Chapter 4

Multiscale modeling of charge-induced deformation of nanoporous gold structures

Recent experimental studies have shown that nanoporous metals undergo dimensional changes when a potential difference is applied in an electrochemical environment. The primary actuation mechanism is the electric-double layer charging of the internal surface in combination with a large surface-to-volume-ratio. To account for the excess charge we have developed an atomistic model that is calibrated to density functional theory. To make a scale transition from the atomistic to the continuum scale, we propose a surface layer model that is informed by atomistic simulations. We use this multiscale approach to study the charge-induced actuation response of ordered (cubic lattices and gyroids) and disordered nanoporous gold (npg) architectures. Results are presented in terms of the charge-induced actuation strain and work density as a function of relative density, ligament size and architectural morphology. The differences between ordered and disordered structures are critically addressed.

4.1 Introduction

Nanoporous metals have attracted much attention recently, because of their potential for a wide range of applications, such as catalysts, sensors, supercapacitors and actuators [27, 31, 89, 164, 202]. The use of nanoporous metals as electrochemical actuator is especially interesting since strain amplitudes comparable to those of piezoelectric ceramics can be generated at much lower voltages (1 V compared to 100 V). This, combined with their relatively high

ductility (compared to ceramics), high specific yield strength [124, 203, 204] and potential for enhanced strain amplitudes [89, 90], makes nanoporous metallic actuators a promising new class of materials.

The actuation response of nanoporous metals is triggered by the electrochemical injection of charge, basically employing their super-capacitance related to the high internal surface area. When charge is injected, a narrow space-charge layer of approximately one to two atomic layers thick is formed at the surface. In these layers the atomic bonding is altered due to the presence of the excess charge, resulting in a lateral atomic equilibrium spacing that differs from that in the bulk. Despite the limited width of this surface layer, macroscopic strains can be generated when the ligament size is on the order of tens of nanometers [15, 29]. Having a very large internal surface area per unit volume (i.e. small ligament width) is key in generating large actuation strokes. The current generation of nanoporous metals are mostly produced using electrochemically-driven dealloying of binary alloys, resulting in a disordered foam-like structure of interconnected ligaments [74, 117, 122, 205, 206], see Fig. 4.1(c). Although these materials feature high internal surface areas, their topological disorder and imperfections will knock-down the mechanical properties [18], leading to a sub-optimal work output against an applied load. However, generating order in metals at the nanoscale is not trivial. Considerable progress has been made recently by utilizing the unique self-assembly properties of block copolymers to synthesize ordered nanoporous metals featuring a gyroidal architecture [207, 208], see Fig. 4.1(b). Clearly, the overall charge-induced deformation of nanoporous metals will be strongly size-dependent due to the surface-charge-driven actuation mechanism. This introduces the ligament size as a characteristic length scale in the problem. In addition to the ligament size, there are two more important parameters: the relative density, and the morphology of the nanoporous architecture, which can both affect the actuation strain and overall mechanical properties. No experimental or theoretical studies exist that contain a detailed analysis of the charge-induced actuation response as a function of relative density, ligament size and morphology. The goal of this chapter is to find these dependencies by studying a range of nanoporous materials with profoundly different morphologies: cubic lattices, ordered gyroids and disordered nanoporous gold structures, see Fig. 4.1. We will use a multiscale modeling approach to bridge the gap between the excess-charge-modified atomic bonding at the metal surface and the overall macroscopic actuation strain and study how this is mediated by the specific morphology of the nanoporous architecture. In chapter 3 we developed an atomistic model in order to bridge the gap between the local electron density redistributions and the overall charge-induced straining of
nanowires. We modified the surface embedded atom (SEAM) potential [192], to take into account the bond strengthening and weakening due to the addition of excess negative and positive charge. The model parameters were calibrated to the surface-stress-charge coefficient of Au(100) surface obtained from DFT simulations [108].

In this chapter we will apply this atomistic model to ordered nanoporous gold structures, i.e., cubic lattices (Fig. 4.1(a)) and gyroids (Fig. 4.1(b)). However, in order to probe the actuation of disordered structures such as nanoporous gold (Fig. 4.1(c)), atomistic simulations become computationally too expensive. To overcome this, we will develop a continuum,
surface-layer, model that is informed by atomistic simulations. We will use the ordered gy-
roidal structures to calibrate the model parameters and then apply the model to simulate the
charge-induced deformation of disordered nanoporous gold.

The chapter is organized as follows. In section 4.2 we briefly discuss the modified
atomistic (SEAM) potential that accounts for the excess charge on the metal surface and
we discuss the proposed continuum model. In section 4.3, we will investigate the actua-
tion stroke and volume-specific strain energy density by subsequently studying the stiffness,
strength and charge-induced deformation of cubic lattices (Sec. 4.3.1), gyroidal structures
(Sec. 4.3.2), and nanoporous gold architectures (Sec. 4.3.3). We discuss the effect of liga-
ment size, relative density and architectural morphology on the actuation response. Finally,
in Section 4.4 we compare the actuation performance of the three different architectures and
draw conclusions.

4.2 Multiscale model: atomistic and continuum approach

In this section we discuss the atomistic and continuum model used to study the charge-
induced deformation of ordered and disordered nanoporous gold. The atomistic model is
informed from the sub-atomic scale through calibration of atomistic (SEAM) potentials to
DFT-obtained surface-stress-charge coefficients, leading to the MSEAM model as discussed
in detail in chapter 3. The MSEAM model is used in this chapter to account for the excess
charge. Since excess charge only localizes at the surface, it is assigned to the atomic layers
which are fully or partially exposed to the surface. The amount of charge assigned to each
layer is proportional to the area projected by each atomic layer onto the surface [192]. Figure
4.2 (left) shows the charged surface and subsurface atoms for an atomistic representation of
nanoporous gold.

