CONTINUUM PERCOLATION THRESHOLD AND IONIC DIFFUSIVITY OF POROUS MEDIA CONSISTING OF ASYMMETRICAL OVOIDAL PORES

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Abstract

Porous networks provide the main transport channels to the active media, which will damage the microstructure and then lead to a subsequent reduction in the strength, serviceability and aesthetic of porous materials. The connectivity of the porous network plays an essential role in the transport properties of these active media. In statistic physics, the percolation threshold ϕ_c is usually used to describe the formation of long-range connectivity in the system and it has been demonstrated that ϕ_c of porous network is highly depended on the geometrical shape of the pores. However, the previous studies focused on the symmetric pores such as spheres, ellipsoids and spherocylinders, etc. How the particle asymmetry affects the percolation behaviour of the porous network and then influences the transport properties of materials is still undiscovered. In this work, a family of asymmetric ovoids is introduced. By combining the geometric model of ovoid with the Monte Carlo simulation, a series of porous composite composed of congruent overlapping pore of asymmetrical ovoids are modelled. Then, the percolation thresholds ϕ_c of composites are obtained by an excluded volume based approximation formula. Furthermore, a general percolation-based effective-medium approximation is adopted to theoretically study the ionic diffusivities of the two-phase porous composites considering their percolation behaviours. The results shed light on the intrinsic and complex interplay of components, structure and transport properties in composites, which can provide some guidance for the development of percolation theory and the design of composites.

Keywords: Asymmetrical ovoid; Porous composites; Continuum percolation; Ionic diffusivity

1. INTRODUCTION

In the geoscience and engineering fields, porous materials are ubiquitous such as zeolites, wood, concrete, ceramic, etc. From the structural perspective, the porous materials could be assumed as a two-phase systems composed by low permeability solid matrix and high permeability porous network [1]. Porous materials, such as concretes and rocks are exposed to harsh environments yet are often expected to last with little or no repair or maintenance for long periods of time (often 100 years or more). However, the active media in the environment (e.g., carbon dioxide, contaminant, ions, fluid, etc.) will penetrate into the porous materials and damage the microstructure of the materials, then lead to a subsequent reduction in the strength, serviceability, and aesthetic of structure [2]. In general, the porous network are the main transport "channels" for those active media and the emergence of system-spanning porous network is the prerequisite of active media transport through the porous materials. Ever since Broadbent and Hammersley [3] modeled the propagation of a fluid in an infinite regular square lattice, the percolation theory has played an abiding role in the study of the connected clusters. The percolation threshold ϕ_c, expressed by critical porosity of porous material, is usually used to characterize the critical emergence of system-spanning path in the system comprising random distributed objects/particles. In the vicinity of percolation threshold, the conductivity, diffusivity and permeability of porous composite materials will have the dramatic changes variation because of the occurrence of the global connectivity. Therefore, accurately obtaining the percolation threshold of porous composites and rigorously incorporating such structural characteristic into the prediction of transport properties of composite is of great significance to illuminate the intrinsic and complex interplay of components, structures and transport properties in porous composites.

From the previous studies [4, 5], it can be concluded that the particle morphology is a very crucial factor for the percolation behavior of the composite. Thus, how to accurately predict the effect of particle shapes on the threshold ϕ_c for different 2D or 3D systems is of great importance for the design of composite. Previous works on the continuum percolation systems mainly focused on symmetrical anisotropic-shaped particles, such as rectangles [5], ellipsoids [6] and spherocylinders [7]. In practice, particulate components in real granular composites are not idealized symmetric particles as mentioned above, as shown in Fig.1. However, how the particle asymmetry affects the percolation behavior of network and then influence the diffusivity of the composite is still undiscovered.

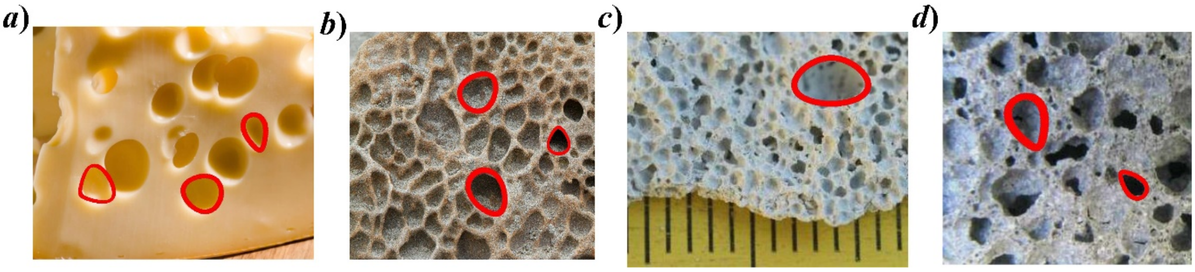

Figure1: The real asymmetrical pores in the porous materials.

