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Nonlinear elastic aspects of multi-component iron oxide core-shell nanowires by means of atom probe tomography, analytical microscopy, and nonlinear mechanics

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1 Nonlinear elasticity

1.1 Components of the Green-Lagrange strain tensor

The Electronic Supplementary Information (ESI) is based on the content of an earlier publication performed by the authors in Ref. [1]. For the sake of simplicity, details found in Sec. 3.2 in [1] is reduced to a point in order to present exclusively the whole non-linear Green-Lagrange (G-L) strain tensor and the final result with respect to the E_{xx} tensor component. These results are also found in Sec. 1.1 to help guide the reader for a deeper understanding of the theory proposed. Following the same route presented in Sec 3.2 in [1] to identify the final bending moment in the form of a non-linear differential equation and consequently, the physical second- and third elastic constants, the G-L tensor yields

$$\mathbf{E}=\frac{1}{2}\begin{bmatrix} (\partial_x u)^2+2\partial_x u+(\partial_x w)^2 & 0 & (1+\partial_x u)\partial_z u+\partial_x w \\ 0 & 0 & 0 \\ (1+\partial_x u)\partial_z u+\partial_x w & 0 & (\partial_z u)^2 \end{bmatrix}. \tag{S1}$$

The most significant elastic response derived from bending originates from the E_{xx} term, therefore the other non-zero components are treated negligibly. As the G-L tensor, $\mathbf{E}$, can be defined in terms of the displacement field, $\mathbf{u}=u(x,z)\vec{i}+v\vec{j}+w(x)\vec{k}$ (using the $\vec{i},\vec{j}$ and $\tilde{\mathrm{k}}$ unit vector notation), and $u(x,z)=u^{\mathrm{o}}-\theta(x)z$ at any x, E_{xx} can now be formulated as a function of the components of $\mathbf{u}$, and its derivatives as

$$E_{xx}=\underbrace{\frac{1}{2}\arctan^2\left[\partial_x w\right]}_{\text{membrane}-\text{strain}}+\underbrace{\frac{1}{2}z^2\frac{\left(\partial_{xx}^2 w\right)^2}{\left(1+(\partial_x w)^2\right)^2}-z\frac{\partial_{xx}^2 w}{1+(\partial_x w)^2}}_{\text{bending}-\text{strain}}. \tag{S2}$$

Eq. S2 represents the E_{xx} tensor component equipped by the full-nonlinearity of the curvature with a quadratic approximation in $\mathbf{u}$ of the displacement field (geometrical non-linearity).

1.2 The P_{xx} component of the 1st Piola-Kirchhoff stress tensor and the bending moment, M

The 1st Piola-Kirchhoff stress tensor, $\mathbf{P}$ describes the stress in the reference configuration, while the non-physical 2nd Piola-Kirchhoff stress tensor, $\mathbf{S}$, can be shown to be energy-conjugate to the G-L strain tensor, $\mathbf{E}$. The $\mathbf{S}$ tensor can be given by the product of the inverse deformation gradient tensor, $\mathbf{F}^{-1}$ and the 1st Piola-Kirchhoff tensor, $\mathbf{P}$. Additionally, in Eqs. 6 and 9 in [1], the relevant components of the corresponding tensors are determined. Thus, a general constitutive law regarding the components of the G-L, and the S tensors as

$$S_{xx}=\phi(E_{xx},E_{xz},E_{zx},E_{zz}) \tag{S3}$$

with some non-linear function ϕ can now be formulated. Assuming the aforementioned negligible contribution of the E_{xz}, E_{zx}, E_{zz} terms, $S_{xx} = \phi(E_{xx})$ is applied. Consequently, P_{xx} yields

$$P_{xx} = (\mathbf{F}\cdot\mathbf{S})_{xx} = (1+\partial_x u)\,\phi\left(\partial_x u + \frac{1}{2}(\partial_x u)^2 + \frac{1}{2}\theta^2\right). \tag{S4}$$

This equation can now be both geometrically and mechanically non-linear. To expand on this point, let $S_{xx} = \phi(E_{xx}) = E_1 E_{xx} + \frac{1}{2}E_2 E_{xx}^2$ be the quadratic approximation of the relation between the 2nd Piola-Kirchhoff stress and the Green-Lagrange strain with constant mathematical parameters of E_1 and E_2. It is worth noting here that this assumption for the stress-strain relation is consistent with the third-order expansion in weakly nonlinear elasticity in which the strain energy is expanded up to the third order in the power of the G-L tensor. In the view of the third-order expansion, Eq. S4 turns into the following form after implementing the quadratic mechanical approximation as