When negative charge is injected onto the metal surface, the electron density increases
in a surface layer of approximately one atom thick, resulting in a smaller equilibrium spac-
ing of the surface atoms. Since contraction of these surface atoms is constrained by the
uncharged core region of the metal, a tensile surface stress develops in the charged surface
region which balances the compressive stresses in the core. We now approximate this pro-
cess in a continuum setting by dividing the metal into an uncharged core region and a charged
surface layer (see Figs. 4.2(b) and 4.2(d)). We account for the charge-induced reduction of
the equilibrium spacing by specifying an eigenstrain \( \epsilon^* \) in the surface layer that is propor-
tional to the surface charge, i.e. negative charge results in a negative eigenstrain and positive
Figure 4.2: Atomistic and continuum representation of nanoporous gold (npg). (a) Atomistic model of npg showing charged surface (gold) and subsurface (red) atoms, and uncharged core atoms (blue). (b) Continuum model of npg showing the surface layer (gold) and core regions (blue). The surface layer is discretized using triangular plate elements and the core region by tetrahedral bulk elements. (c) Zoomed view of a section of the atomistic model indicated by the white arrow in Fig. (a). (d) Zoomed view of a section of the continuum model indicated by the white arrow in Fig. (b).

charge in a positive eigenstrain. Similar to the development of thermal stress in bonded materials with dissimilar thermal expansion coefficients, the strain mismatch between the surface layer and core region results in tensile surface stress and compressive straining when a negative charge-induced eigenstrain is prescribed. A similar approach was proposed to account for edge stresses in graphene sheets [209]. The thickness of the surface layer is
taken approximately equal to the thickness of the charged surface region in the atomistic model. Given the much smaller thickness of the surface layer compared to typical ligament widths of nanoporous structures, we discretize the surface layer by means of plate elements (STRI65 or S4) and the core region by tetrahedral (C3D10) or brick elements (C3D8) [210]. We calibrate the specific value of the eigenstrain by matching the overall actuation strain to that of one atomistic simulation. Details on the model parameters will be discussed in the respective result sections of the different nanoporous architectures (i.e. cubic lattice, gyroid and npg). The continuum calculations were found to be at least a factor 1000 faster than the atomistic simulations.

4.3 Results and Discussion

The performance of an actuator is not only measured in terms of the total actuation stroke $\epsilon_c$, but also on its capability to do work against a certain load. Consider a compressive load applied to the actuator, resulting in an initial compressive strain $\epsilon_{el} = \sigma / E^*$, with $\sigma$ the stress due to the load and $E^*$ the stiffness of the actuator. While the actuator would give an actuation strain (per unit injected charge) of $\epsilon_c$ in the absence of load, the useful strain of the actuator subject to load is $\epsilon_c - \epsilon_{el}$. The work per unit volume done by the actuator against the load is therefore given by [211]

$$W_V = \sigma(\epsilon_c - \epsilon_{el}). \quad (4.1a)$$

Maximizing Eq. 4.1a with respect to $\sigma$ and resubstituting the $\sigma$ for which $W_V$ is maximal (i.e., $\sigma_{max} = E^* \epsilon_c / 2$) back in Eq. 4.1a we arrive at the maximum work density given by

$$W^p_{V} = \frac{1}{4} E^* \epsilon_c^2. \quad (4.1b)$$

Note, however, that this expression is only valid under the assumption that $\sigma_{max}$ is smaller than the yield strength of the material, $\sigma_{pl}^*$. If this is not the case, the maximal work output is limited by the yield strength of the material, leading to

$$W^p_{V} = \sigma_{pl}^*(\epsilon_c - \sigma_{pl}^*/E^*). \quad (4.1c)$$

Following Eq. 4.1b and 4.1c, we characterize the performance of the electrochemical actuators with different architectures through $E^*$, $\sigma_{pl}^*$ and $\epsilon_c$. The goal of this exercise is to obtain the fundamental scaling relations of $\epsilon_c$, $E^*/E_s$ and $\sigma_{pl}^*/\sigma_{ys}$ (with $E_s$ and $\sigma_{ys}$ the size-independent Young’s modulus and yield stress of the solid material) in terms of two fun-
damental parameters: (i) \( \rho^* \), the relative density of the nanoporous material, and (ii) \( V_s/A_s \), where \( V_s \) is the volume of the solid material and \( A_s \) is the surface area of the solid material. The results are presented in the following subsections (4.3.1, 4.3.2 and 4.3.3) for the cubic lattice (Fig. 4.1(a)), gyroidal structure (Fig. 4.1(b)) and nanoporous gold (Fig. 4.1(c)), respectively.

### 4.3.1 Cubic lattice

**Stiffness and strength:** We start our analysis by looking at the simplest nano-porous architecture, a cubic lattice (see Fig. 4.1(a)). The overall stiffness and strength of the cubic lattice can be directly related to the stiffness and strength of the individual struts that make up the lattice. Since cubic lattices are stretching structures, their stiffness and plastic strength can be written as

\[
E^* = E \left( \frac{w}{L} \right)^2 \quad \text{and} \quad \sigma_{pl}^* = \sigma_y \left( \frac{w}{L} \right)^2, 
\]

where \( w \) is the width of the strut, \( L \) is the length of the unit cell and \( E \) and \( \sigma_y \) are the size-dependent Young’s modulus and plastic strength of the strut [167]. Although the exact relation for the relative density of a cubic lattice is given by

\[
\rho^* = 3 \left( \frac{w}{L} \right)^2 - 2 \left( \frac{w}{L} \right)^3, 
\]

in this work we neglect the cubic dependence on \( \frac{w}{L} \), so that

\[
E^* = \frac{E \rho^*}{3} \quad \text{and} \quad \sigma_{pl}^* = \frac{\sigma_y \rho^*}{3}. 
\]

This simplification results in an overestimation of \( E^* \) and \( \sigma_{pl}^* \) by 30% for a relative density \( \rho^* \) of 0.3, and the error decreases with decreasing \( \rho^* \).

