Microstructural modelling of cement-based materials via random packing of three-dimensional ellipsoidal particles

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Abstract

Random packing of particles in cement-based materials plays an important role in microstructural evolution. The preponderance of preview work has focused on the microstructural model by the random packing of spherical or two-dimensional elliptical particles, and little is known about three-dimensional ellipsoidal particles. In the present work, a new random packing model of three-dimensional ellipsoidal particles was developed to simulate microstructure of cement-based materials. It was based on a novel numerical algorithm for detecting the contact of ellipsoidal particles. The accuracy and reliability of the algorithm were verified by a visualization of the random packing of monodispersed ellipsoidal particles with rigid boundary conditions. According to these numerical algorithms, microstructural model of cement-based materials was constructed by the random packing of polydispersed ellipsoidal particles, of which sizes satisfy a specific distribution. Finally, applied stereological tools and serial sectioning analysis technique, microstructure of cement pastes, composed of ellipsoidal cement particles, was characterized and compared with that of spherical cement particles.

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1. Introduction

Cement-based materials are a complex random multi-scale system. At the microscopic and mesoscopic scale, cement-based materials are composed of the random packing of anisotropic grains [1-3]. In addition, the interior structural evolution of cement-based materials is, by and large, dependent on the random packing of grains [4]. Since the macro-mechanical properties of cement-based materials is

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directly related to its microstructure, the simulation of the random packing of particles can get insights about the effect of various characteristic parameters (e.g., particle size, shape, gradation, and distribution, etc.) on the thickness of the interfacial transition zone (ITZs), transport properties and mechanical properties, etc. This will ultimately guide a better design of high-performance cement-based materials and structures.

In the last decade, scientific attention had broadened the study of the macro-mechanical properties and microstructure of cement-based materials, by utilizing the packing behavior of particles. As early as 1985, Wittmann et al. [5] simulated the random sequential packing of two-dimensional aggregates to investigate the macro-mechanical properties and the diffusion of water in the interior structure of concrete. Owing to the limitation of the computational capacity of computers, the simulated structure was restricted in a little number of particles, which could not represent a real structure of concrete. To characterize the microstructural evolution of cement paste during hydration process, van Breugel et al. [6] developed a random sequential spherical particles packing model (HYMOSTRUC Model). Subsequently, applying the technology of digital images, Bentz et al. [7] constructed a random sequential packing model of spherical particles, by which the pore features in the microstructure of concrete was derived. Furthermore, Bentz' work was extended to three-dimensional ellipsoidal particles by Garboczi et al. [8], for studying the percolation theory. Although the technology of digital image could conveniently develop packing models of arbitrary shape particles [9-11], the accuracy of models was limited by the image resolution of equipments (e.g., the ranges of the image resolution by X-Ray CT [12], 3D laser scanner [13], and Atomic Force Microscopy [14] were 5-50μm, 100-500μm, and 0.05-0.1μm, respectively). Afterwards, spherical particle packing model was extensively developed with various approaches, including monodispersed and polydispersed spherical particles [15], as well as random sequential packing and random dynamic packing [16-18]. Unfortunately, these models had a major drawback that the geometrical shape of particles was considered as the simple sphere, which could not represent the true shape of particles in cement-based materials.

Recently, the packing problems of non-spherical particles in cement-based materials had attracted considerable attention [19-22]. For instance, employing Perram contact function [23] to simulate the random sequential packing of two-dimensional elliptical aggregates, Zheng et al. [19, 20] studied the areal fraction and percolation of ITZs in the mesoscopic scale for concrete. Alternatively, Xu et al. [21, 24] presented a new numerical algorithm to construct the elliptical aggregate packing model, and revealed the influence of the shape of ellipses on the packing fraction of aggregates. Furthermore, Wang et al. [22] introduced a convex polygonal random sequential packing model, in which the classical Fourier series was used for particle shape analysis, to simulate mechanical properties of concrete with the assistance of a finite element mesh. In view of the above models, they only worked in two-dimensional space. The researches related to three-dimensional non-spherical particles packing were rare. Therefore, it was necessary to develop a three-dimensional non-spherical particle packing model to characterize microstructure of cement-based materials.

This paper attempted to present a random packing model of three-dimensional ellipsoidal particles to characterize microstructure of cement-based materials. In this approach, five steps were considered. In Section 2, a contact detection algorithm of ellipsoidal particles was illustrated. Then, in Section 3, the accuracy of the three-dimensional ellipsoidal particle packing model was verified. In Section 4, microstructure of cement-based materials was constructed by the random packing of given size distributed ellipsoidal particles in periodic boundary conditions. Finally, microstructure of cement pastes was characterized in Section 5.

2. Contact detection of ellipsoidal particles
The key issue of the random packing of particles was to ensure that each particle did not contact with the others, it was essential to detect contact of ellipsoids for an ellipsoidal particle packing model. In our previous work, a new numerical algorithm of detecting ellipsoids overlapping has been developed [24], in which the ellipsoid \( i \) was converted into a unit sphere with center located at the origin of coordinate system and the ellipse \( j \) was also correspondingly transformed into a new ellipsoid \( j' \) by a series of linear transformations of the coordinate system. Because linear transformations of the coordinate system did not change the relative position of two ellipsoids, the relative position between the unit sphere and the new ellipsoid \( j' \) may represent the ellipsoid \( i \) and the ellipsoid \( j \). Moreover, a novel golden section algorithm developed by Xu et al. [24] was used to calculate the nearest distance from the origin to the new ellipsoid \( j' \) for the purpose of overlapping detection between ellipsoids. In this research, the numerical algorithm was directly employed for simulation of the random packing of the three-dimensional ellipsoidal particles in cement-based materials.

3. Verification of the model

In this section, a three-dimensional cubic model structure with rigid boundary conditions for the random packing of monodispersed ellipsoidal particles was utilized to verify the accuracy and reliability of the model.

For an ellipsoidal particles packing system in the cubic model structure with rigid boundary conditions, particles were not allowed to traverse through the cubic model structure walls and overlap with the others. Thereby, details of the algorithm for the random packing of ellipsoidal particles in rigid boundary conditions were described as follows:

1. Input known parameters: the size of the cubic model structure \( L \), the number of monodispersed particles \( N \), three degrees \((a_i, b_i, c_i)\) of freedom of ellipsoidal particles \( i \), where \( i \leq N \).
2. Randomly generate the center \((x_{0i}, y_{0i}, z_{0i})\) of ellipsoidal particle \( i \) in the interval \((a_i, L-a_i)\).
3. Randomly generate direction angles \((\alpha_i, \beta_i, \gamma_i)\) of elliptical particle \( i \) in the interval \((0, 2\pi)\).
4. Judge whether particle \( i \) contacts with all those preceding \( i-1 \) particles, if overlapping, return to Step (2) and Step (3) to randomly generate particle \( i \) again. Otherwise, return to Step (2) and Step (3) to randomly generate particle \( i+1 \).
5. Iterate Step (2) to Step (4) until all particles are generated.

![Fig.1. Visualizations of (a) random packing of ellipsoidal particles in rigid boundary conditions and (b) intersecting ellipses in the section plane \( z=0.5L \).](image)

To verify the accuracy and reliability of the model, monodispersed ellipsoidal particles were randomly packed in a cubic model structure with rigid boundary conditions, as shown in Fig. 1. Fig.1 (a) displayed a cubic random packing model of monodispersed ellipsoidal particles with \( \kappa = 0.571 \) (oblate), where the packing density was 0.49 and the number of monodispersed ellipsoidal particles was 800. Moreover, a
section plane \( z = 0.5 \) was applied to intercept the cubic random packing model, and the distribution of intersecting ellipses in the section plane was visualized in Fig. 1 (b), where the packing density of intersecting ellipses was 0.51, respectively. Essentially, no contact appeared of ellipsoidal particles. It could be seen from Fig. 1 that the accuracy and reliability of the model for the random packing of ellipsoidal particles in rigid boundary conditions was favourable.

4. Microstructural model of cement-based materials

At the microscopic scale, cement-based materials were considered as a three-phase material composed of aggregate particles, ITZs and cement pastes. It was well-known that characterization of microstructure and properties of cement-based materials had been extensively studied by the computer modelling technology [6, 7, and 17]. Compared with the conventional experimental methods, the computer modelling technology was very convenient and efficient due to its less time-cost as well as high reproducibility. However, most of models were constructed by three-dimensional spherical particles and two-dimensional irregular shape particles. According to the above verified model, a microstructural model was established by random packing of three-dimensional polydispersed ellipsoidal particles, of which sizes satisfied a specific distribution.

The particle size distribution used in cement-based materials could be obtained by the conventional sieve analysis test. In the computer modelling technology, particles were usually assumed to spherical particles for studying the particle size distribution in cement-based materials [17, 25]. However, the ellipsoidal particle size distribution of was seldom reported up to now. In this work, an equivalent diameter, which was defined as the diameter of a sphere having the same volume as that of an ellipsoidal particle [26], was introduced to carry out the ellipsoidal particle size distribution, as expressed in Eq. (1).

\[
D_{eq} = \begin{cases} 
2c\kappa^{\frac{2}{3}} & \text{if } \kappa \leq 1 \\
2c\kappa^{\frac{1}{3}} & \text{if } \kappa \geq 1 
\end{cases}
\]

where \( D_{eq} \) was the equivalent diameter of ellipsoidal particles, \( c \) and \( \kappa \) (if ellipsoid shape was prolate, \( \kappa = a/c \), if ellipsoid shape was oblate, \( \kappa = c/a \)) were semi-minor axis and aspect ratio of the ellipsoidal particle, respectively. Thus, the spherical particle size distribution could be connected with the ellipsoidal particle size distribution.

For instance, a particular distribution function was used to characterize the particle size distribution in cement-based materials normally focused, which was the Rosin-Rammler distribution function, as described in Eq. (2). It was a commonly–used formula to characterize the size distribution of spherical cement particles [6].

\[
F_V(D) = 1 - \exp(-b_0 D^n)
\]

where \( F_V(D) \) was the volume-based cumulative probability, \( b_0 \) and \( n \) were coefficients, \( D \) was the diameter of the spherical particle (\( \mu m \)). Substitution Eq. (1) into Eq. (2), the size distribution of ellipsoidal cement particles were written as
The modified Rosin-Rammler distribution function (Eq. (3)) for the size distribution of ellipsoidal particles was applied to simulate a microstructure of cement pastes. The initial parameters were $b_0=0.005$, $n=1.766$, particle size range of 1-50 $\mu$m, $\kappa=2.25$, 0.66 and $W/C=0.40$. According to Eq. (4), the relationship between the volume fraction of the cement particle and $W/C$ could be obtained.

$$V_c = \left( \frac{W}{C} \cdot \frac{\rho_c}{\rho_w} + 1 \right)^{-1}$$

where $V_c$ was the volume fraction of cement particles, $\rho_c$ and $\rho_w$ were the density of cement and water. Here, $\rho_c$ was assumed as 3150 kg/m$^3$, and $\rho_w$ was 1000 kg/m$^3$.

Fig.2. The relationship between equivalent diameters of the ellipsoidal particle and the probability density of the ellipsoidal cement particle.

Fig.3. The microstructure model of ellipsoidal cement pastes with $\kappa=0.66$. 

$$
\begin{cases} 
F_v(c) = 1 - \exp\left(-2^n b_0 c^n \kappa^{\frac{2n}{3}}\right) & \kappa \leq 1 \\
F_v(c) = 1 - \exp\left(-2^n b_0 c^n \kappa^{\frac{n}{3}}\right) & \kappa \geq 1 
\end{cases}
$$
Fig. 2 displayed the relationship between equivalent diameters of the ellipsoidal particle and the probability density of the ellipsoidal cement particle with different number of particles (e.g., $N=10^6$, $10^4$ and $10^2$). It could be seen from Fig. 2 that theoretical value of the probability density was more consistent with increasing number of particles. Therefore, in the computer simulation of microstructure of cement pastes, a large number of ellipsoidal cement particles should be generated so that the modelling particle size distribution may precisely represent the theoretical curve.

Based on simulated values of the probability density, the number and volume fraction of the ellipsoidal particle of the corresponding equivalent diameter could be obtained. Consequently, the microstructure model of ellipsoidal cement pastes in a cubic container was established, as shown in Fig. 3.

5. Application of the microstructural model of cement-based materials

Relevant to the design of high performance cement-based materials, insight into the microstructure of cement-based materials and its relationship with cement-based materials properties were of paramount importance. Specifically for early age concrete, the microstructural evolution of solid phase was of high relevance to the development of concrete strength. Nonetheless, opaque materials like cement-based materials did not allow easy access to the three-dimensional material microstructure. Normally, experimental work should provide unbiased information. However, the experimental work was labour-intensive and time-consuming [27]. In addition, although digital images analysis/processing technology could derive some information of three-dimensional materials microstructure, as mentioned earlier, it was limited by the image resolution of equipment [12-14]. Hence, in order to overcome the deficiencies of these approaches, a research strategy was proposed in this study, which was relying on more efficient and practical methodology for characterization of microstructure, i.e., stereological tools and serial sectioning analysis technique.

Stereological theory provided geometrical statistical tools for unbiased estimation of the three-dimensional geometrical parameters of solid phase on the basis of one-dimensional or two-dimensional observations, in other words, measurement of spatial dispersion of solid phase in the stereological theory relied on these geometrical parameters [28]. The most common ones were the area fraction of solid phase ($A_A$), which was an unbiased estimator of the volume fraction of the solid phase ($V_V$). It was generally used to reflect durability of cement-based materials [29, 30]. The perimeter length of solid features per unit test area ($L_A$), allowing for estimating the specific surface area ($S_V$) of solid phase in cement-based materials, which could be linked to physical properties of cement-based materials, such as mechanical [31] and transport properties [32], and the mean free spacing between particles, $\lambda$ (as shown in Eq. (5)). In a sense, pore space was considered to be complementary to solid phase in cement pastes. So, the mean free spacing between solid clusters reflected information on the average pore size [32]. Therefore, these spacing parameters were combined with serial sectioning analysis technique and applied to two-dimensional section planes of actual cement pastes for three-dimensional characterization of microstructure of solid phase.

$$\lambda = \pi \frac{1-V_V}{L_A}$$

(5)

where $\lambda$ was the mean free spacing between particles, $V_V$ was the volume fraction of the solid phase, and $L_A$ was the perimeter length of solid features per unit test area.