$$\begin{aligned} P_{xx} &= (\mathbf{F}\cdot\mathbf{S})_{xx} = (1+\partial_x u)\left[E_1\left(\partial_x u + \frac{1}{2}(\partial_x u)^2 + \frac{1}{2}\theta^2\right)\right] + (1+\partial_x u)\left[\frac{1}{2}E_2\left(\partial_x u + \frac{1}{2}(\partial_x u)^2 + \frac{1}{2}\theta^2\right)^2\right] = \\ &= E_1\left[\frac{1}{2}\theta^2 + \partial_x u\left(1+\frac{1}{2}\theta^2\right) + \frac{3}{2}(\partial_x u)^2 + \frac{1}{2}(\partial_x u)^3\right] + \frac{1}{2}E_2\left[\frac{1}{4}\theta^4 + \partial_x u\left(\theta^2 + \frac{1}{4}\theta^4\right) + (\partial_x u)^2\left(1+\frac{3}{2}\theta^2\right)\right] + \\ &+ \frac{1}{2}E_2\left[(\partial_x u)^3\left(2+\frac{1}{2}\theta^2\right) + \frac{5}{4}(\partial_x u)^4 + \frac{1}{4}(\partial_x u)^5\right]. \end{aligned} \tag{S5}$$

Since $\partial_x u = \varepsilon_0 - \partial_x \theta z$ (see the first derivative of Eq. 5 in Sec. 3.2 in [1] with respect to x), and keeping the terms in $\partial_x u$ and θ to have $P_{xx} = P_{xx}(\partial_x u, (\partial_x u)^2, \theta^2, \partial_x u\theta^2, (\partial_x u)^2\theta^2, (\partial_x u)^3, (\partial_x u)^3\theta^2, \theta^4, \partial_x u\theta^4)$ in Eq. S5, the bending moment, defined as of $M \stackrel{\text{def}}{=} \int_A P_{xx} z \mathrm{d}A$ (where A is defined as the beam cross-section), can also be determined as

$$\begin{aligned} M = \int_A P_{xx} z \mathrm{d}A = &\underbrace{\int_A \mathrm{d}Az\left[E_1\varepsilon_0 + \frac{1}{2}E_1\theta^2 + \frac{3}{2}E_1\varepsilon_0^2 + \frac{1}{2}\varepsilon_0 E_1\theta^2\right] + \int_A \mathrm{d}Az\left[\frac{1}{2}E_2\varepsilon_0^2 + \frac{1}{2}\varepsilon_0 E_2\theta^2 + \frac{3}{4}\varepsilon_0^2 E_2\theta^2\right] + \int_A \mathrm{d}Az\left[\frac{1}{8}(1+\varepsilon_0)E_2\theta^4\right] +}_{\text{terms involving the static moment of inertia vanish after integration}} \\ &+ \int_A \mathrm{d}Az\left[-\partial_x\theta\left(E_1 z + 3E_1\varepsilon_0 z + \frac{1}{2}E_1 z\theta^2\right)\right] + \int_A \mathrm{d}Az\left[\frac{3}{2}E_1 z^2\partial_x^2\theta - \frac{1}{2}E_1 z^3\left(\partial_x^3\theta + h(\varepsilon_0)\right)\right] - \\ &- \int_A \mathrm{d}Az\left[E_2 z\partial_x\theta\left[\varepsilon_0 + \theta^2\left(\frac{1}{2} + \frac{3}{2}\varepsilon_0 + \frac{1}{8}\theta^2\right)\right]\right] + \int_A \mathrm{d}Az\left[\frac{1}{2}E_2 z^3\left(\partial_x^3\theta + h(\varepsilon_0)\right)\left(2+\frac{1}{2}\theta^2\right)\right] - \\ &- \int_A \mathrm{d}Az\left[E_2 z^2\partial_x^2\theta\left(\frac{1}{2} + \frac{3}{4}\theta^2\right)\right], \end{aligned} \tag{S6}$$

where $h(\varepsilon_0)$ represents a function with terms consisting of ε_0. Incorporating the full non-linearity of the curvature defined in Eq. 10 in [1], and applying $-z\partial_x\theta = -z\kappa\partial_x s$, Eq. S6 yields

$$\begin{aligned} M = &-E_1\kappa\partial_x s\int_A dAz^2 + \frac{3}{2}E_1\kappa^2\partial_x^2 s\int_A dAz^3 - 3E_1\varepsilon_0\kappa\partial_x s\int_A dAz^2 - \frac{1}{2}E_1\theta^2\kappa\partial_x s\int_A dAz^2 - \\ &- \frac{1}{2}E_1\left((\kappa\partial_x s)^3 + h(\varepsilon_0)\right)\int_A dAz^4 + \left[\frac{1}{2} + \frac{3}{4}\theta^2\right]E_2\kappa^2\partial_x^2 s\int_A dAz^3 - \\ &- \left[\frac{1}{2}\theta^2 + \frac{1}{8}\theta^4 + \varepsilon_0\left(1+\frac{3}{2}\theta^2\right)\right]E_2\kappa\partial_x s\int_A dAz^2 - \frac{1}{2}E_2\left((\kappa\partial_x s)^3 + h(\varepsilon_0)\right)\left(2+\frac{1}{2}\theta^2\right)\int_A dAz^4. \end{aligned} \tag{S7}$$