In calculating the size-dependent Young’s modulus \( E \), the orientation of the lattice with respect to the crystal orientation enters as an important ingredient that strongly dictates the response [12, 197]. To analyze this we carry out atomistic simulations on the struts by taking the strut length much larger than the width (resembling nanowires) and by analyzing different orientations of the wires cut from the bulk FCC lattice, see Figs. 3.1(a) and 3.1(b). The width ranges from 2.5 - 32 nm (corresponding to \( V_s/A_s \) values ranging from 0.6 to 8.2). The wires are first relaxed to the minimum energy configuration using the conjugate gradient method [196] at \( T = 0 \) K. When the ratio of the energy difference between two successive iterations and the magnitude of the energy is less than or equal to the tolerance value (10\(^{-14}\)), the minimum energy configuration is assumed to be reached. Due to the tensile surface stresses on the surfaces, the wires contract upon relaxation, leading to a size-dependent equilibrium strain [12, 212], see Fig. 3.2 where the magnitude of the equilibrium strain is shown to increase with decreasing ligament width (or, equivalently, decreasing \( V_s/A_s \)).

Next we proceed and study Young’s modulus \( E \) of the nanowires by performing tensile

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Note that \( V_s/A_s \) for the cubic lattice is equal to \( \frac{w^4}{12} \left( 1 + \frac{w}{3(L-w)} \right) \), with \( w \) the width of the struts and \( L \) the length of the unit cell.
tests on the relaxed samples. The degrees of freedom of the atoms (along the pulling direction) in 5 atomic layers on both ends are fixed. A displacement, in increments, is prescribed to the atoms at one of the ends and energy minimization is applied after each increment. The samples are subjected to a total overall strain of 0.5%. The strain is calculated as the ratio of the change in length to the length at the relaxed configuration. The slope of the (average virial) stress-versus-strain curve at zero strain gives the Young’s modulus, which is plotted in Fig. 4.3 as a function of $V_s/A_s$ (normalized by the size-independent continuum value $E_s$). The results show a clear size effect on the Young’s modulus, which is due to the fact that the large equilibrium strains (Fig. 3.2) induce nonlinear elastic deformations in the core of the wires [197]. It turns out that the tangent stiffness increases with compressive strain for the [110] orientation, while it decreases with strain for the [100] orientation, thus increasing or decreasing the modulus with decreasing width, respectively. Note that similar results are obtained by Diao et al. [12] and Liang et al. [197] using different atomistic potentials. Experiments on Au sub-micron columns [131] and npg structures [124, 162, 204] have shown that the yield strength increases with a decreasing cross-sectional size of the ligament or column. In [131] it has been shown that the yield strength of Au columns is independent of the crystal orientation. The size-dependent yield strength of Au columns and nanoporous gold is summarized in [204], and scales with $w^{-0.61}$, where $w$ is the cross-sectional size of the column or the average ligament diameter of npg.
Actuation: Next, we investigate the actuation of the cubic lattice by analyzing the charge-induced deformation of nanowires having two different crystal orientations, see Figs. 3.1(a) and 3.1(b), with widths ranging from 2.5 to 32 nm (corresponding to $V_s/A_s$ values ranging from 0.6 to 8.2). The calculation of the actuation strain of nanowires having different crystal orientations has been discussed in detail in chapter 3. Typical charge densities for nanoporous gold actuators are on the order of 1-10 $\mu$C/cm$^2$ [73]. In this chapter we will analyze the strains that are generated for a specific (freely chosen) charge density in this range (i.e., $q_a = 7.7 \mu$C/cm$^2$) for the three different structures investigated (see Fig. 4.1). The atomistic results in Fig. 4.4 are reproduced from Fig. 3.5(b) for the nanowires using open square and triangular symbols for the [100] and [110] orientation, respectively, clearly showing a strongly increasing actuation strain with decreasing wire dimensions. The actuation strain of the [100] orientation is larger than the [110] orientation due to the larger compliance of the [100] wire [212]. In order to verify the accuracy of the continuum model, we repeat the simulations using the continuum approach. The dimensions of the continuum wires are taken to be equal to those of the atomistic wires of the corresponding crystal orientation in number of lattice constants. The core of the wires is discretized with 8-noded brick elements (C3D8) and the surface layer with 4-noded plate elements (S4) [210]. For the wires of width 9.8 nm (corresponding to $V_s/A_s = 2.45$ nm), the eigenstrain $\epsilon^*$ in the surface layer is tuned such that the overall actuation strain of the wire is equal to that of the atomistic simulations (see Fig. 4.4). The eigenstrain values of the [100] and [110] wires were found to be equal to 0.071 and 0.047, respectively. Subsequently, we use these values of the eigenstrain for the wires with different cross-sectional dimensions. Figure 4.4 shows that for both wire orientations, the strains predicted by the continuum model agree well with the atomistic results. In case of the [100] wire, since all $\{100\}$ surfaces are isotropic, the stress in the surface layer is also isotropic (in both the atomistic and continuum model). For the [110] wire, there are two different surfaces: one surface (001) is isotropic and the other, (1 $\overline{1}$0), is anisotropic. The eigenstrain is modeled as isotropic and it is taken to be the same for both surfaces. The anisotropy of the surface stress on the (1 $\overline{1}$0) face is taken care of by the elastic anisotropy of the surface layer. The magnitude of the stresses in the core is found to be close to the atomistic values for both the [100] and [110] wires, which explains the good agreement between the atomistic and continuum strains in Fig. 4.4. Although we use eigenstrains that are fitted to a single sample, the continuum model can well capture the stresses in the core of the atomistic wires leading to a good agreement between the atomistic and continuum model for the charge-induced strains as a function of width.
Figure 4.4: Comparison of atomistic and continuum actuation strains of [100] and [110] wires at charge density $q_a = 7.7 \, \mu\text{C/cm}^2$ plotted as a function of $V_s/A_s (\approx w/4)$. The data points shown in circles are used to tune the eigenstrains of the continuum model.