To provide a theoretical framework to address this lacuna, a family of single axil asymmetrical ovoids, also known as "tapered ellipsoids", is introduced in this paper. From a geometric modeling perspective, ovoid is a natural extension of the ellipsoid and the surface of ovoid can be expressed by Eq. (1). Fig.2 illustrates the morphologies of ovoids with different c/a and T.

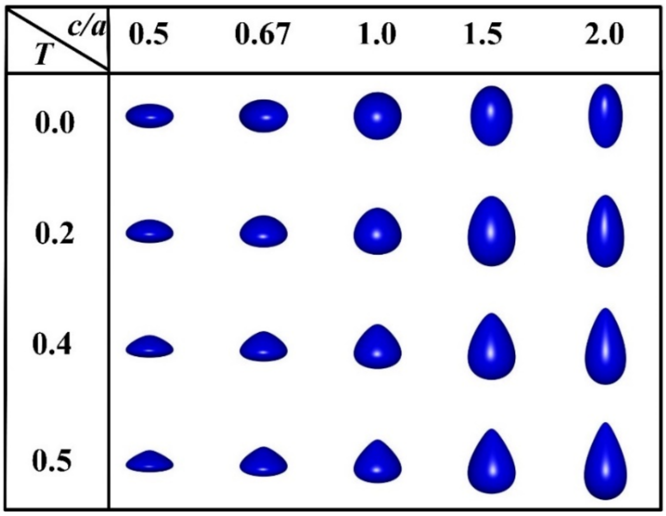

Figure 2: Illustration of the morphologies of ovoids with different *T* and *c*/*a*.

$$F_{ov}(x,y,z)=\left(\frac{1}{T\frac{z}{c}+1}\times\frac{x}{a}\right)^2+\left(\frac{1}{T\frac{z}{c}+1}\times\frac{y}{b}\right)^2+\left(\frac{z}{c}\right)^2-1=0 \tag{1}$$

where a, b and c denote the semi-axis lengths of ovoid in x, y and z directions, and $T\in[0, 0.5]$ is the tapering parameter ($T = 0$ for symmetric ellipsoid).

In this study, the porous systems consist of homogeneous solid matrix and porous network composed of overlapping asymmetric ovoids are generated firstly by combining with the Monte Carlo simulation. Then, the percolation threshold ϕ_c of the congruent overlapping ovoids are obtained by the excluded based approximation formula. To explore the effect of ϕ_c on the diffusivity of systems, the percolation-based generalized effective medium approximation is further applied. Finally, the normalized ionic diffusivity in the saturated porous composite is theoretically predicted and the reliability of the prediction is verified by comparison with the experimental measurements.

2. CONTINUUM PERCOLATION OF OVERLAPPING OVOIDS

In continuum percolation model, the porous composite can be simplified to be the congruent random distributed overlapping asymmetric ovoids, as shown in Fig.3. The porous network is assumed to be the intersected ovoids and the remaining zones are described to be the solid matrix. Once the intersected superovoids long enough to form the system-spanning cluster, the percolation of the porous network is deemed to be realized. In the previous studies [8], we have studied the percolation of ovoids with c/a in [0.5, 2] and an excluded volume based approximation formula is proposed to estimate the effect of shape parameter (i.e., c/a and T) on the threshold ϕ_c, as expressed by Eq. (2).