Since $\int_A dAz^2 = I$ is the second moment of inertia ($R^4\pi/4$ for circular cross-section), $\int_A dAz^3 = 0$ by symmetry, $\int_A dAz^4 = I_{4th}$ is the fourth moment of inertia ($R^6\pi/8$ for circular cross-section) and by neglecting ε_0, Eq. S7 finally becomes

$$\begin{aligned} M = -F(L-x) = &\underbrace{E_1\kappa\partial_x sI}_{\text{I}} + \underbrace{\frac{1}{2}E_1\theta^2\kappa\partial_x sI + \frac{1}{2}E_1(\kappa\partial_x s)^3 I_{4th}}_{\text{II}} + \\ &+ \underbrace{\left(\frac{1}{2}\theta^2 + \frac{1}{8}\theta^4\right)E_2\kappa\partial_x sI}_{\text{III}} + \underbrace{\frac{1}{2}E_2\left(2+\frac{1}{2}\theta^2\right)(\kappa\partial_x s)^3 I_{4th}}_{\text{IV}}, \end{aligned} \tag{S8}$$

where F is the applied concentrated force at the free end of the beam, L represents the total length of the beam (see also Fig. 1 in the main article).

Furthermore, the tensor component P_{xx} can also be formulated as the following,

$$\begin{aligned} P_{xx} = \frac{1}{2}E_1\theta^2 + \frac{1}{8}E_2\theta^4 - z\left[E_1\kappa\partial_x s + \frac{1}{2}\theta^2\left(E_1 + E_2\left(1+\frac{1}{4}\theta^2\right)\right)\kappa\partial_x s\right] + \\ + z^2\left[\frac{3}{2}E_1\kappa^2\partial_x^2 s + E_2\left(\frac{1}{2}+\frac{3}{4}\theta^2\right)\kappa^2\partial_x^2 s\right] - z^3\left[\left[\frac{1}{2}E_1 + \frac{1}{2}E_2\left(2+\frac{1}{2}\theta^2\right)\right]\kappa^3\partial_x^3 s\right]. \end{aligned} \tag{S9}$$

To expand the overall description of a non-linearly deflected nanowires, another important quantifier similar to Young's modulus in isotropic linear elasticity can be introduced. For this purpose, the incremental stretch modulus can be introduced to study the nonlinear elastic response of an isotropic material. The role of this elastic modulus is to reflect stiffening (or softening) in a material under strong loading. The gradient of the 1st Piola-Kirchhoff stress tensor, **P**, with respect to the deformation gradient, **F**, or equivalently, the gradient of **P** with respect to the displacement gradient, $\mathbf{F}-\mathbf{I}$, provides the definition of the incremental stretch modulus, $\tilde{\mathbf{Y}}^{incr}$, as

$$\tilde{\mathbf{Y}}^{incr} = \frac{\partial \mathbf{P}}{\partial(\mathbf{F}-\mathbf{I})}. \tag{S10}$$

Applying Eq. S5, the incremental stretch modulus yields its final closed form in terms of derivatives of the deflection function as

$$\begin{aligned} \tilde{\mathrm{Y}}^{incr} = \frac{\partial P_{xx}}{\partial(F_{xx}-1)} = \frac{\partial P_{xx}}{\partial(\partial_x u)} = E_1(1+\partial_x u)^2 + \left(\frac{1}{2}\theta^2 + \partial_x u + \frac{1}{2}(\partial_x u)^2\right)\times \\ \times\left(E_1 + E_2\left[\frac{1}{2}\left(\frac{1}{2}\theta^2 + \partial_x u + \frac{1}{2}(\partial_x u)^2\right) + (1+\partial_x u)^2\right]\right), \end{aligned} \tag{S11}$$

where $\partial_x u = -z\kappa\partial_x s$ (see also in Sec. 1.1) and we take into considerations made in Eq. S5 up to the terms of $\partial_x^3 u$ and θ^4.

References

[1] M. Jacob, R. Lawitzki, W. Ma, C. Everett, G. Schmitz, G. Csiszár, Beyond linearity: bent crystalline copper nanowires in the small-to-moderate regime, Nanoscale Adv., 2020 (2), 3002-3016.