Next, we use the continuum model to study the charge-induced deformation of a [100] cubic lattice consisting of [100] struts that have a square cross-section. The core of the lattice is meshed with 10-noded tetrahedral elements (C3D10) and the surface is meshed with 6-noded triangular elements (STRI65). Since the ligaments have a [100] crystal orientation, we apply the same eigenstrain as used for the single [100] wire. We create lattices with three different relative densities (0.1, 0.2 and 0.3). Figure 4.5 shows that the strains are larger for the low density lattices but remain less than that of the individual [100] nanowires. This is due to the fact that the nodes/junctions in a cubic lattice have no free surfaces so that the volume in the nodes does not deform due to surface charge and therefore does not contribute to the overall strain of the sample. The effect of the junction can be captured by the simple analytical relation $\epsilon^*_c = (1 - w/L)\epsilon_c$, where $\epsilon^*_c$ is the strain of the lattice and $\epsilon_c$ is the size-dependent strain of the wire. Clearly, the strain of the lattice converges to that of the wire when the relative density (or, equivalently, $w/L$) goes to zero. The magnitude of the strains obtained from the above relation (using the size-dependent single wire results as input for $\epsilon_c$) was found to be in close correspondence to the values obtained from the continuum model. The effect of the relative density ($w/L$) on the magnitude of the actuation strain, however, is much smaller than the effect of $V_s/A_s$ and we will therefore ignore the density effect in the scaling relations.
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Figure 4.5: Actuation strains $\epsilon_c$, obtained from the continuum model, of the [100] wire and the [100] cubic lattices of different relative densities as a function of $V_s/A_s$. The data points of the cubic lattice are fitted by a $(V_s/A_s)^{-1}$ scaling relation (dashed line).

4.3.2 Gyroids

In this subsection we will subsequently investigate the stiffness, strength and actuation strain of gyroidal structures (see Fig. 4.1(b)).

Stiffness: To generate an atomistic model of a gyroid, we start with a cubic block of FCC gold and subsequently remove atoms according to the equations for a gyroidal isosurface [213, 214]. Gyroids are generated with their principal axes (X,Y,Z) along different crystal directions of the FCC lattice. The samples are named after the crystal direction along the X-axis. For example, the gyroid with a crystal orientation as shown in Fig. 3.1(a) is represented by g100, the one with orientation in Fig. 3.1(b) is represented by g110. The third sample, g111 has directions [111], [ 1 1 2] and [1 1 0] along the X-, Y- and Z-axes, respectively, see Fig. 3.1(c). Gyroids with different relative densities, crystal orientations and $V_s/A_s$ values are created and relaxed to the minimum energy configuration, resulting in contraction of the samples due to surface stress effects. The equilibrium strains in the X-direction are calculated in a similar manner as for the wires and are plotted in Fig. 4.6(a) as a function of $V_s/A_s$ for a relative density $\rho^* = 0.3$. Clearly, the larger the surface area over volume ratio, the larger the surface-driven contraction, leading to larger equilibrium strains. Subsequently, we calculate the Young’s modulus of the gyroids by performing tensile tests in the X-direction on the relaxed samples. The procedure for the tensile test is the same as that for the wires, described in section 4.3.1. Gyroidal samples of $n \times n \times n$ unit cells are used for the tensile test. We have
investigated cell-size effects [215, 216] by varying \( n \), and found that \( n = 3 \) is sufficient to get converged, sample-size-independent stiffness values. Therefore, all simulations are carried out on cubic blocks containing three gyroidal unit cells along the sides. We carried out tensile tests on gyroids with different orientations, relative densities and \( V_s/A_s \) values. The effect of the relative density and crystal orientation was found to be much larger than the effect of \( V_s/A_s \). For each relative density and crystal orientation, the effect of \( V_s/A_s \) quickly dies out and the results converge to the bulk, size-independent continuum value, \( E^* \), for that specific orientation and density. To analyze the influence of \( V_s/A_s \), we plot the Young’s modulus of each sample, \( E^*_g \), normalized by \( E^* \), in Fig. 4.6(b), showing that the stiffness at small surface areas slightly increases, but this effect is much smaller compared to that of the crystalline wires (see Fig. 4.3). This is due to the variation of the crystal orientations of the struts in a gyroid: in each gyroidal unit cell there are six different orientations of the struts, with the axis of each strut oriented along different crystal directions. In addition, the surfaces of the wires are planar, while the surface of the struts in the gyroids are curved, therefore probing different surface architectures along the length of the strut. On average, these effects results

Figure 4.6: (a) Atomistic calculations of the equilibrium strain plotted as a function of \( V_s/A_s \) for gyroids of different crystal orientations with a relative density \( \rho^* = 0.3 \). The solid line is a curve fit to the data. (b) Young’s modulus of gyroids, \( E^*_g \), as a function of \( V_s/A_s \). The size-independent continuum stiffness, \( E^* \) (which still depends on crystal orientation and relative density), is used to normalize \( E^*_g \). Filled symbols represent gyroids along the [100] direction and open symbols represent gyroids along the [110] direction. Squares: \( \rho^* = 0.17 \), circles: \( \rho^* = 0.23 \), upward triangles: \( \rho^* = 0.30 \) and downward triangles: \( \rho^* = 0.32 \). The solid line is a curve fit to the data.
in a mild stiffening (Fig. 4.3), induced in a similar way as for the nanowires by nonlinear elastic effects in the core of the struts.

Next, we proceed by investigating the effect of the relative density and crystal orientation on the size-independent stiffness $E^*$, by using a continuum representation of the gyroid structure. To generate a continuum representation of the gyroid structure we use the equations for a gyroidal isosurface [213, 214]. We start with a cubic stacking of voxels and remove those that fall outside the gyroidal surface, thus leaving a gyroidal volume of voxels. The surface of the gyroid is discretized with 3-noded triangular elements and the bulk with 4-noded tetrahedral elements using the iso2mesh software [217]. The gyroidal mesh is further processed in ABAQUS [210] to convert the 3-noded triangular elements into 6-noded plate elements (STRI65) (to be used for actuation) and the 4-noded tetrahedral bulk elements into 10-noded tetrahedral elements (C3D10). We account for anisotropic elastic properties associated to the specific crystal orientation (g100, g110, g111). The results of $E^*$ are plotted in Fig. 4.7 (discrete data points, left axis). The stiffness results can be accurately represented by a power-law dependence on relative density through the relation $E^*/E_s = C_{g1}\rho^{2}$ (solid lines in Fig. 4.7), where $\rho^*$ is the relative density, $C_{g1} = 0.84$ is a dimensionless prefactor associated with the architectural morphology of gyroids and $E_s$ is the Young’s modulus of the solid material for that specific crystal orientation ($E_s = 42.3, 80.9, 116.2$ GPa for the [100], [110] and [111] directions, respectively [218]). The dependence of $E^*$ on $\rho^{*2}$ indicates that the gyroid is a bending dominated structure [167].

**Strength.** To obtain the plastic collapse stress of the gyroid structure as a function of crystal orientation and strut dimensions, detailed atomistic simulations are required which are beyond the scope of this work. Here, we will primarily focus on the scaling of the overall plastic strength with relative density and ignore the effect of the crystal orientation. To do so, we assume the solid material to be elastically and plasticity isotropic and use $J_2$-flow theory [201] to probe the plastic yield strength $\sigma_{pl}^\epsilon$. We take $E_s = 79$ GPa, $\nu_s = 0.44$ and $\sigma_{ys} = 200$ MPa. The yield strength $\sigma_{pl}^\epsilon$ is taken as the stress value at the 0.2% offset strain. The results are shown in Fig. 4.7 (discrete data points, right axis). The results can be nicely represented by the scaling relation $\sigma_{pl}^\epsilon/\sigma_y = C_{g2}\rho^{3/2}$, with $C_{g2} = 0.55$ a dimensionless prefactor associated with the architectural morphology of gyroids and $\sigma_y$ the yield stress of the struts. The Young’s modulus $E^*$ is taken as the slope of the linear part of the (elasto-plastic) stress-strain curve, and follows the scaling relation $E^*/E_s = C_{g3}\rho^{2}$, where $C_{g3} = 0.83$ and $E_s = 79$ GPa. Although neglected in our analysis, the yield stress of the struts, $\sigma_y$, is in-
Figure 4.7: Variation of the size-independent Young’s modulus $E^*$ of gyroids of different crystal orientations (left vertical axis) and the yield strength $\sigma^*_{pl}$ of gyroids having isotropic elasto-plastic properties (labeled “g_iso”) as a function of relative density. The elastic data points are fitted by a $\rho^{s2}$ scaling relation and the plastic data points to a $\rho^{s3/2}$ relation (solid lines, see text for details).

herently size-dependent at the micron and sub-micron scale associated to the predominantly bending-dominated loading situation. Hodge et al. [124] found the size-dependent yield strength $\sigma_y$ of the ligaments in nanoporous gold to scale with $w^{-0.5}$ (with $w$ the diameter of the ligaments). We will get back to this in section 4.3.3.

Actuation: Since charge redistribution on a metal surface is a quantum-chemical phenomenon, DFT studies are needed to analyze the amount of charge on each layer, edges and corners. So far, one DFT study has been performed on the charge redistribution on crystal surfaces [88], which, however, is only qualitative in nature, showing that a small portion of the injected charge penetrates into the subsurface atomic layer. In the atomistic studies on gold crystal surfaces, Haftel and co-workers [192] adopted a strategy for charge redistribution in which they assigned excess charge to each atomic layer in proportion to the percentage of area projected by each layer onto the surface. This strategy is in qualitative agreement with the DFT results [88], showing that excess charge does not penetrate deeply into the metal, but remains localized to the layers which are fully or partially exposed. According to this strategy, and depending on the orientation of the crystal surface, 55-90% should be assigned to the outer surface layer and 10-45% to the subsurface layer of planar crystal surfaces [212]. While implementation of this strategy is straightforward for planar surfaces, for gyroids, however, it is not obvious how to calculate the area projected by each atom onto the
Figure 4.8: Atomistic representation of a gyroid of $\rho^* = 0.1$, $V_s/A_s = 6.1$ nm. Gold atoms are surface atoms with 80% charge, red atoms are sub-surface atoms with 20% charge and blue atoms are core atoms with zero charge. The gyroid shown has dimensions (16 $\times$ 16 $\times$ 16) nm.

surface (and assign charge accordingly) due to the nonuniform crystal orientation of the surface. To simplify the procedure we therefore chose to assign 20% charge to the subsurface layer (which is midway the range valid for planar surfaces, 10-45%, see [212]) and 80% to the surface layer.

The surface and subsurface atoms are indexed using nearest neighbor criteria. In an FCC bulk crystal lattice the number of first and third nearest neighbors of an atom is 12 and 24, respectively. Since the surface atoms have partial coordination, their number of nearest neighbors is less than that of the nearest neighbors of the bulk atoms. By counting the nearest neighbors of the atoms in the gyroid structure, we found that surface atoms can be identified by those atoms that have less than 11 first nearest neighbors ($n_1$). Similarly, subsurface atoms are identified by the condition $n_1 > 10$ and $n_3 < 22$, where $n_3$ is the number of third nearest neighbors. This strategy is adopted for all gyroidal structures analyzed, see Fig. 4.8 for an example, showing a gyroid structure of relative density $\rho^* = 0.1$ and $V_s/A_s = 6.1$ nm.

An area specific charge $q_a = 7.7 \mu$C/cm$^2$ is injected onto the surface of the relaxed gyroids in increments with energy minimization after each increment. The strain is calculated for gyroids of different crystal orientations and varying $V_s/A_s$ values with a relative density of 0.3 (see discrete points in Fig. 4.9(a)). Our study shows that samples with three unit cells in each orthogonal direction are sufficiently large to get converged results. Therefore, all the
atomistic calculations are done on samples with three unit cells.

