Chapter 3

Charge-induced deformation of gold nanowires

Experimental studies have shown that electrolyte-immersed nanoporous metals, with nano-wire-resembling ligaments as building blocks, can undergo considerable dimensional changes when a potential difference is applied. The primary actuation mechanism is the electric double-layer charging of the internal surface. To study the fundamental physical mechanism, we explore the charge-induced deformation of a gold nanowire using atomistic simulations. The excess charge is taken into account by modifying the embedding function of the surface embedded atom method (SEAM) as informed by density functional theory (DFT) calculations. Our atomistic simulations indicate that the charge-induced deformation increases considerably for reduced cross-sectional dimensions of the wire, and depends sensitively on the crystallographic orientation. We found that anisotropy-driven surface distortions play an important role in transducing the atomistic charge-induced forces into dimensional changes. To capture the fundamental mechanisms, we present a simple analytical model for the charge-induced strain of gold nanowires that is found to be in excellent agreement with the atomistic simulations.

3.1 Introduction

Actuator materials are able to generate mechanical energy through the conversion of electrical, chemical or magnetic energy. They find application in a wide variety of fields such as robotics, optical communication and in nano- and microelectromechanical devices [183]. Currently, piezoelectric and ferroelectric ceramics are mostly used as actuators, but they require rather high voltages (100 V). The quest for low-voltage alternatives has led to a new

class of promising materials: electro-active nanoporous metals [29, 89, 90, 184, 185]. In the pioneering work of Weissmuller and coworkers [29] it was demonstrated that nanoporous metals can generate reversible strain, which is comparable in magnitude to those of commercial piezoceramics, in response to an applied voltage which is two orders of magnitude lower than the normal actuating voltages. Recently, even considerably larger strain amplitudes were generated by adding an additional length scale in the nanoporous microstructure [90]. The key feature is the material’s high surface-to-volume-ratio which is exploited to electrochemically inject charge on the internal surface by applying an electric potential. The injected charge changes the electron density distribution of the surface atoms, which modifies the local atomic bond strength, leading to macroscopic dimensional changes of the nanoporous metal. Clearly, the ligament size should be small enough so that the modified surface stresses (acting in a surface layer of roughly 1 atom thick) are able to induce ligament deformations. The goal of this chapter is to explore the fundamental mechanisms that lead to the size-dependent charge-induced ligament deformation by studying gold nanowires having different cross-sectional dimensions and crystallographic orientations.

Nanoporous metals expand upon injection of positive charge and contract when negative charge is injected. This reversal of strain with charge excludes electrostatic effects to have a dominant effect and it now well-accepted that quantum-chemical effects are responsible for the charge-induced deformation [29, 73, 88, 185]. In the absence of excess charge, metals have tensile surface stresses, which is supported by detailed DFT calculations [186, 187] and explained qualitatively by Ibach [188]. In his model, due to partial coordination, the surface electrons redistribute into the region between the surface atoms, which increases their bond strength, and thus decreases the equilibrium interatomic distance. However, the contraction of the surface layer is constrained by the atoms in the core, leading to tensile stresses in the surface and compressive stresses in the core region. When negative charge is injected on the metal surface, excess electrons enter the region between the surface atoms, which further increases their bond strength, giving rise to contraction of the metal. The opposite happens when positive charge is injected; i.e. the surface electron density reduces so that the equilibrium bond length increases, resulting in expansion of the metal. Umeno et al. [88, 108] carried out ab initio (DFT) studies on charged surfaces of gold to study the exact sub-atomic redistribution of surface charge.

