Characterization of hybrid piezoelectric nanogenerators through
dynamic asymptotic homogenization

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Abstract. In the framework of energy scavenging for applications in flexible/stretchable electronics, hybrid piezoelectric nanogenerators, made up with Zinc oxyde nanorods, embedded in a polymeric matrix, and growth on a flexible polymeric support, are investigated. The ZnO nanorods are arranged in clusters, forming nearly regular distributions, so that periodic topologies can be realistically assumed. Focus is on a dynamic multi-field asymptotic homogenization approach, proposed to grasp the overall constitutive behaviour of such complex microstructures. A set of applications, both in static and dynamic regime, is proposed to explore different design paradigms, related to nanogenerators based on three working principles. Both extension and bending nanogenerators are, indeed, analysed, considering either extension along the nanorods axis, or orthogonally to it. The study of the wave propagation is, also, exploited to comprehend the main features of such piezoelectric devices in the dynamic regime.

Keywords: Energy scavenging, hybrid piezoelectric nanodevices, ZnO nanorods, periodic microstructure, multi-field homogenization, Bloch wave propagation.

1 Introduction

In the last decades, energy harvesting is increasingly becoming a topic of great interest in different engineering fields. The key idea is that the energy, naturally available in the environment (for instance in the form of heat or kinetic energy) is captured and converted into electrical energy, used to power small devices, such as wireless sensors and micro electronics, no longer requiring electro-chemical batteries. Among others, piezoelectric generators, exploiting their intrinsic electro-mechanical coupling, are competitive solutions in energy harvesting, as witnessed by the growing number of applications, ranging from structural monitoring, to automobiles, up to Internet of Things.

More recently particular attention has been drawn to emerging applications, such as biomedical monitoring, wearable technology, pervasive computing, micro and nano robotics, tire condition monitoring and extreme technology. To this aim, cutting-edge research has been devoted to design piezoelectric devices characterized by smaller and smaller size and high performances. Starting from the pioneering work by Wang and Song (2006), piezoelectric nanogenerators have been successfully proposed, based on different electro-active materials and working principles (Briscoe and Dunn, 2015; McCarthy et al., 2016; Jin et al., 2016; Zhang et al., 2016; Ahmed et al., 2017; Li et al., 2017; Saadatnia et al., 2017; Wang et al., 2018).
2017; Liu et al., 2018; Askari et al., 2019). Relevant examples concern either the use of piezoelectric zinc oxide (ZnO) nanowire arrays grown on conductive rigid supports (Yi et al., 2005; Wang and Song, 2006), or the adoption of lead zirconate titanate (PZT), polyvinylidene fluoride (PVDF) and barium titanate (BT).

An important improvement in the design of ZnO nanorods-based piezoelectric generators has been achieved by adopting flexible substrates made of electro-active polymeric materials. The main advantage is, indeed, the possibility of exploiting relevant flexural mechanisms, besides the standard direct compression of the device. In Fan et al. (2016) different typologies of flexible nanogenerators are presented and critically commented. Also patterned growth of ZnO nanowires can be exploited to enhance the performances of flexible nanogenerators, as discussed in Yang et al. (2017).

Further benefits can be obtained by resorting to so-called hybrid nanogenerators, made up by embedding the ZnO nanorods within a polymeric matrix. More specifically, Stassi et al. (2015) propose highly oriented ZnO nanotubes in a porous polycarbonate (PC) matrix. The result is an efficient nanogenerator based on such a highly flexible ZnOPC composite. Moreover, in Choi et al. (2017) a hybrid piezoelectric structure made of ZnO nanowires and a matrix of PVDF polymer is investigated in order to obtain a power enhancement. The authors, indeed, find that the ZnO nanowires are able to deliver internal strain to the PVDF, which increase the electrical power output of the hybrid nanogenerator.

Based on the aforementioned considerations, with the aim of energy harvesting from green and sustainable energy resources, our focus is on hybrid flexible nanogenerators, made up with clusters of ZnO nanorods embedded into a polymeric matrix and growth on a flexible support. The choice of ZnO nanorods, is motivated by their relatively simple forming processes using low temperature. In particular, by exploiting innovative growth techniques, it is possible to synthesize ZnO nanorods clamped on top of a flexible support, which is typically realized by sandwiching a polymer base and a layer of conductive fluorine-doped tin oxide (FTO). Concerning the zinc oxyde, the most stable crystalline structure is the Wurtzite (Wz), characterized by an hexagonal structure and a stacking sequence such that the nanorod axis coincides with the [0001] crystalline direction (see Wang (2004) for details). It follows that, the resulting nanorods have hexagonal cross section and principal axis nearly orthogonal to the base support. The overall material is, thus, characterized by a pronounced uni-axial anisotropy and the spontaneous polarization direction coincides with the axis of the nanorods. The ZnO nanorods, having roughly constant section sizes and heights, arrange themselves in clusters characterized in general by nearly regular distributions. It is important to emphasize that, during the synthesis process of such material, it is possible to tune both the density and the heights of the nanorods. The electro-active polymeric matrix is subsequently added, filling the gaps between the nanorods. Moreover, different clusters can be stacked together along the nanorods axis direction, in order to enhance their piezoelectric performances. The device is complemented by the presence of two electrodes located at the opposite external top and bottom faces. Due to the nearly regular distribution of the nanorods, for the sake of simplicity, it is possible to consider pe-
iodic topologies, in which the nanorods are equally spaced. The resulting material is a microstructured piezoelectric composite, whose global response is strongly influenced by its microstructure, i.e. by the geometry and materials properties of each constituents and by their collaborative behaviour.

With a view to investigating such kind of materials, a possibility is resorting to micromechanical approaches, in which the material is described in detail, but generally they result in cumbersome analyses.

In order to overcome these drawbacks, multiscale techniques, based on homogenization approaches, are a very valuable tool to gather both a synthetic and thorough description of the complex material behaviour. The investigation of the overall static and dynamic behaviour of periodic elastic composite materials has been performed resorting either to asymptotic approaches (Bakhvalov and Panasenko, 1984; Gambin and Kröner, 1989; Allaire, 1992; Boutin, 1996; Fish and Chen, 2001; Andrianov et al., 2008; Tran et al., 2012; Bacigalupo, 2014), or to variational-asymptotic approaches (Smyshlyaev and Cherednichenko, 2000; Peerlings and Fleck, 2004; Bacigalupo and Gambarotta, 2012, 2014), or also to identification techniques, among which computational approaches (Forest and Sab, 1998; Kouznetsova et al., 2004; Bacigalupo et al., 2016; Fantoni et al., 2017; De Bellis and Bacigalupo, 2017; Fantoni et al., 2018).

Generalized homogenization approaches have been proposed to date to handle multi-field problems, ranging from thermo-elastic, thermo-diffusive, to piezoelectric and thermo-piezoelectric problems (Gałka et al., 1996; Pettermann and Suresh, 2000; Aboudi et al., 2001; Berger et al., 2005; Kanouté et al., 2009; Zhang et al., 2007; Deraemaeker and Nasser, 2010; Zah and Miehe, 2013; Salvadori et al., 2014; Bacigalupo et al., 2016; Fantoni et al., 2017; De Bellis and Bacigalupo, 2017; Fantoni et al., 2018).

In this context, we propose a dynamic multi-field asymptotic homogenization approach for the analysis of hybrid piezoelectric nanogenerators with periodic microstructure. The key point of such approach is that the microscopic displacement and the electric potential fields are asymptotically expanded and plugged into the microscopic governing equations. It follows that a series of recursive differential problems are defined, in terms of the sensitivities of the microscopic fields. Such problems give rise to down-scaling relations, hierarchical cell problems, in terms of perturbation functions, and so-called average field equations of infinite order. The overall constitutive tensors and the overall inertial terms are, thus, rigorously derived from the generalized macro-homogeneity condition, properly relating the macroscopic Lagrangian and the microscopic mean Lagrangian, referred to a representative portion of the material either at the macroscopic or at the microscopic scale. By truncating the asymptotic expansion of the microscopic mean Lagrangian at different orders, either first order or higher order equivalent homogeneous continua can be identified. As an alternative, first and higher order approximations can be also obtained by solving, via perturbative approaches, the average field equations of infinite order.
The dispersive wave propagation in the hybrid piezoelectric nanogenerators has been, then, investigated and the frequency band structure has been determined consistently with the Floquet-Bloch theory. Moreover, the dispersion functions in equivalent homogeneous materials are derived, able to accurately approximate the acoustic branches of the Floquet-Bloch spectrum in the long wavelength regime. Applications has been devoted both to the static and dynamic analysis of periodic hybrid piezoelectric nanogenerators. In the framework of a first order homogenization approach, the equivalent constitutive properties are determined, as a function of the heights and the density of the nanorods, since such geometric parameters can be easily controlled, in the synthesis of the material, in order to tune the overall piezoelectric response. Considering a benchmark test of an extensional microstructured nanogenerator, the reliability of the proposed homogenization model has been proved by comparing the analytical homogenized solutions with the corresponding solutions of the heterogeneous model.