For samples with \( V_s/A_s \) values larger than 5 nm the computations become excessively expensive and we resort to the continuum model (see Fig. 4.2) for samples with \( V_s/A_s > 5 \) nm. Due to the varying crystal orientation of the surface in gyroidal structures, the surface is assumed on average to have an isotropic surface-stress-charge coefficient. This is accounted for in the continuum model by using isotropic eigen strains and isotropic elastic properties \( (E_s = 79 \text{ GPa and } \nu = 0.44) \) in the surface layer. For the g100 gyroid with surface-to-volume-ratio \( V_s/A_s = 3.2 \text{ nm} \), the eigen strain \( \epsilon^* \) of the surface layer in the continuum model is fitted to match the actuation strain \( \epsilon_c \) of the corresponding atomistic model (see circle in Fig. 4.9(a)). We use that specific value of eigen strain \( \epsilon^* \) for all other gyroidal structures with different \( V_s/A_s \) values and crystal orientation. For g100, except at the smallest \( V_s/A_s \), we see a good agreement between the strain values obtained from the atomistic and continuum models, see Fig. 4.9(a). The deviation at smaller sizes can be explained on the basis of the stress distribution in the cross-section of the gyroid (see Fig. 4.10). When a positive charge is injected on the surface, the magnitude of the pre-existing tensile surface stresses

\[ \rho^* = 0.20 \]
\[ \rho^* = 0.30 \]
\[ \rho^* = 0.35 \]

\( V_s/A_s = 3.2 \text{ nm} \) (shown in circle) is fitted to match the actuation strain \( \epsilon_c \) of the corresponding atomistic model.

\( l^* = 0.20 \)
\( l^* = 0.30 \)
\( l^* = 0.35 \)
in the relaxed sample decreases resulting in a negative stress change $S_{xx}$, while in the core, the magnitude of the compressive stresses decreases resulting in a positive stress change $S_{xx}$. Atoms on the surface of a gyroid have varying coordination numbers compared to the flat surfaces of nanowires, for instance, where atoms have a unique coordination number. The non-uniformity of coordination number is more dominant for samples with small $V_s/A_s$ values, which is due to the presence of steps on the surface, see Fig. 4.10(a). The difference in the coordination of surface atoms results in a nonuniform stress distribution in the surface atoms and those underneath the surface, which causes a nonuniform stress distribution in the core of the ligaments as well (see Fig. 4.10(a)). However, as $V_s/A_s$ increases the effect of the discrete steps decreases and the stress in the core becomes more uniform (with the non-uniformity of stress being restricted to only a few atomic layers underneath the surface), see Figs. 4.10(b) and 4.10(c). At these $V_s/A_s$ values the continuum results agree well with the atomistic simulations.

Finally, we use the continuum model to investigate the effect of the relative density and $V_s/A_s$ on the actuation strain of the g100 gyroid (see Fig. 4.9(b)). Clearly, no effect of $\rho^*$ can be observed, while the $V_s/A_s$ dependence nicely follows a power law with exponent $-1$.

![Figure 4.10](image)

**Figure 4.10**: (a) Stress distribution $S_{xx}$ in a slice of a g100 gyroidal structure of relative density 0.3. (a) $V_s/A_s = 0.96$ nm (b) $V_s/A_s = 1.07$ nm (c) $V_s/A_s = 3.76$ nm. The scale bars have length 2 nm (a), 6 nm (b), 8 nm (c).

### 4.3.3 Nanoporous gold (npg) structures

Nanoporous gold (npg) samples were produced by free corrosion of an Au30-Ag70 alloy in concentrated nitric acid (70%). The details of the dealloying process can be found in
The relative density of the samples was found to be 0.35 and random measurements of the width of several ligaments in scanning electron micrographs yielded an average ligament diameter of about 40 nm. Some researchers [182] consider the topology of NPG to be mimicked by spinodally decomposed structures, given the similarities in the physics of dealloying. Despite some similarities, however these two types of structures are not completely topological equivalent [132]. In this study, we will obtain the real morphological model of npg by means of nanotomography on the dealloyed samples [219]. The basic idea of nanotomography is to remove material in serial cross-sectional slices using a focused ion beam (FIB) and to image the area of interest using scanning electron microscope (SEM) after every slice. Npg was vacuum infiltrated with an epoxy resin (AralditeBY158/Aradur21, ratio: 4:1), which allows the ligament cross-sections to be imaged in the cross-sectional plane with sufficient contrast. FIB serial sectioning was performed on the infiltrated npg with a slicing distance of about 6 nm between two successive cuts. After each FIB sectioning, the cross-section was imaged with the electron beam. Correcting for intensity gradients and viewing angle [220], the images were registered (i.e. aligned in the image plane) and then stacked along the slicing direction. Subsequently, the grey scale images were binarized using the image processing toolbox of MATLAB. Following a series of carefully optimized image morphological operations to eliminate noise and rough ligament boundaries, a voxel mesh was prepared from which a tetrahedral finite element mesh was generated using the iso2mesh toolbox [217]. To generate samples of relative densities between 0.2 and 0.5, the original voxel image with $\rho^* = 0.35$ is subjected to either three-dimensional morphological image dilation [217] (i.e. adding surface voxels uniformly) or erosion (uniform removal of surface voxels). While the connectivity of ligaments is guaranteed during dilation, the erosion algorithm from iso2mesh does not necessarily maintain the connectivity. In fact, we do find loss of connectivity at some locations for relative densities below 0.35.

Given the large number of atoms in the disordered npg structures, we will study the mechanical and actuation performance of npg using the continuum approach. The core is meshed with 10-noded tetrahedral elements (C3D10) and the surface with 6-noded plate elements (STRI65). Similar to the gyroids, the npg structures are generated with their X-axis oriented along the [100] and [110] crystal directions, and are named accordingly: npg100 and npg110.

