

Discrete element study on the influence of initial coordination numbers on the sintering behaviour

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Abstract

A particle-based simulation approach using the discrete element method (DEM) to simulate solid-state sintering is extended in order to account for variable coordination numbers. The model is applied to green particle configurations with different coordination numbers, but similar green densities. For both, configurations with mono-sized particles and particles having a size distribution, it is shown that a decrease in initial coordination number strongly retards densification. This observation is independent of the selected green density.

Keywords

sintering, modelling, simulation, ceramics, discrete element method

Various ceramic forming methods are commonly used to prepare green parts for subsequent sintering. These shaping processes result in powder structures for which both the relative density and the average number of contacting particles (the so-called coordination number) may differ from technique to technique. While most numerical sintering models developed so far take into account the initial relative density, they either ignore the potential influence of the initial coordination number [1, 2] or assume that its value is a function of green density [3, 4, 5, 6]. For particle based models like the discrete element method (DEM), however, the coordination number is a property that is easily accessible. The DEM considers each grain as a distinct spherical particle that interacts with neighbouring grains by specific force laws, for details see [7]. Therefore, the evolution of particle coordination can be tracked conveniently.

Finding an adequate estimate for the initial coordination number Z_0 , however, is quite challenging. While contact numbers are well-known for ordered structures of mono-sized particles, there is no established rule to determine the coordination number of a randomly distributed particle structure of particles with different sizes. In many works [8, 9] the maximum achievable coordination number is indicated to be around 6 with decreasing values for broader particle size distributions. Only few publications deal with sintering configurations of reduced initial coordination numbers as for example Jauffrès [10], who analysed partially sintered structures. Olmos et al. [11] determined experimentally the coordination number of an assembly of mono-sized copper particles with the help of X-ray microtomography obtaining a value around 4.5. Further they used the recorded particle configuration as input for DEM sintering simulations. In both works mentioned above though, the small coordination number comes along with a reduced initial relative density. In accord with the hypothesis of the present paper, Agnolin et al. [12], however, state that different methods to generate initial particle configurations can lead to different coordination numbers, even if the density is the same. In this paper, therefore, sintering of samples with initial coordination numbers ranging from 4 to 6 but of similar relative density is simulated. In this way it is possible to study the influence of the coordination number independently of side effects introduced by changing green densities. The configurations studied in the following also consider different particle size distributions and green densities.

The initial particle structures were generated by a procedure which is described in [8, 13]. First, spherical particles - mono-sized or with a given particle size distribution - are set randomly into a box avoiding overlaps of adjacent particles until a prescribed relative density is reached. To facilitate this filling procedure, the radius of each particle is set to half of the intended value. In a second step, the particle radii are expanded successively up to their intended values while strong repulsive forces between adjacent particles inhibit overlaps. This step typically results in small coordination numbers as there is enough space between particles to allow them to avoid touching each other. In a third step, a DEM simulation with a long-range pairwise potential is used to attract the particles to each other and, therefore, increase the coordination again. Two particles are said to be in contact if $r_{ij} < \eta (r_i + r_j)$ with $\eta = 1.008$, where r_{ij} is the distance between

the particle centres and r_i the radius of particle i , i.e. the contact radius is extended by a small value compared to the actual particle radius [13]. Measuring the influence on coordination number while varying η shows that there is hardly no change between $\eta = 1.001$ and $\eta = 1.02$, which motivated the choice of $\eta = 1.008$.

The samples for the simulations below were obtained by interrupting the structure generation in step 3 at a desired coordination number Z_0 and saving the corresponding particle configuration. With this procedure, the following initial setups were generated:

- i. Setup 1 with a green density $\rho_0 \approx 55.6\%$ containing 49.000 mono-sized particles with radius $R = 75$ nm
- ii. Setup 2 with $\rho_0 \approx 56.5\%$ containing 33.000 particles with log-normal distributed particle sizes ($\sigma_{log} = 0.3$, mean radius $R = 75$ nm) The distribution parameters are according to data of a commercial alumina powder (TM-DAR) [8]
- iii. Setup 3 with $\rho_0 \approx 63.0\%$ containing 56.000 mono-sized particles with $R = 75$ nm
- iv. Setup 4 with $\rho_0 \approx 63.1\%$ containing 38.000 particles with the same particle size distribution as in setup 2

Each setup is cubic with an edge length $5.4 \mu\text{m}$, which is around 36 times the average particle size. Figure 1a shows a typical simulation setup.

