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Polar and toroidal electromechanical properties designed by ferroelectric nano-metamaterials

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ABSTRACT

The recent advance in metamaterials provides a promising route to efficiently tailor and design a variety of material properties through rationally engineered building blocks. To further exploit the metamaterial concept with respect to electromechanical properties, we investigate electromechanical responses in ferroelectric nano-metamaterials using a phase field model based on Ginzburg-Landau theory. A wide magnitude range for apparent piezoelectric coefficients, which are strongly dependent on the internal structure, are obtained in ferroelectric nano-metamaterials, manifesting ferroelectric nano-metamaterials possess great versatility for tailoring the piezoelectricity. Unusual positive transverse piezoelectric coefficients, and consequently positive piezoelectric anisotropy can be achieved in ferroelectric nano-metamaterials. These unusual coefficients go beyond those which typically occur in homogenous ferroelectrics. We further introduce and demonstrate a new functionality of piezotoroidicity, which represents a new type of electromechanical coupling between ferrotoroidic ordering and mechanical excitation, emerging in ferroelectric nano-metamaterials. The present study thus opens exciting opportunities for the tailoring and design of electromechanical properties through deliberate control of the internal structure of ferroelectric nano-metamaterials by further extension of the metamaterial concept to electromechanical nano-metamaterials.

1. Introduction

Control of the properties of materials, going beyond the limit that is accessible with naturally existing or chemically synthesized substances, has become a reality with the advent of metamaterials [1,2]. Being introduced just over a decade ago, metamaterials, advanced artificial materials composed of tailored structural building blocks, have triggered significant interest due to numerous remarkable breakthroughs based on the realization of many tunable, extreme, or even unprecedented material properties in electromagnetism or optics [3–9], and recently in mechanics [10–16]. Metamaterials are thus rapidly emerging at the frontier of science involving physics, material science, engineering, and chemistry [17]. This deceptively simple but extraordinarily powerful concept of metamaterials, i.e., tuning material properties by deliberately engineered structures rather than chemical constituents, offers an entirely new route to further enhance the design of material properties at will.

Inspired by the outstanding progress in electromagnetism and mechanical metamaterials, we have previously proposed and demonstrated the concept of ferroelectric nano-metamaterials as a new stream of metamaterial concepts [18]. The proposed concept allows variety of unusual and complex yet controllable domain patterns to be achieved, in which a coexistence between hierarchical ferroelectric and ferrotoroidic polarization occurs, even in a simply branched network composed of connected ferroelectric nanowires. A key design parameter to realize such complex patterns was explored based on the parity of junctions that connect constituent nanostructures, and the formation of characterized polarization patterns in ferroelectric nano-metamaterials was also discussed [18]. As a characteristic of ferroelectric materials, spontaneous polarization and its arrangement (i.e., domain

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configuration) is crucial to determine the ferroelectric and related piezoelectric and dielectric properties [19–21]. The rich diversity of complex domain patterns that emerge in ferroelectric nano-metamaterials provides an ideal playground to determine not only distinct ferroelectricity, but also related properties, the most important of which is piezoelectricity, which places ferroelectric materials at the heart of many advanced technologies, such as sensors, actuators, and transducers in micro(nano)electromechanical systems (MEMS/NEMS) [22,23]. In addition, the emergence of polarization vortex configuration, which is characterized by a distinct ferrotoroidic order parameter rather than the common polarization order, is quite promising for the realization of unique electromechanical responses to external fields, and gives rise to novel functionalities in ferroelectric nano-metamaterials. Thus, knowledge regarding the electromechanical response of ferroelectric nano-metamaterials is essentially important to satisfy the ever increasing demand for the further improvement of ferroelectric devices. However, a deep understanding of the ferroelectric and/or ferrotoroidic response to external mechanical fields in ferroelectric nano-metamaterials has remained elusive due to the complexity of their non-trivial electro-elastic cross-coupling, which has impeded the application of ferroelectric nano-metamaterials in advanced nano-electromechanical devices.

In this work, polar and toroidal electromechanical responses of ferroelectric nano-metamaterials to mechanical excitation are investigated using a state-of-the-art phase-field model based on Ginzburg-Landau theory. A wide range of apparent piezoelectric coefficients are obtained, which makes them more available with respect to the control and manipulation of piezoelectricity. In addition, a new effect of piezotoroidicity is introduced to characterize the electromechanical response of the polarization vortex in ferroelectric nano-metamaterials to mechanical strain. We further discuss the effect of the nano-metamaterial internal structure on the tailoring of piezoelectric and piezotoroidic functional properties.

