The number of nearest neighbors in the model of a disordered porous medium

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Abstract. The paper considers a model of a disordered porous medium consisting of chaotically located intersecting spheres of various sizes. Based on the model and the analytical approach, the number of nearest neighbors is calculated for each pore in from the pore radius. In conclusion, an analysis of this dependence is presented for packages with different pore size distributions.

1. Introduction

Currently, the "nanoporous medium – non-wetting liquid" systems are of great interest from a practical point of view, because of the large nonlinear response, such systems can be used in temperature sensitive sensors, passive protection systems, for example in fire extinguishing systems, in drug delivery systems [1], in systems with controlled permeability for liquids or gases.

Recent studies show that such a response may be connected with a multiparticle pore correlations in a disordered porous medium, collective phenomena and correlations in the mutual arrangement of clusters of liquid in a random porous medium [2].

One of the important parameter in describing the local pore configuration is the number of nearest neighbors (coordination number). It is widely used in the evaluation of structural properties and bonds between pores, including strength characteristics [3, 4], heat and mass transfer [5] and phase formation [6]. Two methods are widely used for the investigation and determination of the number of nearest neighbors: the experiment [7, 8] and computer simulation [9, 10]. In works [15–18] devoted to modeling the motion of liquids/gases through a porous medium, the importance of understanding the pore configuration, the dependence of coordination numbers on pore size distribution, is noted.

This article is devoted to the theoretical method of investigation.

The study of the number of nearest neighbors, generally, is focused on two aspects:

• determination of the relationship between the number of nearest neighbors and porosity
• determination of the relationship between the number of nearest neighbors and the distribution of pores by size [11].

The current understanding of the relationship between the number of nearest neighbors and the pore size distribution is very limited. One of the most important characteristics of porous media is the pore size distribution function (PSDF). In the nanopore region, the experimental methods for the getting of PSDF are based on information on the hysteresis loop. In this case, the PSDF is calculated from its adsorption and desorption branches.
The calculation of the PSDF for mesoporous media is based on the capillary condensation theory. As a rule, the considered hysteresis loop is typical for porous medium with a corpuscular structure. The stochastic geometry of corpuscular porous medium is very complicated. For this reason, when analyzing the experimental data, the first approximation is the model of effective spherical or cylindrical pores [12].

In 1945, Wheeler, taking as a basis the model of an open cylindrical capillary, proposed a method for calculating the PSDF. Later his approach was developed in the works of Barrett Joyner-Halenda, Creston-Inkley and Dolimer Hill. On the basis of Wheeler’s approach, a generalized equation was proposed that makes it possible to obtain a PSDF for pores of spherical, cylindrical, and slit forms.

In this paper, the model of a disordered porous medium is proposed consisting of chaotically located intersecting spheres of various sizes. The pore space represents the voids inside the spheres, the rest of the space represents a solid phase. This model allows to take into account multiparticle pore correlations and within the framework of the model it becomes possible to analytically calculate the number of nearest neighbors in each pore taking into account the pore size distribution [13]. In addition, the calculation of the number of nearest neighbors of such a system will allow to reconstruct the pore size distribution function in view of their correlations. This fact makes it possible to describe the thermodynamic states of a liquid in a nanoporous disordered medium as an ensemble of quasiparticles consisting of clusters of liquid in neighboring pores.

2. Main part
A model of chaotically located spheres was proposed by Weissberg to describe disperse and porous media. The model is a system of chaotically located intersecting particles of a spherical shape that do not correlate with each other. The probability of finding an arbitrarily chosen center of a particle at a certain point in space does not depend on the location of the remaining centers. This model is universal, because allows us to describe both the structure of the body skeleton and the structure of the pore space. The simplest case of this model is a system of spheres of the same radius [14]. Let us consider a system of chaotically located intersecting cavities of spherical shape with concentration \( n \). In this model, by porosity is meant the ratio of the volume outside the spheres to the total volume of the medium. That is, the porosity is equal to the probability that an arbitrary point of space is in the space of pores; in other words, it is the probability that no center is in the sphere of radius \( R \).

Let us find the probability that the volume \( V_0 (V_0 \ll V) \) does not contain any center, i.e. all the centers are located in the volume \( V - V_0 \). \( V \) is the total volume of the medium.

Then the probability that an arbitrarily chosen center is outside the volume \( V_0 \) is equal to:

\[
P(V_0) = \left( \frac{V - V_0}{V} \right)^{nV} \tag{1}
\]

In this case, the total number of particles \( nV \) is large, and the product \( nV_0 \) is finite, so we can use the definition of the number \( e \) as the limit of the expression \((1 - \alpha)^{-1/\alpha}\) for \( \alpha \to 0 \).

Then the probability becomes:

\[
P(V_0) = e^{-nV_0} \tag{2}
\]

where \( V_0 = \frac{4}{3} \pi R^3 \) is a volume of one sphere.

From the expression for the probability we get the value of porosity:

\[
\varphi = e^{-\alpha} \tag{3}
\]

where \( \alpha = \frac{4}{3} \pi R^3 n \) is a dimensionless parameter.
The pore structure is a random lattice, the nodes of which correspond to voids, and the connections to the throats. By the number of nearest neighbors (or coordination number) is meant the number of points of contact of one pore, in other words the number of links originating from the node. Too large and too small numbers of nearest neighbors are unlikely.

The probability \( P_z \) that an arbitrarily chosen cavity has \( Z \) throats is equal to the probability that exactly \( Z \) lies inside a sphere of radius \( 2R \) from \((n-1)\) centers of cavities located in a unit volume containing the chosen cavity, centered at the center of the selected cavity:

\[
P_z = C_{n-1}^z \left( \frac{4}{3} \pi (2R)^3 \right)^z \left( 1 - \frac{4}{3} \pi (2R)^3 \right)^{n-1-Z} = \frac{(8\alpha)^Z e^{-8\alpha}}{Z!}
\]  

(4)

The average number of nearest neighbors is

\[
\bar{Z} = \sum ZP_z = 8\alpha
\]  

(5)

Consider a system of \( N \) sort of spheres.

\[
\begin{align*}
1\text{-sort} & : a_1 R, b_1 n_1, \text{where } a_1 = 1, b_1 = 1 \\
2\text{-sort} & : a_2 R, n_2 = b_2 n_1 \\
3\text{-sort} & : a_3 R, n_3 = b_3 n_1 \\
& \vdots \\
N\text{-sort} & : a_N R, n_N = b_N n_1
\end{align*}
\]

(6)

Then the dimensionless parameter \( \alpha \) takes the form:

\[
\alpha_j = \frac{4}{3} \pi R^3 \frac{n_j}{b_j} \sum_{i=1}^{N} a_i^3 b_i
\]  

(7)

The average number of nearest neighbors is

\[
\bar{Z}_k = \sum_{k=1}^{N} \frac{(a_j + a_k)^3 b_j \alpha_j}{\sum_{i=1}^{N} a_i^3 b_i} = \frac{4}{3} \pi n_j \sum_{k=1}^{N} (r_j + r_k)
\]  

(8)

3. Results and discussion

In the course of this study, a numerical experiment was conducted, the technique of which is as follows. The initial simulated region is a cube with a linear dimension \( L = 32 \). The cube is filled with spheres of various sizes that can overlap. Generation of a sphere occurs by assigning its coordinates to the center and radius. In turn, the center refers to an arbitrarily given point inside the cube, and the radii of the spheres obey the Gaussian distribution. As a result, the space outside the spheres will represent the skeleton of the porous body, and the voids inside - the pore space.

To verify the numerical experiment, at the start the monodisperse sphere approach was applied (Eq. (5)).
Figure 1. Dependence of the average number of nearest neighbors on the porosity of the system

In the case of polysperpic spheres, the dependence of the number of nearest neighbors for three variants of pore size distribution was studied:

- Narrow distribution with parameters: $\mu = 1, \sigma = 0,1$
- Wide distribution with parameters: $\mu = 1, \sigma = 0,4$
- Normal distribution with parameters: $\mu = 1, \sigma = 0,2$

where $\mu$ is the mean dimensionless radius and $\sigma$ is variance.

Figure 2. Three cases of pore size distribution
3.1. Narrow pore size distribution

Figure 3. The average number of nearest neighbors, depending on the porosity of the system

3.2. Normal pore size distribution

Figure 5. The average number of nearest neighbors, depending on the porosity of the system

Figure 4. The average number of nearest neighbors at the pore radius $r$

Figure 6. The average number of nearest neighbors at the pore radius $r$
3.3. Wide pore size distribution

**Figure 7.** The average number of nearest neighbors, depending on the porosity of the system.

**Figure 8.** The average number of nearest neighbors at the pore radius $r$.

In the course of the work, a model of chaotically located overlapping spheres of various sizes was considered. Within the framework of this model, a formula was obtained that describes the dependence of the number of nearest neighbors on the radius of spheres. The distribution of the nearest neighbor numbers was plotted as a function of the pore radius for different values of porosity and the dependence of the number of nearest neighbors on the pore radius $r$. The exact experiment was verified for the case of monodisperse spheres. It was shown that the results obtained from the formula are consistent with the data obtained in the course of the numerical experiment.

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