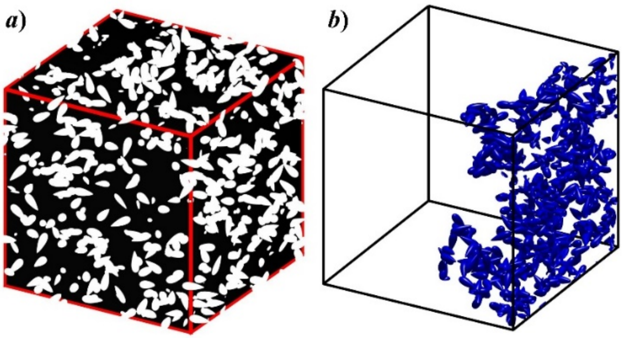

Figure 3: Visualization of *a*) the two-phase porous system consisting of homogeneous solid matrix (black parts) and porous network (white inclusions) composed of overlapping ovoids. *b*) the connected pore cluster in the two-phase porous system.

$$\phi_c = 1 - \exp\left(\frac{-G(c/a,T)}{V_{dex}}\right) \tag{2a}$$

$$\begin{aligned} G(T,c/a) = {} & 2.730 + 0.037\exp(T) - 0.089\ln(c/a) - 0.025\exp^2(T) \\ & - 0.212\ln^2(c/a) + 0.064\exp(T)\ln(c/a). \end{aligned} \tag{2b}$$

$$V_{dex} = \frac{V_{ex}}{V} \tag{2c}$$

where V is the volume of the discrete pore and V_{ex} refers to the volume that is inaccessible to other particles as a result of the presence of the first one [9]. To avoid the size effect of the particle, the dimensionless excluded volume V_{dex}, defined as the ratio between the excluded volume and the volume of particle, is usually employed.

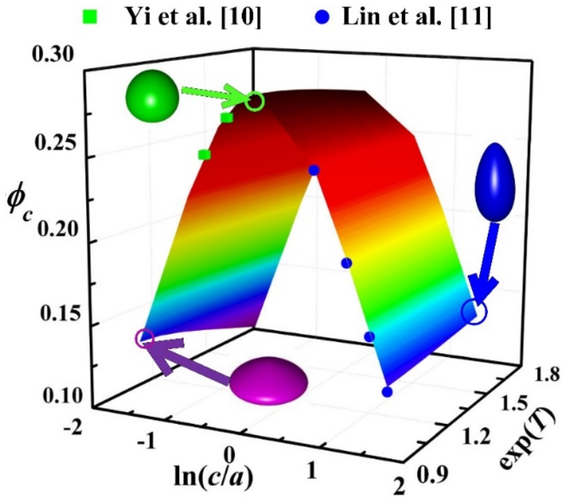

Figure 4: The dereived results of ϕ_c by approximation formula versus the simulated values in Refs. [10, 11].

In this paper, we calculated the V_{dex} of the ovoids with $c/a \in [0.2, 5]$ and the results are shown in Table 1. By combining the V_{dex} in Table 1 with Eq. (2), the thresholds ϕ_c are obtianed. Fig.4 illustrates the thresholds ϕ_c and comparising the theoretical results with the simulated values in previous researchs [10, 11]. It can be seen that the theoretical results are in weel aggrement with the simulated values, which indicates the reliability of our derived results.

Table 1: The dimensionless excluded volume V_{dex} for ovoids with different *c*/*a* and *T*.

c/a T	0.2	0.4	0.6	0.8	1.0	2.0	3.0	4.0	5.0
0.00	15.10	9.95	8.57	8.11	8.00	9.08	10.91	12.96	15.10
0.10	15.24	10.01	8.60	8.13	8.01	9.08	10.90	12.94	15.09
0.20	15.63	10.18	8.70	8.19	8.05	9.07	10.88	12.90	15.03
0.30	16.25	10.45	8.86	8.29	8.12	9.07	10.84	12.84	14.94
0.40	17.06	10.81	9.06	8.42	8.21	9.07	10.79	12.75	14.81
0.50	18.04	11.24	9.32	8.59	8.33	9.06	10.72	12.64	14.66

3. TRANSPORT PROPERTIES OF SATURATED POROUS CEMENT PASTE

For the cement paste, the effective ionic diffusivity D_{eff}, the porosity and diffusivity of porous network are assumed to be ϕ and D_p, and that of solid matrix to be $(1-\phi)$ and D_m. In this case, McLachlan et al.[12] established the relationship between the effective ionic diffusivity and the percolation threshold of porous materials based on the effective medium approximation and percolation theory, as shown by Eq. (3).

$$\frac{D_{eff}}{D_m}=\left(1-\frac{\phi}{\phi_c}\right)^t \quad \text{for } \phi<\phi_c \tag{3a}$$

$$\frac{D_{eff}}{D_p}=\left(\frac{\phi-\phi_c}{1-\phi_c}\right)^t \quad \text{for } \phi>\phi_c \tag{3b}$$