Although ab initio calculations have gained new insights on the fundamental mechanism of charge-induced strain of the metals, they are computationally too expensive to perform on larger systems, including nanowires. Therefore, in this work we resort to atomistic sim-
ulations to bridge the gap between the local electron density redistributions and the overall charge-induced straining of nanowires. Atomic interactions in a metal can be accurately modeled by the embedded atom method (EAM) [189], initially developed for bulk metallic behavior. For situations where surface phenomena (growth, morphology) play an important role, the surface embedded atom method (SEAM) has been developed [190–192], which is calibrated to both bulk properties (elastic constants, lattice constants and vacancy formation energy) and surface properties (e.g., surface energy and surface reconstruction) [193, 194]. In this chapter we present a new atomistic model, based on the SEAM [192], that accounts for the strengthening and weakening of surface bonds due to the addition and removal of surface charge.

### 3.2 Modified SEAM for excess charge on a metal surface

The energy of an atomic system described by the SEAM [192] is given by

$$E = \sum_{i < j} V(r_{ij}) + \sum_i F(\rho_i),$$  \hspace{1cm} (3.1)

where $V$ is a repulsive pair potential between atoms $i$ and $j$, $r_{ij}$ is the distance between atoms $i$ and $j$, and $F$ (a binding term) is the embedding energy of an atom. In this description, the functional form $F$ is only dependent on the species of the embedded atom. This electron density (normalized with respect to the bulk equilibrium electron density $\rho_0$) is defined as

$$\rho_i = \sum_{j \neq i} \phi_j(r_{ij}),$$  \hspace{1cm} (3.2)

where $\phi_j$ is the (normalized) electron density of atom $j$ at site $i$. In the viewpoint of EAM, $\rho$, is the local electron density at site $i$, which is constructed by a superposition of neighboring atomic electron densities. The energy of an atom at site $i$ is then assumed to be the same as if it were embedded in a uniform electron gas of that particular density.

An important consequence of the embedded atom formulation (both EAM and SEAM) is that the partial coordination at the surface leads to a lower $\rho$ at the surface atoms (60-85%) compared to the bulk atoms. The specific functional form of the embedding function leads to an enhancement of attractive forces when $\rho$ is reduced, resulting in tensile surface stresses, in accordance to experiments. Haftel and Rosen [192] studied charged metal surfaces in a metal-electrolyte environment by taking excess charge into account by changing $\rho$ at the metal surface. However, this method predicts expansion of a metal when negatively charged
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(increased $\rho$) and contraction when positively charged (decreased $\rho$), which is opposite to the trends observed in the experiments on gold nanoporous actuators [73] and DFT calculations [108] on gold surfaces. The opposite trend is an obvious outcome of the functional form of the embedding function of the EAM and SEAM where a reduction of $\rho$ leads to an increase in attractive forces.

In order to catch the experimental trend, we modify the embedding function of SEAM by adding an extra term that explicitly accounts for the modified bond strengthening and weakening by the excess negative and positive surface charge, respectively. The modified surface embedding function is given by

$$F(\rho) = \left( F_1(\rho) + b_c \frac{q_v}{e_0} \right) \rho \ln \rho + F_2(\rho), \quad (3.3a)$$

with

$$F_1(\rho) = \begin{cases} A & (\rho \leq \rho_m), \\ b_1 + b_2 \rho + b_3 \rho^2 & (\rho > \rho_m), \end{cases} \quad (3.3b)$$

and

$$F_2(\rho) = \begin{cases} B \rho & (\rho \leq \rho_m), \\ b_0 \rho + C |\rho - 1|^\alpha & (\rho > \rho_m), \end{cases} \quad (3.3c)$$

where $b_c$ (eV) is a fitting parameter, $q_v$ is the excess charge volume density of the surface atom, $e_0$ is the elementary charge, and $A, B, C, \rho_m, b_i \ (i=0, 1 \ldots 3)$ and $\alpha$ are potential parameters of SEAM [191, 192]. The excess charge term is simply added to $F_1(\rho)$ in Eq. 3.3a, thus making the modified functional form compatible with that of SEAM. For non-zero excess charge the modified embedding energy curve is shifted up or down relative to that of SEAM (depending on the sign of the charge), thus increasing or decreasing the bond strength. When no excess charge is present, the embedding function of SEAM is retrieved. From now onwards, the modified SEAM is shortly called MSEAM. The parameter $b_c$ in Eq. 3.3a is obtained by fitting MSEAM to the surface-stress-charge coefficient, $\zeta = d\tau/dq_a$, of an Au(100) surface [108], where $\tau$ is the surface stress and $q_a$ is the area specific charge. The volume and area charge densities are related by

