

Microstructural Percolation

Iwan Schenker, Frank T. Filser and Ludwig J. Gauckler

Nonmetallic Materials, Department of Materials
ETH Zurich, Zurich CH-8093, Switzerland

`iwan.schenker@alumni.ethz.ch`

November 9, 2010

Abstract

The macroscopic mechanical properties of colloidal particle gels strongly depend on the local arrangement of the powder particles. Experiments have shown that more heterogeneous microstructures exhibit up to one order of magnitude higher elastic properties than their more homogeneous counterparts at equal volume fraction. In this paper, packings of spherical particles are used as model structures to computationally investigate the elastic, rheological properties of coagulated particle gels as a function of their degree of heterogeneity. The simulations are performed using the discrete element method. The forces included in the model comprise a linear elastic contact law, particle bonding and damping. The simulation parameters were calibrated using a homogeneous and a heterogeneous microstructure originating from earlier Brownian dynamics simulations. A quantitative agreement between the modelled and the experimental plateau storage moduli was achieved. A systematic study of the elastic properties as a function of the degree of heterogeneity was performed using two sets of microstructures obtained from Brownian dynamics simulation and from the recently developed void expansion method. In terms of degree of heterogeneity, both sets of microstructures cover a broad and to a large extent overlapping range. The simulations have shown that the elastic properties as a function of the degree of heterogeneity are independent of the structure generation algorithm and that a power law relates the elastic plateau storage modulus to the degree of heterogeneity. The presence of a critical degree of heterogeneity suggests a phase transition between a phase with finite and one with zero elastic properties, which is interpreted as microstructural percolation.

1 Introduction

Random sphere packings are ubiquitous model systems for the study of the structural and mechanical properties of granular matter or colloids. Geomechanics [10], granular flow [20] and mixing and segregation of granular materials [19] are but a few examples. The mechanical properties of granular systems depend on various parameters such as the volume fraction [33], the particle size distribution [11], material properties as, for example, the particles' friction coefficients [25] or adhesive forces [18]. Furthermore, as predicted in [8] and discussed in more detail in the following, the mechanical properties strongly depend on the microstructure, i.e., the local arrangement of the particles.

The influence of the microstructure on the mechanical properties is often observed implicitly in experimental and computational mechanical tests on structures differing in preparation history. Macroscopic stress profiles, for example, were found to strongly depend on the sample preparation procedure and thus its microstructure [2]. However, systematic investigations of the mechanical properties as a function of the microstructure are scarce, for two reasons: first, a systematic study requires the possibility of an unambiguous characterization of the microstructural arrangement of the particles in terms of the structure's degree of heterogeneity

(DOH). Such a quantification of the DOH by means of scalar measures has been introduced in [22]. Three distinct structure characterization methods in conjunction with parameters in fit functions or integrals were shown to allow for a clear quantification and thus classification of the DOH of particle structures. Second, and equally important, a systematic study of the microstructure-dependent mechanical properties relies on the possibility of a reproducible generation of microstructures with distinct local arrangements of the particles at constant volume fraction.

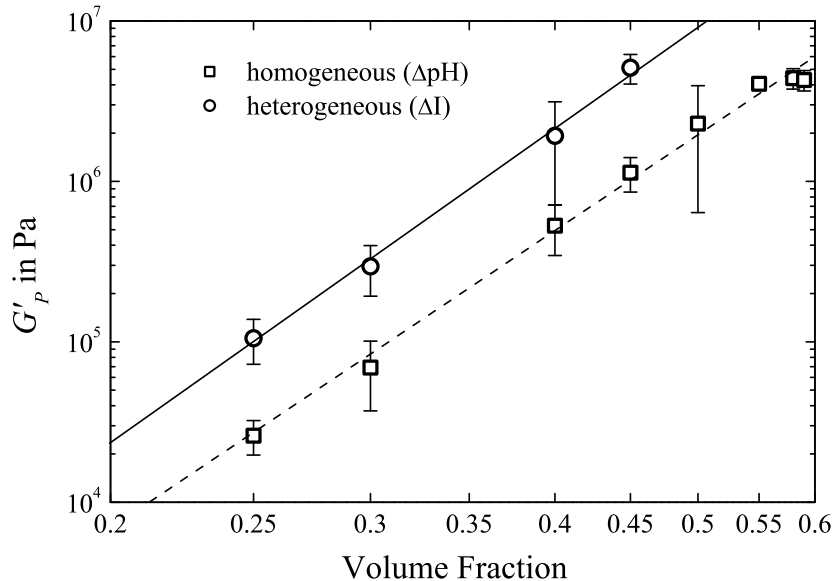


Figure 1: Experimental elastic plateau storage modulus G'_p of alumina particle suspensions (average particle diameter $d_o = 0.4 \mu\text{m}$) formed by the ΔpH - and the ΔI -method of the direct coagulation casting process in dependence of the volume fraction [28].

