Structure Simulation of Concentrated Suspensions of Hard Spherical Particles

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A Monte Carlo technique is applied to simulate the structure of concentrated suspensions of hard spherical particles that obey lognormal distribution. With this technique, the random loose packing, with packing density Φ_m, is obtained first, and then the particles in the packing are randomly separated to achieve a specified solid-volume fraction Φ. The simulated structure is evaluated both in the microscale, the neighboring number distribution, and the distribution of gaps between neighboring particles; and in the macroscale, the distribution of the solid-area fractions on a series of parallel cross sections. Results show that, at the same solid-volume fraction, the increase in the standard deviation of particle diameters leads to the decrease in the mean neighboring number and leads to the increase in the mean gap. The mean relative gap obtained from the simulation is larger than that from theoretical prediction, $\delta = [(\Phi_m/\Phi)^{1/3} - 1]$. With particles of lognormal distribution, both the gap sizes and the neighboring numbers distributed over broader ranges than that with equal particles. Results also show that, with equal particles and particles of lognormal distribution, there is no significant difference between the distributions of the solid-area fractions on the cross sections. The structures obtained in this study are shown to be completely random, homogeneous, and isotropic by statistical tests.

Introduction

Concentrated suspensions are processed in many industries, such as in the chemical, powder material, pharmaceutical, and food industries. Understanding of the structure of concentrated suspensions is of significance in different disciplines, such as in predicting the metastability and glass transition, the thermodynamic properties, the electrical conductivity, and the rheology of these kinds of materials during processes.

The structure of concentrated suspensions can be characterized by different geometric statistic parameters corresponding to different physical properties. Hoover et al. (1979) and Sastry et al. (1998) applied analytical and simulation techniques to determine the free-volume (the volume over which the center of a given particle can translate) and corresponding surface-area distributions that are directly related to thermodynamic quantities of a suspension system. Sastry et al. (1998) also obtained the cavity-volume (the volume of the connected region of space available for the addition of another particle) distribution indirectly from the free-volume distribution. The cavity-volume distribution makes it possible to calculate the chemical potential in the vicinity of the freezing transition. Lado and Torquato (1986) investigated the dependence of the effective electrical conductivity and the effective bulk modulus of a concentrated suspension on its structure.

The mean relative gap δ, the ratio of the mean gap between neighboring particles to particle diameter, is another important geometric parameter in predicting the rheological properties of concentrated suspensions. If the particle packing density Φ_m is known and it is assumed that, by adding a liquid medium, the particles are equally separated to a solid-volume fraction of Φ, then by theoretical analysis δ is given by (Frankel and Acrivos, 1967; Hoffmann and Kevelam, 1999)

$$\delta = (\Phi_m/\Phi)^{1/3} - 1. \quad (1)$$

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This parameter has been employed in many viscosity models (Krieger and Dougherty, 1959; Frankel and Acrivos, 1967; Kitano et al., 1981; Probstein et al., 1994). These models are based on the idea that, at high concentration, the flow of suspensions is dominated by the interaction between neighboring particles. The interaction force, and hence the viscosity, is proportional to δ^{-1}. At high solid-volume fraction the viscosity significantly increases as δ decreases, and as δ approaches zero the suspension becomes immobile.

Theoretical analysis provides a simple way to study concentrated suspensions through structures. However, it cannot give more detailed structure information, such as the configurations of a large number of particles, which is a prerequisite to studying suspension flow using the Stokesian dynamic simulation technique (Brady et al., 1983; Chang and Powell, 1993; Toivakka and Eklund, 1996). By this technique a suspension is treated as a discrete system, and then interactions between neighboring particles and their instantaneous positions are computed step by step. Thus, the macroscopic rheological properties of the suspension can be determined by appropriate temporal and spatial averaging of the microstructure information. A computer simulation technique has been applied to study the structure of concentrated suspensions (Lee and Torquato, 1988; Sevick et al., 1988; Rintoul and Torquato, 1996; Sastry et al., 1998). In these simulations, however, either the particles were restricted to equal size or the number of particles was very limited.