However, it should be noted that the diffusivity near the percolation threshold cannot be measured by Eq. (3), as illustrated in Fig. 5. To overcome this shortcomings, a generalized effective medium theory (GEMT) [13], as expressed by Eq. (4), is proposed. Then, by combining the thresholds with GEMT, a so called percolation threshold based generalized effective medium approximation (PT-GEMA, see Eq. (5)) is present to link the ionic diffusivity with the percolation behaviors of the cement paste comprising uniform overlapping asymmetrical pores.

$$\frac{\phi(D_p^{1/t}-D_{eff}^{1/t})}{D_p^{1/t}+\frac{1-\phi_c}{\phi_c}D_{eff}^{1/t}}+\frac{(1-\phi)(D_m^{1/t}-D_{eff}^{1/t})}{D_m^{1/t}+\frac{1-\phi_c}{\phi_c}D_{eff}^{1/t}}=0 \tag{4}$$

where t is a transport-percolation coefficient refers to the complexity of the porous networks.

$$\frac{D_{eff}}{D_p} = \left\{ \Omega + \sqrt{\Omega^2 + \frac{1-\exp[-G/V_{dex}]}{\exp[-G/V_{dex}]}\left(\frac{D_m}{D_p}\right)^{\frac{1}{t}}} \right\}^t \tag{5a}$$

$$\Omega = \frac{1}{2}\left\{ \left(\frac{D_m}{D_p}\right)^{\frac{1}{t}} - \frac{1-\exp[-G/V_{dex}]}{\exp[-G/V_{dex}]} - \frac{\phi}{\exp[-G/V_{dex}]}\left[\left(\frac{D_m}{D_p}\right)^{\frac{1}{t}} - 1\right] \right\} \tag{5b}$$

Afterwards, we utilize PT-GEMA to compute the normalized chloride diffusivity D_{eff}/D_p in cement paste and compare the derived results with the experimental measurements [14, 15]. Referring to the study by Oh et al. [16], the realistic values for t and D_m/D_p are expected to be 2.7 and 2.0E-4 for cement pastes. It can be clearly seen in Fig.5 that the derived results from PT-GEMA are in agreement with the experiment measurements, which indicates that PT-GEMA can accurately predict the ionic diffusivity of cement paste. Moreover, the derived D_{eff}/D_p of cement paste in Fig.5 by the asymmetrical ovoids are closer to the experiment measurements than the results by sphere.

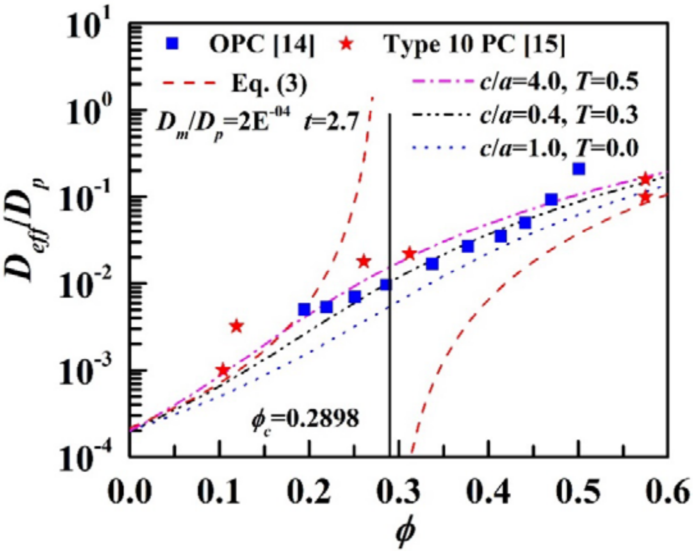

Figure 5: Comparisons of the predicted results of normalized chloride diffusivity from PT- GEMA with experimental data.

4. CONCLUSIONS

The percolation threshold of ovoids with $c/a \in [0.2, 5]$and $T \in [0, 0.5]$ are calculated in this paper. For a constant T in [-0.5, 0.5], ϕ_c shows an initially increasing and then decreasing trend with the increase of c/a and the inflection point located at $c/a = 1.0$, which is consistent with the previous studies. The ionic diffusivities of the cement paste comprising overlapping asymmetrical ovoidal pores are theoretically derived by PT-GEMA and the reliability of PT-GEMA is verified by comparing the derived results from PT-GEMA with the experimental measurements. The results demonstrate that the porous systems composed of asymmetrical shaped pores are closer to the realistic porous materials than the systems comprising spherical pores.

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