Experimentally, the reproducible control of the DOH of colloidal microstructures with volume fractions between 0.2 and 0.6 is achieved using direct coagulation casting [12, 26], which is an *in situ* enzyme-catalyzed destabilization method. It allows for the coagulation of electrostatically stabilized colloidal suspensions to stiff particle structures by either shifting the pH of the suspension to the particles' isoelectric point or by increasing the ionic strength of the suspension without disturbing the particle system. Shifting the pH leads to “more homogeneous” microstructure through diffusion-limited aggregation while increasing the ionic strength results in “more heterogeneous” microstructures via reaction-rate-limited aggregation. These differences in heterogeneity have been observed using various experimental techniques such as diffusing wave spectroscopy [30], static light transmission [30] or cryogenic scanning electron microscopy [29].

Rheological and uniaxial compression experiments on coagulated colloidal particle structures obtained by direct coagulation casting have revealed that those with a more heterogeneous microstructure have significantly higher elastic moduli than their more homogeneous counterparts [3, 28, 31]. The rheological properties, which are the subject of the computational part of this study, were investigated experimentally using a Bohlin rheometer (Model CS-50, Bohlin Instruments, Sweden) equipped with a measuring tool of plate/plate geometry (rough surface, 25 mm plate diameter). Oscillatory measurements were performed at a fixed frequency of 1 Hz with increasing strain amplitude. Figure 1 summarizes the measured elastic plateau storage moduli G'_p of alumina particle suspensions (average particle diameter

$d_0 = 0.4 \mu\text{m}$) destabilized by the ΔpH - and the ΔI -method, respectively, as a function of the volume fractions. For this system, approximately four times higher elastic properties are measured for heterogeneous than for homogenous microstructures at corresponding volume fractions [28, 4].

A variation of the ΔpH -method allowing for a controlled introduction of heterogeneities is the use of alkali-swellable polymer particles. Small amounts of these particles, 80 nm in diameter, are admixed to the suspended powder particles under acidic conditions. The polymer particles swell upon changing pH during the internal gelling reaction of the direct coagulation casting process and enfold to $0.7 \mu\text{m}$ in diameter, thereby rearranging the powder particles and thus producing more heterogeneous microstructures. These more heterogeneous samples exhibit much higher mechanical properties in comparison to samples without polymer particles. In particular, they present comparably high mechanical properties as samples with heterogeneous microstructures produced by the ΔI -method [14, 13].

In summary, strong evidence is given that the differences in macroscopic mechanical properties of coagulated particle suspensions are controlled by the differences in heterogeneity. A yet unanswered question is how these microstructural differences on the length scale of a few particle diameters can have such a dramatic influence on the mechanical properties.

The aim of this study is to perform a systematic computational analysis of the elastic rheological properties of particle packings at constant volume fraction of $\Phi = 0.4$ and to correlate these properties with the structures' DOH.

2 Materials and Methods

In a first part of this section, the discrete element method, which is the simulation method used throughout this study, is introduced. Second, the methods, by which the two sets of initial microstructures are obtained are briefly presented. Then, the method and fit function that is used in order to quantify the structures' DOH is explained and finally, the simulation setup is presented.

2.1 Discrete Element Method

The discrete element method [9] is an iterative simulation method, in which complex structures are built up from primary spherical particles. At each point in time, the total force on each particle is calculated. The time step is chosen small enough to assume a constant force during the time step, which allows linearizing the equations of motion, thereby enabling the efficient calculation of the particles' next positions and velocities. In particular, the simulations presented in this paper are performed using the particle flow code in three dimensions PFC^{3D} [1], which is an implementation of the discrete element method and uses a central difference scheme for the numerical integration of the equations of motion.

Our model comprises a linear elastic contact law between particles, particle bonding and damping. The linear elastic contact law relates the contact forces acting on two particles in contact linearly to the relative displacement between the particles. In PFC^{3D} a soft-contact approach is used, wherein the rigid particles are allowed to overlap at contact points. The magnitude of the normal contact force F_n is given by

$$F_n = k_n U_n, \quad (1)$$

where k_n denotes the normal stiffness and U_n is the overlap. The shear stiffness k_s relates incremental displacements in shear direction ΔU_s to the shear contact force ΔF_s via

$$\Delta F_s = k_s \Delta U_s. \quad (2)$$

The linear elastic contact law is thus parameterized by the normal and shear stiffnesses.

Parameter	Symbol	Value
Number of particles	N	8 000
Particle radius	r_0	0.25 μm
Normal particle stiffness	k_n	50 – 150 N/m
Shear particle stiffness	k_s	5 – 15 N/m
Normal bond strength	F_n^B	10^{-4} N
Shear bond strength	F_s^B	10^{-6} N
Damping coefficient	α	0.9
Friction coefficient	μ	0.0
Volume fraction	Φ	0.4
Particle density	ρ	3 690 kg/m ³

Table 1: Simulation parameters.

A bond between particles can be envisioned as a pair of elastic springs with constant normal and shear stiffness acting at the contact point. These two springs have specified normal and shear strengths, F_n^B and F_s^B , respectively. A bond breaks if either the normal or the shear bond strength is exceeded in normal and shear direction, respectively.

Energy dissipation is simulated via a local damping term added to the equations of motion [7]. This damping force, characterized by the damping coefficient α , is proportional to the force acting on the particle and is opposed to the particle’s velocity. Thereby, only accelerating motion is damped [1].

In conclusion, the simulation model is characterized by five microscopic parameters: the stiffness of the particles and the bond strength both for normal and shear direction, and the damping coefficient. These parameters, in the following referred to as microparameters, are compiled in Table 1. In particular, the normal to shear particle stiffness ratio $k_n/k_s = 10$ is kept constant and a value of 0.9 is chosen for the damping coefficient, which corresponds to the values used in previous studies [22, 23].

2.2 Initial Microstructures

Two sets of microstructures are used as initial particle configurations for the simulation of the elastic properties. A first set originates from previous Brownian dynamics (BD) simulations [16, 15] where the coagulation of electrostatically stabilized colloidal suspensions to stiff particle structures was simulated. The presence and depth of a secondary minimum in the inter-particle potential, described by the Derjaguin-Landau-Verwey-Overbeek theory [21], was shown to account for the variations in the DOH of the resulting particle structures and is adjusted via the surface potential Ψ_0 . For $\Psi_0 = 0$ mV, the electrostatic double layer repulsion is zero and the inter-particle potential is only given by the attractive van der Waals potential. For the set of simulation parameters used in [16, 15], a secondary minimum appears for $\Psi_0 \geq 12$ mV and an energy barrier between the local maximum and the secondary minimum emerges. For $\Psi_0 = 15$ mV, a repulsive barrier of $5.65 k_B T$ is present. The model further contains the frictional Stokes’ drag force and a random Brownian force caused by the suspending liquid. In this paper, BD-microstructures generated with $\Psi_0 = 0, 12, 13, 14$ and 15 mV are used, exhibiting an increasing DOH with increasing Ψ_0 [22].

In particular, the most and least heterogeneous BD-microstructures have been shown to nicely correspond to experimental silica structures using the pair correlation function [29]. These two structures are thus used here to calibrate the microparameters in order for the simulations to reproduce the experimental values given in Fig. 1.

The second set of initial microstructures is obtained using the void expansion method (VEM) presented in [24]. In contrast to BD, which simulates the physical processes during co-

agulation according to established laws and methods, VEM is a purely stochastic method inspired by the experimental generation of heterogeneous microstructures using alkali-swelling polymer particles. This method employs so-called void-particles that mimic the polymer particles. The void-particles, having a small initial diameter, are randomly placed into the simulation box containing the structure-particles. The core part of VEM is the repeated increase in the void-particles' diameter. During this procedure, the structure-particles are rearranged and finally pushed into contact. As shown in [23], VEM allows generating microstructures presenting a broad range of DOH, which is controlled by the void- to structure-particle number ratio. In particular, VEM-microstructures cover an approximately 20% larger range of DOH, slightly shifted to higher values than the BD-microstructures. In this study, the number of void-particles N_V ranges between 1000 and 16000. The void-particles' normal and shear stiffness are $k_{n,V} = 10^2$ N/m and $k_{s,V} = 10^{-2}$ N/m, respectively.

All structures are submitted to the same relaxation procedure before undergoing the simulated mechanical testing. Bonds between neighboring particles having an inter-particle separation distance smaller than $d_\epsilon = (1 + \epsilon)2r_0$ with $\epsilon = 0.01$ are installed. Then, several calculation steps are performed, where, after each step, the translational and rotational velocities are set to zero. This allows for an efficient reduction of particle overlaps and thus of the internal strain energy in the structures without significant changes in the particle positions. In particular, the bonds between the particles prevent these particles from separating and consequently the coordination number distribution is conserved.

