Knudsen Diffusion in Ordered Sphere Packings

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Knudsen diffusion of gases through porous media is of interest in a number of applications where transport is dominated by molecule-pore wall interactions. The diffusivity in straight uniform cylindrical pores is given as (Knudsen, 1928):

$$D_k = (4r/3)(2RT/\pi MW)^{1/2}[(2-f)/f] \qquad (1)$$

For transport in porous media, an effective diffusivity is usually defined as (Satterfield, 1970):

$$D_e = \epsilon D_k/\tau \qquad (2)$$

The tortuosity factor, τ, is a correction factor that reduces the effective diffusivity due to numerous factors including pore cross-sectional shape, pore size distribution, direction orientation, degree of interconnectivity, and pore constrictions. The magnitude of τ cannot be predicted from first principles, but is usually found to vary from 1 to 8 when measured experimentally.

Sphere packings are used often as model porous media for transport studies. Several studies of bulk diffusion in beds of randomly packed uniform spheres have been reported. Currie (1960) measured hydrogen diffusion in smooth glass sphere packings of three different sphere diameters. Sample porosity was in the range of 0.375 to 0.405 and the tortuosity was found to be 1.48 ± 0.02. For packings of sand particles with wider particle size distribution and more surface roughness, porosity varied from 0.355 to 0.424 and τ was 1.60 ± 0.03. For glass spheres with a diameter 1.0–1.25 mm and porosity of 0.43, Hoogschagen (1955) reports a τ of 1.42.

It is apparent that τ is a function of how r is defined for a given solid when Knudsen transport is considered. However, defining the mean pore radius for porous media is not straightforward (Wang and Smith, 1983). The application of mercury porosimetry or capillary condensation techniques will provide information related to the size of the smallest restriction in a particular pore (Lowell, 1979). In contrast, defining the mean pore radius as twice the ratio of pore volume to surface area, as Satterfield (1970) suggests, is a measure of the entire pore network. Smith and Huizenga (1984) have simulated Knudsen diffusion in random beds of uniform spheres. Tortuosity values of 1.40 and 1.72 were calculated for porosities of 0.386 and 0.483, respectively, when the mean pore size ($\bar{r}$) is defined as twice the the ratio of pore volume to surface area. For uniform smooth spheres, $\bar{r}$, is a function of ϵ and sphere size only:

$$\bar{r} = (2/3)[\epsilon/(1-\epsilon)]r_s \qquad (3)$$

Huizenga and Smith (1986) have measured Knudsen diffusion through random assemblages of uniform spheres. The average porosity was 0.363 ± 0.030 and tortuosity factors were found to range from 1.45 to 1.51 for four non-adsorbing gases.

In this work, experimental measurements of Knudsen diffusion through *ordered* assemblages of uniform spheres are reported for the first time. These materials have the advantage that transport in pores of nonuniform cross-section/shape may be studied with a minimum of complications due to pore size distributions (i.e., the pores are not cylindrical but of known shape and all the pores are of similar size and shape).

Experimental

Monodisperse silica spheres were synthesized in a manner similar to a process described by Stober and Fink (1968). Tetraethyl orthosilicate (TEOS) solutions of about 0.28 M in ethyl alcohol were hydrolyzed by the addition of an NH_4OH-ethyl alcohol solution. Precipitation of monodisperse silica spheres was completed by stirring overnight. Powder was recovered by filtering and subsequent drying at ≈373 K. The recov-

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ered powder was dispersed in water with ultrasound and the suspension pH was kept several pH units above or below the isoelectric point. The dispersion (5–10 wt. % solids) was centrifuged to form ordered compacts. After the top clear liquid layer was removed, the ordered compacts were air dried at room temperature for several days and then heat-treated at ≈473 K for 2 hours.

SEM micrographs of the fracture surfaces in the compacts have been taken after gold coating. TEM micrographs of the dispersed powders were taken for size determination. Powder density was determined by helium pycnometry. Mercury porosimetry runs were undertaken with an Autoscan 33 mercury porosimeter. Nitrogen adsorption was measured with a Quantachrome Autosorb-1 analyzer. D_e for nitrogen at 296 K was determined using a flow apparatus described elsewhere (Huizenga and Smith, 1986).

