A Perspective on Methods to Computationally Design the Morphology of Aerogels

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Reconstructing aerogel morphology presents significant challenges, in particular, if 3D visualizations of their mesoporous network are desired. Available microscopic and tomographic tools find it difficult to probe into all types of aerogels for the purposes of reconstructing their 3D nanoporous morphology. This is where computational approaches have shown promising efforts. Herein, diverse models that can be applied to describing different aerogels are explored. To begin with, cluster-cluster aggregation models are examined for simulating the sol-gel process and the resulting morphologies in fractal aerogels, e.g., silica-based. Gaussian random field models and polymerization-induced phase separation models are explored for modeling organic non-fractal aerogels, e.g., resorcinol-formaldehyde (RF) ones. This is followed by Langevin-dynamics-based discrete element models that are explored for simulating gelation in fibrillar aerogels, e.g., those from biopolymer sources. Lastly, modified Voronoi approaches are investigated for describing the 3D fibrillar morphology, also of fibrillar aerogels, like those from biopolymers. A perspective is presented highlighting the strengths as well as shortcomings in each of the model approaches. Possibilities to either extend available approaches or explore new ones are briefly discussed at every interval.

1. Some Introductory Remarks

Aerogels are fascinating materials that exhibit a highly openporous nanostructured morphology. They typically possess very low densities ($<0.2 \text{ g cm}^{-3}$), high porosity (up to 99.98% v/v), low thermal conductivities (up to 0.01 W m⁻¹K⁻¹), and sound velocities as low as 20 m s⁻¹.^[1] The combination of such properties makes aerogels a very interesting class of materials for

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industry and research alike. Aerogels are prepared from inorganic and organic sources, can be carbonized to synthesize carbon aerogels, and can be developed in a hybrid as well as a composite setting.^[1,2] There are two degrees of freedom in the aerogel development, viz. the choice of starting material and the process after gel formation.^[3] Maneuvering through both these degrees of freedom can result in the generation of aerogels with very different morphologies. Most aerogels, such as silica, organic ones such as resorcinolformaldehyde (RF), melamine-formaldehyde (MF), and carbon aerogels exhibit a particleaggregated morphology. There, the growth of the aerogel networks or aggregates can occur through aggregation either driven by nucleation or microphase separation. On the other hand, a few aerogels such as those from bio-based sources, exhibit a fibrillar morphology. There, the aerogel network is formed from 3D-interconnected fibers that are formed from aggregating

polymer chains of e.g., the unit-structured polysaccharide. These microstructures are typically visualized by means of microscopy images as obtained from either scanning electron microscopy (SEM) or transmission electron microscopy (TEM). Neither of these imaging methods give a direct possibility to reconstruct or visualize the 3D network morphology. To this end, tomographic methods are sought after. A few authors have reported the application of tomographic methods such as micro-computed tomography,^[4-6] nanoholotomography,^[7] TEM tomography,^[8] and 4D scanning transmission X-ray microscopy combined with ptychographic tomography.^[9,10] While all these approaches have vielded 3D visualizations of aerogels, one thing common in all these approaches is the limitation of length scale that can be explored. All of these approaches can characterize the aerogels only in the macroporous region, while most of the pore-space and subsequently interesting properties arise out of the mesoporous (and in some case, microporous) region in the aerogels. These are not captured by the state-of-the-art techniques. However, to the best of the knowledge of the author, there has been one report illustrating the nanostructure of fumed silica and silica aerogels by means of advanced electron tomography.^[11] There, the network morphology was investigated by quantifying the obtained structure in terms of porosity, tortuosity, and network connectivity. This methodology needs to be explored to further investigate nanostructured materials like aerogels. One might ask, why is the 3D reconstruction of the aerogel morpholgy of an importance?

A significant proportion of the aerogels' material development has taken place at a laboratory level. With a larger goal of reverse engineering, the improvement of the material properties of aerogels demands the need for theoretical and computational models of aerogels. This is because most of the interesting features in aerogels arise from their structure-property relations. While several analytical methods, e.g., nitrogen porosimetry, small-angle scattering methods, dynamic light scattering, etc. provide significant information about the aerogel structure, they remain implicit. They do not deliver information about the 3D nanostructure nor correlate synthesis parameters to structural parameters explicitly. The easiest way of developing a computational model of a material is to design a 3D network, which is often done by tomography followed by 3D reconstruction. Generating such tomographic models can assist the studies of the structureproperty relations, in particular for aerogels the simulation of the thermal or mechanical transport through the material. This, followed by the correlation of model parameters to the synthesis ones, can help reverse engineer the properties of the aerogels even before the lab-scale development. However, the shortcomings arising from the length-scale limitations of these methods have been briefly discussed earlier. To this end, the development of numerically modeled microstructures that adhere to experimentally characterized aerogels' morphology is requisite.

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Computational modeling of aerogels and their properties has advanced significantly in the last decade. Modeling approaches have primarily opted two routes. First, molecular simulations, and the other, mesoscale ones. Molecular models of aerogels, particularly those using molecular dynamics-based investigations, have evolved steadily since the first study on modeling silica aerogels by means of negative rupturing of silica.^[12] While this approach has been used by several authors^[13–17] since then to model silica aerogels, it only is strictly capable of modeling porous silica. It does not account for processes, such as condensation reactions, that are relevant to develop molecular models. Howbeit, for predicting structureproperty relations, they have proven to be worthy. They have also been extended to model structure-property relations in fiberreinforced aerogel composites at the molecular level.^[18,19] Recently, molecular models to describe porous graphene^[20] and their applicability to model graphene aerogels^[21] have been proposed. While these molecular-dynamics-based models have been developed, they remain fully atomistic. Thus, their applicability to model the morphology of aerogels, as seen through SEM or TEM images, remains questionable. Although, with increasing computer power, significantly large molecular models can be developed. The largest atomistic model for silica aerogels has been 100 nm \times 100 nm \times 100 nm.^[16] This is a large enough scale to describe structural features as well as thermal and mechanical properties of aerogels. However, they demand superior computational resources and establishing correlations between atomistic morphologies and real aerogel morphologies can be challenging. Furthermore, as described earlier, none of the above-mentioned molecular modeling approaches describe or mimic the synthesis process of aerogels at the molecular level. This has led to several gaps between molecular models and lab-based material development. However, the premise is promising given that such molecular dynamics-based simulations have addressed important issues in describing hydrogels.^[22-26]

 Table 1. Summary of various methods applied to computationally design and model aerogels. DLCA: Diffusion-limited cluster-cluster aggregation, BA: Ballistic aggregation, CG-MD: Coarse-grained molecular dynamics, MD: All-atom molecular dynamics, CM: Constitutive model, GRF: Gaussian random field model, PIPS: Polymer-induced phase separation, LD-DEM: Langevin dynamics with discrete element method.

Type of aerogel	Methods				
Silica aerogel	DLCA	BA	CG-MD	MD	CM
Organic aerogel	GRF	PIPS	СМ		
Carbon aerogel	DLCA				
Graphene aerogel	MD				
Biopolymer aerogel	Voronoi	LD-DEM	СМ		
Aerogel composites	MD	СМ			

With respect to aerogels, this is an important subject that needs to be addressed, however, more elaboration at this point may drift the reader of this article off-topic. To this end, molecular dynamics-based models will not be considered in this article, but a special focus will be on mesoscopic models and their applicability to design the 3D morphology of aerogels.

In this article, the author desires to overview and comment on the available approaches to computationally model aerogels, such that they can be applied to characterize aerogels at different scales. Aerogel morphology can be categorized into either particleaggregated or colloidal and fibrillar. Thus, it is important to first know the art of the aerogel network, before proceeding with the choice of the modeling approach. With respect to the approaches, there are again primarily two model hypotheses. On the one hand, the model may describe the entire process through the network formation up to the final state of the morphology. On the other hand, approaches may utilize a shorter path, skipping the network formation process and directly giving the final picture of the aerogel as an output. Both approaches have pros and cons and these, within the context of aerogel modeling, will be addressed. The different modeling methodologies in application to designing aerogel networks are summarized in Table 1. These approaches will be discussed in the following sections.