The structures investigated in this study have equal volume fraction of $\Phi = 0.4$, consist of $N = 8000$ monodispersed spherical particles having a radius $r_0 = 0.25 \mu\text{m}$ and are contained in a cubic simulation box with periodic boundaries and edge length L_{box} given by

$$L_{box} = r_0 \left(\frac{4N\pi}{3\Phi} \right)^{1/3}. \quad (3)$$

2.3 Degree of Heterogeneity

In [22], three distinct methods allowing for a quantification of the degree of heterogeneity using scalar measures were introduced. Here, the DOH is characterized by means of the cumulative pore size distribution $P(r_P > r)$ estimated using the exclusion probability [27]. Equation (4) was shown to nicely fit $P(r_P > r)$ of both the VEM- and the BD-microstructures [22, 23].

$$P(r_P > r) = 1 - \operatorname{erf} \left(\frac{r/r_0 - b}{a\sqrt{2}} \right). \quad (4)$$

The DOH is quantified by the width of the error function measured by parameter a . The values of a for the various microstructures are summarized in Table 2. Parameter b represents the location of the maximum of the underlying Gaussian distribution, i.e., the most probable pore to particle radius ratio.

2.4 Simulation Setup

The simulation setup is schematically shown in Fig. 2. The structure (white particles) is placed between periodic boundaries in x- and y-direction. In z-direction, the boundary conditions are imposed via three additional particle layers (gray), obtained from the periodic repetition of the structure. The lower layers, representing the lower plate in the shear experiment, are immobile whereas the upper layers shear the sample periodically along the x-axis with a fixed frequency of 1 Hz ($\omega = 2\pi$). The shear amplitude is increased after each oscillation. In particular, ten oscillations with a linearly increasing deflection of the upper plate up to a maximum deflection of 0.1% L_{box} are performed. Spherical regions, so-called measurement spheres [1], are defined in different heights monitoring the mean stress tensor in

their respective region. The absolute value of the complex modulus G is obtained by dividing the peak shear stress value with the actual strain of each oscillation. G' is then calculated by multiplication with the cosine of the phase angle between excitation and response, which corresponds to the evaluation of G' according to [32].

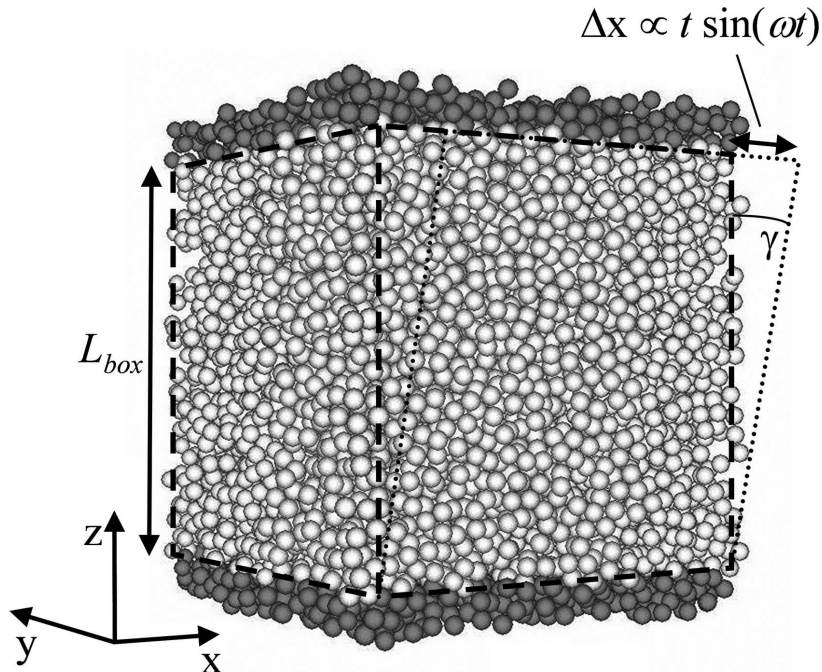


Figure 2: Rheological simulation setup.

3 Results and Discussion

The particle stiffness has been calibrated using the most homogeneous and the most heterogeneous BD-microstructures ($\Psi_0 = 0$ mV and $\Psi_0 = 15$ mV, respectively). Its influence on the mechanical properties of these two structures is shown in Fig. 3 (left graph). The experimental values are shown on the right.

The simulated values for G'_p quantitatively agree with the experimental values within the experimental error for normal stiffness values ranging between 50 and 150 N/m. For both microstructures, a linear dependency is found between G'_p and k_n , which is expressed in a constant ratio between the G'_p -values for the heterogeneous and homogeneous microstructure as a function of k_n : $G'_p{}^{HE}/G'_p{}^{HO} \approx 3.4$. This is in good agreement with the average experimental G'_p -ratio of 3.6 at $\Phi = 0.4$. For all further simulations the particle normal stiffness is fixed to 100 N/m.

