Three-dimensional granular dynamics simulations of polydisperse and bidisperse nanopowders compaction processes

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Abstract. Nanopowder uniform compaction processes are simulated by the three-dimensional granular dynamics method. The interaction of particles in addition to wide-known contact laws involves the dispersion forces of attraction and possibility of interparticle solid bridges formation, which have a large importance for nanopowders. Different model systems are investigated: monosize systems with particle diameter of 10, 20 and 30 nm; polydisperse systems corresponding to the log-normal particle size distribution law with different width; bidisperse systems with different content of small (the diameter is 10 nm) and large (30 nm) particles. The deviations of compact density in polydisperse systems from the density of corresponding monosize system are found to be minor. Non-monotone dependence of compact density on the weight fraction $\omega_m$ of small particles is revealed in the bidisperse systems, where the density maximum is found to be about 7–8% in the vicinity of $\omega_m = 0.35$.

1. Introduction

Processes of the cold compaction of nanosize powders are the grave problem for manufacturing the nanostructured ceramics by the powder metallurgy methods. Large forces of interparticle adhesion, which result from intermolecular dispersion forces of attraction, and high strength of nanoparticles require to use very high pressures (of gigapascal range) to achieve densities desired at the compaction stage [1–6]. Theoretical search of most effective conditions of compaction processes takes here on special significance and topicality. However it is hampered by absence of a valid phenomenological theory describing the powder body properties. Thereupon the direct simulations of nanopowders by the granular dynamics method, also known as the discrete element method [4, 5, 7–11], have attractive prospects. Different regularities of nanopowder systems, for example, the size effect in nanopowder compaction processes, have been already investigated in the framework of the granular dynamics method [4, 5, 12–14]. Heretofore objects for numerical experiments are monodisperse systems [8, 12–14], which consist of particles of the same size, or systems with very artificial particle size distributions, for example, the uniform distribution into the given narrow range of sizes [9]. This situation differs drastically from real experimental conditions [1–3, 6].

It is unlikely that the influence of particle size distribution on the powder compressibility could be detected by full-scale experiments since here there are too many factors, which have
Figure 1. Particle size distribution function $f_n$ (a) for polydisperse systems, equation (1), and the function $f_m \propto d^3 f_n(d)$, which describes the particle mass distribution (b). Lines correspond to the parameter $\sigma = 0.47$ (lines 1), 0.30 (lines 2) and 0.15 (lines 3); $d_{mp} = 20$ nm.

an influence at one time. However some data are rather evidence of presence such influence [6]. Attempts of studying this problem in the frames of numerical experiments have been made earlier, for example, in papers [7,11,15]. However, in references [7,11] powders of micron sizes have been simulated. Interparticle interactions in such powders have essential distinctions from the nanoparticle interactions, namely dispersion attraction of particles is negligible, the plastic deformation of particles play an important role, and so on. Investigation [15] has been performed for two-dimensional (2D) geometry, and the present work continues that study.

2. Objects of study and investigation method

The aim of the present study is to analyze the influence of particle size distribution upon the compressibility of nanopowder systems. To achieve the aim the processes of the uniform compaction have been simulated by granular dynamics method in three-dimensional (3D) geometry. The following systems are simulated: equigranular (or monodisperse) systems with particles diameter $d = 10, 20$ and $30$ nm; polydisperse systems, which are described by the log-normal size distribution law with maximum at the diameter $d_{mp} = 20$ nm and different widths; bidisperse systems with different content of small (the diameter is $d_1 = 10$ nm) and large (the diameter is $d_2 = 30$ nm) particles.

The particle size distribution for polydisperse systems is determined in the form of truncated log-normal law:

\[
  f_n(x) = \frac{f(x)}{I_n}, \quad f(x) = \frac{1}{x} \exp\left[-\frac{(\mu - \ln x)^2}{2\sigma^2}\right],
\]

where $\mu = \sigma^2 + \ln(d_{mp})$, $d_{mp} = 20$ nm, $I_n$ is the normalization integral,

\[
  I_n = \int_{d_{min}}^{d_{max}} f(x) \, dx, \quad d_{max} = d_{mp} \exp\left(\pm\sigma\sqrt{2\ln 6}\right),
\]

and the limits $d_{min}$ and $d_{max}$ are determined by the condition of the function $f(x)$ reduction by 6 times with respect to the maximum at $x = d_{mp}$. Beyond the bounds of $(d_{min}, d_{max})$ the normalized function $f_n(x)$ is fixed to zero. The systems with different distribution width are
Figure 2. Examples of initial powder structures: (a) a bidisperse system with the relative fraction of small particles $\omega = 0.95$ ($d_{rep} = 20$ nm); (b) a polydisperse system, where the particle size distribution is described by the function of (1) with parameters $\sigma = 0.47$ and $d_{mp} = 20$ nm.