2. Particle-Aggregated Aerogels

A major class of aerogels prepared from organic and inorganic sources exhibit a particle-aggregated morphology. Figure 1 shows a TEM image of a silica aerogel and an SEM image of an RF aerogel. One can visualize the network structure of these aerogels to be formed from the aggregation of particles. The images show the appearance of well-defined particles. Note that the scale in images is nearly 2 orders of magnitude apart. Classical silica aerogels show particle sizes in the order of a few nanometers,^[27] while flexible silica aerogels, e.g., from the methyltrimethoxysilane recipe, exhibit particle sizes up to a few micrometers.^[28] In contrast, classical RF aerogels from the recipe of Pekala^[29] show particle sizes in a few nanometers, while those from the recipe of Schwan and Ratke^[30] as shown in this image, exhibit much larger particle sizes. While both the above-illustrated aerogels show a similar morphology, their structural features are quite different. Silica aerogels show a fractal





Figure 1. a) A transmission electron microscopy (TEM) image of silica aerogel and b) a scanning electron microscopy (SEM) image of an resorcinol-formaldehyde (RF) aerogel, illustrating the well-defined particle-aggregated morphology.

morphology, meaning that they exhibit self-similar features. Although seemingly similar, (most) organic aerogels do not show such fractal features.^[31,32] The process of network formation in these two aerogels is very different. Silica aerogels form bonds purely from nucleation and growth. This means monomers form oligomers through the condensation reactions. These evolving entities (sol particles) undergo stochastic or nonstochastic motions inside the solution forming clusters, and these clusters and new oligomers further aggregate forming the network. On the other hand organic aerogels, e.g., RF, exhibit smoothsurfaced domains, indicating that the synthetic opportunity afforded by kinetic growth processes is not demonstrated. The dominant processes that determine the structure in organic aerogels are developed near equilibrium, accounting for the smoothsurfaced domains correlated in a non-self-similar fashion. It was subsequently shown that the growth in such aerogels implicates microphase separation, induced and limited by cross-linking as the dominant process leading to the observed morphology.^[31] To this end, in this section, several approaches to computationally reconstruct the morphology of both types of aerogels will be discussed.

2.1. Fractal Aerogels

As described earlier, silica aerogels are excellent examples of fractal materials. They are synthesized by means of the sol-gel process. In this process, sol particles are typically formed as a result of chemical reactions from dissolved precursor solutions and these particles undergo Brownian motion and in the process start diffusing, thus, initiating aggregation and adding up to gelation. Chemically this process is called condensation followed by subsequent gelation. Fully gelled solutions are obtained after aging. These gels, hydrogels or alcogels, are then dried supercritically to obtain aerogels. It remains a common assumption that the gel structure is unaffected while drying under supercritical conditions. Thus, the network in the fully gelled state and in the aerogel state are treated the same. This process of generating the fully gelled network can be meticulously captured by means of the diffusion-limited aggregation (DLA)^[33] approach. Here, the diffusion-limited cluster-cluster aggregation (DLCA)^[34] is typically chosen because the clusters being formed during the sol-gel process are themselves mobile, thus rendering the classical DLA model useless. Hasmy et al.^[35] in 1994 first showed that the scattering intensity results obtained using small-angle neutron scattering on silica aerogels can be matched by the scattering curves obtained on model structures of silica aerogels described using the DLCA model. The surface area, which for aerogels, is fractal in nature, as well as the pore volume and size distributions could be very well captured by such models as well as validated with experimental data. That the aerogel models could describe the fractal region of the scattering intensity very well was already shown by Hasmy et al.^[35] Since this publication, the application of DLCA for describing silica aerogel networks has become well-known.

DLCA works in the following way. One starts with defining a simulation box with periodic boundary conditions. This is followed by initializing N number of particles in the box. These can be typically placed randomly or in an arranged manner in the box. The former is preferred to agree with the real state of sol particles. The algorithm is illustrated in Figure 2. First, Figure 2a shows the particles initialized in the box. These particles follow the random walk theory, and whenever a particle comes in contact with another particle, it diffuses and is considered to bond. To model contact, typically, a critical distance δ_{crit} is defined, such that if particle A comes within a distance x with particle *B*, where $x \leq \delta_{crit}$, it diffuses. This continues up to the point that all particles and clusters are fully connected forming one aggregate. This is important, because in a real aerogel one has only a single network. However, it must be noted that cluster-cluster aggregation may not always accurately depict the morphology of all silica aerogels. Hüsing and Schubert^[2] briefly outlined the influence of the pH on the growth mechanism of silica gels and aerogels. This is sketched in Figure 3a. In the literature, however, aerogels are generally modeled using the DLCA model, the mechanism of which was illustrated and explained earlier. The (modified or poisoned) Eden growth model^[36] has not been generally applied to study the structural features in silica aerogels. This issue of choosing either of the two growth mechanisms needs addressing to develop accurate digital twins of silica aerogel networks, thus taking the pH dependence





Figure 2. Graphic illustrating the diffusion-limited cluster-cluster aggregation (DLCA) modeling process mimicking mechanistically the sol-gel process of gel formation. The red particles represent single (sol) particles, while the purple ones illustrate clusters. Images generated in the authors' research group.



Figure 3. a) Influence of pH on the growth mechanism in silica (aero)gels. Image is based on Ref. [2]. b) A model silica aerogel generated by the DLCA algorithm with a box size of $250 \text{ nm} \times 250 \text{ nm} \times 250 \text{ nm}$. Image generated in the authors research group.

into account. A fully connected 3D network of a model silica aerogel, modeled by means of DLCA, can be visualized in Figure 3b. Here, the model parameters include N, the number of particles initialized, d, diameter of the particles, and s, step-size of the particles. The latter demonstrates how fast a particle moves. While sufficiently large N should eliminate any size-effects in the model, the parameter d can be correlated with experimental data by following either small-angle scattering data or dynamic light scattering one. It can be chosen to have a constant value or possess a distribution. s may also be correlated with experimental data. The box size together with the particles size and number of particles dictates the relative density or porosity of the model aerogel.

Alternatively, one may choose to apply other aggregation models for describing aerogels. A simple extension to this modeling approach is the chemically or reaction-limited cluster-cluster aggregation (RLCA).^[37] This algorithm is largely the same as DLCA, with the only modification being that not every collision may result in aggregation. It is here that a probability is defined to simulate diffusion. While these two approaches undergo Brownian motion, thus appearing similar, some authors have suggested applying ballistic aggregation for modeling aerogels.^[38] In the ballistic aggregation approach, a particle undergoes a linear motion up to the collision. If it does not collide with another particle even after reaching the boundary, it is given a different trajectory. Good agreement was reported with experimental data using such an approach. While all three approaches can model silica aerogels, the DLCA or RLCA is more physically inclined toward the sol-gel process, and since Hasmy et al.^[39] demonstrated the suitability of applying DLCA to model aerogels among all other possible algorithms, most of the authors have used this approach ever since. After this pioneering work of Hasmy et al.,^[35] the next significant step in the application of DLCA came in the year 2000, when Ma et al.^[40] applied this modeling approach to describe the mechanical properties of silica aerogels. Now, DLCA is a purely mathematical construct driven by the physics of Brownian motion at the mesoscale. Since atomic degrees of freedom are neglected, there exists no interatomic potential that can be used to calculate the energy and forces in the network subjected to deformation. To circumvent this limitation, Ma et al.^[40] ignored the particles in the modeled network and exported the bonds between the particles into a finite element program and treated them as beams. First, the bond was designed by joining the centers of any two particles as obtained in the DLCA model. Second, these were modeled as beams because bonds under deformation can undergo three modes of deformation, viz. stretching, bending, and torsion. All these modes can be captured by means of a beam element. Ma et al.^[40] simulated the imported network structure under hydrostatic compression and evaluated the bulk modulus. They determined a power-law scaling between the bulk modulus K and the relative density ρ , and was expressed as $K \propto \rho^{3.6}$. Generally, in the aerogel literature, such relations have been used to describe the relation between Young's modulus *E* and ρ . For silica aerogels, this relation usually is shown to be between 3 and 4. Ma et al.^[40] also argued upon the role of dead-ends in contributing to the compliance of aerogels. They developed models with as well as without dead-ends, and subjected the local network structure to hydrostatic compression, always yielding an exponent value of