The inter-particle bond strength was strictly speaking not part of the calibration process. In order to focus on the initial elastic properties, its value was chosen high enough to prevent any bond breakage for the deformations considered in this study. The chosen normal bond strength $F_n^B = 10^{-4}$ N, in conjunction with the particle normal stiffness $k_n = 100$ N/m allows for a maximum particle separation distance of 10^{-6} m, which corresponds to two particle diameters. Given the maximum shear displacement of $0.001 L_{box}$, where L_{box} is of the order of roughly 20 particle diameters, this value is never exceeded. Typical stress and strain curves

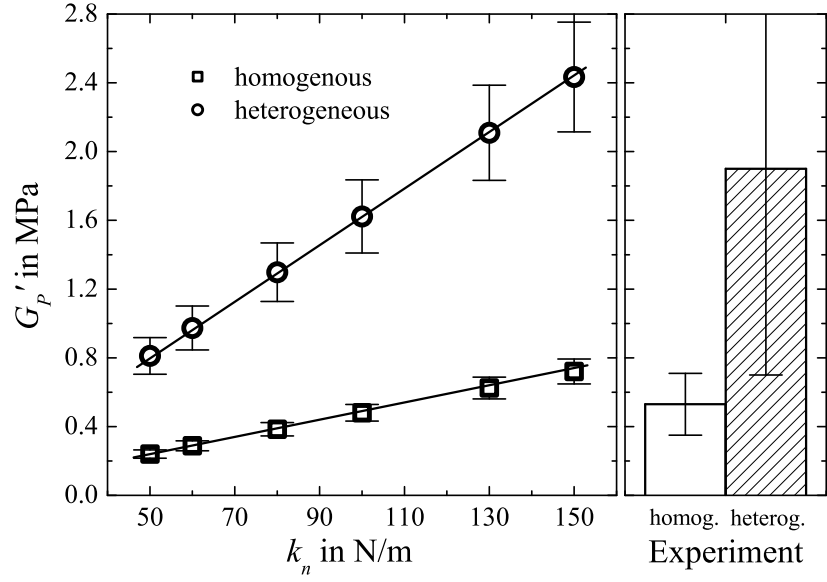


Figure 3: Simulated plateau storage moduli G'_p of the most and least heterogeneous BD-microstructure as a function of the particle normal stiffness k_n . Right: Experimental G'_p -values for alumina particle structures (cf. Fig. 1). $\Phi = 0.4$ for all microstructures.

are shown in Fig. 4, presenting the shear stress σ_{12} (open squares, left scale) and the applied shear deflection γ_{12} (full circles, right scale) as a function of the shear oscillation cycle. σ_{12} increases linearly with γ_{12} and no phase shift between excitation and response is observed, which confirms that these simulations present a purely elastic behavior.

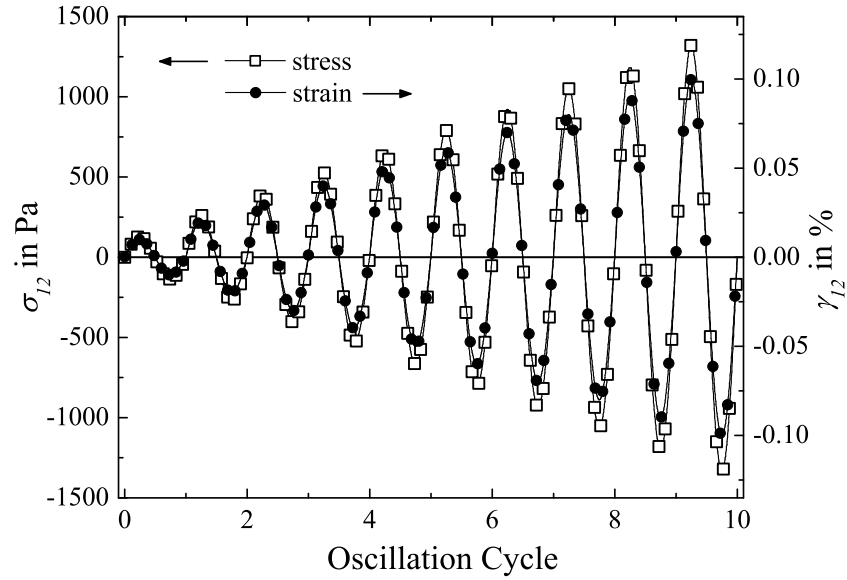


Figure 4: Stress σ_{12} (open squares, left scale) and strain γ_{12} (full circles, right scale) as a function of shear oscillation cycle.