In this article we apply a Monte Carlo technique to simulate the structure of concentrated suspensions of spherical particles obeying lognormal distribution, which is the best fit of particle-size distribution (Rumpf, 1990). This simulation technique is a further development based on our recent work on particle random packings (He et al., 1999). There is a rich literature on computer simulation of particle packings, and the features of different simulation models were reviewed in the work just cited. At a given solid volume fraction Φ, we characterize the structure both in the microscale, the distributions of neighboring number and the gaps between neighboring particles; and in the macroscale, the distribution of the solid area fractions on a series of parallel cross sections. The simulation algorithm is described in the next section. Then we present the simulation results. The final section presents our conclusions.

Simulation Algorithm

The simulation algorithm is composed of four steps, the generation of particle diameters and initial positions, the relaxation of overlaps, the expansion of the packing space, and the random separation of contact particles. For convenience, we normalize the mean particle diameter to one unit; thus hereafter we use "gap" instead of "relative gap."

The probability density function of particle diameter d obeying lognormal distribution is given by [note that $\bar{d} = 1.0$ and $\ln(\bar{d}) = 0$]

$$f(d) = \frac{1}{\sqrt{2\pi}\sigma d} \exp^{-[\ln(d)]^2/2\sigma^2}, \tag{2}$$

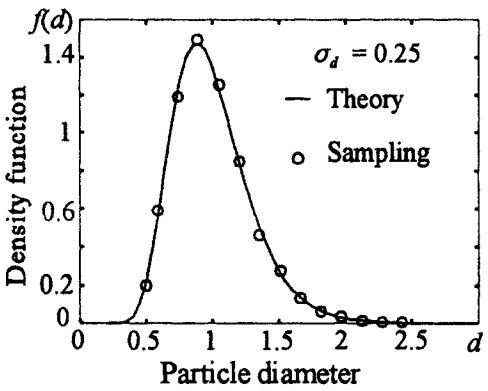

Figure 1. Numerical sampling vs. probability density function of lognormal distribution.

where σ is the standard deviation of $\ln(d)$ but not of d. The diameters $(d_1, d_2, \ldots, d_n)$ of n particles are generated by the following steps. First we sample a set of random numbers $(p_1, p_2, \ldots, p_n)$, obeying uniform distribution over (0,1). Then applying two transformation functions, $t_i = \sigma(-\ln p_i)^{1/2}\sin(2\pi p_i + 1)$ and $d_i = \exp(t_i)$, we obtain the particle diameters $(d_1, d_2, \ldots, d_n)$ that obey lognormal distribution. The standard deviation of d is given by $\sigma_d = [\Sigma(d_i - 1)^2/n]^{1/2}$. Figure 1 shows the agreement of the numerical sampling with the theoretical probability density function. The initial position $\boldsymbol{R}_i$ of a particle is randomly generated within a cubic space, and its projections (x_i, y_i, z_i) all obey uniform distribution over $(0 + d_i/2, L_o - d_i/2)$. Here, L_o is the initial size of the cubic space that is given by

$$L_o = \left[\frac{1}{\Phi_o}\sum_{i=1}^{n}\frac{\pi}{6}d_i^3\right]^{1/3} \tag{3}$$

where Φ_o is the initial packing density and n is the total number of particles. In this study 0.75 is taken as the value of Φ_o. The random close packing density of equal particles is around 0.63 (Scott, 1960; Nolan and Kavanagh, 1994). Therefore, in the initial positions most particles overlap each other.

