total number of voids visited, number of bounces, and overall travel length are also counted, but are not necessary for calculating the effective diffusivity.

Calculation of Effective Diffusivity

As done by many other researchers, the effective diffusivity is calculated by comparing the fractions of molecules transmitted to increasing depths within the solid. Evans et al. (1980) showed that the fraction of molecules transmitted to a certain depth is proportional to the reciprocal penetration depth with a slope related to the effective diffusivity.

$$f_T = 4D_K^e\sqrt{\frac{\pi M}{8RT}}\,(1/L) \tag{4}$$

As shown by Abbasi et al. (1983), the fraction transmitted must be reduced to account for those molecules outside the solid that do not hit a void opening. This is because the flux equation used to derive Eq. 4 represents the total number of molecules that hit the solid, yet the SPM simulation places all molecules in a throat. A simple entrance correction factor for this is the fraction of throat area on the surface, t^2.

The penetration depth is determined by counting the number of cells traveled in the X direction and multiplying by the cell length (in this work it is of nominal unit length). Therefore, all molecules penetrate to at least a depth of one before the entrance correction factor is applied. A time-saving feature is to only allow the molecule to penetrate a certain distance—in

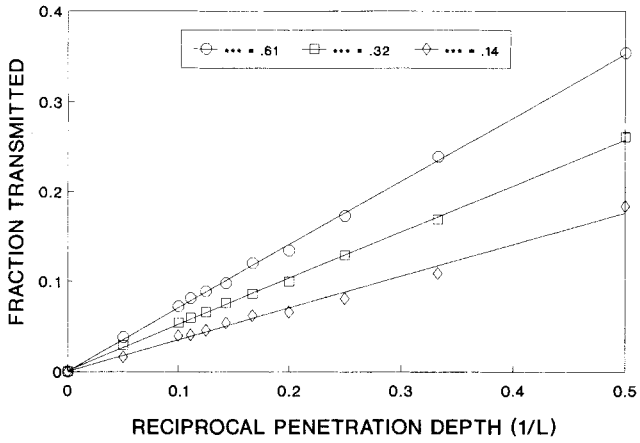

Figure 2. Knudsen diffusion simulation using SPM cells with various porosities and a constant throat to pore size ratio of 0.5.

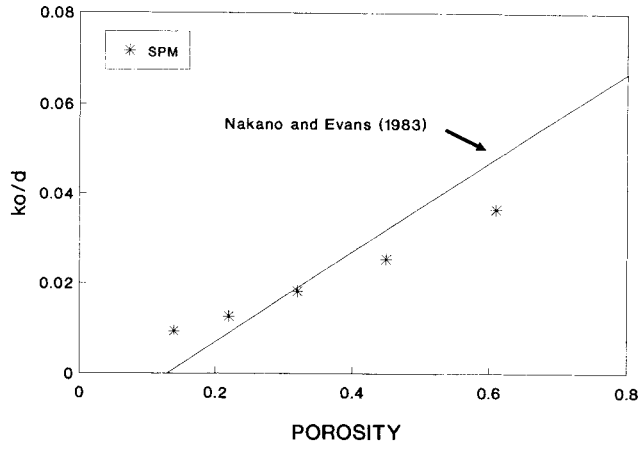

Figure 4. Knudsen diffusion length parameter calculated: the SPM vs. empirical Eq. 10 in Nakano and Evans (1983).

this study 20 cells deep. The fraction transmitted that far is very small, and enough points have been measured to calculate an accurate slope from Eq. 4. The total number of steps increases dramatically as the molecule penetrates deeper into the solid.

Results and Discussion

Figures 2 and 3 show the fraction transmitted vs. reciprocal penetration depth for solids with a nominal cell length of one. The entrance correction factor is not yet applied to the fraction transmitted, so all molecules penetrate to a depth of one cell. Effective diffusivities for actual solids could be calculated by scaling the cell size so that the pores and throats are of sizes found by mercury porosimetry.