To characterize microstructure of cement pastes, a three-dimensional model of cement particles packing should be constructed, as illustrated in Section 4. It was worth noting that boundaries of the model were not periodic conditions, but semi-periodic conditions (as shown in Fig. 4), in which the top
and low boundary planes of the cubic container were defined as rigid conditions, and the other four boundary planes were set as periodic conditions.

![Fig.4](image_url) **Fig.4.** Visualization of the polydispersed ellipsoidal cement particle packing in semi-periodic boundary conditions: the top and low gray planes were rigid boundary conditions, and black planes were serial sectioning planes.

Now, for a given particle size range of 1-50 μm and a given $W/C=0.40$, a comparison for the dependence of microstructure of cement pastes on particle shape (ellipsoidal particles ($\kappa=0.66$) and spherical particle) was presented. In order to guarantee the statistical reliability of the result, 100 model samples were generated for each particle shape. Fig.5 (a), Fig.5 (b) and Fig.5 (c) displayed the statistical result of $V_f$, $L_A$ and $\lambda^2$ vs. distance to the rigid boundary plane, respectively.

It could be seen from Fig.5 that curves of $V_f$, $L_A$ and $\lambda^2$ vs. distance were both symmetrical in the interval between the top and the low boundaries with rigid conditions. Due to significant structure-sensitivity of $V_f$ and $\lambda^2$, the curves of $V_f$ and $\lambda^2$ vs. distance presented a weak oscillation, in other words, 100 model samples could not satisfy the structure-sensitivity of $V_f$ and $\lambda^2$. However, the shape of the curve of $V_f$ was basically divided into ascending and horizontal parts, as well as the shape of the curves of $L_A$ and $\lambda^2$ was very similar and consisted of three regions: ascending, descending and horizontal region.

![Fig.5](image_url) **Fig.5.** Comparisons between ellipsoidal cement particles ($\kappa=0.66$) and spherical cement particles on: (a) $V_f$ vs. distance, (b) $L_A$ vs. distance, (c) $\lambda^2$ vs. distance.

Fig.5 (a) illustrated a comparison between ellipsoidal cement particles ($\kappa=0.66$) and spherical cement particles on the statistical result of $V_f$ vs. distance to the rigid boundary plane. It could be seen that the curve of $V_f$ of the ellipsoidal particle packing system was basically consistent with that of the spherical particle packing system, the result agreed with our previous findings on two-dimensional elliptical particles [30]. However, the peak value and the horizontal value of $L_A$ corresponding to the ellipsoidal particle packing system were remarkably higher than that of the spherical particle packing system, as shown in Fig.5 (b). It was of interest to note from Fig.5 (b) that distances corresponding to the peak value and the horizontal value of $L_A$ were almost the same for both shapes of particle, respectively. Similarly,
Fig. 5 (c) represented a comparison of $\lambda^{-2}$ curves for ellipsoidal as well as spherical particles. That indicated that the mean free spacing of ellipsoidal cement particles was lower than that of spherical cement particles, in other words, the average pore size for the ellipsoidal particle packing model was lower than that of the spherical cement particle packing model. The reason was that under the same particle size distribution as well as the same volume fraction of solid, the specific surface area of the polydispersed ellipsoid particle system was greater than that of the polydispersed sphere system (i.e., $S_{V_{e}}(ellipsoid) > S_{V_{s}}(sphere))$ [33].

6. Conclusions

In this study, a microstructural model for the random packing of three-dimensional ellipsoidal particles in cement-based materials has been developed. By the visualization of the monodispersed ellipsoid random packing structure with rigid boundary conditions, the accuracy and reliability of the ellipsoid packing model has also been verified. Further, based on the advanced size distribution function of ellipsoidal particles, microstructural model of cement pastes was constructed. Applied stereological tools and serial sectioning analysis technique, the comparison of the dependence of microstructure of cement pastes on ellipsoidal cement particles and on spherical cement particles has been presented, and the comparing results revealed that: (1) $V_{f}$ curve of the ellipsoidal particle packing system was consistent with that of the spherical particle packing system. (2) The peak value and the horizontal value of $L_{A}$ corresponding to the ellipsoidal particle model were remarkably higher than that of the spherical particle model. (3) The mean free spacing $\lambda$ of ellipsoidal particle packing structure was lower than that of spherical particle packing structure. To comprehensively investigate the influence of the shape of ellipsoidal particles on the microstructure of cement-based materials, random packing models of ellipsoidal particles with various shapes needed to be utilized to characterize microstructure of cement-based materials in the future work.

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