$$q_v = \frac{c_p q_a A_s}{n_s v_a}, \quad (3.4)$$

where $A_s$ is the surface area on which the charge is injected, $n_s$ is the number of surface atoms in a surface layer, $v_a$ is the volume of an atom in a bulk FCC crystal which is 16.973
Å³ and $c_p$ is the fraction of the total charge $q_aA_s$ assigned to a particular layer of atoms. Since charge redistribution on a metal surface is a quantum-chemical phenomenon, DFT studies are required to give accurate, quantitative results on the amount of charge on each layer, edges and corners. Since such a quantitative analysis has not been performed so far, we adopt the strategy proposed by Haftel and co-workers [192], i.e., to assign 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 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. To assess the modified embedding function in Eq. 3.3a, we carried out molecular statics simulations using LAMMPS [195] and fitted $b_c$ to the surface-stress-charge coefficient $\zeta$ of the Au(100) surface, obtained from DFT calculations [108]. A detailed explanation of the assessment is provided in Appendices A and B.

| Table 3.1: Fraction of total charge $c_p$ assigned to the surface layers. |
|---------------------------------|---------------------------------|---------------------------------|
| (010) | (001) | (001) | (110) | (112) | (110) |
| I layer | 0.79 | 0.79 | 0.79 | 0.55 | 0.33 | 0.55 |
| II layer | 0.21 | 0.21 | 0.21 | 0.45 | 0.33 | 0.45 |
| III layer | - | - | - | - | 0.33 | - |

### 3.3 Results and discussion

#### 3.3.1 Model details

Nanowires of different orientations (see Fig. 3.1) are cut from the bulk FCC material. The wires have free surfaces in all three directions with cross-sectional dimensions ranging from 2.5 nm to 32 nm. The wires are first relaxed to the minimum energy configuration using the conjugate gradient method at $T=0$ K [196]. Full model details are provided in Appendix C. Due to the tensile surface stresses on the side surfaces, the nanowires contract upon relaxation, until a specific equilibrium strain is reached [12, 197]. The equilibrium strain for the three wires with different orientations is shown in Fig. 3.2 (discrete data points). For all wires the equilibrium strain increases with a decrease in the cross-sectional dimension of the wire due to increasing surface effect at lower cross-sectional dimensions [12, 197]. For a given width, the magnitude of the equilibrium strain is higher for the [100] wire, which
is primarily due to the lower Young’s modulus along the [100] direction (42.3 GPa) and it decreases for the [110] and [111] wires in the order of their Young’s moduli (80.9 GPa and 116.2 GPa, respectively).

The surface atoms feature an enhanced bond strength compared to the core atoms, which, upon relaxation, leads to an equilibrium stress distribution in which the surface atoms attain a tensile stress state and the core atoms a compressive stress state. For different cross-sectional sizes, the virial stress distribution [198] in the [100] wires along the length direction (i.e. $\sigma_{11}$) is shown in Fig. 3.3. The tensile stresses are localized to a single (surface) layer and have larger magnitude than the magnitude of the compressive stresses in the core. For the larger cross-sectional sizes the stress distribution is uniform in the surface layer and core, but for the smallest dimension, uniformity is lost, leading to lower tensile stresses at the edges and varying stresses in the core. Unlike the surfaces of the [100] wire, the surface stresses on the lateral surfaces of the [111] wire surfaces, (\(\bar{1}T2\)) and (\(1\bar{1}0\)), are anisotropic owing

Figure 3.1: Nanowires of different orientations used to study the equilibrium strain and charge-induced actuation strain as a function of their cross-sectional dimension $w$. 

(a) [100] wire  
(b) [110] wire 
(c) [111] wire
Figure 3.2: Equilibrium strain $\varepsilon_e$ as a function of cross-sectional size for the three different wires. The discrete data points are obtained using atomistic simulations, while the solid lines correspond to the analytical relation shown in Eq. 3.6 (using $w \ll L$).

to their two fold symmetry [199], see Table 3.2. Table 3.2 contains the surface stresses of infinitely large surfaces of specific orientations as obtained using atomistic simulations. Due to the anisotropic nature of the surface stresses, the stress state is nonuniform leading to a distortion of the cross-sectional dimensions and a nonuniform distribution of surface and core stresses, especially for the smaller wire, see Fig. 3.4.

Table 3.2: Surface stresses (N/m) on infinitely large planar surfaces, following the notation as depicted in Fig. 3.6. The values are obtained using atomistic simulations (for details, see Appendix A).

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{12}$</th>
<th>$\tau_{13}$</th>
<th>$\tau_{21}$</th>
<th>$\tau_{23}$</th>
<th>$\tau_{31}$</th>
<th>$\tau_{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>3.51</td>
<td>3.51</td>
<td>3.51</td>
<td>3.51</td>
<td>3.51</td>
<td>3.51</td>
</tr>
<tr>
<td>[110]</td>
<td>1.97</td>
<td>2.78</td>
<td>3.55</td>
<td>3.55</td>
<td>2.80</td>
<td>1.97</td>
</tr>
<tr>
<td>[111]</td>
<td>4.29</td>
<td>4.30</td>
<td>2.72</td>
<td>3.40</td>
<td>2.51</td>
<td>2.24</td>
</tr>
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</table>

A characteristic feature of the [111] wire is that the middle portion of the surfaces have much higher tensile stresses than the regions near the edges. At the location where these regions meet, a non-uniform stress-state is induced in the core of the wire, resulting in regions of tensile stresses in an otherwise compressive background. Like the [111] wire the two lateral surfaces of the [110] wire have different atomic symmetries and thus different surface stresses. The surface stress on the (110) face is anisotropic owing to its two fold symmetry, while the (001) surface has isotropic stresses due to the four fold symmetry [12, 199], see Table 3.2. Similar to the [111] wires, for the smaller cross-sectional sizes, the surface effects
are dominantly present, which, in combination with the anisotropic nature of the surface stresses results in random atomic distortions (see Fig. D.1 of the Appendix D).

Next, charge is injected onto the surface of the relaxed nanowires through the modified embedding function (Eq. 3.3a) of the surface atoms. The charge distribution to the surface layers, $c_p$, is given in Table 3.1. Model details can be found in Appendix A. The actuation strain for the [100] wire is depicted as a function of charge $q_a$ in Fig. 3.5(a). For a given charge density, the strain increases with a decrease in the cross-sectional dimensions. Fig. 3.5(b) shows the slope of the linear strain-charge curves as a function of wire size $w$ for the three different wire orientations. For all wires, the magnitude of the strain increases with a decrease in the cross-sectional dimensions. The magnitude of the charge-induced strains compares well with the experimental values reported for nanoporous gold at similar ligament widths as the wires [73, 90].

When positive charge is injected on the wire surfaces the bonding between the surface atoms reduces (due to a local reduction of electron density), leading to a decrease in the tensile surface stress. As a result, the compressive core stresses also decrease (to satisfy force equilibrium) leading to a relaxation of the wire and thus a positive actuation strain.

**Figure 3.3:** Stress distribution $\sigma_{11}$ (in GPa) in the relaxed [100] nanowires.
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\[ w = 2.5 \text{ nm} \]

\[ w = 5.6 \text{ nm} \]

\[ w = 15.7 \text{ nm} \]

Figure 3.4: Stress distribution $\sigma_{11}$ (in GPa) in the relaxed [111] nanowires.