In addition, three piezoelectric microstructured nanogenerators, based on different working principles, are investigated as a set of geometrical parameters changes. More specifically, microstructured extension nanogenerators, bending nanogenerators and transversal extension nanogenerators are taken into account and their static behaviour is critically discussed, in order to provide broad guidelines to maximize their efficiency.

Finally, a dynamic characterization of the piezoelectric periodic nanostructured material is performed for the purpose of analysing Bloch waves propagations. Focus is on detecting detect possible partial or total band gaps, strongly characterizing the dynamic response of the composite material. A good agreement has been found between the dispersion functions analytically obtained by the homogenized model, and the acoustic branches of the Floquet-Bloch spectrum of the heterogeneous material.

2 Piezoelectric material modelled at two-scales

Let us consider a heterogeneous piezoelectric material, with periodic microstructure, which phases are described as a first order continuum in the framework of the linear theory of piezoelectricity. Each material point is identified by its position vector $\mathbf{x} = x_1 \mathbf{e}_1 + x_2 \mathbf{e}_2 + x_3 \mathbf{e}_3$, referred to a coordinate system with origin at point $O$ and orthogonal base with the fixed set of basis vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$, see Figure 1. Under the action of external sources, i.e. body forces $b(x, t) = b_i(x, t)\mathbf{e}_i$ and free charge densities $\rho_e(x, t)$, the microscopic displacement field $\mathbf{u}(x, t) = u_i(x, t)\mathbf{e}_i$ and the microscopic electric potential field $\phi(x, t)$ are induced. The fields depends both on point $\mathbf{x}$ and on time $t$. By exploiting the periodicity of the medium, a Periodic Cell $\mathcal{A} = [-d/2, d/2] \times [-d/2, d/2] \times [-h/2, h/2]$ is identified, denoted by the three orthogonal periodicity vectors $\mathbf{v}_1 = d\mathbf{e}_1 = \varepsilon \mathbf{e}_1, \mathbf{v}_2 = d\mathbf{e}_2 = \varepsilon \mathbf{e}_2$ and $\mathbf{v}_3 = h\mathbf{e}_3 = \eta \mathbf{e}_3$, being $\varepsilon$ the characteristic size of the cell $\mathcal{A}$, see Fig. 1(b). Consistently with standard asymptotic homogenization approaches, the Unit Cell $\mathcal{Q} = [-1/2, 1/2] \times [-1/2, 1/2] \times [-\eta/2, \eta/2]$ is obtained by applying the rescaling factor of $\varepsilon$ to the Periodic Cell $\mathcal{A}$. In agreement with (Mindlin, 1974), the partial differential equations governing the
piezoelectric problem, in component form, are

\[
\frac{D}{Dx_j} \left( C^{(m,\varepsilon)}_{ijkl} \frac{Du_k}{Dx_l} \right) + \frac{D}{Dx_j} \left( e^{(m,\varepsilon)}_{ijk} \frac{D\phi}{Dx_k} \right) + b_i = \rho^{(m,\varepsilon)} \frac{D^2u_i}{Dt^2},
\]

where \( C^{(m,\varepsilon)}_{ijkl} \) are the components of the fourth order micro elasticity tensor, \( e^{(m,\varepsilon)}_{ijk} \) are the components of the third order piezoelectric stress-charge coupling tensor, with the following relation between the components \( \tilde{e}^{(m,\varepsilon)}_{ijk} = e^{(m,\varepsilon)}_{jki} \), \( \beta^{(m,\varepsilon)}_{il} \) are the components of the second order dielectric permittivity tensor, and \( \rho^{(m,\varepsilon)} \) is the mass density. In Equations (1) the superscripts \( m \) and \( \varepsilon \) refer to microscopic fields, and to the characteristic size of the Periodic Cell, respectively. Note that the derivatives are intended in a generalized sense.

The constitutive tensors and the mass density are characterized by \( \mathcal{A} \)-periodicity, i.e.

\[
C^{(m,\varepsilon)}_{ijkl} (x + v_\alpha) = C^{(m,\varepsilon)}_{ijkl} (x),
\]

\[
e^{(m,\varepsilon)}_{ijk} (x + v_\alpha) = e^{(m,\varepsilon)}_{ijk} (x),
\]

\[
\beta^{(m,\varepsilon)}_{il} (x + v_\alpha) = \beta^{(m,\varepsilon)}_{il} (x),
\]

\[
\rho^{(m,\varepsilon)} (x + v_\alpha) = \rho^{(m,\varepsilon)} (x), \quad \alpha = 1, 2, 3, \quad \forall x \in \mathcal{A},
\]
therefore, they only depend on the variable $\xi = x/\varepsilon$, so that the $Q$-periodicity holds, as

\begin{align*}
C_{ijkl}^{(m,\varepsilon)}(x) &= C_{ijkl}^{(m,\varepsilon)}\left(\xi = \frac{x}{\varepsilon}\right), \\
\varepsilon_{ij}^{(m,\varepsilon)}(x) &= \varepsilon_{ij}^{(m,\varepsilon)}\left(\xi = \frac{x}{\varepsilon}\right), \\
\beta_{il}^{(m,\varepsilon)}(x) &= \beta_{il}^{(m,\varepsilon)}\left(\xi = \frac{x}{\varepsilon}\right), \\
\rho^{(m,\varepsilon)}(x) &= \rho^{(m,\varepsilon)}\left(\xi = \frac{x}{\varepsilon}\right), \quad \forall \xi \in \Omega.
\end{align*}

(3)

It is assumed that the body forces are $L$-periodic with period $L = [-L/2, L/2] \times [-L/2, L/2] \times [-\eta L/2, \eta L/2]$, and have zero mean values on $L$. Moreover, $L$ can be considered as a representative portion of the whole body, under the assumption that the structural length $L$ is much greater than the microstructural size $\varepsilon$ ($L >> \varepsilon$), consistently with the scale separation principle. As a consequence, the microscopic fields can be expressed in the form $u_i(x, \xi = x/\varepsilon, t)$ and $\phi(x, \xi = x/\varepsilon, t)$, where $x$ and $\xi = x/\varepsilon$ play the roles of macroscopic variable (slow variable), and microscopic variable (fast variable), respectively.

Due to this double $\Omega$- and $L$-periodicity, finding the solution of partial differential equations (1) is, in general, very burdensome adopting numerical approaches and very difficult via analytic approaches. This implies that valuable alternative approaches are found. In particular, homogenization techniques, allowing to replace the periodic medium with an equivalent homogeneous one, provide an efficient tool to accurately describe the overall behaviour of the microstructured piezoelectric material, with low computational costs. We here derive a macroscopic equivalent piezoelectric continuum, which overall constitutive tensors are analytically obtained in terms of the actual geometric and physical properties of the microstructure. In particular, at the macroscopic scale the variables $U(x, t) = U_i(x, t) e_i$ and $\Phi(x, t)$ are consistently defined, depending both on the macroscopic point $x$ and on time $t$.

3 Asymptotic expansion of microscopic field equations

The microscopic fields, involved in the governing equations, can be expressed through an asymptotic expansion in terms of the microscopic characteristic size $\varepsilon$, \textcolor{red}{(Bakhvalov and Panasenko, 1984)}. Consistently with the principle of scale separation, the slow and fast variables are kept separate, and the following expressions hold

\begin{align*}
u_k\left(x, \frac{x}{\varepsilon}, t\right) &= \sum_{l=0}^{+\infty} \varepsilon^l u_k^{(l)}\left(x, \frac{x}{\varepsilon}, t\right) = u_k^{(0)}\left(x, \frac{x}{\varepsilon}, t\right) + \varepsilon u_k^{(1)}\left(x, \frac{x}{\varepsilon}, t\right) + \varepsilon^2 u_k^{(2)}\left(x, \frac{x}{\varepsilon}, t\right) + O\left(\varepsilon^3\right), \\
\phi\left(x, \frac{x}{\varepsilon}, t\right) &= \sum_{l=0}^{+\infty} \varepsilon^l \phi^{(l)}\left(x, \frac{x}{\varepsilon}, t\right) = \phi^{(0)}\left(x, \frac{x}{\varepsilon}, t\right) + \varepsilon \phi^{(1)}\left(x, \frac{x}{\varepsilon}, t\right) + \varepsilon^2 \phi^{(2)}\left(x, \frac{x}{\varepsilon}, t\right) + O\left(\varepsilon^3\right).
\end{align*}