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3.6. They concluded that the decrease in the fraction of bonds bearing the mechanical load in the aerogel model with decreasing density is what makes the aerogel network so compliant.^[41] The dead-ends had no contribution to the mechanical stiffness of the material. For low-density aerogels, the few bonds connecting larger clusters become sources of stress concentration, leaving the larger clusters unloaded. In a subsequent study, they also showed that about 70% of the network strain energy comes from the bending of beams.^[42] As for the rest, the contribution from axial stretching energy.

Recently, this modeling approach was further extended by Abdusalamov et al.^[43] for describing the macroscopic properties of aerogels using the DLCA network structure. In this work, we modeled the structural and fractal features of the silica aerogels by means of the DLCA model. The fractal properties were validated with the synthesized silica aerogels. While simulating the mechanical properties, Ma et al.^[40] simulated only the local network structure by subjecting it to hydrostatic compression. In our work, we applied the periodic boundary conditions in the finite element method, which means that the bulk mechanical properties of the representative volume element (RVE) of the aerogel could be determined. The RVE was then subjected to uniaxial compression, a test typically chosen for describing the mechanical properties of aerogels. Interestingly, the simulation could show the regions of stress concentration very clearly and it was also shown that the majority of the bonds remained stressfree (see Figure 4). The presence of backbone paths could be visualized in 3D. This is again an important result, thus, the inclusion of Figure 4 in this article. Such kind of backbone paths, those that bear the majority of the subjected load leaving the rest of the network stress-free, are observed in colloidal materials.^[44,45] Since uniaxial compression was simulated, we obtained a power-law scaling for their Young's modulus, and it was shown to be $E \propto \rho^{3.61}$. This agreed well with available experimental data.^[46,47] Before moving the discussion forward, the author would like to point out that better connectivity, purely from a computational perspective, is achieved using the on-lattice algorithm for simulating DLCA, compared to the off-lattice one. Using a purely off-lattice algorithm may result, in some occasions, in not having a well-formed backbone in the material. This might explain the reason why Ma et al.^[40] used the on-lattice algorithm.

Other authors have also shown the applicability of DLCA toward the description of silica aerogels. For example, very recently, Borzecka et al.,^[48] developed 2D DLCA and RLCA models to study the gelation kinetics in aerogels. They obtained the condensation kinetics curves and qualitatively compared the results to those obtained experimentally. There, quantitative agreement could not be achieved as the models were only 2D, while aerogels form 3D networks. However, the study was promising such that application of 3D models to do the same and perhaps reverse engineer the gelation process of aerogels can be realized. Another interesting report on modeling aerogels by means of DLCA came in 2000 by Haard et al.^[49] There DLCA

agreement could not be achieved as the models were only 2D, while aerogels form 3D networks. However, the study was promising such that application of 3D models to do the same and perhaps reverse engineer the gelation process of aerogels can be realized. Another interesting report on modeling aerogels by means of DLCA came in 2000 by Haard et al.^[49] There DLCA was applied to model helium-aerogel systems for providing estimates of the quasiparticle mean free path and inter-surface spacing. They simulated DLCA with particles not with a constant size but rather the network having a distribution of particle sizes. The mean free path was found to depend simply on the inverse of the aerogel density. In another application of DLCA, Liu et al.^[50] developed a two-level model, a particle-particle interaction model and a cluster-cluster model. The prior one described the interactions between primary particles, where the polymerization reaction between the primary particles was considered and the neck properties were numerically modeled. They modeled the neck stiffness by short-range interactions, which were modeled by means of a modified Hertzian elastic contact theory. The fracture of the interparticle neck was modeled using a critical stress criteria, which was calculated by dividing the pull-off force with the neck cross-section area. The cluster model was described by means of the DLCA approach. The simulations were performed using the discrete element method (DEM), where the motion of particles are realized by solving their equations of motion. Model sizes of up to 64 000 particles were simulated. The effect of the primary particle size on the mechanical properties was studied. A power-law scaling relation of $E \propto \rho^{3.88}$ was obtained for model systems with a constant particle size. On accounting for the variation in connectivity and particle sizes, exponents in the range of 3.06-3.88 could be obtained. Reasonable quantitative agreement of the Young's modulus and tensile strength of silica aerogels was achieved after accounting for the primary particle size effects. It was thus shown, that the tensile properties of silica aerogels are significantly dependent on the primary particles sizes. Their group subsequently applied DLCA together with a fiber model to describe the properties of fiber-reinforced silica



Figure 4. a) RVE from a DLCA model aerogel network in reference configuration, b) under deformed configuration after 10% compression, and c) zoomed version showing the critical backbone paths. Reprinted (adapted) with permission from.^[43] Copyright 2021 American Chemical Society.



aerogels.^[51] As one can observe, most of the investigations using computational approaches have investigated the structural and mechanical properties of aerogels. First, using an approach similar to that of Ma et al.^[40] or Abdusalamov et al.^[43] one can trivially simulate the thermal transport through the aerogel network. Second, it is perhaps seldom reported due to that fact that aerogels, being thermally superinsulating materials, have undergone intensive lab-based experimental research for improving their thermal characteristics. The mechanical properties remained relatively less within the focus, as many insulation applications do not require the material to bear mechanical loads, however, this has seen a significant change in the last decade, with literature on improving mechanical stiffness and flexibility of aerogels seeing a steep rise. Concerning the application of DLCA to simulate the thermal properties, an interesting study was reported by Zhao et al.,^[52] where they applied the DLCA model within a finite volume framework for predicting the total thermal conductivity in silica aerogels. In this study, they modified the DLCA algorithm by restricting the aggregation growth within the simulation box, thus resulting in a non-periodic structure. There, solid-gas coupling, conduction, and radiation were accounted for. For model aerogels with $\rho = 110 \text{ kg m}^{-3}$, total thermal conductivity as low as $0.0154 \text{ W m}^{-1}\text{K}^{-1}$ at 300 K and 1 bar could be achieved. For pressures <100 kPa, conductivity as low as $0.0047 \text{ W m}^{-1}\text{K}^{-1}$ could be modeled. So far, the application of DLCA has been focused on studying silica aerogels. However, recently Pang et al.^[53] modeled carbon aerogels using the DLCA model to study the hydrogen adsorption characteristics. This was simulated by applying the grand canonical Monte Carlo method. They studied the influence of particle diameter, aerogel density, temperature, pressure, and the specific surface area on the hydrogen adsorption capacity. Interestingly, the specific surface area of the modeled aerogel was higher than that of the experimentally measured one, despite other parameters such as the porosity having similar values. A similar model approach was applied to study nitrogen adsorption in silica aerogels using the DLCA method.^[54] There too, notably, the specific surface areas of the modeled aerogels were comparatively higher than that of the experimentally measured ones. In fact, there, the particle size was adjusted so as to obtain agreeable surface area calculations. This discrepancy in the measured and calculated specific surface area could be attributed to the difference in size scales. DLCA (or most other) models are limited to a simulation box size, which although is supposed to be representative of the entire network structure, this may not always be the case. Moreover, the larger pores, those that are few but account for lowering the specific surface area, are usually not accounted. Furthermore, the applicability of DLCA to model carbon aerogels needs investigation. It was clearly shown by Pekala and Alviso^[55] that carbon aerogels do not show fractal characteristics. Thus, the applicability of DLCA-generated fractal networks to study such aerogels is questionable.