The overlap rate between two particles, particle i and particle j, for example, is defined as $(d_i/2 + d_j/2 - l_{ij})/(d_i/2 + d_j/2)$, where l_{ij} is the center-to-center distance and $l_{ij} < (d_i/2 + d_j/2)$. The following relaxation technique is applied to reduce or eliminate the overlaps. For each particle, particle i, for example, a search of particles that overlap particle i is conducted first. Then from each of the overlapping particles, particle j, for example, a new position can be calculated by

$$\boldsymbol{R}_{ji} = \boldsymbol{R}_j + (\boldsymbol{R}_i - \boldsymbol{R}_j)\frac{d_i + d_j}{2l_{ij}}, \tag{4}$$

where $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ are the positions of particles i and j. If particle i is overlapped by n_i particles, then by Eq. 4 n_i positions can be obtained. The new position of particle i is given by

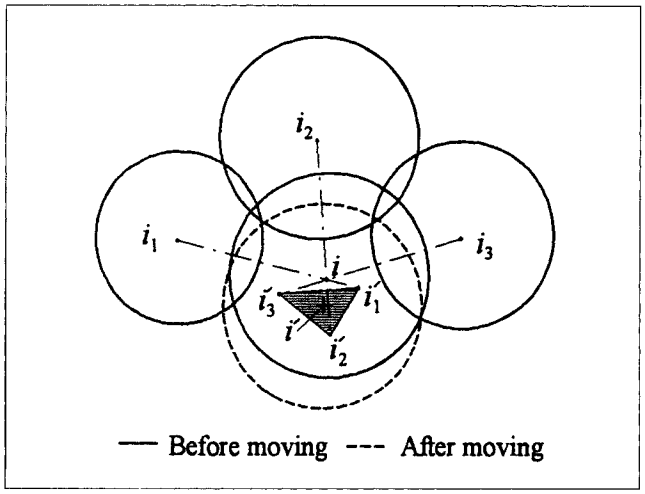

Figure 2. One-step motion of particle *i* from its overlapping neighbors.

$$\boldsymbol{R}'_i = \frac{1}{n_i}\sum_{j=1}^{n_i} \boldsymbol{R}_{ji}. \tag{5}$$

Figure 2 shows the two-dimensional (2-D) case of moving particle i by one step. This relaxation is applied to every overlapped particle. After one iteration each overlapped particle has been relocated to a new position. By repeating the relaxation iteration the mean overlap rate gradually decreases. After a given number of iterations, we expand the packing space to $L = \alpha L_o$, where α is the expanding factor that is greater than one and is proportional to the present mean overlap rate. The relaxation and expansion steps are repeated, and the random packing is obtained as the mean overlap rate drops below a preset tolerance. In this study 2×10^{-4} is accepted as the tolerance that ensures that the relative error in the final packing density Φ_m is less than 10^{-3}.

The final step is the random separation of particles from the packing. If the random packing density obtained from the preceding simulation is Φ_m and the solid volume fraction of a concentrated suspension is Φ, then the separation factor is defined as $\lambda = (\Phi_m/\Phi)^{1/3}$. The following equation is applied to separate particles to simulate the structure of a suspension with solid-volume fraction of Φ

$$\boldsymbol{R}_{i,s} = \lambda \boldsymbol{R}_{i,p} + \frac{d_i}{2}(\lambda - 1)\Delta \boldsymbol{R}_i, \tag{6}$$

where $\boldsymbol{R}_{i,p}$ and $\boldsymbol{R}_{i,s}$ are the positions of particle i before and after separation, and $\Delta \boldsymbol{R}_i$ is a random vector whose module obeys uniform distribution over (0,1) and whose direction obeys uniform distribution in three-dimensional space. As shown in Figure 3, by the first term on the right hand of Eq. 5, each particle is separated from others and is placed in the center of a spherical space with a radius of $\lambda d_i/2$. By the second term this particle is randomly placed in a position within the spherical space. The second term is used to realize the random distribution of gaps between neighboring particles.