(4)
Moreover, recalling the derivation rule valid for the function $f ( \textbf{x, } \xi = \frac{\textbf{x}}{\varepsilon} )$, that is

$$ \frac{D}{Dx_j} f ( \textbf{x, } \xi = \frac{\textbf{x}}{\varepsilon} ) = \left( \frac{\partial f}{\partial x_j} + \frac{1}{\varepsilon} \frac{\partial f}{\partial \xi_j} \right) \bigg|_{\xi = \frac{\textbf{x}}{\varepsilon}} = \left( \frac{\partial f}{\partial x_j} + \frac{1}{\varepsilon} f_j \right) \bigg|_{\xi = \frac{\textbf{x}}{\varepsilon}}, \quad (5) $$

and plugging the asymptotic expansions (4), into the governing equations (1), the asymptotic expansion of microscopic field equations is obtained as

$$ \left\{ \begin{array}{l}
\varepsilon^{-2} \left( \left( C_{ijkl} u_{k,l}^{(0)} \right)_{,j} + \left( e_{ijk} \phi_{k}^{(0)} \right)_{,j} \right) + \varepsilon^{-1} \left[ \left( C_{ijkl} \left( \frac{\partial u_{k}^{(0)}}{\partial x_l} + u_{k,l}^{(1)} \right) \right)_{,j} + \frac{\partial}{\partial x_j} \left( C_{ijkl} u_{k,l}^{(0)} \right) + \\
+ \left( e_{ijk} \left( \frac{\partial \phi_{k}^{(0)}}{\partial x_l} + \phi_{k}^{(1)} \right) \right)_{,j} + \frac{\partial}{\partial x_j} \left( e_{ijk} \phi_{k}^{(0)} \right) \right] + \left[ \left( C_{ijkl} \left( \frac{\partial u_{k}^{(1)}}{\partial x_l} + u_{k,l}^{(2)} \right) \right)_{,j} + \frac{\partial}{\partial x_j} \left( C_{ijkl} u_{k,l}^{(1)} \right) + \\
+ \left( e_{ijk} \left( \frac{\partial \phi_{k}^{(1)}}{\partial x_l} + \phi_{k}^{(2)} \right) \right)_{,j} + \frac{\partial}{\partial x_j} \left( e_{ijk} \phi_{k}^{(1)} \right) \right] + \\
- \rho u_{i}^{(0)} + \mathcal{O} (\varepsilon) \right\} \bigg|_{\xi = \frac{\textbf{x}}{\varepsilon}} + b_i (\textbf{x}) = 0, \\
\varepsilon^{-2} \left( \left( e_{klm} u_{k,l}^{(0)} \right)_{,i} - \left( \beta_{il} \phi_{l}^{(0)} \right)_{,i} \right) + \varepsilon^{-1} \left[ \left( e_{klm} \left( \frac{\partial u_{k}^{(0)}}{\partial x_l} + u_{k,l}^{(1)} \right) \right)_{,i} + \frac{\partial}{\partial x_i} \left( e_{klm} u_{k,l}^{(0)} \right) + \\
- \left( \beta_{il} \left( \frac{\partial \phi_{l}^{(0)}}{\partial x_l} + \phi_{l}^{(1)} \right) \right)_{,i} - \frac{\partial}{\partial x_i} \left( \beta_{il} \phi_{l}^{(0)} \right) \right] + \left[ \left( e_{klm} \left( \frac{\partial u_{k}^{(1)}}{\partial x_l} + u_{k,l}^{(2)} \right) \right)_{,i} + \frac{\partial}{\partial x_i} \left( e_{klm} u_{k,l}^{(1)} \right) + \\
+ \frac{\partial}{\partial x_i} \left( e_{klm} \left( \frac{\partial \phi_{l}^{(1)}}{\partial x_l} + \phi_{l}^{(2)} \right) \right)_{,i} - \frac{\partial}{\partial x_i} \left( \beta_{il} \phi_{l}^{(1)} \right) \right] + \mathcal{O} (\varepsilon) \right|_{\xi = \frac{\textbf{x}}{\varepsilon}} - \rho_c (\textbf{x}) = 0.
\end{array} \right. \quad (6) $$

After proper manipulations, by collecting the terms with equal power $\varepsilon$, a hierarchical set of recursive partial differential problems, in terms of the sensitivities $u \sub{0} \sub{k} (\textbf{x, } \xi = \frac{\textbf{x}}{\varepsilon})$ and $\phi \sub{0} (\textbf{x, } \xi = \frac{\textbf{x}}{\varepsilon})$, is obtained. The statement and the solution of such recursive problems are reported in Appendix A. In particular, the solution of the $\varepsilon^{-2}$-order problem, in (43), takes the following form, where the dependence on the microscopic variable disappears

$$ u \sub{0} \sub{k} (\textbf{x, } \xi, t) = U_k (\textbf{x}, t), \quad \phi \sub{0} (\textbf{x, } \xi, t) = \Phi (\textbf{x}, t). \quad (7) $$
Analogously, the solution of the $\varepsilon^{-1}$-order problem, in (44), results in

$$
\begin{align*}
&u_k^{(1)}(x, \xi, t) = N_{kpq_1}^{(1)}(\xi) \frac{\partial U_p}{\partial x_{q_1}} + \tilde{N}_{kpq_1}^{(1)}(\xi) \frac{\partial \Phi}{\partial x_{q_1}}, \\
&\phi^{(1)}(x, \xi, t) = W_{q_1}^{(1)}(\xi) \frac{\partial \Phi}{\partial x_{q_1}} + \tilde{W}_{p_{q_1}}^{(1)}(\xi) \frac{\partial U_p}{\partial x_{q_1}},
\end{align*}
$$

(8)

where $N_{kpq_1}^{(1)}$, $\tilde{N}_{kpq_1}^{(1)}$, $W_{q_1}^{(1)}$, $\tilde{W}_{p_{q_1}}^{(1)}$ are the first order perturbation functions, only depending on the geometric and physical properties of the microstructure, that will be evaluated in the following.

Finally, the solution of the $\varepsilon^0$-order problem, in (46), is

$$
\begin{align*}
&u_k^{(2)}(x, \xi, t) = N_{kpq_{12}}^{(2)}(\xi) \frac{\partial^2 U_p}{\partial x_{q_1} \partial x_{q_2}} + \tilde{N}_{kpq_{12}}^{(2)}(\xi) \frac{\partial^2 \Phi}{\partial x_{q_1} \partial x_{q_2}} + \tilde{N}_{kp}^{(2)}(\xi) \tilde{U}_p, \\
&\phi^{(2)}(x, \xi, t) = W_{q_{12}}^{(2)}(\xi) \frac{\partial^2 \Phi}{\partial x_{q_1} \partial x_{q_2}} + \tilde{W}_{p_{q_{12}}}^{(2)}(\xi) \frac{\partial^2 U_p}{\partial x_{q_1} \partial x_{q_2}} + \tilde{W}_{q_{12}}^{(2)}(\xi) \tilde{U}_p,
\end{align*}
$$

(9)

being $N_{kpq_{12}}^{(2)}$, $\tilde{N}_{kpq_{12}}^{(2)}$, $\tilde{N}_{kp}^{(2)}$, $W_{q_{12}}^{(2)}$, $\tilde{W}_{p_{q_{12}}}^{(2)}$, and $\tilde{W}_{q_{12}}^{(2)}$ are the second order perturbation functions. The perturbation functions are determined, in turn, by solving two sets of hierarchical differential problems referred to as cell problems. The cell problems are obtained by properly manipulating the recursive problems, reported in Appendix A, and exploiting the structure of the sensitivities in (7)-(9), according with [Smyshlyaev and Cherednichenko 2000]. [Fantoni et al. 2017]. It is remarked that the source terms involved in such cell problems are characterized by zero mean values in the Unit Cell $\Omega$. As a consequence, they admit sufficiently regular and $\Omega$-periodic solutions. Moreover, the uniqueness of cell problems solutions is guaranteed by enforcing the normalization condition of the perturbation functions, i.e. assuring zero mean values in $\Omega$.

The two cell problems at the order $\varepsilon^{-1}$ read

$$
\begin{align*}
\left(C_{ijkl}^{m} N_{kpq_{1},l}^{(1)}\right)_{,j} + \left(e_{ijk}^{m} \tilde{W}_{pq_{1},l}^{(1)}\right)_{,j} + C_{ijkl}^{m} m_{pq_{1},j} &= 0, \\
\left(e_{ijkl}^{m} N_{kpq_{1},l}^{(1)}\right)_{,i} - \left(\beta_{d}^{m} \tilde{W}_{pq_{1},l}^{(1)}\right)_{,i} + e_{ijkl}^{m} m_{pq_{1},i} &= 0,
\end{align*}
$$

(10)

$$
\begin{align*}
\left(C_{ijkl}^{m} \tilde{N}_{kpq_{1},l}^{(1)}\right)_{,j} + \left(e_{ijk}^{m} W_{pq_{1},l}^{(1)}\right)_{,j} + e_{ijk}^{m} m_{pq_{1},j} &= 0, \\
\left(e_{ijkl}^{m} \tilde{N}_{kpq_{1},l}^{(1)}\right)_{,i} - \left(\beta_{d}^{m} W_{pq_{1},l}^{(1)}\right)_{,i} - e_{ijkl}^{m} m_{pq_{1},i} &= 0,
\end{align*}
$$

(11)
in terms of the first order perturbation functions.