For each of these four setups, three test samples with different initial coordination numbers were generated, that is $Z_0 = 4$, $Z_0 = 5$ and $Z_0 = 6$. Figure 1b shows the relative densities of the individual test samples and Figure 1c the relative frequencies of coordination numbers for setup 1 and 2 (setups 3 and 4 are similar). Apparently, the relative density (computed as sum of particle volumes divided by closest box volume) is almost constant within one setup whereas the coordination number varies considerably.

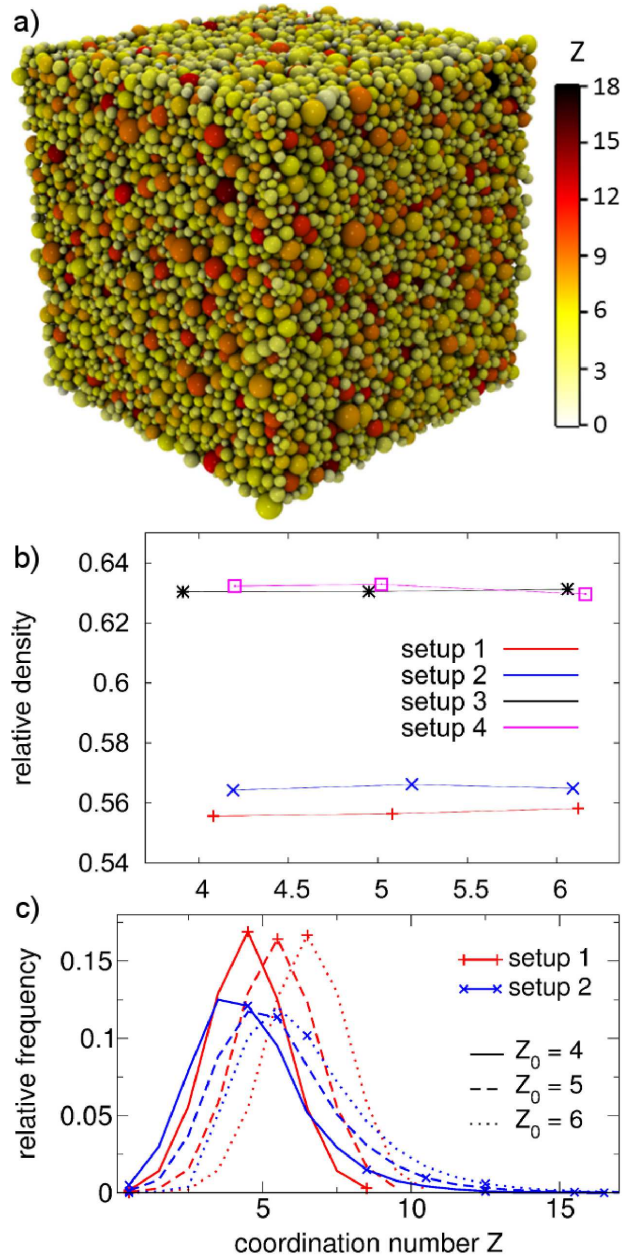


Figure 1: (a) Setup 2 (colour coding according to initial coordination number Z_0); (b) initial relative densities and coordination numbers for all samples; (c) relative frequencies of coordination numbers of initial configuration setup 1 (red) and setup 2 (blue).

The applied simulation method is based on a procedure described in detail in [13] and the force calculation of Riedel and Svoboda [14, 15]. It is used to simulate the initial and intermediate stages of solid-state sintering with a discrete element method assuming that grain boundary diffusion is the dominant transport mechanism, neighbouring contacts do not interact and the surface of the pores is in equilibrium. The assumption of isolated grain contact areas, i.e. open

porosity, limits the range of validity of the DEM approach to relative densities below about 90%. The normal force between two spherical grains contains an attractive part F_a and a viscous repulsive part F_v [15]:

$$F_n = F_a + F_v = \gamma_s(2\kappa A + L\sin\psi) + \frac{\pi c^4 k_B T}{8\Omega \delta D_b} v_{ij}^n \quad (1)$$

with k_B being the Boltzmann constant, T the temperature, Ω the atomic volume and δD_b the grain boundary thickness times the grain boundary diffusion coefficient. $A = \pi c^2$ is the grain contact area with radius c , L the length of its perimeter, κ the curvature of the surface, γ_s the specific surface energy, ψ the dihedral angle, and v_{ij}^n the component of the relative grain-grain velocity perpendicular to the contact area.

