Received: 24 June 2020 | Accepted: 18 November 2020

DOI: 10.1002/pamm.202000099

Analysis of the fractal properties of silica aerogels using diffusion-limited aggregation

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Silica aerogels are highly porous solids with very low densities and thermal conductivities. Their high porosity results in a fractal morphology which has a strong influence on mechanical properties. In this work, the diffusion-limited cluster aggregation (DLCA) method is implemented to model silica aerogel aggregates. A preliminary model based on this approach demonstrates good agreement with experimental data [1]. The influence on the fractal properties of different input parameters as for example the particle size is investigated. Moreover, the resulting geometries are compared to fractal features of silica aerogels determined by experimental data from small angle X-ray scattering (SAXS). The mechanical response of these aggregation models is analyzed by a finite element analysis (FEA) for the generated representative volume elements (RVE). The effect of varying densities on the mechanical properties, for e.g., Young's modulus, is further elucidated.

1 Introduction

Silica aerogels are highly nanostructured porous materials, synthesized by the sol-gel process. In addition to their superinsulating properties, the structural features and mechanical properties gain more relevance given the widening of their application spectrum. Their mechanical properties have been investigated by molecular dynamics simulations [2] and coarse-grained modeling [3, 4]. Hasmy et al. [5, 6] concluded that the microstructure of silica aerogels can be described best with diffusion-limited aggregation-based models.

In this work, highly porous structures were generated using the diffusion-limited cluster aggregation (DLCA) method. The generated structures were subsequently compared to experimental data from small angle X-ray scattering (SAXS) measurements and the mass fractal behavior was determined. A finite element (FE) simulation of a representative volume element (RVE) was performed by modeling all particle bonds with beams. The aim of the FE simulation was to investigate the bulk mechanical properties of the structures created by means of the aggregation algorithm and compare them to experimental values of silica aerogels for a given porosity.

2 Generation of models using DLCA

The DLCA algorithm uses Brownian motion of particles in the form of random walks to generate structures. In a box with periodic boundary conditions, a total number of N_{all} particles are initialized. These particles can be divided into N_{S} seeds and N_{W} walkers. They all can move freely throughout the defined periodic box. If a walker surpasses a critical distance d_{crit} to a seed it diffuses and is bound to it. Thus, clusters are formed over time, which also can be connected if any two particles of two clusters exceed a critical distance. The algorithm ends when all particles are connected to each other. The implementation of the code was perfomed in MATLAB R2018B. It is possible to compare the generated structure with scanning electron microscopy (SEM) images showing real aerogel microstructures (see Figure 1). In order to compare the geometric similarity of the two structures, the fractal dimensions are determined and compared.

3 Correlation to experimental SAXS measurements

Since the lateral length L of the simulated box is known, the volume fraction c can be determined using N_{all} and the particle radius r as:

$$c = \frac{V_{\text{particles}}}{L^3} \quad \text{with} \quad V_{\text{particles}} = N_{\text{all}} \cdot \frac{4\pi}{3} R^3 \, .$$

For the structure shown in Figure 1, the lateral length was $L = 200\,\text{nm}$ and in total 3591 seeds were created. The measured particle size was determined with a radius of $r = 3.1\,\text{nm}$, which was also used in the DLCA model. Thereby, a volume

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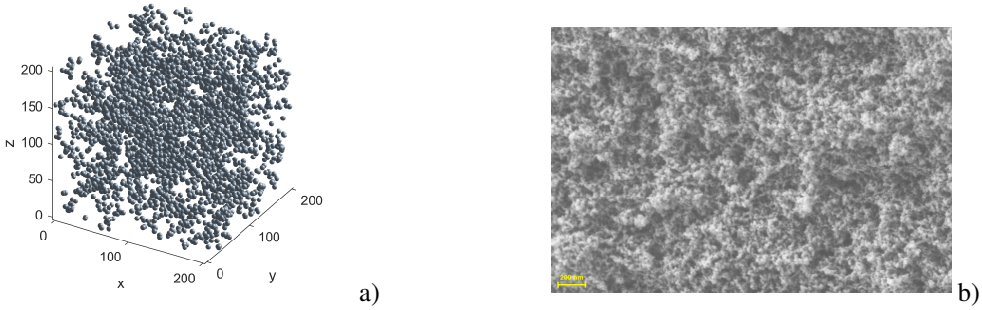


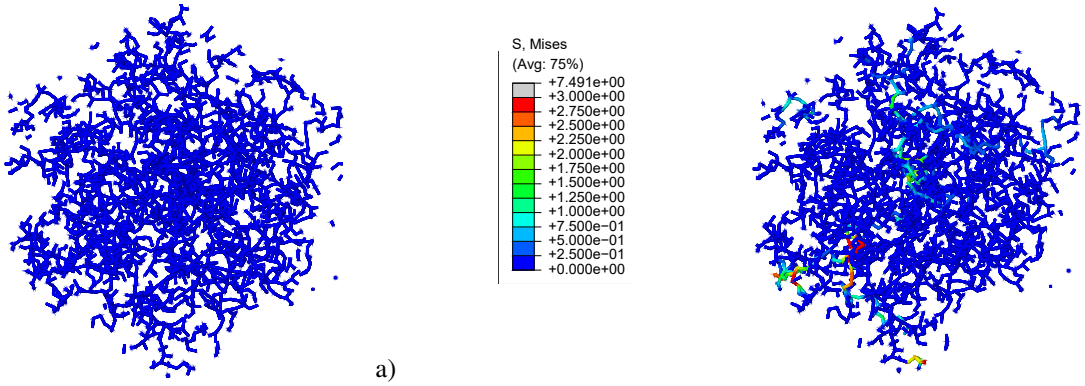
a) b)

Fig. 1: **a** Generated DLCA structure, **b** nanostructured assembly of particles forming aggregates in a silica aerogel is observed in the scanning electron microscopy (SEM) image.

fraction of $c = 0.056$ was determined, resulting in a porosity of $\phi = (1 - c) = 94.4\,\%$. The fractal dimension determined by the SAXS experiment was identified with $d_{\mathrm{f,\,exp}} = 2.51 \pm 0.07$. For the generated structure the fractal dimension of 2.58 was calculated. This shows good agreement between the model results and the experimental findings.

4 Finite element simulation

In order to create input decks in ABAQUS/CAE 2017, a export function was implemented in MATLAB. Beam elements were created, where the particle coordinates were specified as nodes and the particle bonds as elements. A circular cross-section of the beam elements is assumed where the diameter equals $10\,\%$ of the particle radius. Beam elements are especially suitable since bending, torsion and tension/compression can be modeled. These deformation states are generally observed in molecular mechanics. All nodes at the boundary surfaces of the box are connected to each other using periodic boundary conditions by coupling the three translational and the three rotational degrees of freedom. Thus, a desired strain can be specified by dummy nodes. The resulting deformations can be seen in Figure 2, where the RVE was subjected to $10\,\%$ compressive strain.



a) b)

Fig. 2: FE simulation of RVE: Visualization of von Mises stresses under an applied compression of 10% **a** undeformed and **b** deformed state.

Acknowledgements We acknowledge Markus Heyer and Rebekka Probst from DLR for synthesizing the silica aerogel and preparing the SEM picture, respectively. We also acknowledge Christian Scherdel and Gudrun Reichenauer from ZAE Bayern for providing the SAXS data.
Open access funding enabled and organized by Projekt DEAL.

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