Finally, the three cell problems at the order $\epsilon^0$ are

\begin{align*}
\left(C_{ijkl}^{(2)} \tilde{N}_{pq}^{(2)} \right)_{ij} &+ \left(C_{i j k l}^{(2)} \tilde{W}_{pq}^{(2)} \right)_{ij} + \frac{1}{2} \left[ \left(C_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} \right)_{ij} + C_{ijqk}^{(1)} + C_{iqkl}^{(1)} N_{pq}^{(1)} + \left(e_{ijqk}^{(1)} \tilde{W}_{pq}^{(1)} \right)_{ij} 
\right. \\
&+ e_{ij}^{(1)} \tilde{W}_{pq}^{(1)} + \left(C_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} \right)_{ij} + C_{iqlk}^{(1)} + C_{iqkl}^{(1)} N_{pq}^{(1)} + \left(e_{ijql}^{(1)} \tilde{W}_{pq}^{(1)} \right)_{ij} + e_{iqkl}^{(1)} \tilde{W}_{pq}^{(1)} 
\left. \ight] = \frac{1}{2} \left( C_{ijkl}^{(1)} + C_{iqlk}^{(1)} N_{pq}^{(1)} + C_{iqkl}^{(1)} N_{pq}^{(1)} + C_{ijql}^{(1)} \tilde{W}_{pq}^{(1)} \right),
\end{align*}

\begin{align*}
\left( e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} \right)_{ij} &+ \left( e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right)_{ij} + \frac{1}{2} \left[ \left( e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} \right)_{ij} + e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} + \left( e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right)_{ij} + e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right],
\end{align*}

\begin{align*}
\left( e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} \right)_{ij} &+ \left( e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right)_{ij} + \frac{1}{2} \left[ \left( e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} \right)_{ij} + e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} + \left( e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right)_{ij} + e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right] = \frac{1}{2} \left( e_{ijkl}^{(1)} + e_{ijkl}^{(1)} \tilde{N}_{pq}^{(1)} + e_{ijkl}^{(1)} \tilde{W}_{pq}^{(1)} \right).
\end{align*}

in terms of the first order perturbation functions, where a proper symmetrization with respect to indices $q_1$ and $q_2$ has been introduced. The symbol $\langle (\cdot) \rangle = 1/|\Omega| \int_{\Omega} (\cdot) d\xi$ has been introduced, $|\Omega| = \eta$, and $\delta_{pi}$ is the Kronecker delta function.

After determining the perturbation functions, by solving the cell problems, the so-called down-scaling relations can be rigorously determined. In particular, by plugging the terms in (7)-(9) into the asymptotic
expansion (4), the following down-scaling relations are found

\[
\begin{align*}
  u_k (x, \xi, t) &= U_k (x, t) + \varepsilon \left( N_{kpq_1}^{(1)} (\xi) \frac{\partial U_p}{\partial x_q} + N_{kq_1}^{(1)} (\xi) \frac{\partial \Phi}{\partial x_q} \right) + \varepsilon^2 \left( N_{kpq_1q_2}^{(2)} (\xi) \frac{\partial^2 U_p}{\partial x_q \partial x_{q_2}} \right. \\
  & \quad + \left. N_{kq_1q_2}^{(2)} (\xi) \frac{\partial^2 \Phi}{\partial x_q \partial x_{q_2}} + \widetilde{N}_{kp}^{(2)} (\xi) \frac{\partial \Phi}{\partial x_q} \right) \quad + \mathcal{O} (\varepsilon^3), \\
  \phi (x, \xi, t) &= \Phi (x, t) + \varepsilon \left( W_{q_1}^{(1)} (\xi) \frac{\partial \Phi}{\partial x_q} + \widetilde{W}_{pq_1}^{(1)} (\xi) \frac{\partial U_p}{\partial x_q} \right) + \varepsilon^2 \left( W_{q_1q_2}^{(2)} (\xi) \frac{\partial^2 \Phi}{\partial x_q \partial x_{q_2}} \right. \\
  & \quad + \left. \widetilde{W}_{pq_1q_2}^{(2)} (\xi) \frac{\partial \Phi}{\partial x_q} \right) \quad + \mathcal{O} (\varepsilon^3),
\end{align*}
\]

where the microscopic fields are made dependent on the corresponding macroscopic ones.

The up-scaling relations are, in turn, determined as

\[
\begin{align*}
  U_k (x, t) &= \left\langle u_k \left( x, \frac{x}{\varepsilon} + \zeta, t \right) \right\rangle, \\
  \Phi (x, t) &= \left\langle \phi \left( x, \frac{x}{\varepsilon} + \zeta, t \right) \right\rangle,
\end{align*}
\]

where \( \zeta \in \Omega \) is a translation variable, such that the vector \( \varepsilon \zeta \in \mathcal{A} \) defines a translation of the heterogeneous medium with respect to \( \mathcal{L} \)-periodic source terms (Smyshlyaev and Cherednichenko 2000; Bacigalupo 2014). It is pointed out that the perturbation functions fulfil the invariance property satisfied by \( \mathcal{L} \)-periodic functions \( g(\xi + \zeta)|_{\xi=x/\varepsilon} \), such that \( \int g(x/\varepsilon + \zeta) d\zeta = \int g(\xi + \zeta) d\zeta = \int g(\xi + \zeta) d\xi \).

### 4 Identification of the homogenized constitutive tensors

The macroscopic piezoelectric constitutive properties and the macroscopic inertial term are derived by exploiting a generalized macro-homogeneity condition, establishing an energy equivalence between the macroscopic and the microscopic scales. To this aim, the generalized microscopic mean Lagrangian \( \overline{L}_m \), inspired by (Smyshlyaev and Cherednichenko 2000; Bacigalupo 2014), and the corresponding generalized macroscopic Lagrangian \( \mathcal{L}_M \) are taken into account. Note that focus is on the identification of a first order homogenized continuum.

More specifically, the generalized microscopic mean Lagrangian is defined on the basis of the microscopic kinetic energy density \( t_m \) and of the microscopic electric enthalpy density \( h_m \), as

\[
\begin{align*}
  \overline{L}_m &= \int_{\mathcal{L}} \left[ \frac{1}{|\Omega|} \int_{\Omega} \left( t_m \left( x, \frac{x}{\varepsilon} + \zeta, t \right) - h_m \left( x, \frac{x}{\varepsilon} + \zeta, t \right) \right) d\zeta \right] d\mathbf{x} = \\
  &= \int_{\mathcal{L}} \left( t_m - h_m \right) d\mathbf{x},
\end{align*}
\]

(17)
where the down-scaling relations have been exploited to express the densities \( t_m \) and \( h_m \) as asymptotic expansions in terms of the macroscopic displacement \( U_t \) and electric potential \( \Phi \), respectively, i.e.

\[
\begin{align*}
t_m &= \frac{1}{2} \rho^m u_i u_i = \frac{1}{2} \rho^m \dot{U}_i \dot{U}_i + \mathcal{O}(\varepsilon), \\
h_m &= \frac{1}{2} C_{ijhk}^m \frac{D U_i}{D x_j} \frac{D u_h}{D x_k} + e^{m}_{ijh} \frac{D \phi}{D x_h} \frac{D u_i}{D x_j} - \frac{1}{2} \rho^m \frac{D \phi}{D x_i} \frac{D \phi}{D x_j} = \\
&= \frac{1}{2} \left[ C_{ijhk}^m \left( \delta_{ip} \delta_{jq} + N_{ipq,j}^{(1)} \right) \right] \frac{\partial U_p}{\partial x_i} \frac{\partial U_q}{\partial x_j} + \left[ C_{ijhk}^m \left( \delta_{ip} \delta_{jq} + N_{ipq,j}^{(1)} \right) \right] \frac{\partial U_p}{\partial x_i} \frac{\partial \phi}{\partial x_j} - \frac{1}{2} \left[ \beta_{ij}^m \left( \delta_{jq} + W_{qj}^{(1)} \right) \right] \\
&= \left( \delta_{hr} + W_{r,h}^{(1)} \right) + e^{m}_{ijh} \tilde{N}_{hr1,j} W_{qj}^{(1)} - \beta_{ij}^m \tilde{W}_{qj}^{(1)} \left( \delta_{ir} + W_{r1,i}^{(1)} \right) \\
&- \beta_{ij}^m \tilde{W}_{qj}^{(1)} \left( \delta_{hr} + W_{h1,r}^{(1)} \right) + \mathcal{O}(\varepsilon). \\
\end{align*}
\]

(18)

Analogously, the generalized macroscopic Lagrangian is given as

\[
\mathcal{L}_M = \int_{\mathbb{E}} \left( t_M (\mathbf{x}, t) - h_M (\mathbf{x}, t) \right) d\mathbf{x},
\]

(19)
in terms of the macroscopic kinetic energy density \( t_M \) and of the macroscopic electric enthalpy density \( h_M \), express in the following form

\[
\begin{align*}
t_M &= \frac{1}{2} \rho \ddot{U}_i, \\
h_M &= \frac{1}{2} C_{pq1sr1} \frac{\partial U_p}{\partial x_q} \frac{\partial U_s}{\partial x_r} + e_{pq1r1} \frac{\partial U_p}{\partial x_q} \frac{\partial \phi}{\partial x_r} - \frac{1}{2} \beta_{q1r1} \frac{\partial \phi}{\partial x_q} \frac{\partial \phi}{\partial x_r},
\end{align*}
\]

(20)
involving the components of the macroscopic constitutive tensors and of the macroscopic inertial term of the piezoelectric first order continuum.