Apart from the application of DLCA to model silica aerogels, a simplified beam-based unit cell was modeled to describe silica aerogels by Lei and Liu.^[56] They modeled a silica aerogel RVE made up of cubic-shaped unit cells having dead-ends. They compared the mechanical properties of the model with dead-ends and without, and concluded that the dead-ends have no role to play in Young's modulus of the material, but do have a

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significant contribution in their compressive strength. This, together with the reports of Ma et al.^[40-42] confirm that dead-ends have no role to play in the mechanical stiffness of aerogels. It is my opinion, that the random connectivity and the pearl-necklacelike morphology are critical factors in describing the mechanical properties of aerogels. While there are several reports, using DLCA, that take into account the random connectivity in aerogels, almost no study has analytically or computationally investigated the influence of the pore-wall features on the structural and mechanical properties of aerogels. This subject was addressed only recently, when Rege et al.^[57] illustrated the influence of the pearl-necklace-like morphology and the variations in the neck sizes on the mechanical properties of the pore walls. Having such a morphology as against the pore wall having a constant crosssection results in significantly different maximal axial and bending stresses and critical buckling loads in the pore walls, which may provide insights into the bulk failure mechanisms subject to variations in the particle-neck sizes.

To summarize the application of DLCA to model fractal morphologies in aerogels and then subsequently investigate their mechanical and even thermal properties, while the abovementioned studies report significant progress in modeling silica aerogels, it is still in nascent stages. Material modeling has today evolved into a separate category of science that is not only used to model particular behavior, but to rather predict material behavior and properties as well as accelerate the synthesis of new materials. The advent of artificial intelligence has significantly boosted the efforts toward rapid materials development. In the case of modeling aerogels, DLCA has so far only focused on finding out the power scaling relationships between the aerogel density and the target property, thus from a mechanical perspective, focused only on the linear elastic regime of deformation. Since periodic boundary conditions have been applied within a finite element setting, it must be possible to simulate the macroscopic stress-strain curves of silica aerogels under large deformations, those that are in agreement with experimental data. This will validate the modeling approach very strongly, as well as provide insights into the damage and failure in the aerogel networks. This could also very well set the first step toward using computational approaches towards tailoring and reverse engineering aerogels. Machine learning (ML) models have been so far applied to optimize the thermal and optical performances of aerogels for energy-saving applications in glazing systems.^[58,59] However, there have been very few articles exploiting ML approaches to optimize and design the network architecture of aerogels. To this end, recently an ML model was developed to predict the fractal dimension in an aerogel given DLCA model parameters (see Figure 5), where the model showed an R^2 score of 0.973.^[60] This was a first-of-its-kind ML model for predicting structure-property relations in aerogels. Moreover, the same neural network was inverted to predict model parameters for a target material property. The model was quite successful in doing so. However, like many previous studies using DLCA to model silica aerogels, quantifying purely the structural characteristics and the fractal properties is not going to bring research on the modeling of aerogels forward. Direct quantitative measurements of mechanical and thermal properties using such models are necessary. To this end, efforts have been made to develop an ML model for predicting the mechanical properties of silica





Figure 5. A first-of-its-kind artificial neural network (ANN) for structure-property prediction in silica aerogels. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry.

aerogels, and subsequently applying a reinforcement learning approach for inverse designing the aerogels for target mechanical properties.^[61] However, these investigations find themselves in preliminary stages.

2.2. Non-Fractal Aerogels

Aerogels such as those from RF form networks due to microphase separation. Here, unlike silica aerogels, self-similar kinetic growth processes are not dominant. Many authors report a lack of observation of a fractal behavior in RF aerogels.^[31,32] It may be possible that aerogels have very low densities or else those prepared from other recipes may exhibit a fractal nature. However, this is still to be explored. Having said that, like silica aerogels, RF aerogels do show a pearl-necklace-like morphology of the clusters. This appearance could be attributed to the transition from nucleation and growth to spinodal decomposition. Pekala and Schaefer^[31] proposed microphase separation as the mechanism driving the growth of the gel in such materials. This was attributed to a persistent observation of peaks in the scattering curves, absence of fractal behavior, and observation of short-scale smooth-surfaced morphology, thus implying the occurrence of network formation near equilibrium. The degree of branching is controlled by the catalyst concentration used in polymerization.

There are not many studies reporting on modeling the phase separation-driven growth of porous networks in RF or other organic aerogels. Roberts^[62] first developed an approach based on Gaussian random fields (GRF) to describe the morphology of organic, in particular RF, aerogels. GRFs were chosen because they have in the past shown to describe networks arising in spinodal decomposition,^[63] microemulsions,^[64] and porous rocks.^[65] He realized that the standard 1-cut GRF model cannot create aerogel-like porosities, while a 2-cut model would exhibit only sheetlike structures. To overcome this challenge, he modeled the open-porous network by defining the solid phase

occupying two regions, where these regions were statistically independent GRFs. This independence allows the calculation of correlation functions. To correlate the model to experimental data, he subsequently derived the surface area and scattering intensity. Roberts obtained good validation for RF aerogels synthesized with R/C ratios of 300 and 50, with respect to the surface area and matching of the scattering intensity curves. Similar to specific surface area predictions in the case of DLCA models, the calculated surface areas in the GRF models of RF aerogels were always higher compared to the experimental ones. Gommes and Roberts,^[32] then building up on Roberts' previous work, showed that neither approach, aggregation, or phase-separation, when considered alone, fully satisfies the description of such aerogels. This means that both forms of aggregation must not be considered mutually exclusive for network formation.

The modeling approach can be elucidated as follows. Two statistically independent GRFs y(x) and z(x) are considered, with mean equal to zero and variance equal to one. Given two thresholds α and β , the solid skeleton of the gel is defined as the regions of space where both $\alpha \leq y(x) \leq \beta$ and $\alpha \leq z(x) \leq \beta$. To this, a field-field correlation function must be defined. In the work of Gommes and Roberts,^[32] they defined a simple function with two parameters, viz. the correlation length ξ and the domain scale *d*. This was chosen in a way that guarantees that the specific surface area of the level-cut morphology remains finite. Thus, the model approach is very straightforward and not complex. Determining the surface areas and pore-size distributions result in the possibility of achieving validation of the structures against those of that of real aerogels. Figure 6 illustrates exemplary structures of RF aerogels generated by means of GRFs. The network structures generated here agree with the comments of Pekala,^[31] that they exhibit smooth-surfaced domains. In the study by Gommes and Roberts,^[32] they proposed two hypotheses: a) the structure of the gel was considered to be biphasic comprising of a polymer phase and a liquid phase with conservation of the total volume of the polymer during gel formation, and b) the



Figure 6. Gaussian random field models having different porosities are illustrated. a) 90%, b) 93%, and c) 95%. Images generated in the authors research group.

morphology was considered to have two different length scales, one that was mesoporous and the other that was microporous. To this end, two models were developed: in model A, the small-scale structure was a colloidal polymer suspension that filled the pores of the skeleton; in model B, the small-scale structure consisted of micropores within the gel's skeleton. The behavior of model A corresponded to the aggregation theory of gel formation, similar to the one discussed in Section 2.1. The intersection model did exhibit pearl-necklace-like structures and the polydispersity could be controlled by the factor ξ/d . In contrast, model B mimicked the microphase separation theory of gel formation. This was studied by modeling the time evolution of the model networks. To do this, one can study the evolution of morphological parameters during the formation of the gel by means of small angle scattering studies, and then mimick these onto the model parameters, thus being able to simulate the growth of aerogel networks. They showed that while aggregation and microphase separation seem to be two distinct processes, in the case of RF aerogels, both scenarios lead to very similar morphologies. This can be agreed by reviewing SEM or TEM images of, e.g., silica and RF aerogels. Thus, the proposed two-point function sufficed in constructing the aerogel morphology. As one can now correlate, structures similar to DLCA can be generated (see Figure 6). Of course, here, no well-defined particles can be observed. This is because, here, the internal surface of the microstructure is modeled as an isosurface of the GRF. However, visual similarities in the network appearance with the DLCA can be observed.