**Stiffness and strength:** We perform tensile tests in the X-direction to probe the stiffness and strength. The procedure is the same as that for the wires and gyroids. First, we analyze
the effect of relative density and crystal orientation on the size-independent stiffness $E^*$ (see Fig. 4.11(a)). Comparison with Fig. 4.7 shows that the stiffness is much smaller than the stiffness of the gyroidal structures and that the effect of the crystal orientation in npg is negligible compared to that in case of gyroids. To analyze the plastic strength of npg we assume elastically and plastically ($J_2$-flow) isotropic material behavior using a Young’s modulus of 79 GPa, Poisson ratio of 0.44 and yield stress of 200 MPa. Figure 4.11(b) shows that also the plastic strength is much lower than that of the gyroids (Fig. 4.7, right axis). These effects are likely to be related to the very disordered architecture of the nanoporous gold structures, resulting in a much more compliant structure than the ordered gyroids. This difference is also reflected in the unusual scaling behavior of npg $E^*/E_s = 1.33\rho^{*4.0}$ and $\sigma_{pl}/\sigma_y = 1.05\rho^{*3.5}$ (see Fig. 4.11(b)), compared to the $\rho^{*2}$ and $\rho^{*1.5}$ scaling, respectively, for gyroids (see Fig. 4.7).

In order to explore the high scaling exponents for stiffness and strength, we carefully investigated the morphological architecture of the npg as a function of density. Two observations were made. First, below relative densities of around 0.35, the change in morphological architecture with decreasing density is not only reflected in a change in slenderness of the
struts but also in an increasing loss of ligament connectivity. This loss of connectivity results in a much stronger decrease in stiffness and strength [221] with decreasing density than in-tact bending-dominated structures, leading to a higher power-law exponent. Second, for densities equal to and above 0.35 we analyzed the change in ligament slenderness ratio (ligament width \( w \) divided by ligament length \( L \)) with increasing relative density and found that the slenderness ratio \( w/L \) increases linearly with relative density, \( \rho^* \propto w/L \), as was also found experimentally [112]. This linear scaling is in contrast to the typical quadratic scaling in macroscopic open cell foams, and reflects the complex morphological architecture of npg. Substituting \( \rho^* \propto w/L \) in the typical scaling relation for bending-dominated structures, \( E^* \propto (w/L)^4 \) [167], leads to a fourth-order dependence of stiffness on relative density: \( E^* \propto \rho^* E_s \), similar to our simulation results in Fig. 4.11(b). Similarly, the plastic strength \( \sigma_{pl}^* \) of bending-dominated structures is proportional to \((w/L)^3\), leading to \( \sigma_{pl}^* \propto \rho^{3.5} \), which corroborates the higher exponent (3.5) in the scaling relation of the plastic strength of npg.

Hodge et al. [124] experimentally determined the yield strength of npg samples of different ligament diameters with relative densities ranging from 0.20 to 0.42. They used the standard scaling relation for the yield strength of open-cell macroscopic foams, \( \sigma_{pl}^*/\sigma_y = 0.3 \rho^{1.5} \) [167], to back-calculate the yield strength of the solid ligament material, and came up with a size-dependent strength of the npg-ligament of \( \sigma_y = (200 + 9821w^{-0.5}) \) MPa, with \( w \) the diameter of the ligament. However, if we confront our scaling relation for the plastic strength, \( \sigma_{pl}^*/\sigma_y = 1.05 \rho^{3.5} \), against the experimental results, the yield strength of the npg-ligaments becomes unrealistically high, even higher than the theoretical shear strength of Au (4.3 GPa [222]). A possible explanation of this discrepancy is that Hodge et al. [124] calculated the relative density of npg directly from the composition of Au in the Au/Ag alloy before dealloying. As a result, the study does not account for the volume shrinkage of the sample during dealloying, which is often reported in the literature [90, 130]. Liu and Antoniou [112] calculated the relative densities from the electron micrographs of npg samples available in the literature (including the samples of Hodge et al.) [117, 121, 124, 126, 162, 163, 177, 178, 204, 223] and found that the values range from 0.53 to 0.69, which are far higher than the values calculated by Hodge et al. [124] using the Au composition in the alloy. The increase in relative density due to the volume shrinkage ranges from 20 to 100% [112, 130]. Assuming that the relative density increases by 60% (i.e., midway between 20 and 80%) due to the shrinkage, we back-calculate the yield strength of the ligaments, using \( \sigma_{pl}^*/\sigma_y = 1.05 \rho^{3.5} \), from the experimentally obtained yield strength of the npg [124]. The yield strength of ligaments follow \( \sigma_y = (200 + 12051w^{-0.6}) \) MPa, see Fig.
Figure 4.12: Yield strength of the ligaments of npg. The data points are back-calculated from the yield strength of npg [124] using $\sigma_{pl}/\sigma_y = 1.05\rho^{-3.5}$ and the solid line is fitted to the data using a $w^{-0.6}$ scaling relation.

4.12. The exponent $-0.6$ is close to the value of Hodge ($-0.5$) [124] and is (almost) equal to the value of Volkert ($-0.61$) [204].