The generalized macro-homogeneity condition is, thus, defined by

\[
\overline{\mathcal{L}}_m^0 \doteq \mathcal{L}_M,
\]

(21)
where \( \overline{\mathcal{L}}_m^0 \) identifies the generalized microscopic mean Lagrangian truncated at order 0-th, i.e. retaining only the coefficients of \( \varepsilon^0 \). It follows that the components of macroscopic piezoelectric constitutive
properties and the macroscopic inertial term result as

\[ \rho = \langle \rho^m \rangle, \]
\[ C_{pq1, sr1} = \frac{1}{2} \left( C_{ijh}^m \left( \delta_{ip} \delta_{jq1} + N_{ipq1,j}^{(1)} \right) \left( \delta_{hs} \delta_{kr1} + N_{hrs1,k}^{(1)} \right) + 2e_{ijh}^m \left( \delta_{ip} \delta_{jq1} + N_{ipq1,j}^{(1)} \right) \tilde{W}_{sr1,h}^{(1)} + \beta_{pq1}^m \tilde{W}_{pq1,h}^{(1)} \right) \cdot \]
\[ e_{pq1r1} = C_{ijh}^m \left( \delta_{ip} \delta_{jq1} + N_{ipq1,j}^{(1)} \right) \tilde{W}_{hr1,k}^{(1)} + e_{ijh}^m \left( \delta_{ip} \delta_{jq1} + N_{ipq1,j}^{(1)} \right) \left( \delta_{hr1} + W_{r1,h}^{(1)} \right) + \right. \]
\[ + e_{ijh}^m \tilde{N}_{ir1,j}^{(1)} W_{pq1,h}^{(1)} - \beta_{ijh}^m \tilde{W}_{pq1,j}^{(1)} \left( \delta_{ir1} + W_{r1,i}^{(1)} \right) \left( \delta_{hr1} + W_{r1,h}^{(1)} \right) \cdot \]
\[ \beta_{q1r1} = \frac{1}{2} \beta_{ijh}^m \left( \delta_{jq1} + W_{q1,i}^{(1)} \right) \left( \delta_{ir1} + W_{r1,i}^{(1)} \right) - C_{ijh}^m \tilde{N}_{iq1,j}^{(1)} \tilde{N}_{hr1,k}^{(1)} - 2e_{ijh}^m \tilde{N}_{iq1,j}^{(1)} \left( \delta_{hr1} + \tilde{W}_{r1,h}^{(1)} \right) \right), \]

(22)

expressed in terms of the perturbation functions and in terms of the components of the microscopic constitutive tensors and of the microscopic inertial term.

A more accurate description of the response of the heterogeneous material can be consistently obtained resorting to higher order homogenization approaches, in which the generalized macro-homogeneity condition is properly modified, both taking into account higher order terms in the asymptotic expansions at the microscopic scale, and nonlocal constitutive tensors and inertial terms at the macroscopic level. An alternative approach is schematically reported in Appendix B. It consists in solving the so-called average field equations of infinite order (48), via perturbation methods. An infinite hierarchical set of macroscopic partial differential problems is, thus, obtained and higher order approximations can be obtained by properly truncating the asymptotic expansion of \( U_i \) and \( \Phi \).

5 Characterization of dispersive wave propagation in piezoelectric periodic materials

The problem of characterizing the wave propagation in piezoelectric periodic materials can be addressed through the Floquet-Bloch theory able to deduce the frequency band structure of the material characterized by periodic microstructure. Nevertheless, this approach can eventually be computationally cumbersome in the case of very complex microstructural topologies. In this respect, a valuable alternative is the use of homogenization techniques, adopting either local or non-local approaches. More specifically, when first order approaches are used, an accurate description is obtained in the case of in the long wavelength regime.

With this in mind, in the following Section 5.1 the heterogeneous material is investigated to determine its frequency spectrum, with both acoustic and optical branches, while the Section 5.2 is devoted to deter-
mine the dispersive functions approximating only the acoustic branches in the long wavelength regime, adopting a first order asymptotic homogenization approach.

5.1 Frequency band structure of the heterogeneous material with periodic microstructure

In this Section, consistently with the rigorous Floquet-Bloch theory (Floquet 1883, Bloch 1928, Brillouin 1960), a generalization to piezoelectric materials is used to study the band structure of the microstructured periodic material. To this aim we apply the time Fourier transform to the partial differential equations (1) at the microscopic scale, in the case of zero source terms, i.e. \(b_i=0\) and \(\rho_e=0\). For the sake of completeness, we recall the time Fourier transform for a generic \(g(x, t)\) is defined as

\[
\mathcal{F}_t [g(x, t)] = \int_{-\infty}^{+\infty} g(x, t)e^{-i\omega t} \, dx = \tilde{g}(x, \omega),
\]

where the angular frequency \(\omega \in \mathbb{R}\). The resulting generalized Christoffel equations are, thus, obtained as

\[
\begin{align*}
\frac{D}{Dx_j} \left( C_{ijkl}^{(m,\varepsilon)} \frac{Du_k}{Dx_l} \right) + \frac{D}{Dx_j} \left( e_{ijkl}^{(m,\varepsilon)} \frac{D\tilde{\phi}}{Dx_k} \right) + \rho^{(m,\varepsilon)} \omega^2 \tilde{u}_i &= 0, \\
\frac{D}{Dx_i} \left( \tilde{\varepsilon}_{ijkl}^{(m,\varepsilon)} \frac{Du_k}{Dx_l} \right) - \frac{D}{Dx_i} \left( \beta_{il}^{(m,\varepsilon)} \frac{D\tilde{\phi}}{Dx_l} \right) &= 0,
\end{align*}
\]

in which the the well-known property \(\mathcal{F}_t \left( \frac{\partial^n g(x, t)}{\partial t^n} \right) = (i\omega)^n \tilde{g}(x, \omega)\) has been exploited.

Due to the periodicity of the microstructured medium, only the Periodic Cell \(\mathcal{A}\) is analysed, subject to the Floquet-Bloch boundary conditions, that is

\[
\begin{align*}
\tilde{u}_i^+ &= \tilde{u}_i^- e^{i k_j v_j^{(p)}}, \\
\tilde{\phi}^+ &= \tilde{\phi}^- e^{i k_j v_j^{(p)}}, \\
\tilde{\sigma}_{lr}^+ &= -\tilde{\sigma}_{lr}^- (m_r^{(p)})^- e^{i k_j v_j^{(p)}}, \\
\tilde{d}_r^+ (m_r^{(p)})^+ &= -\tilde{d}_r^- (m_r^{(p)})^- e^{i k_j v_j^{(p)}},
\end{align*}
\]

being \(v_j^{(p)}\) the components of the vector of periodicity \(v_p = v_j^{(p)} e_j\), and \((m_r^{(p)})^\pm\) the components of the outward normal \(m_p^\pm = (m_j^{(p)})^\pm e_j\) to the boundary \(\partial \mathcal{A}\), \(j, p = 1, 2, 3\). Moreover, the apexes \(\pm\) are referred to the positive part \(\partial \mathcal{A}^+\) (with outward normal \(m_1^+\)) and the corresponding negative parts \(\partial \mathcal{A}^-\) (with outward normal \(m_1^-\)) of the Periodic Cell boundary. Note that for the generic function \(\tilde{g}\) the following notation is used, i.e. \(\tilde{g}^\pm = \tilde{g}(x^\pm)\) where \(x^\pm \in \partial \mathcal{A}^\pm\), and \(x^+ = x^- + v_p\). Finally, \(k_j\) are the components of the wave vector \(k\). In this context, the dimensionless first Brillouin zone \(\mathcal{B} = [-\pi, \pi] \times [-\pi, \pi] \times [-\pi, \pi]\) is defined in the space of the dimensionless wave vectors (whose components are \(k_1 d\), \(k_2 d\) and \(k_3 h\)) and
is associated to the Periodic Cell $\mathfrak{A}$. Such Brillouin zone is characterized by three orthogonal vectors $\pi n_i$, parallel to $e_i$, with $i=1,2,3$.

### 5.2 Dispersion functions in the first order homogeneous material

A first order asymptotic homogenization approach is here adopted to study the dispersion functions piezoelectric periodic material. The equations of motion for the homogenized continuum, in the absence of source terms take the following form

\[
\begin{align*}
C_{ijkl} \frac{\partial^2 U_p}{\partial x_{q_1} \partial x_{q_2}} + e_{ijk} \frac{\partial^2 \Phi}{\partial x_{q_1} \partial x_{q_2}} &= \rho \ddot{U}_i, \\
\tilde{e}_{ikl} \frac{\partial^2 U_p}{\partial x_{q_1} \partial x_{q_2}} - \beta_{il} \frac{\partial^2 \Phi}{\partial x_{q_1} \partial x_{q_2}} &= 0,
\end{align*}
\]

(29)

where $C_{ijkl}$ are the components of the fourth order macro elasticity tensor, $e_{ijk}$ are the components of the third order macroscopic piezoelectric stress-charge coupling tensor, with the following relation between the components $\tilde{e}_{ijk} = e_{jki}$, $\beta_{il}$ are the components of the second order macroscopic dielectric permittivity tensor and $\rho$ is the macroscopic mass density, reported in Equation (22). Equations (29) are here properly manipulated, by first exploiting the time Fourier transform, see equation (23), and then the space Fourier transform in the macroscopic space, that is hereafter recalled

\[
\mathcal{F}_x [\bar{g}(x, \omega)] = \int_{\mathbb{R}^2} \bar{g}(x, \omega) e^{-ikx} dx = \bar{\bar{g}}(k, \omega),
\]