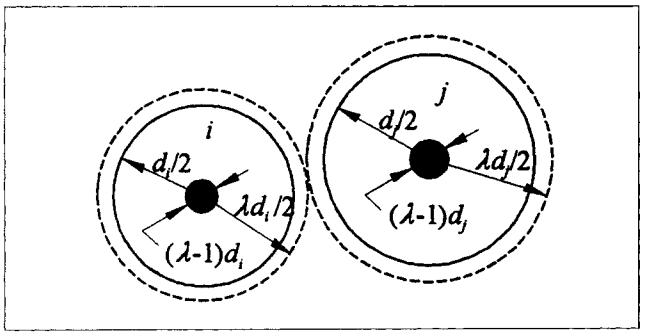

Figure 3. Separation of two neighboring particles.

The center of particle i obeys uniform distribution within the shadowed circle.

Simulation Results and Discussion

We applied the previous model each time ten thousand particles were simulated. Figure 4 shows the three-dimensional views and two-dimensional cross-section views of the random packing and the structure of a concentrated suspension with a solid-volume fraction of 0.45. The simulation results are presented as follows.

Distributions of neighboring numbers, gap sizes, and solid area fractions on cross sections

By experiment, Bernal and Mason (1960) found that in a random packing of particles there exist both close contacts

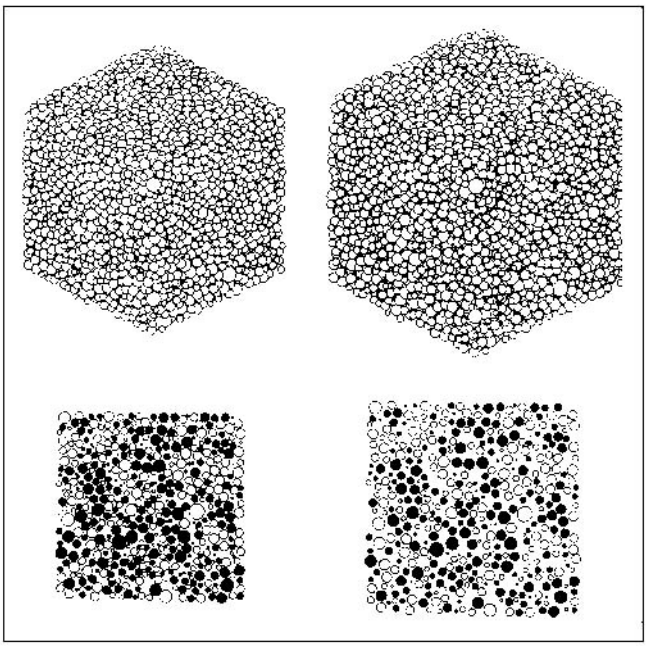

Figure 4. 3-D and 2-D cross sections of random packing (left) and concentrated suspension with solid-volume fraction of 0.45 (right), $\sigma_d = 0.20$.

Centers of darkened particles are in front of the cross sections.

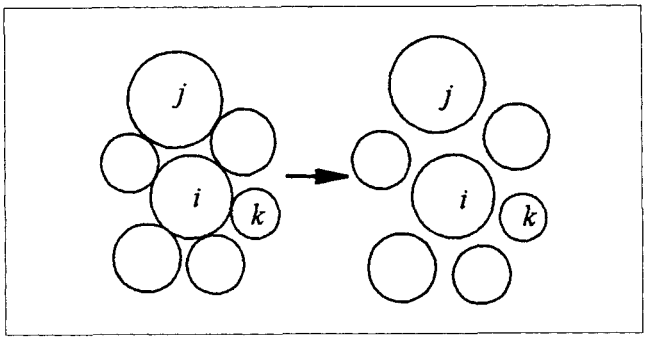

Figure 5. Particles in random packing (left) and in suspension (right).