	Structure	a	G'_p in MPa
VEM	$N_V = 1\ 000$	0.605	1.73 ± 0.383
	$N_V = 2\ 000$	0.530	1.83 ± 0.136
	$N_V = 4\ 000$	0.472	1.62 ± 0.190
	$N_V = 8\ 000$	0.431	1.32 ± 0.237
	$N_V = 13\ 000$	0.411	1.32 ± 0.267
	$N_V = 16\ 000$	0.401	1.17 ± 0.231
BD	$\Psi_0 = 0\ \text{mV}$	0.375	0.480 ± 0.049
	$\Psi_0 = 12\ \text{mV}$	0.405	1.19 ± 0.141
	$\Psi_0 = 13\ \text{mV}$	0.413	1.05 ± 0.124
	$\Psi_0 = 14\ \text{mV}$	0.474	1.46 ± 0.120
	$\Psi_0 = 15\ \text{mV}$	0.538	1.62 ± 0.213

Table 2: DOH-parameter a [22, 23] and simulated plateau storage moduli of the various VEM- and BD-microstructures.

3.1 Elastic Properties as a Function of the DOH

Using a particle normal stiffness of 100 N/m, the plateau storage moduli of the various VEM- and BD-microstructure were simulated. The resulting G'_p -values are summarized in Table 2 and are shown in Fig. 5 as a function of the structures' DOH expressed by parameter a . Triangles and circles correspond to BD- and VEM-microstructures, respectively.

Two conclusions can be drawn from Fig. 5: first, the elastic properties present a clear dependence on the microstructure's heterogeneity such that G'_p increases for increasing DOH-parameter a . Second, the behavior is independent of the structure generation algorithm. Indeed, the elastic moduli of the VEM- and the BD-microstructures agree within the error bars for microstructures with comparable DOH.

The solid line in Fig. 5 represents a power law fit given by

$$G'_p \propto (a - a_0)^\beta, a \geq a_0, \quad (5)$$

with $a_0 = 0.373 \pm 0.001$ (shown as dashed line in Fig. 5) and $\beta = 0.207 \pm 0.033$. The use of this fit function is inspired by percolation theory where a power law scaling is found for the elastic properties as a function of the volume fraction [5, 6]. In view of this analogy, this fit function suggests a phase transition with a_0 the critical DOH. Below this value, the elastic properties are zero; above this value, they increase for increasing a . A DOH-value $a = 0.265$ below a_0 was found for the stabilized colloidal microstructures with repulsive inter-particle potentials [22]. In the model used in this work, this microstructure would indeed present negligible elastic properties since there would be no bonds between the particles.

4 Summary and Conclusions

In this paper, the relation between the microstructure and the elastic properties of packings of spherical particles was investigated computationally using the discrete element method. Two distinct sets of initial microstructures were subjected to strain-controlled oscillatory shear simulations. The first set originated from Brownian dynamics simulations [16, 15] where the physical processes during coagulation were simulated. The second set was obtained using the void expansion method [24]. In contrast to Brownian dynamics simulations, the latter is a purely stochastic method. Both sets cover a broad range of degrees of heterogeneity, which, in this work, was characterized using the width of the pore size distribution.

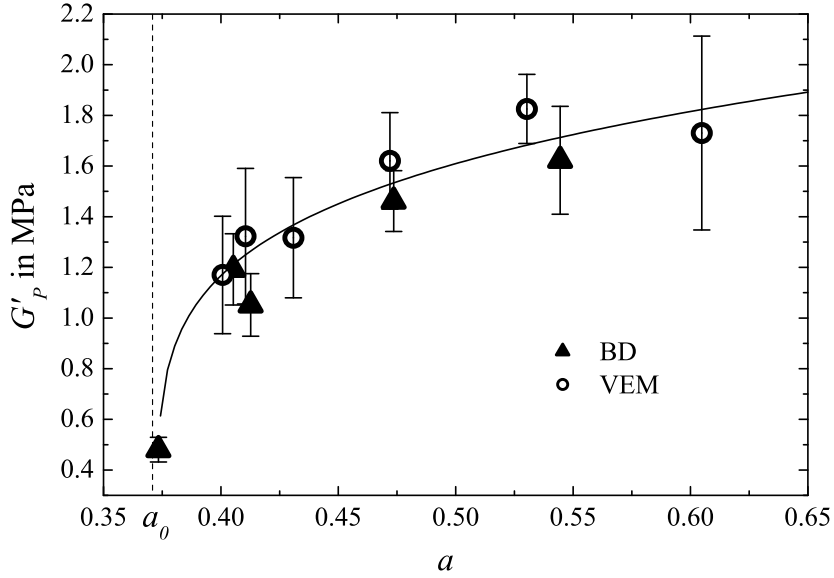


Figure 5: Simulated plateau storage moduli G'_p of the various microstructures ($\Phi = 0.4$, $r_0 = 0.25 \mu\text{m}$) as a function of the DOH in terms of parameter a and power law fit (solid line).