(30)

where $k \in \mathbb{R}^2$ is the wave vector, and recalling the property $\mathcal{F}_x (\frac{\partial^n \bar{g}(x, \omega)}{\partial x^k}) = (ik_j)^n \bar{\bar{g}}(k, \omega)$ the following governing equations in the frequency and wave vector space are obtained

\[
\begin{align*}
- C_{ijkl} k_j \bar{U}_k - e_{ikj} k_j k_k \bar{\Phi} + \rho \omega^2 \bar{U}_i &= 0, \\
- \tilde{e}_{ikl} k_j \bar{U}_k + \beta_{il} k_j k_k \bar{\Phi} &= 0.
\end{align*}
\]

(31)

The Equation (31) can be rewritten in an equivalent form, after simple manipulations, in terms of the phase velocity and of the propagation direction, as

\[
\begin{align*}
- C_{ijkl} n_j n_l \bar{U}_k - e_{ikj} n_j n_k \bar{\Phi} + \rho c^2 \bar{U}_i &= 0, \\
- \tilde{e}_{ikl} n_j n_l \bar{U}_k + \beta_{il} n_j n_k \bar{\Phi} &= 0,
\end{align*}
\]

(32)
where the phase velocity is \( c = \omega / k \), the wave number is \( k = ||k||_2 \) and the unit vector of propagation is \( \mathbf{n} = \mathbf{k} / k \) with components \( n_j \).

A static condensation is, at this stage, performed so that from the second equation in (32) we obtain
\[
\tilde{\Phi} = \tilde{\varepsilon}_{ikl} n_l \tilde{U}_k / (\beta il n_i) \quad \text{and, after substituting in the first equation in (32), the eigenproblem governing the Bloch-wave propagation, expressed in terms of phase velocity and the transformed displacement components, is obtained as}
\]
\[
\left( C_{ijkl} n_j n_l + e_{ijq} n_j n_q \frac{\tilde{\varepsilon}_{pkl} n_l n_p}{\beta rs n_s n_r} - \rho c^2 \delta_{ki} \right) \tilde{U}_k = 0, \quad i = 1, 2, 3,
\]
(33)

where \( \tilde{\varepsilon}_{pkl} = e_{klp} \) is exploited. Note that for any unit vector of propagation \( \mathbf{n} \), the eigenvalues \( c^2 \) are the square of the wave velocity in the first order homogenized continuum. The corresponding eigenvectors, whose components \( \tilde{U}_k \) correspond to the time and space Fourier transform of the components of the macroscopic displacement in the first order homogenized continuum, identify the components of the polarization vector.

### 6 Illustrative applications

In this Section some illustrative examples are shown. We refer to the realistic assumption of materials with periodic cells characterized by orthogonal periodic vectors, as schematically shown in Figure 1. First, the components of the homogenized constitutive tensors, characterizing the composite material with periodic nano-structure, are shown for different geometric parameters, i.e. the height of the nanorods and their volumetric density. Then, both the results obtained with a micromechanical model and with a first order piezoelectric homogenized model are compared with each other, in the case of an extensional nanoscopic generator. Moreover, the influence of the volumetric density on the overall efficiency of such extensional nanostructured devices has been investigated in order to provide broad guidelines to maximize their efficiency.

Both analytic and numerical solutions are considered. Concerning the latter ones, finite elements analyses have been performed adopting fully coupled tetrahedral second order elements with displacements and electric potential independent degrees of freedom.

#### 6.1 Homogenized piezoelectric properties

We consider a hybrid piezoelectric nanogenerator made of equispaced ZnO-nanorods embedded in a polymeric matrix and sandwiched in two homogeneous polymeric layers. The homogenized constitutive properties of the piezoelectric material are investigated with reference to the Periodic Cell, shown in Figure 2(a). The Periodic Cell \( \mathcal{A} = [-d/2, d/2] \times [-d/2, d/2] \times [-h/2, h/2] \) is characterized by the three orthogonal periodicity vectors \( \mathbf{v}_1, \mathbf{v}_2 \) and \( \mathbf{v}_3 \). We assume \( d=200 \ \text{nm} \), the nanorod has hexagonal section.
with edge 80 nm, while the height in the polarization direction is $h = 1100$ nm, and the thickness of both top and bottom layers is 50 nm. Such average geometric values are representative of actual ZnO-rods based nanostructures, see [Wang (2004)].

The nanorod with hexagonal section is made of Zinc oxide with polarization along the vertical axis $e_3$. Considering the ZnO material, see [Yang, 2004], the non-vanishing components of the elasticity tensor are:

- $C_{1111}^m = 2.097 \cdot 10^{11}$ Pa, $C_{2222}^m = 2.097 \cdot 10^{11}$ Pa, $C_{3333}^m = 2.111 \cdot 10^{11}$ Pa, $C_{1122}^m = 1.211 \cdot 10^{10}$ Pa, $C_{1133}^m = 1.053 \cdot 10^{10}$ Pa, $C_{2233}^m = 1.053 \cdot 10^{10}$ Pa, $C_{1212}^m = 4.237 \cdot 10^{10}$ Pa, $C_{1313}^m = 4.237 \cdot 10^{10}$ Pa, $C_{2323}^m = 4.424 \cdot 10^{10}$ Pa.

Moreover, the non-vanishing components of the coupling tensor in the stress-charge form are:

- $\tilde{e}_{311} = -0.567 \, C/m^2$, $\tilde{e}_{322} = 1.3204 \, C/m^2$, $\tilde{e}_{333} = -0.4805 \, C/m^2$. Finally, the non-vanishing components of the dielectric permittivity tensor are $\beta_{11}/\varepsilon_0 = 8.5446$, $\beta_{33}/\varepsilon_0 = 10.204$, where $\varepsilon_0 = 8.854 \cdot 10^{-12} \, C/(V\cdot m)$ is the vacuum permittivity.

A first numerical investigation concerns the influence of the heights of ZnO-nanorods on the overall piezoelectric constitutive response. The values of the actual height of the nanorods $h_{nr}$ are supposed to vary between $0.5 \times h_{nr}^* = 550$ nm and $2 \times h_{nr}^*$, where $h_{nr}^* = 1100$ nm is the reference initial height. In Figure 2(b) the non-vanishing components of the homogenized elasticity tensor, normalized with respect to the corresponding components of bulk ZnO material, are plotted against $\alpha = h_{nr}/h_{nr}^*$. A monotonic increasing variation is found for all the considered components. As expected, $C_{3333}$ (red curve) is the component most affected by the variation of $\alpha$, with a maximum value about three times the initial one. The remaining components exhibit variations significantly lower, see the zoomed plot in Figure 2(b). Similar considerations apply to the components of the coupling tensor, shown in Figure 2(c). Only the component $e_{333}$ (red curve) exhibits remarkable variations. Moreover, also the maximum variations of the components $\beta_{ij}/\beta_{ij}^{ZnO}$ are referred to the component $\beta_{33}$ (red curve), see Figure 2(d).

The second numerical study is devoted to analyse the influence of the volumetric density of ZnO-nanorods on the overall constitutive response of the Periodic Cell. The density is defined as $\delta = V_{NR}/V$, i.e. the ratio between the volume occupied by the nanorods and the volume of a Periodic Cell, neglecting the contribution of the top and bottom layers. We let the density $\delta$ vary between a minimum value of about $\delta = 0.066$, corresponding to the case where $d = 500$ nm in the Periodic Cell $\mathfrak{A}$, and a maximum value of about $\delta = 0.65$, for which $d = 160$ nm, see the sketch in Figure 3(a).

In Figure 3(b) the dimensionless non-vanishing components of the homogenized elasticity tensor $C_{ijkl}/C_{ijkl}^{ZnO}$ are plotted versus the density $\delta$. We observe that all the components monotonically increase, and the $C_{3333}$ (red curve) shows the maximum variation between the extremal $\delta$ values. Moreover, due to the geometrical and material symmetries of the Periodic Cell, the curves related to the components
Fig. 2: (a) Schematic of the Periodic Cell. Components of the homogenized constitutive tensors versus $\alpha = h_{nr}/h_{*nr}$, with $h_{nr}=1000$ nm: (b) components of the elastic tensor (the blue curve is $C_{1111}$, the magenta curve is $C_{2222}$, the red curve is $C_{3333}$, the green curve is $C_{1122}$, the black curve is $C_{1133}$ (nearly indistinguishable from $C_{2233}$), the cyan curve is $C_{1212}$ almost perfectly overlapping $C_{1313}$ and $C_{2323}$); (c) components of the coupling tensor (the blue curve is $e_{113}$, the magenta curve is $e_{223}$, the red curve is $C_{333}$, the green curve is $e_{131}$ and the back curve is $e_{232}$); (d) components of the dielectric permittivity tensor (the blue curve is $\beta_{11}$, the green curve is $\beta_{22}$ and the red curve is $\beta_{33}$).
increasing nanorods density $\delta$