**Actuation:** To study the size-dependent actuation behavior, we explore the effect of the relative density and ligament size by analyzing samples of varying density in the range 0.2-0.36. For each relative density, we simply scale the sample dimensions with different scaling factors, leading to $V_s/A_s$ values in the range 1-15 nm. We analyze two different orientations of the crystal structure, npg100 and npg110. As explained in the beginning of this section (section 4.3.3), we will use the continuum model and account for charge on the surface (marked in gold in Fig. 4.13(a)) by applying eigenstrains in the surface layer. The surface layer is assumed to have similar properties as the surface layer of the gyroidal structures, as explained in section 4.3.2. The actuation strain is calculated by tracking the nodal displacements in two parallel planes, each located near the two ends of the sample. The strain is given by $\epsilon_c = (L_f - L_g)/L_g$, where $L_f$ is the final distance between the two planes and $L_g$ is the distance between the planes before actuation. $L_g$ is chosen such that end effects do not affect the results. The actuation strains of npg for different crystal orientations and relative densities are shown in Fig. 4.13(b). Clearly, we see no effect of relative density, nor crystal orientation on the magnitude of the strain, while the $V_s/A_s$ dependence can be nicely captured by a power $-1$ scaling relation. These trends are similar to the trends observed for the more or-
Figure 4.13: (a) Continuum model of npg reconstructed from tomographic images. The surface layer is shown in gold and the core is shown in blue. (b) Effect of the relative density on the dependence of actuation strain on $V_s/A_s$. Filled symbols indicate npg100 and unfilled symbols indicate npg110. The solid line is fitted to the data points using a $(V_s/A_s)^{-1}$ scaling relation.

4.4 Summary and conclusions

We have investigated the charge-induced deformation, stiffness and plastic strength of three nanoporous gold structures as a function of relative density, surface-to-volume-ratio and crystal orientation, using a multiscale modeling approach. Comparison of Figs. 4.5, 4.9 and 4.13(b) indicates that the actuation strains plotted as a function of $V_s/A_s$ are very similar for the three different nanoporous architectures studied. Despite the fact that these structures are ordered, disordered, bending or stretching dominated, the actuation strain can be captured by a $(V_s/A_s)^{-1}$ scaling law. However, as discussed at the beginning of the results section, the performance of an actuator is not only measured in terms of the total actuation stroke $\epsilon_c$, but also on its capability to do work against a certain load. While doing work, the stresses should not induce plastic yielding of the nanoporous structure. However, the magnitude of the charge-induced strains $\epsilon_c$ was found to be much smaller (by two orders) than the initial
yield strain $\epsilon_{el} = \sigma_{pl}^*/E^*$ due to the load at the plastic yield strength $\sigma_{pl}^*$, indicating that the actuators studied here always operate well below the plastic limit. In the remainder of this section, we will therefore compare the work densities of nanoporous structures of different architectures oriented along the [100] crystal orientation in the elastic limit, based on Eq. 4.1b.

The Young’s modulus and actuation strain of nanoporous structures can be written in terms of two dimensionless parameters, $\rho^*$ and $V_s/A_s/a$ ($a$ is the atomic spacing = 0.2 nm for Au), in the following way.

$$E^*/E_s = c_1(1 + c_2(V_s/A_s a)^\alpha)\rho^{*\beta},$$

$$\epsilon_{c} = c_3(V_s/A_s a)^\gamma,$$

For cubic lattices the size-dependency parameter $\alpha$ is obtained from the scaling relation of the Young’s modulus of [100] wires (see Fig. 4.3), leading to $c_2 = -0.1$ and $\alpha = -2$ (see Table 4.1). For gyroidal structures the size effect on stiffness is very small (see Fig. 4.6(b)); we will therefore neglect the elastic size effects for the gyroids and npg structures, leading to $c_2 = 0$ and $\alpha = 0$, see Table 4.1. The scaling of $E^*$ with $\rho^*$ for the cubic lattice, gyroids and npg has been discussed in Section 4.3.1, 4.3.2 and 4.3.3, respectively, leading to power-law exponent $\beta$ of 1.0, 2.0 and 3.9, respectively. The actuation strains of the three structures scale with $(V_s/A_s a)^{-1}$, leading to $\gamma = -1$. Note that $c_1$, $c_2$ and $c_3$ are dimensionless coefficients that depend on morphology only. For npg, these coefficients have been obtained for one specific sample, using nanotomography. Therefore, the morphological coefficients $c_1$ and $c_3$ might differ slightly from sample to sample or when different dealloying parameters are used [122]. By substituting Eq. 4.2a and Eq. 4.2b in Eq. 4.1b we arrive at

$$W_{V_s}^{max} = \frac{1}{4} c_1 c_3^2 E_s(1 + c_2(V_s/A_s a)^\alpha)(V_s/A_s a)^2 \rho^{*\beta}. \quad (4.2c)$$

Fig. 4.14 shows the normalized work density $W_{V_s}^{max}/E_s$ (Eq. 4.2c) as a function of $V_s/A_s a$ for the three different morphologies at two different densities. For all structures the work increases with decreasing volume-to-surface-ratio $V_s/A_s a$ due to the increasing actuation strain. At the same time the work decreases with decreasing density due to a decrease in stiffness. Clearly, in discussing the size-dependence of actuation it is important to distinguish between situations in which the ligament width is decreased at a fixed ligament length (leading to a lower relative density and lower $V_s/A_s$), or whether it is decreased in proportion to the ligament length (fixed $w/L$ and thus fixed relative density and lower $V_s/A_s$). The latter
Table 4.1: Scaling parameters of $E^*$ and $\epsilon_c$ in the elastic limit for nanoporous structures oriented along the [100] crystal orientation.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic lattice</td>
<td>-2</td>
<td>1.0</td>
<td>-1</td>
<td>0.33</td>
<td>-0.1</td>
<td>$4.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>Gyroid</td>
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<td>-1</td>
<td>0.84</td>
<td>0</td>
<td>$3.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>npg</td>
<td>0</td>
<td>3.9</td>
<td>-1</td>
<td>1.83</td>
<td>0</td>
<td>$2.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

will lead to an increased work density while the former will result in a decrease. Comparison of the three structures shows that the work density increases with increasing order with high density cubic lattices being able to generate the largest work output and low density npg the lowest. Our results indicate that optimal actuation performance is related to our ability to create large surface-to-volume-ratio materials and at the same time minimize their porosity.
Figure 4.14: Work density (in the elastic limit) of nanoporous structures of different architectures and relative densities plotted as a function of the dimensionless parameter \( V_s/A_s a \). Solid and dashed curves represent \( \rho^* = 0.2 \) and 0.3, respectively.