2. Computational details

2.1. Simulation methodology: a phase-field method

A ferroelectric material changes from the paraelectric phase to the ferroelectric phase when the temperature is below its Curie temperature, where spontaneous polarization exists even in the absence of any external field. The phenomenon originates from a change of crystal structure and lattice parameters, so that the spontaneous polarization is intrinsically coupled with mechanical excitation; therefore, all ferroelectrics have piezoelectricity. The piezoelectricity of ferroelectric nano-metamaterials is investigated here using a phase-field approach based on the extended Ginzburg–Landau theory. The present phase-field modeling achieves self-consistency of the electrostatic and elastic interactions, which is essential to describe the electromechanical behavior in ferroelectric nano-metamaterials [24]. The polarization vector $\boldsymbol{P} = (P_1, P_2, P_3)$ is used as the order parameter in the phase-field model to describe the free energies of ferroelectric phases. The total free energy F, of ferroelectric nano-metamaterial is obtained by integrating the total free energy density f, over the entire volume V, of the system [24]:

$$F = \int_V f dV = \int_V \left(f_{\text{Land}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{coup}} + f_{\text{elec}}\right) dV \tag{1}$$

where f_{Land}, f_{grad}, f_{elas}, f_{coup}, and f_{elec} represent the Landau free energy density, gradient energy density, pure elastic energy density, coupling energy density, and electrostatic energy density, respectively.

The Landau free energy density is described by a sixth-order polynomial of the polarization [24–27]:

$$\begin{aligned} f_{\text{Land}} = {} & \alpha_1\left(P_1^2 + P_2^2 + P_3^2\right) + \alpha_{11}\left(P_1^4 + P_2^4 + P_3^4\right) + \alpha_{12}\left(P_1^2P_2^2\right. \\ & \left. + P_2^2P_3^2 + P_3^2P_1^2\right) + \alpha_{111}\left(P_1^6 + P_2^6 + P_3^6\right) \\ & + \alpha_{112}\left[P_1^4\left(P_2^2 + P_3^2\right) + P_2^4\left(P_1^2 + P_3^2\right) + P_3^4\left(P_1^2 + P_2^2\right)\right] \\ & + \alpha_{123}P_1^2P_2^2P_3^2, \end{aligned} \tag{2}$$

where α_1 is the dielectric stiffness, and α_{11}, α_{12}, α_{111}, α_{112}, and α_{123} are higher order dielectric stiffness constants. The dielectric stiffness α_1 is given a linear temperature dependence based on the Curie–Weiss law:

$$\alpha_1 = (T - T_0)/2\kappa_0 C_0, \tag{3}$$

where T and T_0 denote the temperature and Curie-Weiss temperature, respectively, C_0 is the Curie constant, and κ_0 denotes the dielectric constant of a vacuum. The gradient energy density, which represents the energy penalty for the spatial polarization variation, is described by Refs. [24,26,27]:

$$\begin{aligned} f_{\text{grad}} = {} & \frac{1}{2}G_{11}\left(P_{1,1}^2 + P_{2,2}^2 + P_{3,3}^2\right) + G_{12}\left(P_{1,1}P_{2,2} + P_{2,2}P_{3,3}\right. \\ & \left. + P_{3,3}P_{1,1}\right) + \frac{1}{2}G_{44}\left[\left(P_{1,2} + P_{2,1}\right)^2 + \left(P_{2,3} + P_{3,2}\right)^2\right. \\ & \left. + \left(P_{1,3} + P_{3,1}\right)^2\right] + \frac{1}{2}G'_{44}\left[\left(P_{1,2} - P_{2,1}\right)^2 + \left(P_{2,3} - P_{3,2}\right)^2\right. \\ & \left. + \left(P_{3,1} - P_{1,3}\right)^2\right], \end{aligned} \tag{4}$$

where G_{11}, G_{12}, G_{44}, and G'_{44} are the gradient energy coefficients, and $P_{i,j} = \partial P_i/\partial x_j$ denotes the derivative of the ith component of the polarization vector P_i, with respect to the j-th coordinate x_j, and where $i, j = 1, 2, 3$. The elastic energy density induced by mechanical strain is expressed by:

$$\begin{aligned} f_{\text{elas}} = {} & \frac{1}{2}c_{11}\left(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2\right) + c_{12}\left(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{22}\varepsilon_{33} + \varepsilon_{33}\varepsilon_{11}\right) \\ & + 2c_{44}\left(\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{31}^2\right), \end{aligned} \tag{5}$$

where c_{11}, c_{12}, and c_{44} are the elastic constants, and ε_{ij} is the total strain that includes the elastic and electrostrictive strains. The coupling energy density between polarization and strain is given by Refs. [24,26,27]:

$$\begin{aligned} f_{\text{coup}} = {} & -q_{11}\left(\varepsilon_{11}P_1^2 + \varepsilon_{22}P_2^2 + \varepsilon_{33}P_3^2\right) - 2q_{12}\left[\varepsilon_{11}\left(P_2^2 + P_3^2\right)\right. \\ & \left. + \varepsilon_{22}\left(P_1^2 + P_3^2\right) + \varepsilon_{33}\left(P_1^2 + P_2^2\right)\right] - 2q_{44}\left(\varepsilon_{12}P_1P_2\right. \\ & \left. + \varepsilon_{13}P_1P_3 + \varepsilon_{23}P_2P_3\right), \end{aligned} \tag{6}$$

where q_{11}, q_{12}, and q_{44} are electrostrictive constants. The electrostatic energy density, which is obtained through Legendre transformation, is given as follow [24,26,27]: