Received: 24 June 2020 | Accepted: 18 November 2020

DOI: 10.1002/pamm.202000102

# Modeling the microstructure of biopolymer aerogels using Voronoi tessellation method

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The bulk properties of biopolymer aerogels depend on their microstructure, which can be tailored by different synthesis and drying methods. Biopolymer aerogels are characterized by a fibrillar morphology having a cellular-like network. The recently proposed constitutive modeling approach by Rege et al. [1] has shown good predictive capabilities in describing the mechanical behavior of such aerogels. Although the model describes the cellular nature and adheres to the cell-size distributions of aerogels, it is based on the assumption that the network is made up of idealized square-shaped cells. In this contribution, the diversified cellular morphology of aerogels is described computationally using a Laguerre-Voronoi tessellation based approach [2]. The pore-size distribution (PSD) data obtained from experiments accounts for the random cell sizes within the network. Accordingly, Voronoi tessellations are generated to create periodic representative volume elements (RVEs) resembling the microstructural properties of the cellular network. This work is an extension of our previous Voronoi tessellation-based 2-d description of biopolymer aerogels [3].



## 1 Introduction

Due to the biodegradability and biocompatibility of biopolymer precursors, aerogels from polysaccharides have been explored for tissue engineering applications and as carrier for drugs in biomedical industry [4]. In food industry, biopolymer aerogels are also used for food packaging [4]. These applications demand a study on the mechanical properties of biopolymer aerogels for understanding their load bearing capacity. Bulk properties of aerogels depend on their microstructure which can be tailored by different material sources, extracting and processing methods, and also synthesis and drying routes [4]. As an illustration, the fibril diameter, density and pore-size distribution (PSD) of such aerogels were observed to depend on the polysaccharide concentration [1]. Accordingly, the mechanical properties can be directly evaluated based on synthesis parameters. To investigate the substructure evolution of the 3-d porous cellular network of biopolymer aerogels under deformation, a computational model representating their realistic 3-d pore morphologies is necessary.

## 2 Methods

A 2-d model based on Voronoi tessellations was recently proposed to investigate the mechanical properties of cellulose aerogels [3]. In this approach, seed points (in set $S$) are randomly distributed in space and a Voronoi cell $V$ for each seed point $S_i$ $(i = 1, 2, ..., n)$ is generated in a way that each boundary of the cell is equidistant to seed point $S_i$ and its closest point $S_j$. The Voronoi cell of seed point $S_i$ can be expressed as

$$V(S_i) = \left\{ x \in \mathbb{R}^m \,\middle|\, ||x - S_i||_2 \leq ||x - S_j||_2 \right\} \; \forall \, j = 1, 2, ..., n \;\; : j \neq i,$$

where $x$ represent the position of any point in $m$-dimensional space. The classical Voronoi approach limits the control over the cell size distribution due to the randomized spatial distribution of seed points $S$ in 3-d space and the generation of cell boundaries based on equidistance between seed points. Alternatively, the Laguerre-Voronoi tesselation technique based on random closed packing of sphere was evaluated to model the 3-d geometry of biopolymer aerogels.

### 2.1 Sphere packing

Unlike in our previous approach [3], the seed distribution is obtained by random closed packing of polydisperse spheres by assuming the pores of the aerogels to be spherical and interpreting the pore widths to the sphere diameters. Based on the pore volume distribution data of aerogels obtained from experimental nitrogen sorption tests, the number of spheres to be packed in a given domain and the sphere volume distribution corresponding to pore width is obtained and the sphere packing is carried out based on the Lubachevsky–Stillinger algorithm according to [5].

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### 2.2 Laguerre-Voronoi tessellations (LVT)