studied: $\sigma = 0$ (a monodisperse system), $0.15$, $0.30$ and $0.47$. The maximal value $\sigma = 0.47$ corresponds to the real nanosize powders [5], which are produced by the method of electric explosion of wires [16]. Figure 1(a) shows the functions $f_n(x)$ of particle size distribution (1). Figure 1(b) shows the functions $f_n \propto x^3 f_n(x)$, which describe the weight fraction of particles with a given diameter, i.e., the mass or volume distribution functions. It is helpful to note that in spite of the fixed value of most probable diameter ($d_{mp} = 20$ nm) the distribution width increase results in the considerable increase of the diameter, which corresponds to the maximal contribution of particles to the total system mass. For example, it can be seen in figure 1(b) that at $\sigma = 0.47$ the particles with the diameter of 39 nm have the maximal weight fraction of a whole system.

The total number of particles $N_p$ in model cells has been set equal to 4000. At that, as test calculations show, a model cell is a reliable representative volume of the powder body, i.e., the influence of the cell sizes on the model system properties is negligible. The initial density of all model systems has been set equal to $\rho_0 = 0.24$. As the density we have used the relative volume of the model cell, which is occupied by the particles, i.e., $\rho = V_p/V_{cell}$. To generate initial structures the algorithm [12] is used, which allows producing isotropic and homogeneous structures in the form of connected 3D-periodical cluster. Figure 2 shows of initial structures of the bidisperse and polydisperse systems. For the purpose of clearness the figure demonstrates systems consisting of less number of particles (400) by order than the model systems being simulated. It was noted in reference [15] that the model polydisperse system with distribution width $\sigma = 0.47$, see figure 2(b), in 2D-geometry looks like real nanopowder photographs obtained by the scanning electron microscopy.

The parameters of interparticle interactions correspond to oxide nanosize powders with strong agglomeration tendency, i.e., the systems of II type in references [12,13]. The theoretical model [12,13] includes the contact interaction laws, such as the modified Hertz law, which describes the elastic repulsion of particles, the linearized Cattaneo–Mindlin law [17,18], which describes the “friction” forces at particle shift, the Jäger law [18,19], which describes the “pivoting friction” of contact particles, the Lur’e law [20], which describes the contact elasticity to the particle
Figure 3. Compaction curves on the density–pressure plane: the monosystem with the particle diameter \( d = 20 \) nm (line 1) and polydisperse systems described by the log-normal distribution (1) with parameters \( d_{mp} = 20 \) nm, \( \sigma = 0.15 \) (line 2), 0.30 (line 3), and 0.47 (line 4).

rolling, as well as modified Hamaker’s formula [21], which describes the dispersion attractive forces, and the possibility of interparticle solid bridges formation [10]. Note that the dispersion attractions and the agglomeration tendency for the nanosize powders, as distinct from powders of micron (or larger) sizes, take on special significance and, in particular, owing to introduction these factors the size effect in compaction processes, well-known from the experimental studies [1–3,6], is reproduced by the granular dynamics method. All parameters of particle interactions have been described elsewhere [12, 13] in detail.

3. Results and discussion

Figures 3–7 demonstrate the simulation results for polydisperse and bidisperse systems. Figures 3 and 4 show the compaction curves, the curves each constructing on the basis of averaging 5–20 independent numerical experiments. The statistical accuracy of the density amounts to 0.001, as a rule, with the exception of bidisperse systems at low pressure, whose accuracy is shown in figure 6. As the relative fraction of small particles in figures 4 and 6 we imply the quantity \( \omega = N_1/N_p \). The stress tensor \( \sigma_{ij} \), averaged over the model cell, is calculated by the known expression [8–10],

\[
\sigma_{ij} = -\frac{1}{V_{cell}} \sum_{k<l} f^{(kl)}_i r^{(kl)}_j,
\]

where the summation is conducted over all pairs \((k, l)\) of interacting particles. As the compaction pressure in figures 3–7 we have used the main pressure \( p = -\text{Tr}(\sigma_{ij})/3 \).

