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NOTE

EVALUATION OF THE PORE SIZE DISTRIBUTION IN MERCURY POROSIMETRY USING COMPUTER SIMULATIONS OF POROUS MEDIA

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Abstract—The pore size distribution calculated using the Washburn equation was evaluated. The pore-sphere network was selected as a model for porous media since this model could qualitatively describe hysteresis and retention phenomena. 3-Dimensional lattices of square configuration were considered with normal, skewed and bimodal pore size distributions. The calculated pore size distribution was accurate up to the average size pores, but significantly different for larger pores. The fraction of average size pores was always exaggerated. Pore connectivity had larger influence on the pore size distribution than the lattice structures.

INTRODUCTION

Porous structure can be found everywhere in nature and has long been an important subject of research in a variety of fields. However, scientific basis of porous structures has not been firmly established yet. One significant problem is that we cannot characterize porous structures with simple mathematical expressions. Although porosity and pore size distribution are frequently used as independent variables in such expressions, shapes and connectivities of pores should not be neglected to have accurate description of porous structures. To make matters worse, aforementioned variables are hard to measure and even not clear to define.

Mercury porosimetry is frequently used to analyse pore size distribution of porous media. In the experiment, mercury penetrates into and retracts from the porous samples according to the applied pressure, resulting in the pressure-volume (P-V) curve. Pore size distribution is calculated from this P-V curve using the Washburn equation. The inherent assumption of the Washburn equation is that the pores are straight cylinders and do not intersect each other. However, the pores of real porous media have varying diameters and interconnectedness is a distinctive characteristics of most porous media. Therefore, the calculated pore size distribution using Washburn equation usually differs from that of real porous media and its use is limited to provide a relative information which is generated from a standard method.

In the present paper, we extend our previous work for 2-dimensional lattices [1] to 3-dimensional lattices. As pointed out by Dullien [2], 3-dimensional structure is not a simple extension of 2-dimensional structure, but has fundamental differences since two continuous phases can be present simultaneously.

SELECTION OF A MODEL FOR POROUS MEDIA

To proceed computer simulations of mercury porosimetry, we need a model of porous media which is simple enough to be described by mathematical expressions (thus, pore size distribution can be unambiguously defined) and still complex enough to provide the important characteristics of real porous structures. To find an "appropriate" model, we first define what are the important characteristics of porous media. In this paper, a model which showed characteristic behaviors of the P-V curves obtained from penetration-retraction experiment-hysteresis, entrapment and S-shape curves-was considered that it had all the essential characteristics of porous media.

The most sophisticated model of porous media may be the pore-throat network model [3] [The word

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"pore" means a spherical void at the intersections of cylindrical "throats" in this model. Therefore, "throats" are equivalent to "pores" of the pore-network model [4]. To avoid confusions in further discussions, we will use the term "pore-sphere network" instead of pore-throat network. With this new terminology, pores and spheres mean the cylindrical voids and the spherical voids at the intersection of cylindrical pores, respectively.]. The merits of this model were discussed in our previous work [1]. Therefore, we chose the pore-sphere network model in our 3-dimensional simulations as a model for porous media.

GENERATION OF PORE-SPHERE NETWORK STRUCTURE

To generate pore-sphere network structure, a reasonable recipe to distribute various sizes of pores and spheres in a given dimensional space is required. Since there are two constituents, pores and spheres, in pore-sphere network, two distributions are required in this model. The pore size distribution and the sphere size distribution can be completely separated or partially overlaped in view of their size ranges. In this paper, we have used the same method described in our previous work [1], which correlates two size distributions through the introduction of a simple constraint that the diameter of a sphere should be larger than any of the diameters of the pores which intersect. Therefore, sphere size distribution cannot be chosen independent of pore size distribution and our method is consistent with the method of Mayagoita et al. [5] in this sense. This constraint seems arbitrary, but is nearly true in most real porous structures.

In our procedure, pore size distribution was generated first. Three types of pore size distributions were considered; normal distribution, bimodal distribution and skewed distribution. Once the pore size distribution was determined, these pores were distributed randomly over the available dimensional space. Five different configurations were generated for every given pore size distribution to minimize the effect of a specific spacial configuration. Note that different configurations alter the sphere size distribution though the pore size distribution is identical.

We considered 3-dimensional space, but only for the square lattice where the coordinated pores were six. As pointed out by Androutsopoulos and Mann [4], it is the connectivity of pores, not the lattice type, that has strong effect on the penetration-retraction simulations. For this reason and computational simplicity, random lattice structure was not investigated.

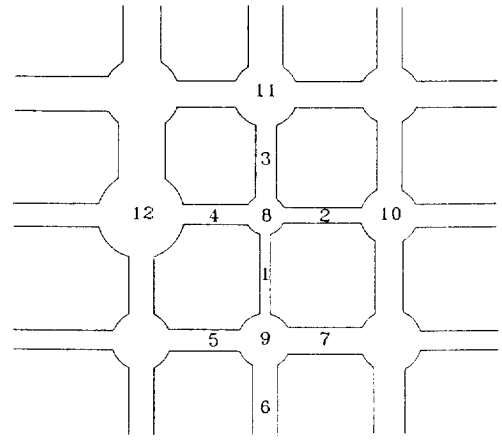

Fig. 1. Schematic diagram for the retraction process in the pore-sphere network.

ALGORITHM FOR THE PENETRATION -RETRACTION SIMULATIONS

Computer simulation of mercury porosimetry we performed is composed of the penetration simulation and the retraction simulation. Details of the algorithms were same as our previous work [1]. These algorithms are equally applicable to square and triangular lattices, and 2-dimensional or 3-dimensional networks. Two things should be mentioned here.

(1) Once all pores and spheres are filled, the applied pressure is lowered. The retraction of mercury starts at the pores which has been filled last and has the smallest diameter. This procedure is based on the hypothesis of coalescence and the starting point of mercury retraction is called the air pocket. Another procedure called the hypothesis of no coalescence has been proposed [6, 7]. In this procedure, multiple air pockets appear during penetration simulations. In our simulations, we accepted the hypothesis of coalescence because mercury porosimetry experiment usually require evacuation step before penetration. In fact, Park and Ihm [6] showed that both of these hypotheses could generate retraction curves which showed hysteresis and retention.

(2) Mechanism of mercury retraction can be explained with Figure 1. Portsmouth and Gladden [8] suggested 3 different mechanisms: (1) In mechanism 1, the evacuation of pores and spheres was proceeded in the order of pore 1, sphere 8, sphere 9, pore 2, sphere 10, pore 4, sphere 12, etc. (2) In mechanism 2, the order was pore 1, pore 2, pore 4-sphere 8, pore 3, etc. (3) Mechanism 3 differs from mechanism 1 only

with respect to the nature of the seeding site for extrusion.

In our simulation, we adopted a different mechanism for mercury retraction. Pore 1 has the smallest diameter and retraction of mercury evacuates pore 1. New mercury-vapor interfaces appear at pore 1-sphere 8 and pore 1-sphere 9. Up to here, this mechanism is same as the mechanism 2 of Portsmouth and Gladden [8]. The applied pressure is then gradually lowered. No mercury is retracted until the applied pressure is low enough to evacuate sphere 8. After evacuation of sphere 8, three new interfaces appear at pore 2-sphere 8, pore 3-sphere 8 and pore 4-sphere 8. The interface at pore 1-sphere 9 remains because sphere 9 has larger diameter than sphere 8. Therefore, our mechanism is a hybrid of mechanism 1 and mechanism 2 of Portsmouth and Gladden [8]. They asserted that mechanism 2 is correct because it successfully evacuates all mercury in case of same pore diameters, but this is also true with our mechanism. In fact, their mechanism 2 does not seem persuasive to us because the pore which have no interface and no air pocket can be evacuated.

DISCUSSIONS ON THE SIMULATION RESULTS

Computer simulations were performed using algorithm of previous section on the 3-dimensional square lattices. Results of such simulations are acceptable only when the models are sufficiently realistic. Since real porous media contains enormous number of pores and spheres, computer simulations have to be performed on large lattices. Results obtained from small systems reflect the effect of system boundaries. Introduction of periodic boundary condition may improve the credibility of simulations, but implementation of it is not obvious for mercury penetration and retraction. Few of reported simulations seriously considered system size effect.

Mercury retention occurs not only due to the presence of ink-bottle network, but also due to the disconnection of retraction paths because some pores in the path are already evacuated. In small systems, this is hardly possible since large fraction of pores are at the surface. In this paper, all simulations were performed on the lattice of 100×100 to avoid the unwanted surface effect.

Figures 2-4 show the results of our simulations. Each figure contains the results for 5 different configurations of same pore size distribution. Difference in configurations affects the amount of retention, resulting in multiple retraction lines. This is partly because different configurations generate different sphere size distributions, but mostly because different configurations alter the retraction paths. In fact, we plotted only one sphere size distribution in Figures 2-4 since the differences in the sphere size distributions were very small.

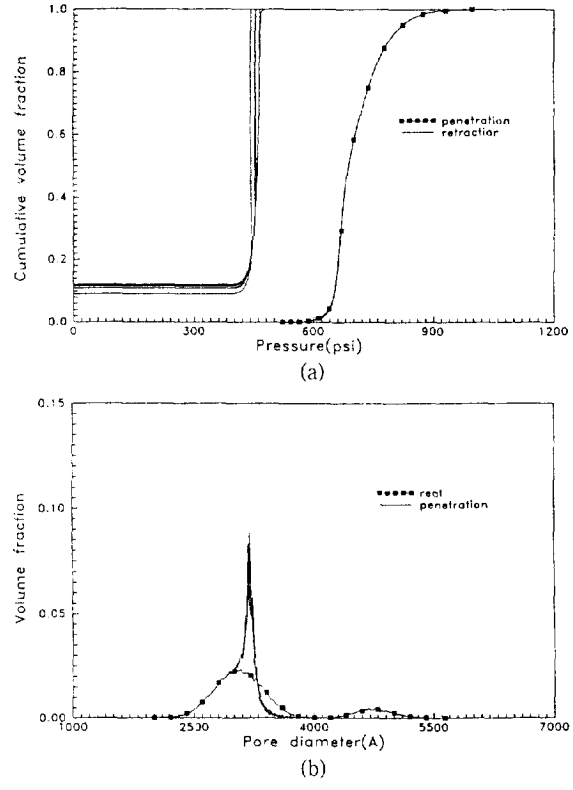

Fig. 2. (a) Pressure-volume curves (normal pore size distribution with $\mu = 3000$ Å, $\sigma = 300$ Å), (b) Comparison of pore size distributions.

It should be noted that the points of inflection on the penetration curve and the retraction curve precisely match the average pore diameter and the average sphere diameter. This fact seems quite reasonable since the limiting steps of penetration and retraction occur at pores and spheres, respectively. The calculated pore size distributions were obtained using the Washburn equation from the penetration part of the P-V curves and denoted as "penetration" in volume fraction-pore diameter plots, so the presence of spheres was not detected in the "penetration" pore size distribution. The known pore size distribution was denoted as "real" for comparison. Note that in Figures 2-4, the horizontal axes of the P-V diagrams are con-

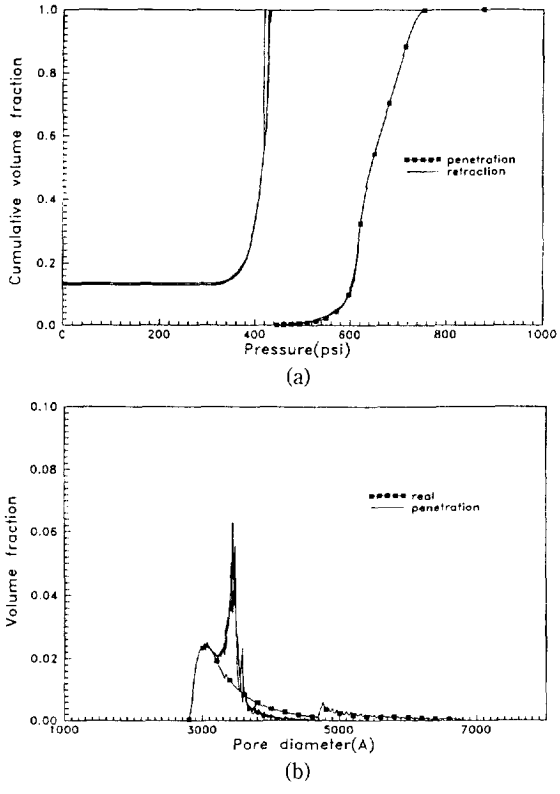

Fig. 3. (a) Pressure-volume curves (skew-left pore size distribution with $\mu=3000$ Å), (b) Comparison of pore size distributions.

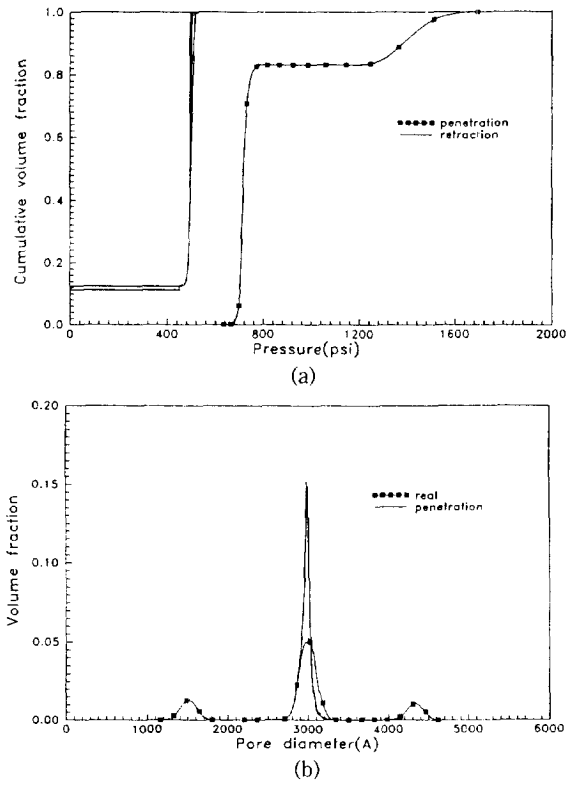

Fig. 4. (a) Pressure-volume curves (bimodal pore size distribution with $\mu1=3000$ Å, $\mu2=1500$ Å, $\sigma=300$ Å), (b) Comparison of pore size distributions.

verted to the corresponding pore diameters using the Washburn equation.

Figure 2 is the results of simulations with the normal pore size distributions. Here, we used the word "normal distribution" only considering the pores. Since the size of a sphere is determined by the sizes of intersecting pores at that point, the size distribution of spheres cannot be a priori defined with a mathematical distribution. We can observe an interesting fact that the "penetration" pore size distribution correctly estimates the average pore diameter, but it exaggerated the fraction of pores in the mean at the expense of bigger pores. This is due to the side-by-side occurence of small pores and big spheres.

The log-normal distribution of pores were investigated in Figure 3. The distribution was skewed to the smaller pores. The pore size distributions were given as Eq. (1)

$$F(D)=\frac{1}{D\sigma(2\pi)^{1/2}}\exp\left[-\frac{(\ln D-\mu)^2}{2\sigma^2}\right] \quad (1)$$

with $\mu=4.5$ and $\sigma=0.8$, and the function truncated at 50 Å. Though S shape of the penetration curve is similar to that of normal distribution, starting tail is longer than ending tail. This is a direct consequence of the skewed pore size distribution; smaller pores are dominant. The average pore diameter of the "penetration" pore size distribution was larger than the mode of "real" pore size distribution. Amplification of the fraction at the average pore diameter and deamplification of the fractions for larger pores were also evident. Fractions of the pores which have much smaller diameters than the average pore diameter were almost exactly reproduced. Note also that the "penetration" pore size distribution has inflection points.