$$L = \sqrt{\frac{\delta V_{nr}}{h_{nr}}}$$

Fig. 3: (a) Schematic of the $5 \times 5$ cluster of nanorods for different values of density $\delta$. Components of the homogenized constitutive tensors versus $\delta$: (b) components of the elastic tensor (the blue curve is $C_{1111}$, the magenta curve is $C_{2222}$, the red curve is $C_{3333}$, the green curve is $C_{1122}$, the black curve is $C_{1133}$, the purple curve is $C_{2233}$, the cyan curve is $C_{1212}$, the yellow curve is $C_{1313}$ and the brown curve is $C_{2323}$); (c) components of the coupling tensor (the blue curve is $e_{113}$, the magenta curve is $e_{223}$, the red curve is $C_{333}$, the green curve is $e_{131}$ and the back curve is $e_{232}$); (d) components of the dielectric permittivity tensor (the blue curve is $\beta_{11}$, the green curve is $\beta_{22}$ and the red curve is $\beta_{33}$).
\( C_{3333}, C_{1133} \) and \( C_{2233} \) are concave upward, while all the others have opposite concavity. The components \( e_{ijh}/e_{ijh}^{ZnO} \) are plotted in Figure 3(c). Again, monotonic variations are observed with maximum values reached for \( e_{333} \). Finally, in Figure 3(d) the dimensionless non-vanishing components \( \beta_{ij}/\beta_{ij}^{ZnO} \) are plotted, confirming monotonic variations that take maximum values for \( \beta_{33} \). Note that the maximum variations are significantly lower than those shown by the components \( C_{3333} \) and \( e_{333} \).

### 6.2 Benchmark test: two-phase piezoelectric hybrid composite

We study the microstructured nanogenerators under compressive loads along the nanorods axis, considering a cluster of \( n \times n \) cells (with base dimension \( L \) and height \( h \)), obtained by repeating the Periodic Cell along the periodicity vectors \( \mathbf{v}_1 \) and \( \mathbf{v}_2 \), see Figure 3(a) where a sketch is shown. A uniform surface compressive load \( q \) is applied on the top horizontal face of the specimen, while the displacements of the points on the bottom face are restricted in \( e_3 \) direction. The electrodes are located along the top and bottom faces. Two alternative cases are considered, depending on the boundary conditions applied on the lateral faces. The Case 1 is characterized by free lateral faces, while in the Case 2 the displacements are restricted along the outward normal to the lateral surface.

In order to reduce the computational costs involved in micromechanical analyses of such piezoelectric nanogenerators, their macroscopic behaviour can be satisfactorily described via a first order equivalent homogeneous material.

The macroscopic field equations of the first order homogenized continuum, specialized to the considered material symmetries, and with zero source terms, result as

\[
\begin{align*}
\frac{\partial}{\partial x_1} \left( C_{1111} \frac{\partial U_1}{\partial x_1} + C_{1122} \frac{\partial U_2}{\partial x_2} + C_{1133} \frac{\partial U_3}{\partial x_3} \right) + \frac{\partial}{\partial x_2} \left( C_{1212} \frac{\partial U_2}{\partial x_1} + \frac{\partial U_1}{\partial x_2} \right) + \frac{\partial}{\partial x_3} \left( C_{1313} \frac{\partial U_3}{\partial x_1} + \frac{\partial U_1}{\partial x_3} \right) + C_{1133} \frac{\partial U_3}{\partial x_1} + \frac{\partial U_1}{\partial x_3} = 0, \\
\frac{\partial}{\partial x_2} \left( C_{2222} \frac{\partial U_2}{\partial x_2} + C_{2233} \frac{\partial U_3}{\partial x_3} + C_{1122} \frac{\partial U_2}{\partial x_2} \right) + \frac{\partial}{\partial x_3} \left( C_{3232} \frac{\partial U_3}{\partial x_2} + \frac{\partial U_2}{\partial x_3} \right) = 0, \\
\frac{\partial}{\partial x_3} \left( C_{3333} \frac{\partial U_3}{\partial x_3} + C_{1133} \frac{\partial U_1}{\partial x_1} + C_{2233} \frac{\partial U_2}{\partial x_2} \right) + \frac{\partial}{\partial x_2} \left( C_{3232} \frac{\partial U_3}{\partial x_2} + \frac{\partial U_2}{\partial x_3} \right) = 0, \\
\frac{\partial}{\partial x_1} \left( e_{113} \frac{\partial U_1}{\partial x_1} + e_{222} \frac{\partial U_2}{\partial x_2} + e_{322} \frac{\partial U_3}{\partial x_3} + e_{113} (\frac{\partial U_3}{\partial x_1} + \frac{\partial U_1}{\partial x_3}) \right) + \frac{\partial}{\partial x_2} \left( e_{222} \frac{\partial U_2}{\partial x_1} + e_{322} \frac{\partial U_3}{\partial x_2} \right) + e_{131} \left( \frac{\partial U_1}{\partial x_1} + \frac{\partial U_3}{\partial x_3} \right) - \frac{\partial}{\partial x_1} \left( \beta_{11} \frac{\partial \Phi}{\partial x_1} \right) - \frac{\partial}{\partial x_2} \left( \beta_{22} \frac{\partial \Phi}{\partial x_2} \right) - \frac{\partial}{\partial x_3} \left( \beta_{33} \frac{\partial \Phi}{\partial x_3} \right) = 0.
\end{align*}
\]
Considering the Case 1, the boundary conditions are \( U_1(x_1 = -L/2) = 0, U_2(x_2 = -L/2) = 0, U_3(x_3 = -h/2) = 0, \Phi(x_3 = -h/2) = 0, \Sigma_{11}(x_1 = L/2) = 0, \Sigma_{22}(x_2 = L/2) = 0, \Sigma_{33}(x_3 = h/2) = -q, d_3(x_3 = h/2) = 0. \)

The solution of this ODE problem takes the following form

\[
U_1(x_1) = -q (2x_1 + L) \Psi^{-1} \left[ C_{1133} e_{223}^2 - (C_{1122} e_{333} - C_{2233} e_{113}) e_{223} - C_{1122} C_{2233} \beta_{33} + C_{2222} (C_{1133} \beta_{33} + e_{113} e_{333}) \right],
\]

\[
U_2(x_2) = q (2x_2 + L) \Psi^{-1} \left[ -C_{2233} e_{113}^2 + (C_{1111} e_{333} - C_{1133} e_{223}) e_{113} + C_{1122} C_{1133} \beta_{33} - C_{2233} \beta_{33} + e_{223} e_{333} \right],
\]

\[
U_3(x_3) = q (2x_3 + h) \Psi^{-1} \left[ -C_{1122}^2 \beta_{33} - 2 C_{1122} e_{113} e_{223} + C_{2222} e_{113}^2 + C_{1111} (C_{2222} \beta_{33} + e_{223}^2) \right],
\]

\[
\Phi(x_3) = q (2x_3 + h) \Psi^{-1} \left[ C_{1122} e_{333} + (-C_{1133} e_{223} - C_{2233} e_{113}) C_{1122} + C_{1133} C_{2222} e_{113} - C_{1111} (C_{2222} e_{333} - C_{2233} e_{223}) \right],
\]

where the constant \( \Psi \) takes the form

\[
\Psi = -\left[ 2 C_{3333} \beta_{33} + 2 e_{333}^2 \right] C_{1122}^2 + \left( (4 C_{2233} \beta_{33} + 4 e_{223} e_{333}) C_{1133} + -4 e_{113} (C_{2233} e_{333} - C_{3333} e_{223}) \right) C_{1122} - 2 \left( C_{2222} \beta_{33} + e_{223}^2 \right) C_{1133}^2 + -4 e_{113} (C_{2222} e_{333} - C_{2233} e_{223}) C_{1133} - 2 \left( C_{1111} \beta_{33} + e_{113}^2 \right) C_{2233}^2 + + 4 C_{1111} C_{2233} e_{223} e_{333} + 2 C_{2222} C_{3333} e_{113}^2 + + 2 \left( C_{3333} e_{223}^2 + C_{2222} \left( C_{3333} \beta_{33} + e_{333}^2 \right) \right) C_{1111}. \]

The strain field and the electric field are consistently derived. The electric displacement field is identically zero, while the only non-vanishing component of the resulting stress field is \( \Sigma_{33} = -q. \)

Concerning, instead, the Case 2, the new set of boundary conditions is \( U_1(x_1 = \pm L/2) = 0, U_2(x_2 = \pm L/2) = 0, U_3(x_3 = -h/2) = 0, \Phi(x_3 = -h/2) = 0, \Sigma_{33}(x_3 = h/2) = -q, d_3(x_3 = h/2) = 0. \) The corresponding solution of the ODE problem is

\[
U_1(x_1) = 0,
\]

\[
U_2(x_2) = 0,
\]

\[
U_3(x_3) = -\frac{q}{2} (2x_3 + h) \Xi^{-1} \beta_{33},
\]

\[
\Phi(x_3) = -\frac{q}{2} (2x_3 + h) \Xi^{-1} e_{333},
\]

with the constant \( \Xi \) expressed in the form

\[
\Xi = C_{3333} \beta_{33} + e_{333}^2.
\]
The components of the electric displacement field are equal to zero, and the non-vanishing components of the stress field are

\[
\begin{align*}
\Sigma_{11}(x_1) &= -q\Xi^{-1} (C_{1133} \beta_{33} + \epsilon_{113} \epsilon_{333}), \\
\Sigma_{22}(x_2) &= -q\Xi^{-1} (C_{2233} \beta_{33} + \epsilon_{223} \epsilon_{333}), \\
\Sigma_{33}(x_3) &= -q. 
\end{align*}
\]

The macroscopic fields, analytical determined, are compared against numerical results obtained with a micro-mechanical model. To this aim, a convergence study is performed considering, at the microscopic scale, clusters of increasing dimensions, in order to detect the minimum size of the cluster such that the results related to the central cell remain almost unchanged. We observe that already for a cluster of 5 \(\times\) 5 satisfactory results are obtained, so that the numerical results presented below are referred to this minimum size cluster geometry.