It is interesting to note that the compaction curves of the polydisperse systems, which are demonstrated in figure 3, intersect at the pressure about 10 MPa. At lower pressures \((p < 10 \text{ MPa})\) the transition from the monosystem to the polydispersity and the increase of log-normal distribution width results in the decrease of attainable compact densities. In the region
Figure 4. Compaction curves on the density-pressure plane: mono- and bidisperse systems with content of small particles $\omega = 1.0$ (line 1), 0.99 (line 2), 0.95 (line 3), 0.70 (line 4), and 0.0 (line 5).

of relatively large densities, at $p > 10$ MPa, we have an inverse effect. The same peculiarity of the influence of polydispersity in the nanosize granular systems was revealed earlier for 2D-geometry [15]. As a whole, as figures 3 and 5 show, in the range of high compaction pressures ($p > 10$ MPa) the transition to polydisperse systems has an insignificant influence on the compact density of the nanosize powder. Density changes do not exceed the value of 0.02. This result justifies the application of monodisperse systems in the frameworks of granular dynamics method to describe the experimental properties of real polydisperse nanopowders, the most probable diameter of size distribution function (1) should be taking the characteristic size. It is worth noting that the last result is quite unexpected. The analysis of mass distribution functions presented in figure 1(b) is seemed to require the considerable increase of the characteristic size, right up to the value of 39 nm at $\sigma = 0.47$. However such an increase of the characteristic size would result in the density shift more than 0.06, i.e., the model system would not be a good prototype of the real polydisperse powder.

Figures 4 and 6 show that for the bidisperse systems at the range of relatively small pressures ($p < 100$ MPa) the chief factor, which determines the change of the compact density, is the size effect: the system with smaller particles ($d_1 = 10$ nm) needs the larger compaction pressure or, in other words, at the given pressure the smaller particles system has smaller value of attainable compact density [1–5,12–14]. The density differences between the systems with particle diameter of 10 and 30 nm amount to value of 0.06 at the pressure $p = 50$ MPa. In the region of large pressures ($p > 1.0$ GPa) the size effect disappears, but due to the density relaxation at the unloading stage the size effect change sign even [14], i.e., the smaller particles system has larger value of attainable compact density. However these differences are little enough and do not exceed by 0.02 of the density. The transition from the monosize system to the bidisperse ones has a lot more impact on the compact densities at large pressures, when $p > 1.0$ GPa. Here, as figures 4 and 6 show, dependences $\rho(\omega)$ of bidisperse systems become non-monotone: there is the
Figure 5. Dependences of the densities of polydisperse systems on the parameter $\sigma$, which determines the width of size distribution (1). Solid lines correspond to the compaction pressures (from the bottom) $p = 0.1$, $1$, $3$, and $5$ GPa; dotted line shows the compact densities after unloading from the maximal pressure ($p = 0$ after $p = 5$ GPa).

maximum at the range of $\omega$ values about 0.95. In the vicinity of the maximum the density values of bidisperse systems can exceed noticeably the densities of corresponding monosize systems. For example, at the pressure $p = 5$ GPa the monosize system densities are 0.756 (30-nm-system) and 0.759 (10-nm-system), and the bidisperse system density at the maximum is 0.812, i.e., the density increases by 7%. At the pressure $p = 1$ GPa the density increase at the maximum is 8% relatively the corresponding densities of monosize systems.

As in the case of 2D-geometry [15], the relative simple considerations can explain rather a sharp increase of the compact density when small number of large particles is added to the initial system of small particles, i.e., in the vicinity of $\omega = 1$. Into the volume being occupied by the large particles added the density of the initial monodisperse system of small particles ($\rho_1 < 1$) has been increased up to the maximal value equal to 1. At the condition that a large particle added does not effect on the density $\rho_1$ of surrounding monodisperse system and also if $d_1 \ll d_2$ and $V_2 \ll V_{\text{cell}}$, where $V_2$ is the volume occupied by the large particles added, it is not difficult to deduce the density change. The density of the initial monodisperse system of small particles and the new density of the bidisperse system are determined by the expressions

$$
\rho_1 = \frac{\pi N_p d_1^3}{6 V_{\text{cell}}}, \quad \rho = \frac{\pi N_1 d_1^3 + N_2 d_2^3}{6 V_{\text{cell}}},
$$

where $N_1 = \omega N$, $N_2 = (1 - \omega)N$. The new number of particles $N = N_1 + N_2$, which are situated into the volume of the initial model cell, is $N = N_p + N_2 - \Delta N_1$. The number $\Delta N_1$ of “displaced” small particles, which was situated into the volume $V_2 = N_2 \pi d_2^3/6$, is $\Delta N_1 = 6V_2\rho_1/(\pi d_1^3)$. 