Theoretical prediction cannot take the gap between particle i and particle j into consideration.

and near contacts (with gaps smaller than $0.1d$). Theoretical analysis does not take the near contacts, such as particle i and particle j shown in Figure 5, into account. However, because the hydrodynamic interaction between these two particles may be stronger than that between particle i and a nearer but smaller particle, such as particle k, it should be taken into account. In the random packing obtained by the simulation, we examined the mean neighboring number m as a function of the gap δ between near particles. For equal particles we found that, as $\delta \le 5\%$ $m = 6.65$, as $\delta \le 10\%$ $m = 8.48$, and as $\delta \le 20\%$ $m = 8.93$, which means that, as $\delta \ge 10\%$, the increase in m is insignificant. In concentrated suspension flow, the interaction between two particles also significantly decreases as the gap increases. Therefore, we only took two particles in the random packing as neighboring particles if the gap between them was smaller than 10% of the sum of their radii. Figure 6 shows the random packing density Φ_m and the mean neighboring number m as functions of the standard deviation σ_d of particle diameters. With equal particles, we got that $\Phi_m = 0.596$, which falls in the generally accepted range of the random loose packing density 0.59 ~ 0.60 (Scott, 1960; Tory et al., 1973; He et al., 1999). The random loose-packing density has been taken as the limit of solid-volume fraction in many viscosity models of concentrated suspensions of noncolloidal particles (Chong et al., 1971; Sudduth, 1993). With particles obeying lognormal distribution, Φ_m significantly increases with σ_d as $\sigma_d > 0.15$. This is because, as σ_d increases, the chance for a small particle to fill the cages among large particles increases. The effect of σ_d on Φ_m quantitatively agrees with the experimental result (Sohn and Moreland, 1968) and qualitatively agrees with other simulation results (Nolan and Kavanagh, 1993; Yang et al., 1996). With equal particles $m = 8.48$, which is much higher than the coordination number of random loose packing, which is about 5.5. This is because, as defined earlier, particles in near contact were taken into account in this study. It agrees with the experimental result of Bernal and Mason (1960). With particles of lognormal distribution, as σ_d increases m decreases, and this effect also becomes significant as $\sigma_d > 0.15$.

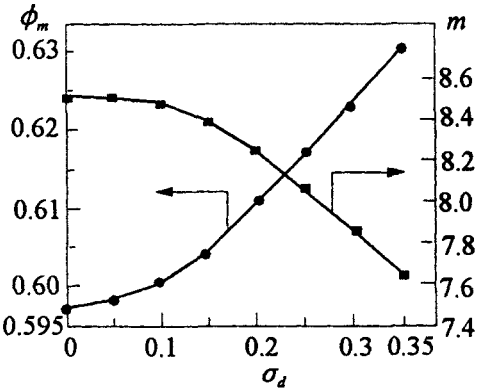

Figure 6. Packing density and neighboring number as functions of σ_d.

Figure 7 shows the mean gap δ as a function of the solid volume fraction Φ and the standard deviation σ_d of particle diameters. Applying the random packing density given in Figure 6, it was found that the mean gap can be well correlated with Φ_m/Φ by the following equation:

$$\delta = 0.018 + \left[(\Phi_m/\Phi)^{1/3} - 1\right]. \tag{7}$$

Comparing Eq. 7 with Eq. 1, it is seen that, since the near-contact particles in the random packing were taken into account, at the same solid-volume fraction the mean gap given by Eq. 7 is greater than that predicted by Eq. 1. At a high solid-volume fraction the relative viscosity of concentrated suspensions of noncolloidal particles is significantly influenced by the particle-size distribution, that is, the higher the standard deviation the lower the viscosity. This can be explained by the effect of particle-size distribution on the mean gap. Taking $\Phi = 0.5$, for example, with $\sigma_d = 0.20$, the mean gap $\delta = 0.091$, that is, about 1.15 times of the mean gap of equal particles, which is about 0.079. The flow of concentrated suspensions of noncolloidal particles is mainly dominated by the hydrodynamic interaction, the lubrication force between neighboring particles, which is proportional to δ^{-1} (Frankel and Acrivos, 1967; Cox, 1974). Thus, for concentrated suspensions with particles of lognormal distribution, the viscosity decreases as σ_d increases.