LVT is a weighted version of the Voronoi tesselation, where the relative value of the weight $\omega$ of two neighbouring seeds determines the position of the cell boundaries by modifying $V(S_i)$ with $||x - S_i||_2 - \omega_i \leq ||x - S_j||_2 - \omega_j$. The weights could be interpreted as the square of the radius of a sphere with its center corresponding to the seed point. The LVT is carried out for the seed set $S$ corresponding to sphere set $s$. For each sphere $s_i = (S_i, r_i)$ in $\mathbb{R}^3$, where $S_i$ is the point corresponding to the center of each sphere and $r_i$ is the weight corresponding to radius of sphere, the distance between $S_i$ and any point $x$ is given by $D_L(x, S_i) = \left[||x - S_i||^2 - r_i^2\right]^{1/2}$. Similarly to the classical Voronoi formulation, the Laguerre-Voronoi cell $V_L$ corresponding to seed point $S_i$ is defined as

$$V_L(S_i) = \left\{ x \in \mathbb{R}^m \;\middle|\; D_L(x, S_i) \leq D_L(x, S_j) \right\} \; \forall \; j = 1, 2, ..., n \;\; : j \neq i.$$

The Laguerre-Voronoi tesselation is carried out for the point set consisting of the sphere centers and the corresponding radii obtained from sphere packing [2].

## 3 Results

In this work, sphere packing and the respective LVT is carried out for a RVE size of 450 nm $\times$ 450 nm $\times$ 450 nm based on the PSD of k-carrageenan aerogels[1] corresponding to the pore width data ranging from 22 nm to 74 nm. The resulting Voronoi diagram (see Fig. 1) is fully periodic and the Voronoi cells correspond to the pores of the aerogels. The proposed approach of generating Voronoi cells is capable of inheriting the pore volume distribution of k-carrageenan aerogels as shown in Fig. 2.

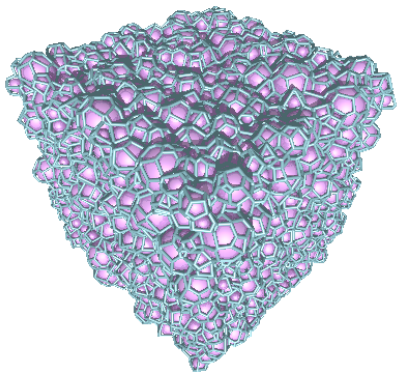

**Fig. 1:** Laguerre-Voronoi diagram based on randomly packed spheres

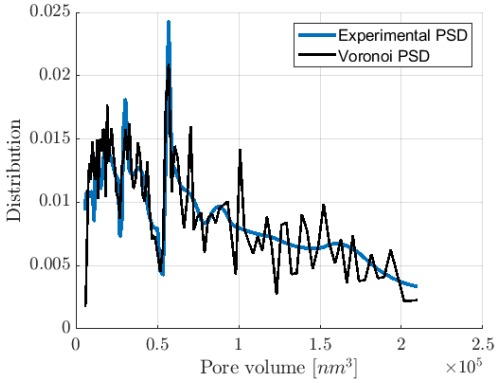


**Fig. 2:** Comparison between the volume distribution of Voronoi cells and k-carrageenan aerogels

## 4 Conclusion

The presented procedure of LVT based on random packing of spheres is capable of reproducing the 3-d morphology of biopolymer aerogels. However, the PSD for very fine range of pore width is required in order to interpret the pore width to sphere diameter for sphere packing. The cell edges of 3-d Voronoi diagram can be meshed to beam elements with circular cross section corresponding to cell wall fibers in the aerogel network and used as a representative volume element (RVE) to obtain the mechanical properties and investigate the effect of microstructural properties on the bulk behavior of aerogels.

**Acknowledgements** We acknowledge Kathirvel Ganesan at DLR for the PSD data of k-carrageenan aerogels.
Open access funding enabled and organized by Projekt DEAL.

## References

[1] A. Rege, M. Schestakow, I. Karadagli, L. Ratke and M. Itskov, Soft Matter 12, 7079-7088 (2016).
[2] Z. Fan, Y. Wu, X. Zhao and Y. Lu, Computational Materials Science **29**, 301-308 (2004).
[3] A. Rege, M. Hillgärtner and M. Itskov, The Journal of Supercritical Fluids **151**, 24-29 (2019).
[4] S. Zhao, W. J. Malfait, N. Guerrero-Alburquerque, M. M. Koebel and G. Nyström, Angewandte Chemie International Edition **57**, 7580-7608 (2018).
[5] V. Baranau and U. Tallarek, Soft Matter **10**, 3826-3841 (2014).
[6] K. Ganesan and L. Ratke, Soft Matter **10**, 3218-3224 (2014).

[1] The k-carageenan aerogels were synthesized by following the recipe in [6]

 