Figure 2 shows the results for solids of different porosities and a constant throat to pore size ratio of 0.5. As expected, the effective diffusivity (proportional to the slope) varies directly with the porosity. The pore and throat sizes can be assigned at random from a distribution but this is not done here for simplicity. Tests using distributions with standard deviations as large as 40% of the mean showed no significant effect on the results.

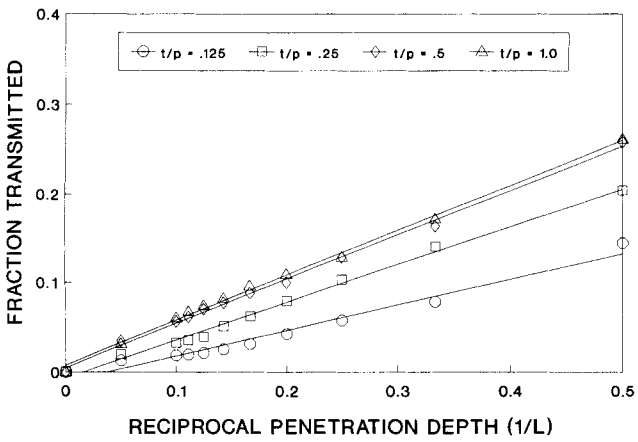

Figure 3. Knudsen diffusion simulation using SPM cells with various throat to pore size ratios and a constant porosity of 0.32.

The results in Figure 3 are for a constant porosity of 0.32 and various pore to throat size ratios. Necking down the throats decreases the effective diffusivity (decreases the slope) in agreement with Nakano et al. (1987).

Evans et al. (1980) derived an expression for a Knudsen diffusion length parameter characteristic of a given porous solid

$$k_0 = \frac{3}{16}(f_T L) \tag{5}$$

where k_0 can be related to the effective Knudsen diffusivity by (Mason et al., 1967):

$$D_K^e = \frac{4}{3}\sqrt{\frac{8RT}{\pi M}}\, k_0 \tag{6}$$

They found for convex and concave pore geometries alike that at constant porosity k_0/d was identical, where d is a mean pore size.

The SPM can be compared to some previously published models by calculating k_0/d. The SPM distinguishes between pores and throats, so the appropriate mean pore size to use is not clear. The parameter is calculated here using the average of the pore and throat sizes as the mean pore size and applying the entrance correction factor:

$$k_0/d = \frac{3}{16}(f_T L)t^2/(p+t)/2 \tag{7}$$

The parameter k_0/d is plotted in Figure 4 for the variable porosity experiment along with the empirical equation determined by Nakano and Evans (1983), which was found to represent real and simulated porous solids. The parameter was also calculated for the variable throat to pore-size ratio experiment and found to be a nearly constant 0.018. The favorable comparison is made simply to verify that the SPM can indeed produce reasonable estimates of the nominal effective

diffusivity. It must be recognized that the absolute value is highly dependent on the assumed entrance correction factor and characteristic length.

There are several limitations to this first-generation SPM as with any specific model. These concern the fixed geometry and topology of the network structure. The connectivity is a constant six and the cells are regularly aligned. As shown by Reyes and Jensen (1986), connectivity is a major factor affecting diffusivity. The model, however, presents an opportunity to explicitly study the effects of connectivity, since it can be easily varied by randomly blocking off throats. This is related to another limitation that all pores are accessible no matter what the porosity is. Once the throats or pores are randomly blocked to vary connectivity, the structure should exhibit the usual percolation threshold for a cubic structure. The cells do not have to be regularly aligned; they can be positioned off-center. In fact, one advantage of the SPM's lack of memory is that no concern is warranted about how the cells all fit together. The geometry of the cells can also be quite flexible. For instance, the cell and its voids can be stretched to model fibrous media or flattened to model plate-like structures.

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Notation

C = length of travel
d = mean pore size
D_K = Knudsen diffusivity
f_T = fraction transmitted to depth L
k_0 = Knudsen diffusion characteristic length
K = entrance correction factor
L = penetration depth
M = molecular weight
p = pore size
R = gas constant
t = throat size
T = temperature
X, Y, Z = spatial coordinates

Greek letters

ϵ = porosity
Φ = azimuthal angle
Θ = polar angle

Superscript

e = effective

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