Simulation Studies for Porosity and Specific Surface Area in the Penetrable-Concentric-Shell Model Pore

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Recent advances in separation science and engineering have taken place in parallel with an improvement in our understanding of the molecular structure of both confined fluids and porous media. For both theoretical and practical approaches in this area,[1-3] one of the commonly used pore systems is the random pore model in which the solid matrix is represented as assemblies of rigid hard-spheres randomly distributed in the pore phase. The concept of the random bed of spheres becomes more useful if the solid spheres are allowed to be partly overlapped or interpenetrated one another. Such a random pore system is the so-called 'cherry-pit model' or 'penetrable-concentric-shell (PCS) model'.[4-7]

In the PCS model pore itself, each sphere of diameter σ is composed of a hard-core of diameter $\lambda\sigma (0 \le \lambda \le 1)$. The PCS model is versatile to construct various interpenetrable-sphere systems by varying the degree of impenetrability factor λ. The two extreme limits of the impenetrability parameters, $\lambda = 0$ and $\lambda = 1$, respectively, correspond to the cases of fully penetrable and totally impenetrable spheres. The latter can be employed in the model systems of random pore media with a discontinuous solid phase and the former in those of materials possessing a continuous solid phase.

For statistically homogeneous media, the simplest morphological quantities are the porosity and the specific surface area. As for the PCS model pore, Rikvold and Stell[4,5] has obtained the analytical expression for low-order structural correlation functions by establishing an isomorphism between the PCS model and the scaled-particle theory. For any arbitrary impenetrability factor $0 \le \lambda \le 1$, the porosity ϕ, which is the pore volume fraction to the total system volume, can be represented as

$$\phi = (1 - \lambda^3\eta)$$
$$\exp\left[-\frac{(1-\lambda^3)\eta}{1-\lambda^3\eta} - \frac{3(1-\lambda)^2(2+\lambda-3\lambda^4\eta)\lambda^3\eta^2}{2(1-\lambda^3\eta)^3}\right] \quad (1)$$

Here,

$$\eta = \frac{\pi}{6}\rho\sigma^3 \quad (2)$$

is a reduced packing density, which is identical to the packing fraction for the system of impenetrable spheres, and ρ is the particle number density. The scale-particle approximation for 3-D systems is known to exact through the level of the third virial coefficient.

For the system of totally impenetrable spheres ($\lambda = 1$), we have

$$\phi = 1 - \eta \quad (3)$$

and the specific pore surface area s_P, which is defined as the interfacial area per unit system volume, is simply written as

$$s_P = \frac{6\eta}{\sigma} \quad (4)$$

In the case of fully penetrable spheres ($\lambda = 0$), one may find

$$\phi = \exp(-\eta) \quad (5)$$

and

$$s_P = \frac{6\eta}{\sigma}\exp(-\eta) \quad (6)$$

As a useful diagnostic tool for investigating model pore systems, the corresponding simulation data can be used to investigate the applicability of theoretical predictions. In this preliminary work, we will first describe the efficient computational method to calculate the structural properties including the porosity and the specific surface area in the PCS model pore. The initialization procedure was first to construct unbiased configurations for equilibrium distributions of identical spheres. For lower η and λ values, this could be done directly by the random inserting method into the fundamental cubic cell. For higher η and λ values, however, such initialization procedures were failed to generate appropriate configurations. In this case, the systems were equilibrated from the regular arrays of the face-centered cubic structure using the standard hard-sphere molecular dynamics simulations.[8] For the purpose of simulations, conventional periodic boundary conditions were imposed at the edges of each cubic cell to reduce the system size effect.

Once the initial configurations were realized, it followed the numerical evaluation of the porosity and the specific surface area in a given set of configuration, and then repeatedly over a large number of independent sets. One of the simplest computational methods is the crude Monte Carlo calculations[9] known as the hit/miss random sampling (hereafter referred to as the 'RS method'), in which the sampling points are randomly thrown into the fundamental system volume and the desired quantities are measured from the ratio of the total number of hits (or misses) to the total number of attempts. The main disadvantage of this method is that computations become inefficient and inaccurate to achieve the statistically acceptable results.