Another interesting way of treating this problem of model network formation by phase separation is using polymerization-induced phase separation (PIPS). Modulating the phase separation during polymerization has shown to be very effective in tailoring the network architecture of RF aerogels.^[66] This presents a motivation for exploring PIPS for computationally describing the structure of such aerogels. While this has not been yet used to model aerogels, Wang et al.^[67] recently applied their previously developed model^[68] to investigate PIPS for modeling porous microstructures within the framework of a phase-field study. Since this model is yet not used to describe aerogels, it will not be explored in detail within the context of this article. However, it presents an interesting approach that needs to be built on to model organic aerogel networks. Basically, the model is based on the Flory–Huggins theory. A simple motivation for

the use of this theory was that it accounted for the degree of polymerization for the free energy mixing. It is known that with an increasing degree of polymerization, the free energy, and the phase diagram become highly asymmetric. The polymer phase remains in the spinodal region, while the solvent phase moves outside thus attaining equilibrium concentration. This observation leads to different diffusion mechanisms for the solvent and polymer phases. The polymer phase is governed by an abnormal diffusion mechanism while the solvent phase is controlled by normal diffusion. Because the driving force for the concentration evolution in the solvent phase after passing through the spinodal point is much greater than the one in the polymer phase, these two phases reach the equilibrium concentration asynchronously, which leads to an asynchronous evolution of the polymer and solvent phases. This asynchronous effect gives rise to the morphological transition from continuous networks to pearl-like dispersed droplets. Within the context of this study, the gelation of these dispersed droplets was not simulated. The gelation of these dispersed droplets is governed by Brownian motion and can be modeled using various approaches. This is in line with the conclusions from Pekala and Schaefer that the network formation is a result of phase separation and kinetic growth. Computationally, this also aligns well with the previous modeling approach involving GRFs and the subsequent discussion presented. The model accounting for both, diffusion and capillary flow, is illustrated in Figure 7. Different forms of morphological transformations under PIPS, such as percolation-to-cluster, cluster-to-percolation, tiny droplets and polymer-ring patterns could be observed.

Both the above-described methods show promising potentials. While GRFs can already model nanostructured networks of organic aerogels, PIPS can be extended to account for aggregation, thus resulting in porous colloidal networks. It is especially interesting to check the applicability of these to model carbon aerogels. These are obtained by pyrolyzing organic aerogels, who then undergo a massive loss in mass and a simultaneous creation of a high amount of micropores resulting from the escaping of gas. Modeling carbon aerogels becomes interesting, particularly owing to their high potential in battery applications.^[69] Another interesting method that can model phase separation along with the other process is the Lattice Boltzmann method (LBM).^[70] This approach has so far, to the best of knowledge of the author, not been applied to create

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Figure 7. Network evolution with time for three different setups: a-c): only diffusion, d-f): diffusion with weak capillary flow, and g-i): diffusion with strong capillary flow. The cyan surface denotes interface of the polymer-rich and polymer-poor phases, while the orange surfaces illustrate the isosurfaces inside the polymer-rich phase. Image reused from ^[67] with permission from Springer Nature.

aerogel nanostructures. However, LBM has been applied to simulate thermal conductivity^[71,72] and phonon heat transport^[73] in aerogels. The method, however, shows tremendous potential in its applicability to design organic and carbon aerogels.

While new methods exist to be explored and the existing methods demand improvements, there are different approaches for modeling fractal and non-fractal aerogels with reasonable accuracy than can be validated with available characterization approaches.

3. Fibrillar Aerogels

While the above-mentioned section and presented models therein have shown to be powerful in computationally generating the porous morphology and subsequent structure–property relations in aerogels having a particle-aggregated morphology, there is a wide class of aerogels that exhibit a fibrillar morphology. This is commonly observed in the case of biopolymer aerogels, in particular polysaccharide-based ones. This is because biopolymer aerogels are synthesized from fibrillar building blocks. As an example, an SEM image of a cellulose aerogel is illustrated in **Figure 8**. The fibrils are typically formed from the aggregation of polymer chains and their physical and chemical crosslinking



Figure 8. A scanning electron micrograph (in-lens) of a cellulose aerogel.

leads to a 3D-interconnected fibrillar morphology. Before the development of computational models describing the 3D morphology in aerogels, there were a few studies that developed constitutive models of such fibrillar aerogels. These models were motivated by the investigations by Gibson and Ashby on open-porous materials.^[74,75] They observed that the microscopic kinematics within such networks dictate their macroscopic



mechanical properties. Thus, models based on deformation in the pore-wall fibrils were developed to study such aerogels.

Since these models do not reconstruct the morphology of the aerogels, they will be only briefly discussed. A first-of-its-kind constitutive model for cellulose aerogels was proposed by Rege et al.^[76] The model was based on the assumption of square-shaped cells representing pores that are distributed homogeneously through the 3D space. This is generally in agreement with cellulose aerogels.^[77] The mechanical properties of the aerogels were modeled by describing the deformation in the pore walls based on the Euler-Bernoulli beam theory, by accounting for large deflections in the pore walls.^[78] This model accounted for only the strain energy from bending. The model showed good agreement against the experimental data of cellulose aerogels, despite the fact that the axial effects were ignored. The model was then extended to account for these axial effects and was then shown to capture the behavior not only in cellulose, but also pectin and κ -carrageenan aerogels.^[79] The reason that the model accounting only for the bending contribution to the strain energy obtained good validation is because the total network strain energy in aerogels is largely dominated by the bending stresses.^[42] A more generalized model describing not only aerogels, but also other open-cellular materials was recently reported.^[80] Thus far, the above-mentioned models only accounted for the active fibrils in the network. This means, once the pore walls collapsed, their contribution to the network strain energy was considered zero. Hence, only the linear-elastic region and the onset of pore-collapse could be captured with this model. Only recently, this model was extended to capture the densification behavior in these aerogels.^[81] Here, the contribution of the open cells as well as that of the collapsed cells to the network strain energy was considered. Very good validation of the model response against the experimental data of cellulose and pectinbased aerogels could be demonstrated. In separate reports, the tensile behavior in aerogels was also described,^[82] as well as the models were extended to capture the influence of hydration in biopolymer aerogels.^[83,84] While the above-mentioned models can be applied for predictive modeling of aerogels, they do not describe the network morphology of the fibrillar aerogels in question. In the following, two approaches to generate this fibrillar

morphology of biopolymer aerogels and subsequently investigate their structure-property relationships will be discussed.

The network formation in fibrillar aerogels is of significant interest to the community. As discussed earlier, the fibrous appearance comes from the aggregation of polymer chains during the gelation process and the subsequent formation of entanglements leading up to a 3D-interconnected network. While this process can be adequately modeled by approaches such as molecular dynamics, as was the case in silica aerogels, it would be computationally exhaustive, due to the presence of various processes involved. Here, limitations arising from time- and length-scale effects present a bottleneck with regard to correlations to available experimental data from analytics. As for silica aerogels, the DLCA model mechanistically mimics the sol-gel process of aerogel synthesis, or as with RF, the PIPS model can describe the phase separation in RF, which can be subsequently extended to account for aggregation and model the aerogel networks. There has been a strong need for a model capable of adequately describing the fibrillar morphology of aerogels. Recently, Depta et al.^[85] proposed a mesoscale model under a DEM-based Langevin dynamics framework for modeling the gelation in Caalginate hydrogels. As an example model system, the Ca-alginate system was chosen, thus, the modeling of alginate polymer systems using Ca⁺ in aqueous media. The aggregation of polymer fibers and the resulting morphology could be captured very well, as shown in Figure 9. The sophisticated modeling approach led to investigations of the impact of various composition and process parameters on the gelation mechanism, those which included ion concentration, polymer concentration, composition of alginate, and molecular weight of the polymer fibers. Interestingly, higher-scale network formation during the gelation on a micrometer length scale and millisecond timescale could be achieved.

The algorithm works as follows. A simulation box is defined, where, the polymer fibers are generated and placed randomly having random orientations. The polymer chains are first abstracted as dimer units, modeled as a set of primary particles, connected by flexible bonds and the interactions between the units and the environment were implicitly described. This is conceptually similar to the bonded-particle-method (BPM).



Figure 9. Illustration of the 3D fibrillar network in Ca-alginate aerogels by means of the discrete element method. The image on the right shows a close-up 2D zoomed view. Adapted with permission.^[85] Copyright 2021, The Authors. Published by American Chemical Society.



A procedure similar to MD is followed. The perfectly linear fibers must be first relaxed without interacting with each other. This lets them get to their normal relaxed state. Equilibration must be followed to avoid and correct overlap between polymer fibers. For simulating the gelation process, three interaction mechanisms were considered, viz. diffusion of units in a solvent, the interaction between the units of different chains, and the interaction of units within a chain through solid bonds. The network model was described using the Markov process. The motion of each particle in the DEM frame is governed by diffusion, solid bonds between the particles, and interaction with other particles. Diffusion was modeled based on Langevin dynamics. Only translational diffusion was considered. The absence of rotational diffusion avoided the necessity of coordinate transformations, thus reducing computational time, while also permitting simulations with larger time steps. The bonded interaction was modeled by accounting for normal and bending components of the force in the bonds. This was primarily dictated by the axial and bending stiffness. This is a typical approach for modeling the elastic energy in bonded chains within, e.g., percolating clusters.^[86] To model the interactions, a Lennard-Jones potential was chosen. The model further included an implicit probabilistic ion model capturing the effects of the ion availability during ion-mediated gelation. The proposed model was implemented in the DEM framework MUSEN.^[87] The model could be verified against the experimental data for the bundle sizes and the pore-size distributions. Good agreement was observed. It remains to see if the model can be extended to account for periodicity within the structure, so that it can in the future be applied to study the structure-property relationships. However, the results showcasing the network formation have been impressive, and the methodology can be trivially adjusted to model other biopolymer aerogel networks.

While it remains interesting to model the evolution of the microstructure, by involving the gelation mechanism in the model generation process, for most instances involving structure-property modeling, it suffices to be able to accurately describe the final resulting microstructure of the material. Since we are on the subject of fibrillar microstructures, it has been pointed out that many fibrillar aerogels, such as those from cellulose, exhibit a foam-like morphology.^[77] This could also be observed in the SEM image from Figure 8. A recognized method for generating randomized microstructures for cellular foams is through Voronoi tessellation. A Voronoi tessellation is simply a partitioning of a given domain in n-dimensional space into m distinct regions based on *m* corresponding points called seeds.^[88] Each consequent region is then referred to as a Voronoi cell. Voronoi tessellations have been used in the past to describe many open- and closed-porous materials. A proof-of-concept study on the application of this method for describing aerogels was first presented by Rege et al.^[89] There, 2D Voronoi tessellations adhering to the pore-area distribution of cellulose aerogels were developed. While Voronoi is principally a randomized network generation approach, a fitting algorithm was applied to make the randomized geometry adhere to the given cell-size distribution. While this was not the most efficient approach, it worked fine in 2D. The 2D tessellations were then imported into a finite element program and the cell-wall properties were chosen as that of the cellulose fibrils that form the aerogel network. These were

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primarily the cell-wall diameter and Young's modulus of the wall. Periodic boundary conditions were applied in FE and the bulk mechanical properties, albeit in 2D, were simulated. The influence of different cell-wall diameters and different cell-size distributions were simulated. The results were in agreement qualitatively with previously reported modeling studies, those that were compared to experimental data. In this case, comparing with experimental data was not possible because the non-trivial out-of-plane connectivity of the aerogel network was not accounted for. Thus for quantitative validations, use of 2D Voronoi tessellations for describing aerogels is not very useful.

To address the challenge of generating the 3D network of such aerogels, a modified Voronoi tessellation approach was developed and proposed by the same group.^[90] Fitting the pore-size distribution of aerogels to the randomized algorithm of the Voronoi diagram in 3D presented a significant bottleneck. It was deemed necessary that the Voronoi network needed to be built upon the basis of the pore-size distribution. To this end, a model using the Laguerre-Voronoi tessellation^[91,92] based on the random closed packing of polydisperse spheres^[93,94] was developed. Laguerre-Voronoi tessellation is basically a weighted version of the Voronoi tessellation. The model flow is straightforward. First, a polydisperse sphere pack that adheres to the pore-size distribution of a given aerogel is generated using the Lubachevsky-Stillinger approach^[95] using a force-biased algorithm.^[96] The sphere-volume distribution adheres to the pore-volume distribution as obtained from experimental characterization. More details on the exact methodology can be found in our previous work.^[90] The Voronoi diagram is then generated on each sphere, where the cell boundaries are generated tangential to the sphere surface at the point of contact between two adjacent spheres of different sizes rather than the typical equidistant positioning. The spheres are then removed from the geometry, thus only forming a template for creating the Voronoi diagram as initially desired. Thus, the pore-size distribution of the generated microstructure now adheres to that of the input one from a true aerogel, thus mimicking the real aerogel network. This model flow is sketched in Figure 10. It must be noted that this is achieved after introducing a corrector step, where the volume of the Voronoi structure is scaled to that of the original sphere pack. In hindsight, it is noteworthy, that although not really accurate, the process mimics the aerogel synthesis process. In Figure 10, one has a network, say of biopolymer fibers, and filled pores, with spheres representing the pores filled with solvent. Then, one extracts the spheres from the model, mimicking, again mechanistically, the effect of the drying process. Anyhow, even without this superficial correlation, highly nanoporous networks adhering to the input pore-size distribution can be formed. In particular, those that have a fibrillar nature. Of special interest, the fiber diameter was not assumed to be constant and that of a particular value. The only input so far to the microstructure was the pore-size distribution of the aerogel. Now, the relative density of the aerogel was measured and taken as an input, and the fiberdiameter distribution was obtained by maintaining the pore-size distribution and relative density simultaneously. This gave a distribution that was well in the range of experimentally measured fiber diameters. This is important because the fibers through the aerogel network are not all of a constant thickness, and experimental analysis only provides an average value for the fiber





Figure 10. Generation of a fibrillar aerogel network by means of sphere-pack combined with Laguerre Voronoi tessellations. The pore-size distribution is first taken as an input to generate a sphere-pack having a volume distribution adhering to that of the aerogels. Voronoi tessellations are then generated over the spheres, only to have then the spheres eliminated leaving an open-porous fibrillar network. The last image shown on the right illustrates a cube-shaped RVE.

thickness, for e.g., from SEM-image analysis. This proposed computational approach can provide a distribution of fiber diameters, thus providing more structural information about the aerogel network. Thus, the modeling approach only involves two material parameters, viz. pore-size distribution and relative density of the aerogel. The developed microstructure was then implemented in a finite element program to simulate the mechanical properties. It is of special importance to highlight that the linear elastic behavior as simulated by this microstructure coalesced the one experimentally tested. This was tested against κ -carrageenan aerogels with three different wt% concentrations of κ -carrageenan. It was observed that unlike in silica aerogels, the stress distribution through the biopolymer aerogel network was very homogeneous. This can be clearly seen from the wellconnected network in the case of biopolymers as shown in Figure 11 as against the fragmented one in the case of silica aerogels in Figure 4. This may very well be the reason why biopolymer aerogels exhibit a power scaling exponent near to 2,^[77] such that the one in the open-cell foam model. This also demonstrates the significance of network connectivity in aerogels and their resulting properties. It was recently illustrated that it is not only



Figure 11. Deformed RVE for κ -carrageenan aerogels showing an even stress-distribution through the model aerogel network. Image reused from Ref.[90].

the density, but also the pore sizes and the pore-wall morphology that dictate the mechanical properties in aerogels.^[97] This was shown by applying the above-mentioned radical Voronoi models, thus demonstrating the capabilities of the modeling approach to (a) design aerogel networks and (b) investigate the structureproperty relations.