The simulations of the mechanical properties have been performed using a discrete element model with five microparameters: the particle stiffness and the bond strength in normal and shear direction, respectively and damping. The inter-particle normal and shear bond strengths were set to a high value in order to prevent any bond breaking for the deformations applied during the shear simulations. This allowed focussing on the initial, purely elastic behavior found in experiment [31]. The particle stiffness was calibrated using the microstructures generated using Brownian dynamics and, in particular, those presenting the highest and lowest degree of heterogeneity. A quantitative agreement with experiment was achieved. For particle normal stiffnesses ranging between 50 and 150 N/m, the absolute values of the experimental elastic moduli are reproduced, as shown in Fig. 3. In particular, the ratio between the elastic moduli of the heterogeneous and the homogeneous microstructures is in good agreement with the experimental value. This latter result is particularly remarkable, since the model used in this study constitutes an important simplification with respect to theoretical models such as the Derjaguin-Landau-Verwey-Overbeek theory [21], giving the inter-particle potential as the sum of the van der Waals attraction and the electrostatic repulsion or the Johnson-Kendall-Roberts theory [17], describing the adhesive force between particles. It emphasizes the strong influence of the differences in microstructure independently of the interaction potential.

Using the calibrated model, the elastic properties of all microstructures generated using the void expansion method and Brownian dynamics were simulated. This investigation has revealed a correlation between the elastic properties and the structures' degree of heterogeneity. It was also shown, that the elastic properties are independent of the structure generation algorithm. Indeed, for structures with comparable degrees of heterogeneity, comparable plateau storage moduli were found. The simulation results suggest a power law relation between the plateau storage modulus and the degree of heterogeneity above a critical value. This indicates a phase transition between a phase with finite and a phase with zero elastic properties. This result is in nice analogy to earlier findings [5, 6], where the elastic properties

were shown to exhibit a power law dependence as a function of the volume fraction. This study thus suggests an extension to percolation theory, where usually the volume fraction constitutes the continuous variable presenting a critical value. Here, the degree of heterogeneity, possessing the same critical behavior as the volume fraction has been identified as an additional variable. This shows that the degree of heterogeneity is particularly useful in order to quantify and characterize the heterogeneity of particle packings since it allows for an unprecedented theoretical description of their elastic properties.

Acknowledgements

The authors would like to thank Hans J. Herrmann and Tomaso Aste for their valuable help throughout this project.

References

- [1] *PFC^{3D} User's Manual*. Itasca Consulting Group, Inc., Minneapolis, Minnesota, USA, 1995.
- [2] A. P. F. Atman, P. Brunet, J. Geng, G. Reydellet, G. Combe, P. Claudin, R. P. Behringer, and E. Clément. Sensitivity of the stress response function to packing preparation. *J. Phys.: Condens. Matter*, 17:S2391–S2403, 2005.
- [3] B. Balzer, M. K. M. Hruschka, and L. J. Gauckler. Coagulation kinetics and mechanical behavior of wet alumina green bodies produced via dcc. *J. Colloid Interface Sci.*, 216:379–386, 1999.
- [4] B. Balzer, M. K. M. Hruschka, and L. J. Gauckler. In-situ rheological investigation of the coagulation in aqueous alumina suspensions. *J. Am. Ceram.*, 84:1733–1739, 1999.
- [5] L. Benguigui. Experimental study of the elastic properties of a percolating system. *Phys. Rev. Lett.*, 53:2028–2030, 1984.
- [6] D. J. Bergman. Exact relations between critical exponents for elastic stiffness and electrical conductivity of two-dimensional percolating networks. *Phys. Rev. E*, 65:026124, 2002.
- [7] E. T. Brown. *Analytical and Computational Methods in Engineering Rock Mechanics*. Ed. London: Allen & Unwin, 1987.
- [8] M. E. Cates, J. P. Wittmer, J.-P. Bouchaud, and P. Claudin. Jamming and static stress transmission in granular materials. *CHAOS*, 9:511–522, 1999.
- [9] P. A. Cundall and O. D. L. Strack. A discrete numerical model for granular assemblies. *Géotechnique*, 29:47–65, 1979.
- [10] A. Fakhimi and T. Villegas. Application of dimensional analysis in calibration of a discrete element model for rock deformation and fracture. *Rock Mech. Rock Engng.*, 40:193–211, 2007.
- [11] B. S. Gardiner and A. Tordesillas. Effect of particle size distribution in a three-dimensional micropolar continuum model of granular media. *Powder Technol.*, 161:110–121, 2006.
- [12] L. J. Gauckler, Th. Graule, and F. Baader. Ceramic forming using enzyme catalyzed reactions. *Mater. Chem. Phys.*, 61:78–102, 1999.