Results and Discussion

A SEM cross section of a pellet fabricated from 272 nm spheres is shown in Figure 1. This figure clearly shows that the individual spheres are intact and a high degree of ordering exists. It should be noted that the cross section was taken at an internal fracture plane, which explains the three-dimensional effect apparent in the figure. The true density of the powder was found to be 2.12 g/cm^3 ± 1%. TEM size analysis resulted in average sphere diameters of 272 nm and 119 nm for the two different particle sizes used. For 150 measured particles, the size standard deviation for the 272 nm and 119 nm spheres was 5 and 17%, respectively.

To insure that D_e measurements are in the Knudsen regime, experiments were conducted over an inlet pressure range of 13.3 to 53.2 kPa. For all pellets studied, D_e was essentially independent of pressure. This indicates that diffusion is in the Knudsen regime and is a strong indication that no measurable surface transport occurred. In order to examine the reproducibility of our diffusion measurement scheme, a duplicate pellet was fabricated from the 272 nm batch of spheres. Effective diffusivities for the two different 272 nm pellets were found to be 0.0297 and 0.0288 cm^2/s. For the 119 nm pellet, D_e was 0.0133 cm^2/s.

Mercury porosimetry and N_2 desorption pore size distributions are shown in Figure 2. For a given sample, the two techniques demonstrate similar size distribution shape but nitrogen desorption predicts a distribution shifted to larger pore size. This discrepancy could be the result of contact angle/surface tension uncertainty, pore shape effects, network effects, and/or sample compression. BET surface area, geometric surface area, and porosity of each pellet is presented in Table 1. The differences in BET and geometric surface area can be attributed to small-scale surface roughness (Wright et al., 1987). The porosities are calculated from the total pore volume obtained by N_2 condensation.

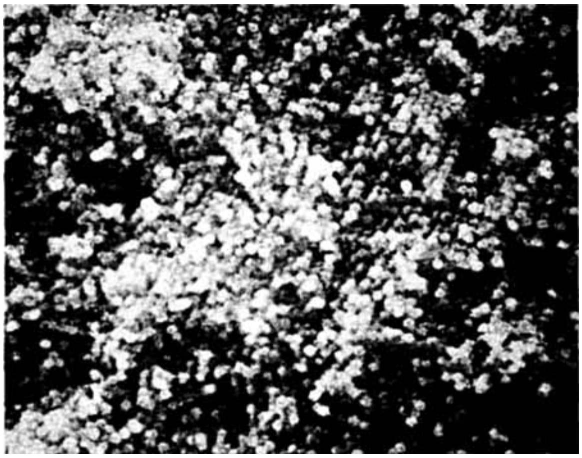

Figure 1. SEM cross section of 272 nm ordered packing.

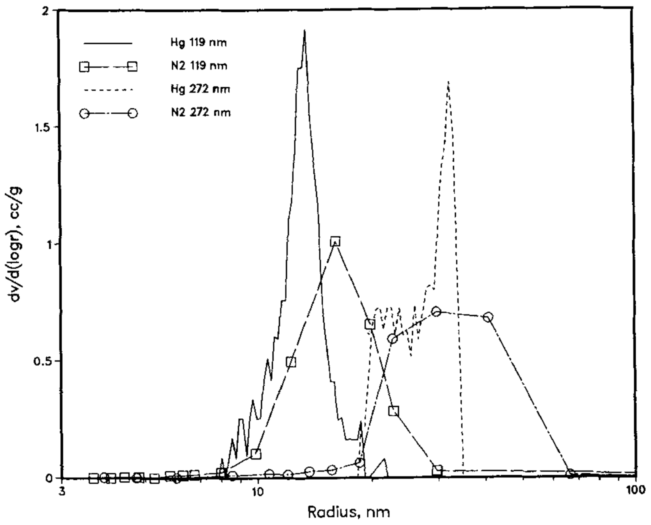

Figure 2. Pore-size distributions for 272 and 119 nm ordered packings.

For porous media, a number of different definitions for $\bar{r}$ may be used. Table 2 is a summary of the calculated tortuosities with the corresponding radius definition. These definitions include the hydraulic radius for smooth spheres (Eq. 3), the actual hydraulic radius, and the maximum in the mercury porosimetry size distribution.

If one invokes a geometric similarity argument for pellets produced from ordered packings of different sphere sizes, the value of the tortuosity factor should be independent of sphere size. The differences in τ when Eq. 3 is used are the consequence of assuming smooth spherical particles. When 2(N_2 PV)/BET SA is used to define the pore radius, which takes into account the surface roughness of the particles, the variation in τ becomes minimal. The porosimetry data, which is a measurement of the smallest restriction in a particular pore, also shows only a slight variation in τ. The fact that the last two radius definitions produce similar τ's is not physically significant since it is a result of two different independent phenomena (surface roughness versus pore constriction). The small-scale (angstroms) roughness will be probed by nitrogen adsorption, but not by mercury penetration.

Table 1. Physical Properties of Ordered Compacts

Pellet	BET Surface Area (m^2/g)	Geometric Surface Area (m^2/g)	ϵ
272-1	13.3	10.4	0.339
272-2	15.4	10.4	0.356
119	30.7	21.8	0.348

Table 2. Experimental Tortuosity Factors for Ordered Compacts

$\bar{r}$ Definition	Pellet	$\bar{r}$(nm)	τ
Equation 3	272-1	46.5	1.68
	272-2	49.7	1.95
	119	21.2	1.75
2(N_2PV)/BET SA	272-1	36.3	1.31
	272-2	33.9	1.33
	119	16.4	1.36
Hg Porosimetry	272-1	36.7	1.32
	272-2	34.6	1.35
	119	16.3	1.35

Table 3. Theoretical Constriction Factors for Ordered Packings

Particle Size (nm)	Cavity Size (nm)	Throat Size (nm)	β	τ
272	39.3	20.9*	3.5	1.9
		30.3–35.8**	1.7–1.2	1.0–1.3
119	18.9	10.1*	3.5	1.9
		14.6–17.2**	1.7–1.2	1.0–1.3

*Smallest.
**Range.

Prior work on these ordered silica compacts (Ciftcioglu et al., 1987) shows a packing efficiency that varies between 66 to 69%, for which a combination of tetragonal and body-centered cubic structures are representative of the ordering nature. Also presented in that work are the theoretical sizes of throats and pores obtained from the sizes of inscribed spheres in the constrictions and cavities of the ordered packings. Because the ordering is a combination of tetragonal and body-centered cubic structures, a range of throat sizes are presented along with the smallest throat size possible. The smallest throat size corresponds to a face-centered cubic structure. Smith (1986) has studied Knudsen diffusion in a single constricted pore using Monte Carlo techniques. He defines a parameter, β, as the maximum cross-sectional area/minimum cross-sectional area and plots the constriction factor as a function of β for $\bar{r}$ defined as the hydraulic radius. If the pores are all aligned in the direction of flow and are all uniform, the inverse of the constriction factor should equal τ. This value should be a reasonable lower bound for the materials studied in this work. Knowing the theoretical sizes of throats and pores, β's were calculated and the theoretical tortuosity factors found. Table 3 presents these tortuosity factors along with the theoretical sizes of throats and pores.

It is expected that few of the pores will correspond to the smallest throat size since this is the result of face-centered packing for which the pore volume should be small as compared to the total pore volume. Taking this into account, the experimental τ's seem to agree reasonably with the τ's calculated from the upper limit throat size value. It should be noted that even though the packing is ordered, the theoretical τ's are a lower limit on the magnitude of τ since the direction of flow may not be aligned exactly with the ordering, causing a slight increase in τ.

Notation

D_k = Knudsen diffusivity
f = sticking coefficient
MW = gas molecular weight
r = pore radius
$\bar{r}$ = mean pore radius
r_s = solid sphere radius
R = gas constant
T = temperature

Greek letters

β = maximum pore cross-sectional area/minimum cross-sectional area
ϵ = porosity
τ = tortuosity factor

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