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This approach to modeling fibrillar nanostructures is much faster than the previous one based on Langevin dynamics. It also is periodic in nature, thus within a finite element setting, it can be used to describe the bulk mechanical and thermal properties of aerogels. Having expressed that, the Langevin dynamics model describes the gelation of such fibrillar aerogels very accurately. It is indeed worth exploring this approach and extending it to be applicable for modeling bulk material properties.

4. Concluding Remarks

This article presents a perspective into different ways of designing or constructing the aerogel morphology using computational approaches. There has been a steady progress in the evolution of the field of computational models describing aerogels. To this end, different approaches are elucidated. Aggregation and phase-separation models are discussed within the context of silica or organic aerogels, while discrete element models and modified Voronoi approaches are reported in the context of biopolymer aerogels. All presented approaches show promising insights into the possibility of designing aerogel networks as well as usability to study structure-property relations. However, there are several shortcomings in the presented approaches, that if overcome, they can be exploited to realize reverse engineering the synthesis process of aerogels, thus initiating data-driven rapid materials development. Since different research groups use different protocols for preparing aerogels, and changes in such protocols, lead to aerogels with different end properties, establishing unified or uniform material properties of aerogels becomes challenging. Here, machine learning approaches can be exploited to solve this issue of consistency in developing material data sheets keeping an overview of the synthesis strategies. However, this requires generating a large amount of dataset, which seems difficult for aerogels at the present laboratory-based development. However, correlating computational models to

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synthesis protocols can be an efficient way of exploiting a way of generating datasets. Datasets from physics-informed computational models can be generated faster, manifold, and much cheaper than laboratory-based syntheses and subsequent characterization. Rapid reverse engineering of aerogels needs joint efforts on both, experimental laboratory-based and computational data-based, ends.

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Conflict of Interest

The author declares no conflict of interest.

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- M. A. Aegerter, N. Leventis, M. M. Koebel, Aerogels Handbook, Springer Science Business Media, Berlin 2011.
- [2] N. Hüsing, U. Schubert, Angew. Chem. Int. Ed. 1998, 37, 22.
- [3] I. Smirnova, P. Gurikov, Annu. Rev. Chem. Biomol. Eng. 2017, 8, 307.
- [4] B. Fu, H. Luo, F. Wang, G. Churu, K. T. Chu, J. C. Hanan, C. Sotiriou-Leventis, N. Leventis, H. Lu, J. Non-Cryst. Solids 2011, 357, 2063.
- [5] H. Zhang, C. Lin, T. Han, F. Du, Y. Zhao, X. Li, Y. Sun, ACS Sustainable Chem. Eng. 2016, 4, 6277.
- [6] F. Ram, B. Biswas, A. Torris, G. Kumaraswamy, K. Shanmuganathan, *Cellulose* 2021, 28, 6323.
- [7] R. Tannert, M. Schwan, A. Rege, M. Eggeler, J. C. da Silva, M. Bartsch,
 B. Milow, M. Itskov, L. Ratke, J. Sol-Gel Sci. Technol. 2017, 84, 391.
- [8] C. Buesch, S. W. Smith, P. Eschbach, J. Conley, J. Simonsen, Biomacromolecules 2016, 17, 2956.
- [9] J. Wu, X. Zhu, D. A. Shapiro, J. R. I. Lee, T. Van Buuren, M. M. Biener, S. A. Gammon, T. T. Li, T. F. Baumann, A. P. Hitchcock, *J. Phys. Chem.* C 2018, 122, 25374.
- [10] H. Yuan, H. Yuan, T. Casagrande, D. Shapiro, Y.-S. Yu, B. Enders, J. R. I. Lee, A. van Buuren, M. M. Biener, S. A. Gammon, T. F. Baumann, A. P. Hitchcock, ACS Appl. Nano Mater. 2021, 4, 621.
- [11] L. Roiban, G. Foray, Q. Rong, A. Perret, D. Ihiawakrim, K. Masenelli-Varlot, E. Maire, B. Yrieix, RSC Adv. 2016, 6, 10625.
- [12] J. Kieffer, A. Angell, J. Non-Cryst. Solids 1988, 106, 336.
- [13] A. Nakano, L. Bi, R. K. Kalia, P. Vashishta, Phys. Rev. Lett. 1993, 71, 85.

