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3D stochastic bicontinuous microstructures: Generation, topology and elasticity

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ABSTRACT

Motivated by recent experimental investigations of the mechanical behavior of nanoporous metal we explore an efficient and robust method for generating 3D representative volume elements (RVEs) with strikingly similar behavior. Our approach adopts Cahn's method of generating a Gaussian random field by taking a superposition of standing sinusoidal waves of fixed wavelength but random in direction and phase. In its theory part, our study describes closed-form expressions for how the solid volume fraction affects the binarization level, mean structure size, specific surface area, averages of mean and Gaussian curvature, and the scaled topological genus. Based on numerical studies we report on criteria for achieving representative realizations of the structure by proper choice of the number of waves and element size. We also show that periodic structures are readily created. We analyze the mechanical properties considering linear and infinitesimal elasticity and evaluate the residual anisotropy (which can be made small) and the effective values of the Young's modulus and Poisson's ratio. The numerical results are in excellent agreement with experimental findings for the variation of stiffness with solid fraction of nanoporous gold made by dealloying. We propose scaling relations that achieve naturally a perfect agreement with the numerical and experimental data. The scaling relation for the stiffness accounts for a percolation-to-cluster transition in the random field microstructure at a finite solid fraction. We propose that this transition is the origin of the previously reported anomalous compliance of nanoporous gold.

1. Introduction

Stochastic bicontinuous microstructures, in which two contiguous phases interpenetrate, are characteristic for many materials formed by decomposition of a homogeneous parent phase. Examples are spinodally decomposed metal alloys [1,2], polymer blends [3,4] or microemulsions [5], foams that can be polymeric, metallic or food [6] and network solids such as nanoporous metals made by dealloying solid solutions [7,8]. The properties of such microstructures depend on geometric or topological characteristics including the specific surface area, the tortuosity of transport paths through one or both of the phases, the characteristic structure size, and measures for connectivity, such as e.g. genus per unit volume. Here, we describe how spinodal-like stochastic microstructures can be generated by a convenient and fast numerical algorithm and we explore their geometric and mechanical properties.

Our study is motivated by recent research in the field of nanoporous metals made by dealloying. A substantial body of experiments explores specifically the mechanical behavior of nanoporous gold made in this way [9–18]. Nanoporous materials made by dealloying can be understood as networks of nanoscale struts or "ligaments", typically with solid volume fractions between 0.25 and 0.50 [7–9]. While their microstructure is stochastic, their mechanical behavior is typically discussed with reference to the Gibson-Ashby scaling relations [6] which have been supported - on the modeling side - by periodic structures. However, the mechanical properties of dealloying-made nanoporous solids are not well described by the Gibson-Ashby scaling relations, and specifically their Young's modulus can be more than an order of magnitude less than predicted [14,19]. While surface excess elasticity has been ruled out as an explanation [20,21], nonlinear elastic behavior of the bulk may contribute [22]. Yet, the decisive issue appears to be

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network connectivity [13,14,23,24], which may systematically vary with ligament size and solid fraction.

Cahn [1] showed that the composition field in the early stages of spinodal decomposition could be approximated by the superposition of waves with random direction but same wavelength. In one of the first computer simulations of microstructure evolution in materials science, Cahn showed that binarizing this composition field indeed yielded the bicontinuous microstructure of spinodally decomposed mixtures [1]. In the present work, we explore a modern numerical implementation of Cahn's algorithm, which efficiently generates 3D stochastic bicontinuous microstructures. We present closed-form expressions for specific surface area and scaled connectivity as a function of the wavelength and solid fraction. Using finite element simulations, we document the elastic behavior and the requirements on the size of the volume element (VE)[1] for achieving representative behavior. The numerical part of our study specifically focuses on the comparison to nanoporous gold, from which the experimental validation of our model emerges. We point out that a percolation-to-cluster transition at finite density can be related to the anomalously low stiffness of experimental nanoporous gold. We bring to the reader's attention an alternative scaling law, suggested by Roberts and Garboczi [25], which accounts for the transition and remains accurate over a wide range of solid volume fraction. Since many numerical simulation approaches use periodic boundary conditions, we show how volume elements with translational periodicity can be generated. We also provide a comparison between the results for aperiodic and periodic microstructures considering the predicted effective elastic properties and demonstrate that they are in very good agreement.