Moreover, a tangential viscous force acts on two particles in contact opposing their relative tangential motion (for details see [13]). The latter is controlled by a phenomenological dimensionless viscosity parameter μ , which determines the sliding behaviour of two particles. Herein, we use the dimensionless description given by [16]. The total force as well as the total torque acting on a particle is calculated from the sum of particle–particle forces and torques. The temporal evolution of the particle system is governed by Newton’s equations of motion. Information on the numerical implementation of the propagation scheme can be found in [13]. No grain coarsening is assumed.

According to [13] and [14], the contact radius c and the attractive force F_a can be described by polynomials that are fitted to numerical results given in [14]:

$$c = X(f, Z, \psi) \cdot R^* \quad (2)$$

$$F_a = \frac{\pi^{2/3} R^* \gamma_s}{3^{1/6} (1-f)^{2/3}} Y(f, Z, \psi) \quad (3)$$

where X and Y are polynomial functions of the porosity f , the coordination number Z and the dihedral angle ψ . R^* denotes the equivalent radius of two particles of different size that is defined as $R^* = 2r_i r_j / (r_i + r_j)$. This generalisation – which has also been used by other authors [16] – is a good approximation up to particle size ratios of 1:4 [17]. For a bcc particle arrangement, the porosity can be written as $f = 1 - \rho_{loc} = 1 - \pi\sqrt{3} (R^*/r_{ij})^3$, where ρ_{loc} is the local relative density measured between two particles.

The numerical values in the polynomial functions X and Y are given in [14] for different dihedral angles ψ and fixed coordination numbers Z . In recent years, our group used the numerical values for the bcc case, hence for $Z = 8$ [8, 13]. Since the coordination number evolves during sintering, it is necessary to modify the polynomial expressions X and Y to be able to deal with continuously changing coordination numbers. For that purpose, the numerical values p_z representing any of the coefficients of X and Y for $Z = 6$ and 8 with $\psi = 60^\circ$ from [14] are extrapolated such that a wider range of coordination numbers is covered. The extrapolated

coefficients of X and Y are assumed to be linear functions $l(Z)$ of the coordination number for $Z > 6$ fulfilling the requirements $l(6) = p_6$ and $l(8) = p_8$. For $Z \leq 6$, the coefficients are extrapolated by a quartic function $q(Z) = AZ^4 + BZ^2 + C$, where the coefficients A, B, C are chosen such that the following conditions are satisfied:

- i. $q(6) = p_6$
- ii. $q'(6) = (p_8 - p_6)/2$, i.e. the slope of q is continuous to the linear part $l(Z)$ at $Z = 6$
- iii. $q(4) = 3p_6/2 - p_8/2$

While the requirement of the conditions i and ii is evident, the third condition is admittedly arbitrary. It is only used to demonstrate the effect of an increasing coordination number on the sintering kinetics. Figure 2 shows the resulting polynomials X and Y for different coordination numbers.

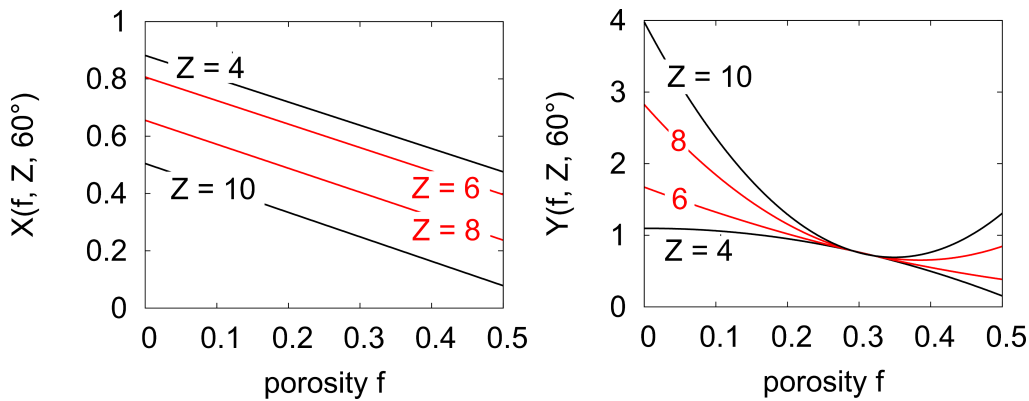


Figure 2: Polynomials X (a) and Y (b) for $Z = 6$ and 8 from [14] (red) and extrapolated for $Z = 4$ and 10 (black).

The extended sintering model is applied to the samples defined above using the model parameters given in [18] except the tangential grain boundary viscosity coefficient that is set to $\mu = 0.027$. The simulation starts at a temperature $T = 1150$ °C which is then increased by 25 K/min up to the hold temperature of 1350 °C.

The simulations are evaluated with regard to the evolution of relative density as shown in Figure 3. Apparently the samples with mono-sized particles (setups 1 and 3) sinter faster than the samples with distributed particle sizes (setups 2 and 4) - an observation which has already been described by other authors [8, 9]. A new aspect, however, is that a reduced initial coordination number Z_0 strongly retards densification independently of particle size distribution or green density. The influence of our model improvement is highlighted for setup 2 (Figure 3c), where simulations performed with the new model (Z is variable) are compared to those performed with the original model assuming the bcc case with a constant model coordination number $Z = 8$.

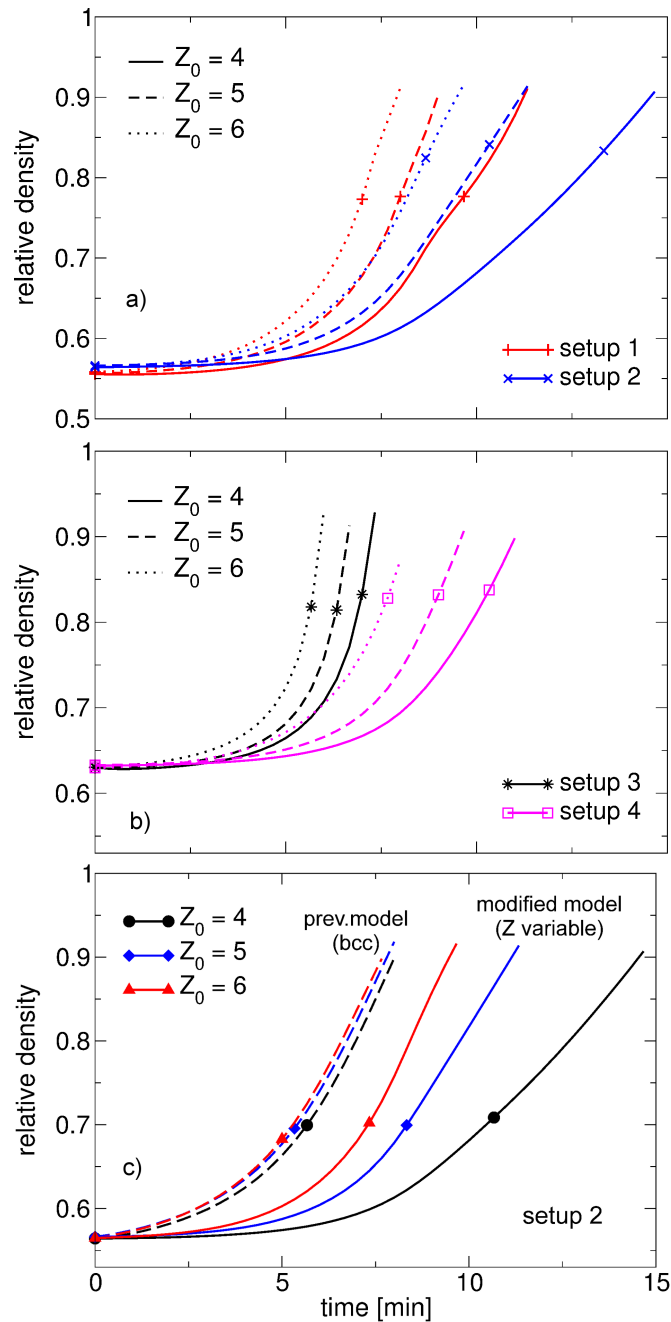


Figure 3: Simulated densification of setup 1 and 2 (a) and setup 3 and 4 (b). (c) Comparison between previous model (dashed) with a constant model coordination number $Z = 8$ and modified model (solid) with variable Z for setup 2.

Looking at the evolution of coordination number in Figure 4 gives the reason for the observed sintering delay. Although the increase of the coordination number is steeper for samples with lower Z_0 , it takes some time until it reaches values comparable to those of samples with high Z_0 and the curves finally converge at relative densities around 85%. A lower coordination number

implies lower attractive sintering forces F_a (compare Figure 2b and Equation (3)) and higher repulsive viscous forces F_v due to an increased contact radius c (compare Figure 2a with Equations (1) and (2)). Both effects lead to a reduced sintering rate. The effect of larger contact radii for samples with smaller coordination is in agreement with observations made by Jauffrès et al. [10].

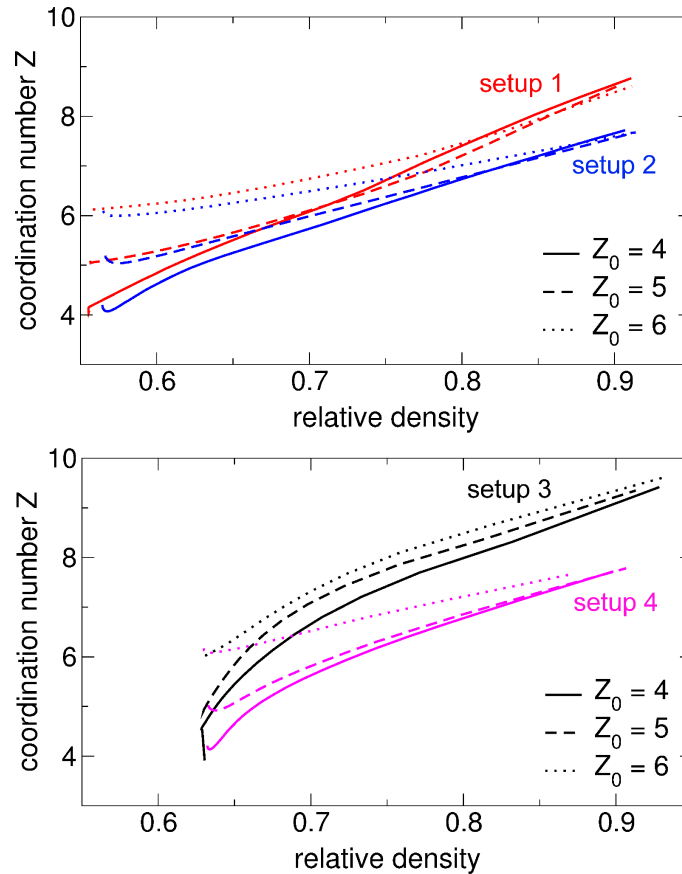


Figure 4: Evolution of coordination number for setup 1 and 2 (a) and for setup 3 and 4 (b).

Two other remarkable effects can be seen in Figure 4: First, the samples with particle size distribution (setup 2 and 4) show a slight decrease in coordination number at the very beginning of sintering. This observation has also been made in previous publications [13, 19] and has been interpreted as a consequence of particle rearrangement. This assumption is supported by our simulations since samples with mono-sized particles do not show such behaviour where the particles probably cannot rearrange as easily as small particles in powders with a size distribution.

Second, the samples with $Z_0 = 4$ of setup 1 and 3 with mono-sized particles show a jump of coordination number before densification starts. This indicates that the initial particle configurations might not be entirely in mechanical equilibrium for those cases since small forces are sufficient to increase the number of contact partners by rearrangement. This assumption is

supported by the fact that a larger rise of the coordination number occurs for the sample with 63% initial relative density for which it is intuitively reasonable to expect a higher degree of mechanical instability at low coordination numbers. On the other hand, as all the other samples do not show such behaviour, it can be assumed that their particle configuration is in equilibrium and the critical samples reach such a state quickly.

Summing up, a modified sintering model was applied to particle configurations with varying initial coordination numbers but similar green densities leading to the result that densification is strongly retarded in the case of low initial coordination numbers. Therefore, our simulations give evidence that considering exclusively the green density as characterization parameter for sintering is not sufficient as the influence of the initial coordination number – which is not implicitly associated with relative density – is important additionally. A validation of our statements by experiments will be quite challenging since determining the coordination number of green particle packings as well as producing particle assemblies with varying coordination numbers but equal green densities is very ambitious. Therefore, only particle-based simulations are able to provide information about the influence of initial coordination in a comfortable way.

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