- [14] J. S. Rivas Murillo, M. E. Bachlechner, F. A. Campo, E. J. Barbero, J. Non-Cryst. Solids 2010, 356, 1325.
- [15] S. P. Patil, A. Rege, Sagardas, M. Itskov, B. Markert, J. Phys. Chem. B 2017, 121, 5660.
- [16] W. Gonçalves, J. Morthomas, P. Chantrenne, M. Perez, G. Foray, C. L. Martin, Acta Mater. 2018, 145, 165.
- [17] S. P. Patil, A. Rege, M. Itskov, B. Markert, J. Non-Cryst. Solids 2018, 498, 125.
- [18] A. Rege, S. P. Patil, Adv. Theory Simul. 2020, 3, 1900211.
- [19] S. P. Patil, P. Shendye, B. Markert, Scr. Mater. 2020, 177, 65.
- [20] Z. Qin, G. S. Jung, M. J. Kang, M. J. Buehler, Sci. Adv. 2017, 3, 1601536.
- [21] S. P. Patil, P. Shendye, B. Markert, J. Phys. Chem. B 2020, 124, 6132.
- [22] Y. Tamai, H. Tanaka, Macromolecules 1996, 29, 6750.
- [23] Y. Tamai, H. Tanaka, K. Nakanishi, Macromolecules 1996, 29, 6761.
- [24] E. Chiessi, F. Cavalieri, G. Paradossi, J. Phys. Chem. B 2007, 111, 2820.
- [25] Z. Han, X. Yue, J.-H. Shao, Food Hydrocolloids 2022, 128, 107537.
- [26] P. Xu, Z. Shang, M. Yao, X. Li, J. Mol. Liq. 2022, 357 119094.
- [27] J. Fricke, A. Emmerling, J. Am. Chem. Soc. 1992, 75, 2027.
- [28] A. V. Rao, S. D. Bhagat, H. Hirashima, G. Pajonk, J. Colloid Interface Sci. 2006, 300, 279.
- [29] R. W. Pekala, J. Mater. Sci. 1989, 24, 3221.
- [30] M. Schwan, L. Ratke, J. Mater. Chem. A 2013, 1, 13462.
- [31] R. Pekala, D. Schaefer, Macromolecules 1993, 26, 5487.
- [32] C. J. Gommes, A. P. Roberts, Phys. Rev. E 2008, 77, 041409.
- [33] T. A. Witten, L. M. Sander, Phys. Rev. Lett. 1981, 47, 1400.
- [34] P. Meakin, J. Colloid Interface Sci. 1984, 102, 491.
- [35] A. Hasmy, E. Anglaret, M. Foret, J. Pelous, R. Jullien, Phys. Rev. B 1994, 50, 6006.
- [36] K. D. Keefer, D. W. Schaefer, Phys. Rev. Lett. 1986, 56, 2376.
- [37] P. Meakin, F. Family, Phys. Rev. A Gen. Phys. 1988, 38, 2110.
- [38] M. Grzegorczyk, M. Rybaczuk, K. Maruszewski, Chaos, Solitons Fractals 2004, 19, 1003.
- [39] A. Hasmy, M. Foret, J. Pelous, R. Jullien, Phys. Rev. B Condens. Matter 1993, 48, 9345.
- [40] H.-S. Ma, A. P. Roberts, J.-H. Prévost, R. Jullien, G. W. Scherer, J. Non-Cryst. Solids 2000, 277, 127.
- [41] H.-S. Ma, J.-H. Prévost, R. Jullien, G. W. Scherer, J. Non-Cryst. Solids 2001, 285, 216.
- [42] H.-S. Ma, J.-H. Prévost, G. W. Scherer, Int. J. Solids Struct. 2002, 39, 4605.
- [43] R. Abdusalamov, C. Scherdel, M. Itskov, B. Milow, G. Reichenauer, A. Rege, J. Phys. Chem. B 2021, 125, 1944.
- [44] A. D. Dinsmore, V. Prasad, I. Y. Wong, D. A. Weitz, Phys. Rev. Lett. 2006, 96, 185502.
- [45] R. Dargazany, A. Rege, M. Itskov, Constitutive Models for Rubber VIII, CRC Press, London 2013, pp. 261–266.
- [46] J. Groß, J. Fricke, Nano Struct. Mater. 1995, 6, 905.
- [47] T. Woignier, J. Phalippou, R. Vacher, J. Mater. Res. 1989, 4, 688.
- [48] N. H. Borzecka, B. Nowak, R. Pakula, R. Przewodzki, J. M. Gac, *Gels* 2021, 7, 2.
- [49] T. M. Haard, G. Gervais, R. Nomura, W. P. Halpern, Phys. B 2000, 284–288, 289.
- [50] Q. Liu, Z. Lu, M. Zhu, Z. Yuan, Z. Yang, Z. Hu, J. Li, Soft Matter 2014, 10, 6266.
- [51] Z. Lu, Z. Yuan, Q. Liu, Z. Hu, F. Xie, M. Zhu, Mater. Sci. Eng. A 2015, 625, 278.
- [52] J.-J. Zhao, Y.-Y. Duan, X.-D. Wang, B.-X. Wang, J. Non-Cryst. Solids 2012, 358, 1287.
- [53] H.-Q. Pang, S. Li, Z.-Y. Li, Int. J. Hydrogen Energy 2021, 46, 34807.
- [54] W.-L. Xie, Z.-J. Chen, Z. Li, W.-Q. Tao, Computation 2016, 4, 2.
- [55] R. W. Pekala, C. T. Alviso, *MRS Proc.* **1992**, *270*, 3.
- [56] J. Lei, Z. Liu, J. Appl. Phys. 2018, 124, 2.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [57] A. Rege, S. Aney, L. Ratke, AIP Adv. 2022, 12 105108.
- [58] S. Zheng, Y. Zhou, Adv. Theory Simul. 2019, 2, 9.
- [59] Y. Zhou, S. Zheng, Energy 2020, 193, 116718.
- [60] R. Abdusalamov, P. Pandit, B. Milow, M. Itskov, A. Rege, Soft Matter 2021, 17, 7350.
- [61] P. Pandit, Master's thesis, RWTH Aachen University, 2021.
- [62] A. P. Roberts, Phys. Rev. E 1997, 55, R1286.
- [63] J. W. Cahn, J. Chem. Phys. 1965, 42, 93.
- [64] S. Marcelja, J. Phys. Chem. 1990, 94, 7259.
- [65] J. A. Quiblier, J. Colloid Interface Sci. 1984, 98, 84.
- [66] G. Hasegawa, T. Shimizu, K. Kanamori, A. Maeno, H. Kaji, K. Nakanishi, *Chem. Mater.* 2017, 29, 2122.
- [67] F. Wang, L. Ratke, H. Zhang, P. Altschuh, B. Nestler, J. Sol-Gel Sci. Technol. 2020, 94, 356.
- [68] F. Wang, P. Altschuh, L. Ratke, H. Zhang, M. Selzer, B. Nestler, Adv. Mater. 2019, 31, 1806733.
- [69] M. Nojabaee, B. Sievert, M. Schwan, J. Schettler, F. Warth, N. Wagner, B. Milow, K. A. Friedrich, J. Mater. Chem. A 2021, 9, 6508.
- [70] T. Krüger, H. Kusumaatmaja, A. Kuzmin, O. Shardt, G. Silva, E. M. Viggen, Springer International Publishing, Vol. 10, 2017, p. 978.
- [71] Z. Qu, Y. Fu, Y. Liu, L. Zhou, Appl. Therm. Eng. 2018, 132, 730.
- [72] A. Kan, S. Mao, N. Wang, B. Shi, J. Therm. Sci. 2021, 30, 248.
- [73] Y.-F. Han, X.-L. Xia, H.-P. Tan, H.-D. Liu, Phys. B 2013, 420, 58.
- [74] L. J. Gibson, M. F. Ashby, G. S. Schajer, C. I. Robertson, Proc. R. Soc. London. Ser. A 1982, 382, 25.
- [75] L. J. Gibson, M. F. Ashby, Proc. R. Soc. London. A 1982, 382, 43.
- [76] A. Rege, M. Schestakow, I. Karadagli, L. Ratke, M. Itskov, Soft Matter 2016, 12, 7079.

[77] S. Zhao, W. J. Malfait, N. Guerrero-Alburquerque, M. M. Koebel, G. Nyström, Angew. Chem., Int. Ed. 2018, 57 7850.

ENGINEERING

www.aem-journal.com

- [78] L. Chen, Int. J. Non-Linear Mech. 2010, 45, 301.
- [79] A. Rege, I. Preibisch, M. Schestakow, K. Ganesan, P. Gurikov, B. Milow, I. Smirnova, M. Itskov, *Materials* **2018**, *11*, 1670.
- [80] A. Rege, S. Aney, B. Milow, Phys. Rev. E 2021, 103, 043001.
- [81] A. Rege, Materials **2021**, 14, 2731.
- [82] A. Rege, M. Itskov, Acta Mech. 2018, 229, 585.
- [83] A. Rege, L. Ratke, S. D. Külcü, P. Gurikov, J. Non-Cryst. Solids 2020, 531, 119859.
- [84] I. D. Külcü, A. Rege, Soft Matter 2021, 17, 5278.
- [85] P. N. Depta, P. Gurikov, B. Schroeter, A. Forgacs, J. Kalmar, G. Paul, L. Marchese, S. Heinrich, M. Dosta, J. Chem. Inf. Model. 2022, 62, 49.
- [86] Y. Kantor, I. Webman, Phys. Rev. Lett. 1984, 52, 1891.
- [87] M. Dosta, V. Skorych, SoftwareX 2020, 12, 100618.
- [88] G. Voronoi, J. Reine Angew. Math. 1908, 1908, 198.
- [89] A. Rege, M. Hillgärtner, M. Itskov, J. Supercrit. Fluids 2019, 151, 24.
- [90] R. Chandrasekaran, M. Hillgärtner, K. Ganesan, B. Milow, M. Itskov, A. Rege, Sci. Rep. 2021, 11, 10198.
- [91] H. Imai, M. Iri, K. Murota, SIAM J. Comput. 1985, 14, 93.
- [92] K. Sugihara, J. Geom. Graphics 2002, 6, 69.
- [93] V. Baranau, D. Hlushkou, S. Khirevich, U. Tallarek, Soft Matter 2013, 9, 12.
- [94] V. Baranau, U. Tallarek, Soft Matter 2014, 10, 3826.
- [95] B. D. Lubachevsky, F. H. Stillinger, J. Stat. Phys. 1990, 60, 561.
- [96] J. Mościński, M. Bargieł, Z. A. Rycerz, P. W. M. Jacobs, *Mol. Simul.* 2006, 3, 201.
- [97] S. Aney, A. Rege, Math. Mech. Solids 2022, 108128652211241.



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