Subsequently, more efficient ways of the sampling algorithm were implemented by Torquato and his co-workers.[6,7] An important feature of their algorithm is the use of the so-called digitized image or digitized grid method (hereafter referred to as the 'DG method'). In such a scheme the digitized grid is generated by dividing the system volume into a regular pixel grid (a square in 2-D and a cube in 3-D) before starting the sampling procedure. This DG method can reduce the computer execution time because it avoids the wasteful sampling time of getting the averages in the pixel grids which are entirely occupied or unoccupied by the spheres. This is particularly true for very low or very high pore systems.

However, the digitization over the large system volume significantly requires an excessive amount of memory in order to reach sufficiently fine resolutions.[10] An alternative way to overcome these difficulties is the multiple-step digitization technique. Lee and Torquato[6] employed the two-step grid method for the 3-D system, in which the system volume was first tessellated into the coarse-grained pixels with a resolution of $64 \times 64 \times 64$ and then each pixel containing partial spherical edges was tessellated further into 27 subpixels. Although a bit-map type of the digitizing procedure may be applicable to reduce the required memory, the DG method is generally restricted for the small system. In fact, the ranges of particle numbers investigated in their previous simulation studies using the DG method were from 64 to 448 spheres in the 3-D case.

A new algorithm employed in this work is based upon the use of spherical test particles with the finite size, which is somewhat similar to the pixel in the DG method. As in both RS and DG methods, the most time-consuming part in computations is searching the neighbor spheres in a given region. Our new algorithm is combined with the linked-cell searching routine. Each spherical test particle (or a circle in 2-D) is sequentially generated into the system volume and only the possible overlapping spheres are checked using the linked-cell list. In our scheme, it is much easier than the DG method to check whether overlapped or not in the test region. Moreover, if partially overlapped with one sphere or linearly overlapped with more than one sphere, the exact analytical formula for the intersection volume is available and a more accurate value can be evaluated comparing with the DG method. Such modifications reduce the computational time significantly. For the complex case of containing multi-overlapping spheres, particle identification numbers with the relative position vectors are saved on temporary arrays and we throw 10,000 points into the test sphere region to determine the overlapping volume fraction.

In Table 1 we report simulation results for the volume fraction of spheres in the two case of fully penetrable spheres ($\lambda = 0$) and totally impenetrable spheres ($\lambda = 1$). For the comparative purposes, all computational parameters were chosen to be the same as in Ref. 6. The statistical errors quoted in this table represent the standard deviation over 1,000 independent configurations. The volume fraction obtained from Eq. (3) for $\lambda = 1$ is exact for all the cases whereas Eq. (5) for $\lambda = 0$ is exact when the system size approaches to infinite. The standard errors for $\lambda = 0$ are larger than those for $\lambda = 1$ due to this system size effect. Among the three methods, as can be seen in Table 1, it is found our method to be the most accurate one to evaluate the resulting porosities. The statistical errors from our simulations are also smaller than either the RS or the DG method. For the case of $\lambda = 1$, where no sphere is allowed to be overlapped each other, our new algorithm gives the exact values within five significant figures.

Our simulation results for $0 < \lambda < 1$ are displayed for the porosity and the specific pore surface area in Figures 1 and 2, respectively. Also shown as the solid lines in these figures are theoretical predictions based on the scaled-particle approximation in the PCS model pore. The specific pore surface area is obtained from the relationship of

$$s_P = -\frac{d\phi(\lambda, \eta)}{dr} \tag{7}$$

where the parameters λ and η are both a function of r. The total number of particles in each given condition were 1,372, which is much larger than the particle numbers employed in the previous DG computations. The independent sets of 100 configurations were used to obtain the resulting statistical errors.

As exhibited in Figures 1 and 2, the agreement between theoretical approximations and the corresponding simulation

Table 1. Monte Carlo simulation data for the volume fraction of spheres (=$1-\phi$) for the cases of $\lambda = 0$ and $\lambda = 1$

$\rho\sigma^3$	N	RS method[a]	DG method[b]	In this work[a]	Exact
			$\lambda = 0$		
0.125	64	0.06337±0.00094	0.06343±0.00075	0.06339±0.00079	0.06335
0.375	192	0.17839±0.00221	0.17798±0.00199	0.17831±0.00021	0.17825
0.625	320	0.27912±0.00341	0.27940±0.00303	0.27933±0.00297	0.27910
0.875	448	0.36762±0.00390	0.36795±0.00440	0.36790±0.00402	0.36755
			$\lambda = 1$		
0.125	64	0.06544±0.00051	0.06545±0.00004	0.06545±0.000001	0.06545
0.375	192	0.19640±0.00082	0.19635±0.00006	0.19635±0.000002	0.19635
0.625	320	0.32718±0.00092	0.32725±0.00000	0.32725±0.000003	0.32725
0.875	448	0.45818±0.00117	0.45816±0.00037	0.45815±0.000003	0.45815

[a] Total sampling numbers were quarter millions. [b] In Ref. 6 using the two-step grid method.
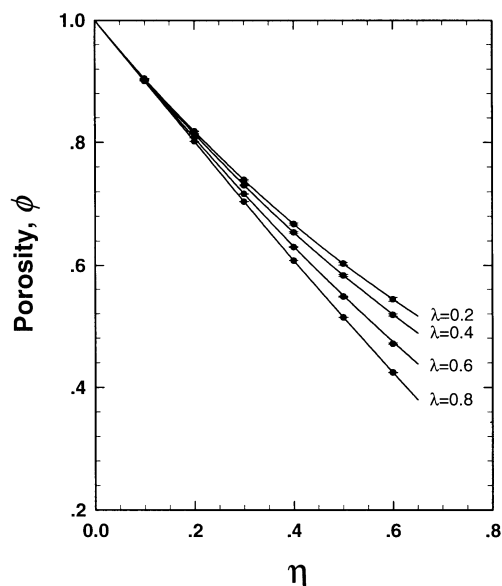
Figure 1. The porosity ϕ as a function of the reduced density η. Shown as solid lines and circles correspond to theoretical predictions based on the scale-particle approximation in the PCS model pore.
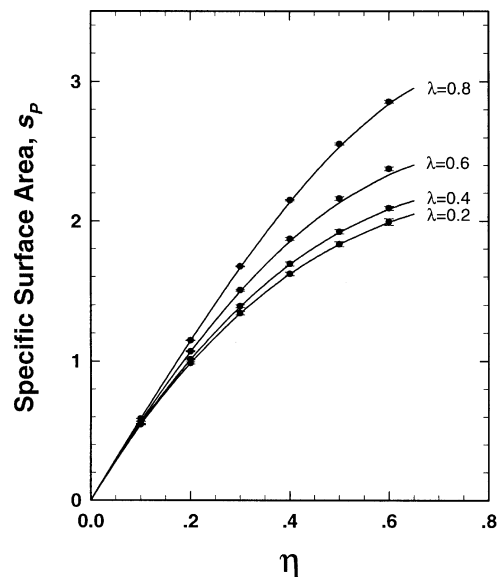
Figure 2. Same as in Figure 1 but for the specific surface area s_P.

results is seen to be excellent. The differences are slightly larger for the specific surface area, particularly in the case of $\lambda = 0.6$ and $\eta = 0.6$ where the relative error between simulation results and theoretical predictions were about 1.83%.

Such differences in the surface area are partly due to the limited sampling numbers compared with the porosity calculations. The statistical errors in these figures are generally smaller than the symbol size itself, ranging over 0.003%-0.03% ($\eta = 0.1$) and 0.09%-0.60% ($\eta = 0.6$) for the porosity and 0.13%-0.49% ($\eta = 0.1$) and 0.34%-1.18% ($\eta = 0.6$) for the specific surface area. Larger relative deviations were found in the case of lower λ-values. This indicates that the overlapping geometries of largely penetrating systems (lower lambda -values) are topologically more complex than those of partly overlapping systems (higher λ-values). In general, the porosity predictions by Eq. (1) can be accurate through second order in η and the applicabilities of theoretical predictions using Eq. (7) is more restricted for the intermediate values of λ.

In summary, our new algorithm to simulate the porosity and specific surface area of random media is found to be more accurate and faster execution time than either the random sampling method or the digitized grid method. We are currently in the process of employing this new algorithm to investigate the structural properties of the PCS model pore including pore-size distributions, nearest-neighbor distribution functions, chord-length distribution functions, and exclusion-volume probability functions. Such simulation results, in conjunction with various theoretical approximations, will provide the quantitative characterization of microporous media at a molecular level.

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