Porous materials may contain more than one pore size distribution. These distributions may or may not overlap. Commercial catalyst pellets have two discrete pore size distributions for the macropores and the micropores. In Figure 4, we investigated the porous media which have bimodal pore size distribution with negligible overlap. The average pore diameters were

1500 Å and 3000 Å, and standard deviation was 150 Å for both distributions. Two plateaus appear on the penetration curve. Note that the retraction curves have no intermediate retention which was observed in the work of Park and Ihm [6]. Since the pores of two distributions were randomly distributed in a given lattice, only one sphere size distribution existed and intermediate retention could not appear in our simulations.

One interesting fact we should point out is that the "penetration" pore size distribution for the 3-dimensional square network (connectivity=6) in Figure 4 is closer to that of the 2-dimensional triangular network (connectivity=6) than that of the 2-dimensional square network (connectivity=4). This may be an indication of the importance of pore connectivity over lattice structures.

Real materials always have 3-dimensional structures. As pointed out by Dullien [2], 3-dimensional structure is not a simple extension of 2-dimensional structure, but has fundamental differences. Generally speaking, however, no qualitative changes were observed other than the amount of retentions; they went down to 10 % for normal, bimodal and skewed distributions. This is another result of increased connectivities in 3-dimensional lattices.

CONCLUSIONS

Pore size distribution is one of the most important parameter for the characterization of porous media. It is routinely obtained from mercury porosimetry, but is based on an unrealistic picture of porous media. It can be affected by the choice of model for the porous media or the choice of equations which convert the P-V curve to a pore size distribution.

The connectivity of pores was the most important factor in porous media while choice of specific lattice types has little effect on the "penetration" pore size distribution. The shape of "real" pore size distribution has minor effect on the "penetration" pore size distribution, but the average pore diameters were shifted. The fraction of average size pores was always exaggerated in "penetration" pore size distributions.

Several different algorithms for mercury retraction has been proposed. We have used slightly different retraction algorithm in our simulations. Since pore-sphere network model was used in our simulations, direct comparison with different algorithms were not possible. We suggest that a "model experiment" should be performed before simulations to choose correct algorithm. "Model experiment" is an actual experiment with mercury on a porous media which has exactly same structure of computer model. In fact, such an experiment was performed on the square pore-network by Lenormand and Zarcone [9]. A model experiment with pore-sphere network is recommended for future workers.

ACKNOWLEDGEMENTS

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NOMENCLATURE

D : diameter of pore [Å]
F(D) : log-normal distribution of pore diameters
μ : mean
σ : standard deviation

REFERENCES

1. Kim, S. Y., Yoo, K.-P. and Lee, K. H.: *Hwahak Konghak*, **31**(1), 16 (1993).
2. Dullien, F. A. L.: "Porous Media Fluid Transport and Pore Structure", Academic Press, San Diego p. 45 (1979).
3. Coner, Wm. C., Lane, A. M., Ng, K. M. and Goldblatt, M.: *J. Catalysis*, **83**, 336 (1983).
4. Androutsopoulos, G. P. and Mann, R.: *Chem. Engng Sci.*, **34**, 1203 (1979).
5. Mayagoitia, V., Cruz, M. J. and Rojas, F.: *J. Chem. Soc., Faraday Trans. I*, **85**, 2071 (1989).
6. Park, C. Y. and Ihm, S. K.: *AIChE J.*, **36**, 1641 (1990).
7. Tsakiroglou, C. D. and Payatakes, A. C.: *J. Colloid Interface Sci.*, **137**, 315 (1990).
8. Portsmouth, R. L. and Gladden, L. F.: *Chem. Engng Sci.*, **46**, 3023 (1991).
9. Lenormand, R. and Zarcone, C.: in Family, F. and Landau, D. P., ed. "Kinetics of Aggregation and Gelation", Elsevier, Amsterdam, p. 177 (1984).