$\epsilon_c$ (see Fig. 3.5(a)). The opposite effect occurs when negative charge is injected, leading to a further strengthening of the surface bonds and thus a further contraction of the wire. The results of Fig. 3.5(b) show that, similar to the relaxation process (Fig. 3.2), the strains increase with decreasing cross-sectional size for all wire orientations.

To capture the fundamental physical mechanisms, we derive a simple analytical model to predict the wire strain as a function of the initial and charge-induced surface stresses. For a nanowire with free surface boundary conditions in three directions, surface stresses develop whose directions are schematically depicted in Fig. 3.6. Since each component of the tensile surface stress induces a compressive stress in the core, the wire is in a triaxial stress state [200]. As the wire is in equilibrium after relaxation, for a given direction, the compressive force in the core is equal and opposite to the tensile force at the surface. The equilibrium
between the surface and core forces is given by

\[
\begin{align*}
2w\tau_{21} + 2w\tau_{31} &= -w^2\sigma_{11}, \\
2w\tau_{12} + 2L\tau_{32} &= -Lw\sigma_{22}, \\
2w\tau_{13} + 2L\tau_{23} &= -Lw\sigma_{33},
\end{align*}
\] (3.5)

where \(\tau_{ij}\) is the surface stress and \(\sigma_{jj}\) is the stress in the core along different directions. According to Hooke’s law, the equilibrium strain \(\epsilon_e\) in the length direction of the wire due to the triaxial stress state in the core is given by

\[
\epsilon_e = S_{11}\sigma_{11} + S_{12}\sigma_{22} + S_{13}\sigma_{33},
\]

where \(S_{11}, S_{12}, S_{13}\) are the compliances obtained by inverting the elasticity matrix for a specific orientation of the wire [201] (see Table 3.3). By substituting \(\sigma_{11}, \sigma_{22}\) and \(\sigma_{33}\) from Eq. 3.5 in the relation for \(\epsilon_e\), we arrive at

\[
\epsilon_e = -\left[2S_{11}\left(\frac{\tau_{21} + \tau_{31}}{w}\right) + 2S_{12}\left(\frac{w\tau_{12} + L\tau_{32}}{Lw}\right) + 2S_{13}\left(\frac{w\tau_{13} + L\tau_{23}}{Lw}\right)\right].
\] (3.6)

When excess charge is injected on the surface of a nanowire, it reaches a new equilibrium configuration due to a change in the surface stresses, \(d\tau_{ij}\). The charge-induced change in the surface stresses \(d\tau_{ij}\) is accompanied by a change in the stresses in the core of the wire, \(d\sigma_{ij}\).
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Then, by using Hooke’s law, a similar expression as Eq. 3.6 can be derived, expressing the charge-induced strain $d\epsilon_c$ as a function of $d\tau_{ij}$. Incorporating the surface-stress-charge relation \[\tau_{ij} = \zeta_{ij} dq_a\] (with $\zeta_{ij}$ the surface-stress-charge coefficient), we arrive at

$$\frac{d\epsilon_c}{dq_a} = \frac{2}{w} \left(S_{11}(\zeta_{21} + \zeta_{31}) + S_{12}\zeta_{32} + S_{13}\zeta_{23}\right).$$

(3.7)

Note that no charge is injected on the surfaces normal to the 1-direction, so that the terms with $\zeta_{12}$ and $\zeta_{13}$ have dropped out in Eq. 3.7, compared to Eq. 3.6. To obtain the initial surface stress $\tau_{ij}$ and the surface-stress-charge coefficients $\zeta_{ij}$, we carried out independent atomistic simulations on infinitely large surfaces with different orientations (see tables 3.2 and Table 3.4). Note that all sides of the [100] wire have (100) faces with four fold symmetry, so that $\tau_{ij}$ and $\zeta_{ij}$ are isotropic [12]. In Fig. 3.2 we compare the atomistic results to the analytical model of Eq. 3.6 for the equilibrium strain $\epsilon_e$. Since the atomistic results are carried out on wires that are long enough not to affect the strains (i.e. the equilibrium strains only depend on $w$), we assume $L \gg w$ in Eq. 3.6 so that the $\tau_{12}$ and $\tau_{13}$ terms drop out, leading to a pure $1/w$ dependence of $\epsilon_e$. The equilibrium strain obtained from the analytical model is in very good agreement with that obtained from the atomistic simulations. For the [110] and [111] wires at smaller sizes, the analytical results slightly deviate from the atomistic results. This might be due to the simplifying assumption in the analytical model, i.e. (i) the surface layer has zero thickness, (ii) the cross-section remains square, and (iii) the stress state in the core of the wire is uniform. A close look at Fig. 3.4 (and Fig. D.1 of the Appendix D) clearly show that this is not the case, especially at smaller wire dimensions. The nonuniform stress-state in the [110] and [111] wires is due to the anisotropic nature of the surface stresses, which, at small cross-sectional dimensions can create relatively large forces to distort the ordered crystal structure of the core of the wires (see Figs. 3.4(a)-3.4(b),

\[\text{Figure 3.6: Schematic representation of a nanowire of with length } L, \text{ a square cross-section of size } w, \text{ with the direction of the surface stresses.}\]
3.4(d)-3.4(e) and D.1 of the Appendix D).

Table 3.3: Compliances (in $10^{-11} m^2/N$) of the wires with different orientations.

<table>
<thead>
<tr>
<th></th>
<th>$S_{11}$</th>
<th>$S_{12}$</th>
<th>$S_{13}$</th>
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<tbody>
<tr>
<td>[100]</td>
<td>2.36</td>
<td>−1.08</td>
<td>−1.08</td>
</tr>
<tr>
<td>[110]</td>
<td>1.24</td>
<td>−1.08</td>
<td>0.05</td>
</tr>
<tr>
<td>[111]</td>
<td>0.86</td>
<td>−0.33</td>
<td>−0.33</td>
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</table>

Next, we compared the charge-induced strains predicted by the analytical model of Eq. 3.7 to the atomistic results using the $\zeta_{ij}$ values from Table 3.4. We found that for the [100] wire, the analytical results are very close to that obtained from the atomistic simulations, but for the [110] and [111] wires, the strains from the atomistic simulations were considerably over-estimated. The lower strain magnitudes of the atomistic results are due to the distortion of the surface atoms from their original lattice positions during relaxation (see Fig. 3.4), leading to a reduction of the charge-induced actuation force along the length direction especially at smaller wire dimensions.

Since the atomic distortion is larger in case of anisotropic surfaces, we modified the $\zeta$ values of the anisotropic surfaces in the length direction to fit the analytical results to the atomistics. By reducing $\zeta_{31}$ of the [110] wire by 25% (to $-1.42$), and $\zeta_{21}$ and $\zeta_{31}$ of the [111] wire by 33% (to $-0.86$ and $-1.18$, respectively) the comparison between the analytical and atomistic results in Fig. 3.5(b) was found to be excellent. Clearly, the atomistic results can be nicely captured by a single analytical expression that only features material parameters of the bulk crystal ($S_{ij}$) and the wire surfaces ($\tau_{ij}, \zeta_{ij}$) for the specific crystallographic orientations.

Table 3.4: Surface-stress-charge coefficients (in Volts) on infinitely large planar surfaces (for details, see Appendix A).

<table>
<thead>
<tr>
<th></th>
<th>$\zeta_{21}$</th>
<th>$\zeta_{23}$</th>
<th>$\zeta_{31}$</th>
<th>$\zeta_{32}$</th>
</tr>
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<tbody>
<tr>
<td>[100]</td>
<td>$-0.90$</td>
<td>$-0.90$</td>
<td>$-0.90$</td>
<td>$-0.90$</td>
</tr>
<tr>
<td>[110]</td>
<td>$-0.90$</td>
<td>$-0.90$</td>
<td>$-1.89$</td>
<td>$-1.48$</td>
</tr>
<tr>
<td>[111]</td>
<td>$-1.28$</td>
<td>$-1.12$</td>
<td>$-1.76$</td>
<td>$-1.61$</td>
</tr>
</tbody>
</table>
3.4 Conclusions

We studied the surface stress-driven relaxation and the charge-induced actuation of gold nanowires of different orientations and cross-sectional sizes. We used an atomistic approach for which we modified the embedding function of SEAM to account for the excess charge on the metal surface. The modified atomic potential (MSEAM) is fitted to the surface-stress-charge coefficient of the Au(100) surface obtained from DFT calculations. The magnitude of the equilibrium strain and actuation strain per unit surface charge is inversely proportional to the cross-sectional dimension of the wire, clearly reflecting the enhanced surface-to-volume-ratio at smaller sizes. The magnitude of the charge-induced strain in nanowires obtained from our MSEAM simulations are on the same order of magnitude as those obtained from experiments on nanoporous gold. Finally, we present a simple analytical model to predict the equilibrium and charge-induced strain in nanowires. For the [100] wire the good agreement between analytical and atomistic strains is due to the isotropic nature of the surface stresses, leading to a limited amount of surface distortion and uniform core stresses. For the [110] and [111] wires, the anisotropic surface stresses cause pronounced surface distortions, effectively leading to reduced surface stresses and surface-stress charge coefficients as compared to planar, undistorted surfaces. The atomistic results can be nicely captured by a single analytical expression that only features material parameters of the bulk crystal ($S_{ij}$) and the wire surfaces ($\tau_{ij}$, $\zeta_{ij}$) for the specific crystallographic orientations. The results contribute to an enhanced understanding of the fundamental atomistic mechanisms that couple the injection of charge to structural alterations in metallic nanowires and nonporous metals.
Appendices

A Calculation of $\tau_{ij}$ and $\zeta_{ij}$ at infinitely large planar surfaces

We have carried out molecular statics simulations (i.e. at $T=0$ K) on samples having dimensions $H \times H \times H/2$ using LAMMPS [195]. The samples have free surfaces perpendicular to the thickness and are periodic in the other two directions. Initially, the uncharged samples are relaxed to the minimum energy configuration using the conjugate gradient method [196]. The surface stress is calculated by using the potential energy method [12], which consists of the following steps. A tensile test is carried out on the sample along one of the two periodic directions, keeping the length in the other periodic direction fixed. The sample is subjected to a tensile strain $\epsilon$ of 1% in 75 steps. The total strain energy $U$ is fitted to the polynomial $U = c_1 \epsilon + c_2 \epsilon^2$. The surface stress at zero charge, $\tau$, is given by $\tau = c_1/2A_s$, with $A_s$ the surface area in the undeformed configuration. The effect of the sample thickness $H/2$ on the results is studied and it was found that at a thickness of 10 lattice constants the results have converged to a thickness-independent value for the surface stress. Similar tensile tests on differently oriented samples yield the associated surface stresses of all lateral surfaces of the three wire orientations depicted in Fig. 3.1. The calculated $\tau_{ij}$ values are listed in Table 3.2 of the main manuscript.