Figure 8 compares the distribution of neighboring numbers of equal and lognormal distributed particles. With equal particles, the neighboring numbers lie between 4 and 12, and about 85% of particles have neighboring numbers between 7 and 10, while with lognormal distributed particles, the neighboring numbers are dispersed in a broader range. Taking $\sigma_d = 0.20$, for example, less than 70% of particles have neighboring numbers between 7 and 10. In a random packing of unequal particles, it is expected that, large particles tend to be surrounded by more neighboring particles, while small particles tend to be surrounded by fewer neighboring particles.

In Figure 9 a solid-volume fraction of 0.5 is used to compare the distributions of gaps in suspensions of equal and lognormal distributed particles. It is seen that, with lognormal distributed particles, the gaps are distributed over a broader range than that with equal particles. The effect of particle-size distribution on the gap distribution is similar to its effect on the distribution of neighboring number. How-

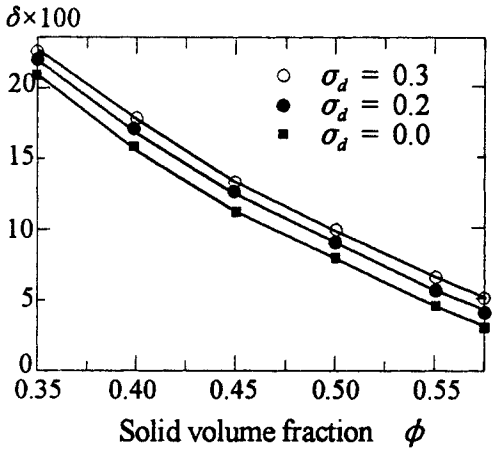

Figure 7. Mean gap as function of solid-volume fraction with different values of σ_d.

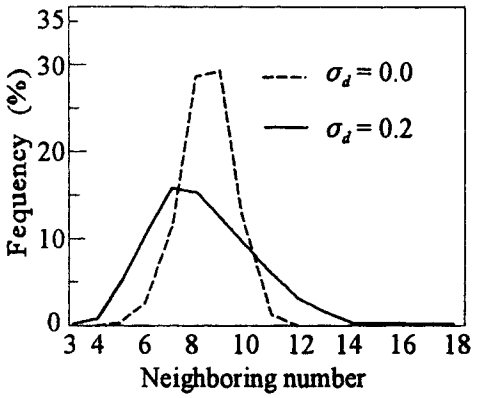

Figure 8. Neighboring number distributions of equal and lognormal distributed particles.

ever, the mean neighboring number of equal particles is higher than that of lognormal distributed particles, while the mean gap between equal particles is smaller than that between lognormal distributed particles.

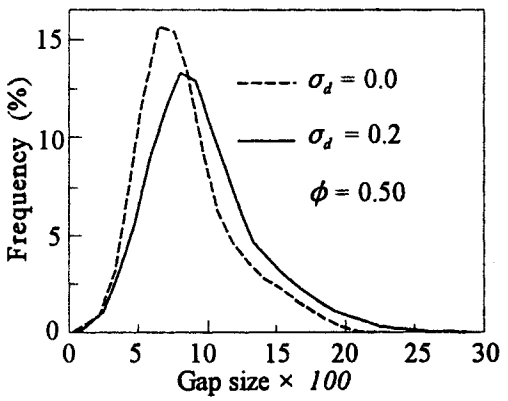

Figure 9. Gap-size distributions of equal and lognormal distributed particles at $\Phi = 50\%$.

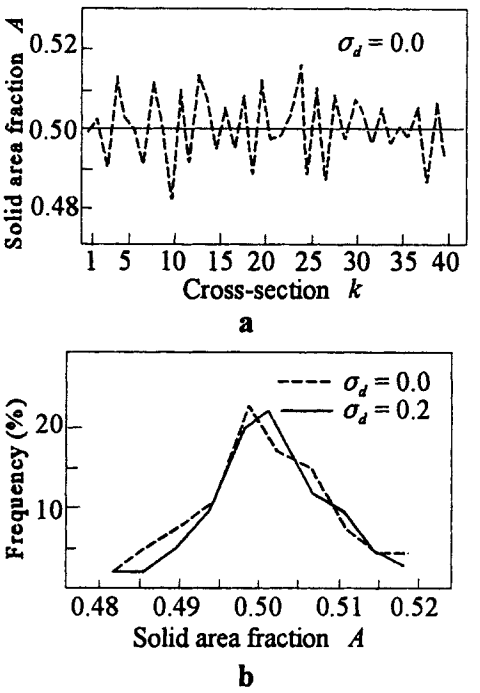

Figure 10. Solid-area fractions (a) on cross sections, and (b) comparison of distributions.

To evaluate the structure in a macroscale, each simulated suspension body was cut by forty equally separated parallel cross sections (see the two-dimensional view of Figure 4), and the distribution of the solid-area fractions was examined. At a solid-volume fraction of 50%, Figure 10a shows a series of solid-area fractions on the cross sections in sequence. Figure 10b compares the distributions of the solid-area fractions of equal and lognormal distributed particles. The mean and the standard deviation of the solid-area fractions are 0.501 and 0.0101, respectively, for equal particles, and are 0.499 and 0.0093, respectively, for lognormal distributed particles. A statistic test shows that there is no significant difference between the two solid-area fraction distributions. However, it may imply that, with particles of the same elemental composition, the particle-size distribution has no significant influence on some of the physical properties of concentrated suspensions, such as the electrical or thermal conductivity that is proportional to the solid-area fraction on the cross section, while, as we discussed earlier, the use of lognormal distributed particles can reduce the viscosity.

The randomness, homogeneity, and isotropy

It is known that during processes such as shearing, the structure of concentrated suspensions may experience the transitions from disordering to ordering due to particle rearrangement from homogeneous to inhomogeneous or from isotropic to anisotropic due to particle immigration (Marshall and Zukoski IV, 1990). To study the transition processes, the structure should be initially random, homogeneous, and isotropic. The following methods were used to test these structure properties.

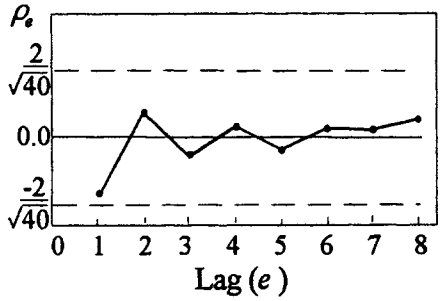

Figure 11. Autocorrelation coefficients of solid-area fractions on cross sections.

Time-series analysis technique (Chatfield, 1989) was employed to test the randomness. The autocorrelation coefficient of the solid-area fractions on the cross sections (see Figure 10a) can be calculated using the following equation:

$$\rho_e = \frac{\sum_{t=1}^{40-e} (A_t - \bar{A})(A_{t+e} - \bar{A})}{\sum_{t=1}^{40} (A_t - \bar{A})^2}, \qquad (8)$$

where A_t is the solid-area fraction on the tth cross section, $\bar{A}$ is the mean solid-area fraction, and e is the lag that should be smaller than one-quarter of the number of the cross sections; here $e < 10$. The time-series analysis technique proves that if the series of area fractions is completely random, which implies that the particles are randomly suspended in the system, then ρ_e is expected to lie between $\pm 2/\sqrt{40}$. The equal-particle autocorrelation coefficients at $e = 1, 2, \ldots, 8$ are plotted in Figure 11. It is seen that all the values of ρ_e lie between the upper and lower limits. For lognormal distributed particles, similar results were also obtained. Therefore, the structures obtained by the simulation are of complete randomness.

To test the homogeneity without considering the particles on the surface, we divided the remainder of each suspension into 64 equal cubic subcells and counted the particles in each subcell. Table 1 is one example of the counting results. Then the chi-square goodness-of-fit test was applied to examine the hypothesis that the particles are uniformly distributed among the subcells. The test statistic of the data of Table 1 is $\chi^2 =$ 17.41. At the 0.05 level, the critical value $\chi^2_{0.05,63}$ is 82.53, which is much greater than the test statistic; therefore, there is no evidence that the hypothesis should be rejected. This implies that the simulated suspensions are homogeneous.

Table 1. Particle Distribution Among Subcells

Top	118	118	122	120	126	111	127	116
Layer	129	107	119	128	113	115	120	110
Second	121	114	124	106	123	112	122	124
Layer	117	119	106	120	115	120	128	122
Third	117	116	116	112	121	125	116	114
Layer	116	109	122	120	125	113	117	128
Bottom	113	125	114	119	116	122	117	118
Layer	109	124	116	108	117	120	117	111

$$\bar{m} = \frac{1}{64}\sum m_i = 117.8 \qquad \chi^2 = \sum \frac{(m_i - \bar{m})^2}{\bar{m}} = 17.41$$

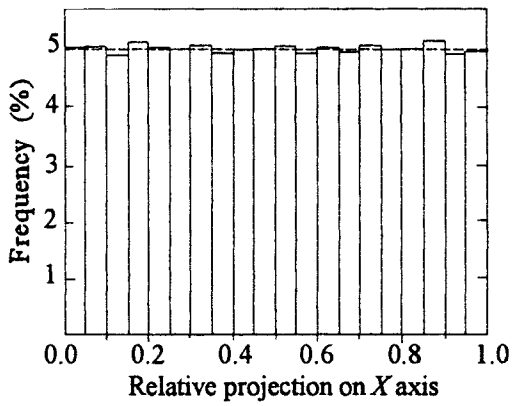

Figure 12. Distribution of relative projections of center-to-center lines between neighboring particles on the X axis.

The distribution of the relative projections of the center-to-center lines between neighboring particles was used to examine the isotropic property of the suspensions. The relative projections of two neighboring particles are defined as

$$px_{ij} = \frac{|x_i - x_j|}{l_{ij}} \qquad py_{ij} = \frac{|y_i - y_j|}{l_{ij}} \qquad pz_{ij} = \frac{|z_i - z_j|}{l_{ij}}, \qquad (9)$$

where l_{ij} is the center-to-center distance. It was proven that (Tory et al., 1974) if px_{ij}, py_{ij}, and pz_{ij} all obey uniform distribution over (0,1), then the structure is isotropic. The mean and variance of a random variable obeying uniform distribution over (0,1), are 0.5 and 0.08333, respectively. For the case shown in Figure 4, the means of the relative projections on X, Y, and Z axes are 0.4990, 0.5002, and 0.4993, and the variances are 0.0836, 0.0832, and 0.0837, respectively. Figure 12 shows the distribution of the projections on the X-axis. The test showed that the projections obey uniform distribution over (0,1). Therefore, the suspensions obtained by this simulation are isotropic.

Conclusion

A Monte Carlo simulation model was used to simulate the structure of the concentrated suspensions of the hard spherical particles obeying lognormal distribution. Using this model, the random loose packing was obtained first, after which particles in the packing were separated to achieve a specified solid-volume fraction. The simulation results show that:

1. The mean gap between neighboring particles δ can be correlated with the random packing density Φ_m and solid-volume fraction Φ by $\delta = 0.018 + [(\Phi_m/\Phi)^{1/3} - 1]$, which is higher than that of the theoretical prediction.

2. For the same solid-volume fraction, increasing the standard deviation of particle diameters decreases the mean neighboring number and increases the mean gap between neighboring particles.

3. As the standard deviation of particle diameters increases, both the gap sizes and the neighboring numbers distribute over broader ranges. In contrast, particle-size distribution has no significant influence on the distribution of solid-area fractions on the cross sections.

4. The structures of concentrated suspensions obtained in this study are random, homogeneous, and isotropic.

The results of this work can be used in the study of the physical properties of concentrated suspensions. For example, in modeling the rheology of concentrated suspensions, and in particular, the numerical study of suspension flow and structure transition.

Acknowledgment

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