- [13] D. Hesselbarth. *Quellfähige Polymerbinder in Aluminiumoxid-Suspensionen*. Ph.D. thesis no. 13404, ETH Zurich, Switzerland, 2000.
- [14] D. Hesselbarth, E. Tervoort, C. Urban, and L. J. Gauckler. Mechanical properties of coagulated wet particle networks with alkali-swellaible thickeners. *J. Am. Ceram. Soc.*, 84:1689–1695, 2001.
- [15] M. Hütter. *Brownian Dynamics Simulation of Stable and of Coagulating Colloids in Aqueous Suspension*. Ph.D. thesis no. 13107, ETH Zurich, Switzerland, 1999.
- [16] M. Hütter. Local structure evolution in particle network formation studied by brownian dynamics simulation. *J. Colloid Interface Sci.*, 231:337–150, 2000.
- [17] K. L. Johnson, K. Kendall, and A. D. Roberts. Surface energy and the contact of elastic solids. *Proc. R. Soc. Lond. A*, 324:301–313, 1971.
- [18] C. L. Martin and R. K. Bordia. Influence of adhesion and friction on the geometry of packings of spherical particles. *Phys. Rev. E*, 77:031307, 2008.
- [19] J. M. Ottino and D. V. Khakhar. Mixing and segregation of granular materials. *Annu. Rev. Fluid Mech.*, 32:55–91, 2000.
- [20] P. G. Rognon, J.-N. Roux, D. Wolf, M. Naaïm, and F. Chevoir. Rheophysics of cohesive granular materials. *Europhys. Lett.*, 74:644–650, 2006.
- [21] W. B. Russel, D. A. Saville, and W. R. Schowalter. *Colloidal Dispersions*. Cambridge University Press, New York, 1989.
- [22] I. Schenker, F. T. Filser, T. Aste, H. J. Herrmann, and L. J. Gauckler. Quantification of the heterogeneity of particle packings. *Phys. Rev. E*, 80:021302, 2009.
- [23] I. Schenker, F. T. Filser, and L. J. Gauckler. Stochastic generation of particle structures with controlled degree of heterogeneity. *Granul. Matter*, 12:437–446, 2010.
- [24] I. Schenker, F. T. Filser, H. J. Herrmann, and L. J. Gauckler. Generation of porous particle structures using the void expansion method. *Granul. Matter*, 11:201–208, 2009.
- [25] L. E. Silbert, D. Ertaş, G. S. Grest, T. C. Halsey, and D. Levine. Geometry of frictionless and frictional sphere packings. *Phys. Rev. E*, 65:031304, 2002.
- [26] E. Tervoort, T. A. Tervoort, and L. J. Gauckler. Chemical aspects of direct coagulation casting of alumina suspensions. *J. Am. Ceram. Soc.*, 87:1530–1535, 2004.
- [27] S. Torquato, B. Lu, and J. Rubinstein. Nearest-neighbor distribution functions in many-body systems. *Phys. Rev. A*, 41:2059–2075, 1990.
- [28] H. M. Wyss, A. M. Deliormanli, E. Tervoort, and L. J. Gauckler. Influence of microstructure on the rheological behavior of dense particle gels. *AIChE J.*, 51:134–141, 2005.
- [29] H. M. Wyss, M. Hütter, M. Müller, L. P. Meier, and L. J. Gauckler. Quantification of microstructure in stable and gelled suspensions from cryo-sem. *J. Colloid Interface Sci.*, 248:340–346, 2002.
- [30] H. M. Wyss, S. Romer, F. Scheffold, P. Schurtenberger, and L. J. Gauckler. Diffusion-wave spectroscopy of concentrated alumina suspensions during gelation. *J. Colloid Interface Sci.*, 241:89–97, 2001.

- [31] H. M. Wyss, E. Tervoort, L. P. Meier, M. Müller, and L. J. Gauckler. Relation between microstructure and mechanical behavior of concentrated silica gels. *J. Colloid Interface Sci.*, 273:455–462, 2004.
- [32] J. A. Yanez, T. Shikata, F. F. Lange, and D. S. Pearson. Shear modulus and yield stress measurements of attractive alumina particle networks in aqueous slurries. *J. Am. Ceram. Soc.*, 79:2917–2965, 1996.
- [33] A. Zaccone, M. Lattuada, H. Wu, and M. Morbidelli. Theoretical elastic moduli for disordered packings of interconnected spheres. *J. Chem. Phys.*, 127:174512, 2007.