Next, an area specific charge $q_a$ (1-10 $\mu$C/cm$^2$), a typical range for gold nanoporous actuators [73] is injected on the surface atoms (which are on the surfaces perpendicular to the thickness direction) of the $H \times H \times H/2$ sample. The amount of charge assigned to each layer of atoms is proportional to the amount of area projected by each layer onto the surface [192], see Table 3.1 of the main manuscript for the charge distribution on different crystal surfaces. After charge injection, separate tensile tests are carried out on samples with different surfaces, yielding the surface stresses ($\tau_c$). Since the surface stress varies linearly with the charge, the surface-stress-charge coefficient $\zeta$ is calculated by using the relation $\zeta = (\tau_c - \tau)/q_a$. Again, by analyzing differently oriented samples, the relevant $\zeta_{ij}$ are obtained, see Table 3.4 of the main manuscript.
B Assessment of the modified embedding function

To fit and assess the value of $b_c$ we considered a sample having dimensions of 20x20x10 lattice constants with $\{100\}$ surfaces on all sides. Separate tensile tests on uncharged and charged samples yield the corresponding surface stresses $\tau$ and $\tau_c$. The parameter $b_c$ is tuned to ensure that the $\zeta$ obtained from the atomistics, using the relation $\zeta = (\tau_c - \tau)/q_a$, corresponds to the $\zeta$ of DFT calculations (i.e. $\zeta = -0.9$ V), resulting in $b_c = -2.48$ eV. To verify the accuracy of the obtained $b_c$ value, we have carried out an additional atomistic simulation on a Au(111) surface (using the same procedure as described above), predicting a surface stress-charge coefficient of $\zeta = -1.96$ V, which is in close agreement with the value obtained from DFT calculations (-1.86 V) [108].

C Model details for calculating the equilibrium and charge-induced strain of nanowires

The wires have free surfaces in all three directions. The cross section is square for the $[100]$ wire due to symmetry. For the $[110]$ and $[111]$ wires, the cross-section is made as square as possible. For the $[100]$ wire the cross-sectional dimension $w$ is the length of the lateral side, while for the $[110]$ and $[111]$ wires the cross-sectional dimension $w$ is taken to be the average of the two lateral dimensions. The cross-sectional dimension for all three wires ranges from 2.5 nm to 32 nm. The wires are relaxed to the minimum energy configuration using the conjugate gradient method 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 side surfaces, the nanowires contract upon relaxation. The compressive strain after relaxation is often referred to as the equilibrium strain [12, 197]. To obtain the equilibrium strain of the wires we track the distance between two parallel planes of atoms during relaxation. The equilibrium strain is calculated from $\epsilon_e = (L_f - L_g)/L_g$, where $L_f$ is the final distance between the two planes of atoms after relaxation and $L_g$ (the gage length) is the distance before relaxation. Our studies indicate that a length of $w$ should be left on each end of the wire to ignore the effects of the free ends on the equilibrium strain, leading to a gage length $L_g = L - 2w$. We carried out a convergence study on the effect of the wire length $L$ on the equilibrium strain and found that for a length to width ratio of 4 the wire length does not affect the relaxation result.
In case of charging, the wire is relaxed initially (as described in the previous paragraph), after which the charge is injected on the surface (through the modified embedding function of the surface atoms), followed by energy minimization at each step. The charge is injected on the surfaces parallel to the length of the wire. For all cross-sectional sizes, the length of the wire was taken large enough to ensure that the actuation strains are independent of the wire length. For the [100] wire the side surfaces have a [100] orientation, leading to a fraction $c_p = 0.79$ that is assigned to the first layer and a fraction of 0.21 assigned to the second layer. In the [110] wire, for the side surface having a (110) orientation, 55% of charge is assigned to the first layer and 45% to the second layer, while for the (001) surface the charge distribution is the same as that of the (100) face. Finally, for the side surface having (112) orientation in the [111] wire, because three atomic layers are equally exposed, each layer is assigned 33.3% charge, see Table 3.1 of the main manuscript.

**D Stress distribution in the [110] nanowires**

![Stress distribution in the [110] nanowires](image)

**Figure D.1:** Stress distribution $\sigma_{11}$ (in GPa) in the relaxed [110] nanowires.