2. Methods of 3D generation of nanoporous metal microstructures

The 3D geometry of the microstructure of nanoporous gold has been characterized in experiment by tomographic reconstruction. Approaches were based on transmission electron microscopy [26–29], X-ray nanotomography [30–32], focused-ion-beam (FIB) sectioning [23,24,33,34] and atom-probe tomography [35]. These approaches reveal a random network of ligaments which are interconnected in nodes. The surface is found dominated by convex and saddle-shaped patches [33], so that the average of the mean curvature is positive [26,33]. The connectivity density is less than in regular geometric networks such as the gyroid structure [23], and it varies little when the mean structure size is varied by annealing-induced coarsening [24,33]. Experimental 3D microstructures have been used as the basis for numerical simulation of the mechanical response of nanoporous gold [23,24,32]. Studies working with large volume elements, as better representatives for macroscopic material response, find strength and stiffness in qualitative agreement with experimental mechanical tests [23,24].

While experimental reconstructions are distinguished by their realistic geometry, they are also restricted to specific realizations within the family of possible structures with the same stochastic building principles. Furthermore, systematic experiments exploring variations of the microstructure of nanoporous gold with solid fraction remain yet to be reported. Numerical simulation approaches, and specifically atomistic approaches such as molecular dynamics, also often require models that are compatible with 3D translational periodicity. In each instance, the available experimental database for 3D structures is not yet sufficient for comprehensive numerical studies. This highlights the need for the computational generation of model structures.

Computational generation methods often use deterministic periodic unit cell-based idealizations. This may involve heuristic constructions or constructions of (analytical) level surfaces, e.g., triply periodic minimal surface-based unit cells. The Kelvin model [36] consisting of a regular packing of tetra(kai)decahedra, its variations by Waire and Phelan [37] and the model of Gibson and Ashby [6,38] are among the most widely used idealized unit cells for nanoporous metals. Agglomeration of the mass in junctions is considered making use of modified rectangular unit cells in Refs. [39,40]. Periodic diamond cubic unit cells were recently used for modeling nanoporous gold samples [21].

Constructions of triply periodic bicontinuous cubic microdomain morphologies, which are generated by making use of triply periodic continuous minimal surfaces [41,42], constitute another attractive direction. These level surfaces and the developed microstructures have the symmetries of a crystallographic group such as cubic, tetragonal, rhombohedral, and orthorhombic symmetries. Their smooth surfaces allow incorporation of theories accounting for surface curvature effects more realistically. For the use of triply periodic minimal surface based microstructures in modeling of nanoporous gold samples, see e.g. Refs. [23,43,44]. Gyroids as approximants to nanoporous metal foams were investgated in Ref. [45]. Moreover, microstructures made up of single and double gyroids were used in computation of the specific surface area of nanoporous materials in Ref. [46].

Although periodic unit cell idealizations prove efficient and simple, they fall short in reflecting certain key morphological, topological and mechanical characteristics of nanoporous metals. On the morphological part, the 3D reconstructions emphasize a random, as opposed to periodic, structure. So far, no evidence of anisotropy in the mechanical response has been reported for nanoporous gold and the reconstructions appear isotropic. On the contrary, the structures generated by making use of the aforementioned heuristic constructions or constructions of (analytical) level surfaces show cubic anisotropy with high polarity in terms of their directional dependence of Young's modulus.

It is possible to bridge this gap by considering stochastic disorder in cell structures, see, e.g., [47–49]. Voronoi or Laguerre tessellations constitute a more systematic method in forming stochastic cells [50–53]. A specific step in this direction was the introduction of disorder in the diamond-based network structure of Ref. [21], which indeed provided qualitatively improved agreement with experiments.

Computational generation of stochastic bicontinuous geometries of nanoporous metals are often created at considerable computational expense. With attention to modeling dealloying-made metal network structures, several studies have used the simulation of spinodal decomposition via phase-field [54–56] or kinetic lattice Monte Carlo approaches [19,57]. These approaches achieve a striking similarity to the experimental reconstructions of dealloying-made metal network structures.

A computationally more efficient method of modeling phase-separation dynamics, i.e., the phase-ordering dynamics of thermodynamically unstable phases, is the use of cell dynamical systems [58–60], e.g., coupled maps and cellular automata.

Making use of leveled Gaussian random fields, in which the interfaces between cells are defined by level cuts of random fields [61], in computational generation of stochastic bicontinuous geometries constitutes an even more efficient approach. Leveled-wave models for random morphologies, which were initially proposed for bicontinuous material morphologies formed due to phase-separation [1], have found attention in various applications [25,62–64].

[1] A volume element does not have to be adequate in size to cover sufficient microstructural features and, thus, encapsulate the effective properties, as an RVE does.