Figure 6. Dependences of the densities of bidisperse systems on the relative fraction $\omega$ of small particles. Notations are analogous to figure 5. The statistical errors are shown on the curve at $p = 0.1$ GPa; dashed lines are the asymptotes in accordance with the equation (5).

Combining above listed expressions and (3) we get

$$\Delta \rho = \rho - \rho_1 = \frac{(1 - \omega)\rho_1(1 - \rho_1)(d_2/d_1)^3}{\omega + (1 - \omega)\rho_1(d_2/d_1)^3}. \quad (4)$$

In the limit of $\omega \to 1$ this expression gives the asymptotic dependence of the bidisperse system density on the content in the form of

$$\rho(\omega) = \rho_1 + (1 - \omega)\rho_1(1 - \rho_1)(d_2/d_1)^3. \quad (5)$$

The asymptotic dependences of (5) are shown by dashed lines in figure 6 for curves $\rho(\omega)$ corresponding the compaction pressures $p = 0.1$ and 5 GPa, and for the unloading density curve.

As it was supposed in the paper [15] the increase of the exponent in (5) in comparison with the similar equation in 2D-geometry (three instead of two) results in the considerable rise of the maximum on the dependences $\rho(\omega)$. In 2D-geometry the density maximum is about 0.02 only as against 0.06 in figure 6. Noticeable deviations of simulation curves $\rho(\omega)$ from the asymptotes (5) in the limit $\omega \to 1$ are connected with weak implementation of the condition $d_1 \ll d_2$ in the bidisperse systems being studied, where we have $d_2/d_1 = 3$.

In addition to the density dependences on the relative fraction of small particles $\rho(\omega)$ presented in figure 6 it is interesting to analyze the density dependences on the particle weight fraction $\omega_m$, which is connected with parameter $\omega$ by the following relation:

$$\omega_m = \frac{\omega}{\omega + (1 - \omega)(d_2/d_1)^3}. \quad (6)$$
Figure 7. Dependence of bidisperse system densities on the weight fraction $\omega_m$ of small particles. Notations are analogous to figure 5. Dashed lines are the asymptotes with accordance of the equation (7).

Figure 7 presents the dependences of $\rho(\omega_m)$. The asymptotic law (5) in the terms of parameter $\omega_m$ takes a simple form of

$$\rho(\omega_m) = \rho_1 + (1 - \omega_m)\rho_1(1 - \rho_1).$$

(7)

Figure 7 shows that the attainable density maximum is situated at the values of weight fraction of small particles about 30–40%, i.e., the small particles should take about 1/3 of total mass. In 2D-geometry [15] the analog of the parameter $\omega_m$ is the area fraction occupied by small particles, $\omega_s$. The analysis of data presented in the paper [15] shows that density maximum of bidisperse systems in 2D-geometry corresponds to the value of $\omega_s \simeq 1/3$ as well.

4. Conclusion

Compaction processes of mono-, bi- and poly-disperse nanopowder systems are simulated by the granular dynamics method in 3D geometry. The main results of the research are as follows:

- The compressibility of polydisperse systems with log-normal particle size distribution law has been studied. It is revealed that the increase of the distribution width, which is determined by the parameter $\sigma$, from zero (a monodisperse system) up to the value $\sigma = 0.47$ that corresponds to real nanopowders, has an insignificant influence on the compact density. This result justifies the application of monodisperse systems in the frameworks of granular dynamics method to describe the experimental properties of real polydisperse nanopowders.
- The influence of the content of bidisperse systems (composed of particles with diameter $d_1 = 10$ nm and $d_2 = 30$ nm) on the powder compressibility has been studied. The non-monotone density dependence on the relative fraction of small particles $\omega = N_1/(N_1 + N_2)$ has been revealed; namely, the dependence $\rho(\omega)$ has a maximum in the vicinity of values
\( \omega = 0.95 \), where the bidisperse system density can exceed the densities of corresponding monodisperse systems by 7–8%. In the terms of small particle weight fraction the maximum is situated at the values about 1/3.

In particular, the last result opens up possibilities of attainable densities increase at fixed compaction pressure owing to the special preparation of a nanopowder mixture with bidisperse form of particle size distribution. In accordance with simulation fulfilled for particle fractions, size particles of whose differs by three times, the mixture content should be close to the following: 1 mass part of small particles and 2 mass parts of large particles.

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