A first investigation is referred to the behaviour of the nanogenerators as the volume fraction of PANI nanoscopic particles varies within the matrix and the top and bottom layers, i.e. for dielectric permittivity \(\varepsilon_{rP/PANI}^{P/PANI}\) ranging from 5 to 10000. We, indeed, assume that the matrix and the layers are characterized by very high values of dielectric constants, varying with the volume fraction of PANI nanoscopic particles dispersed in the polymeric matrix. In Figure 4(a) the macroscopic dimensionless potential differences \(\Delta\Phi \sqrt{\beta_{33}^{\text{ZnO}}/(\sqrt{\eta}h)}\) obtained from the heterogeneous model via up-scaling relations (solid plots) and from the equivalent homogenized model (dotted plots) are shown. Two densities are considered for both Case 1 and Case 2. In particular, blue and green curves refer to Case 1 and Case 2, respectively, considering a density \(\delta=0.415\), while red and black curves refer to Case 1 and Case 2, respectively, considering a density \(\delta=0.104\). We observe that the macroscopic analytical solutions are in very good agreement with the macroscopic numeric results obtained via up-scaling from the heterogeneous model. A non-linear trend is observed, with potential differences increasing as the the volume fraction of PANI decreases. Better performances are obtained for low values of \(\varepsilon_{rP/PANI}^{P/PANI}\). Note that the maximum values of potential differences are observed for the Case 1 with lower density. For both the densities, the Case 1 exhibits better performances.

A further investigation is devoted to study the influence of the height of the nanorods, considering the parameter \(\alpha = h/h^*\), as the height \(h\) varies between 550 nm and 2200 nm, with \(h^*=1100\) nm. In Figure 4(b) the macroscopic dimensionless potential differences \(\Delta\Phi \sqrt{\beta_{33}^{\text{ZnO}}/(\sqrt{\eta}h^*)}\) are, thus, plotted versus \(\alpha\). Also in this plot, blue and green curves refer to Case 1 and Case 2, respectively, considering a density \(\delta=0.415\), while red and black curves refer to Case 1 and Case 2, respectively, considering a density \(\delta=0.104\). The solid lines refer to the solution of the micromechanical problems, while the dotted lines are the analytical solutions. Again, a nearly perfect match is observed. In this case, nearly linear variations are found as \(\alpha\) varies. As expected, higher values of nanorods’ heights are associated with better
performances. Also in this case, the Case 1 is more effective than Case 2 irrespective of the considered density.

A more comprehensive investigation concerns the comparison between dimensionless potentials and di-

Fig. 4: Comparison of the macroscopic dimensionless potential differences obtained from the heterogeneous model via up-scaling relations (solid plots) and from the equivalent homogenized model (dotted plots). (a) $\Delta \Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{qh})$ versus $\varepsilon_{r}^{P/PANI}$ for $\delta=0.415$ (the blue curves is for the Case 1, the green curves is for the Case 2), and for $\delta=0.104$ (the red curves is for the Case 1, the black curves is for the Case 2); (b) $\Delta \Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{qh^*})$, with $h^*=1100$ nm, versus $\alpha$ for $\delta=0.415$ (the blue curves is for the Case 1, the green curves is for the Case 2), and for $\delta=0.104$ (the red curves is for the Case 1, the black curves is for the Case 2)

mensionless displacement components, evaluated along the top surface of the central Periodic Cell in the Cluster, adopting the heterogeneous model and the corresponding quantities derived from the first order homogenized model. In particular, in Figure 5(a) the dimensionless macroscopic and microscopic electric potentials, $\Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{qh})$ and $\phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{qh})$, respectively, evaluated along the top surface of the central Periodic Cell, are plotted, confirming the effectiveness of the homogenized model in predicting the averaged behaviour of the heterogeneous model. Finally, in Figure 5(b), both the dimensionless macroscopic and the microscopic displacement components, $U_3 \sigma_{3333}^{ZnO} / (qh)$ and $u_3 C_{3333}^{ZnO} / (qh)$, respectively, are compared with each other, again in good agreement.

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Fig. 5: Comparison between the heterogeneous model (blue surfaces) and the equivalent homogenized model (red surfaces). (a) Dimensionless potential of the heterogeneous model $\phi \sqrt{\beta_{33}^{\text{ZnO}}/(\sqrt{q}h)}$ and dimensionless potential of the homogenized model $\Phi \sqrt{\beta_{33}^{\text{ZnO}}/(\sqrt{q}h)}$ along the top surface of the central Periodic Cell; (b) Dimensionless displacement component of the heterogeneous model $u_3 C_{3333}^{\text{ZnO}}/(q h)$ and dimensionless displacement component of the homogenized model $U_3 C_{3333}^{\text{ZnO}}/(q h)$ along the top surface of the central Periodic Cell.

7 Applications of the asymptotic piezoelectric homogenization to microstructured nanogenerators

In this Section, the behaviour of three piezoelectric microstructured nanogenerators, with different working principles, is investigated as a set of geometrical parameters changes. Both extension and bending nanogenerators are taken into account, considering either extension along the nanorods axis, or orthogonally to it. The influence of either the height of nanorods and their density on the overall behaviour of such devices is analysed. These geometric parameters can be, indeed, properly modified during the synthesis process of the ZnO-nanorods cluster, in order to tune the overall piezoelectric response and obtain improved performances, to possibly orient a final user towards optimal design choices.

In Subsection 7.1 microstructured extension nanogenerators are investigated. In this case, mechanical loads act along the nanorods axis and the related potential differences are evaluated. Moreover, in Sub-
section 7.2. Microstructured bending nanogenerators are analysed. The bending behaviour is induced by properly defined boundary conditions. Finally, in Subsection 7.3, microstructured transversal extension nanogenerators are taken into account. The extension/contraction behaviour is due to the adoption of appropriate boundary conditions. In all the considered cases, the homogenized equivalent response of the device at hand is examined. Finite elements analyses have been performed adopting fully coupled tetrahedral second order elements with displacements and electric potential independent degrees of freedom. Note that we are particularly interested in determining the potential difference $\Delta \Phi$ measured between the top and bottom faces of the nanogenerator.

### 7.1 Microstructured extension nanogenerators

We consider a microstructured device made of a cluster of $5 \times 5$ Periodic Cells, with base dimension $L$ and height $h$. Electrodes are present on the upper and lower surfaces of the device. The heterogeneous material is ideally replaced by a homogeneous equivalent piezoelectric first order continuum, obtained by exploiting the proposed asymptotic homogenization approach, see Figure 6 where a sketch is shown.

![Microstructured extension generator](image)

![First order equivalent material](image)

**Fig. 6:** Two-scales description of the extensional nanogenerator made by a cluster of $5 \times 5$ Periodic Cells.

Two loading conditions are alternatively taken into account, i.e. a uniform surface load, and a load with fixed resultant, both applied on the top horizontal face. Moreover, the multiscale analyses are performed assuming either free (*Case 1*) or restrained (*Case 2*) lateral vertical faces of the cluster, according to what proposed in the previous Section 6.2.

The initial investigation relates the influence of the nanorods density $\delta$ on the overall piezoelectric response of the devices. In Figure 7 a set of clusters made of $5 \times 5$ Periodic Cells, corresponding to various densities is reported.

We first consider the uniform surface load. In Figure 8, the overall response of the nanogenerators is
Fig. 7: Schematic of the extensional nanogenerator as the density $\delta$ varies, while the height of the ZnO nanorods is kept constant.

Fig. 8: Uniform surface load: (a) dimensionless potential difference $\Delta \Phi \sqrt{\beta_{33}^{\text{ZnO}}} / (\sqrt{q h})$ versus $\delta$; (b) dimensionless displacement component $U_3 C_{3333}^{\text{ZnO}} / (q h)$ versus $\delta$. Blue curves refer to the case with free lateral faces, while red curves to the case with fixed lateral faces.
Fig. 9: Load with fixed resultant: (a) dimensionless potential difference $\Delta \Phi \sqrt{\frac{\beta_{33}^{ZnO}}{\sqrt{R}}}$ versus $\delta$; (b) dimensionless displacement component $U_3 C_{3333}^{ZnO} h / R$ versus $\delta$. Blue curves refer to the case with free lateral faces, while red curves to the case with fixed lateral faces.

reported in terms of averaged values, referred to the central Periodic Cell of the cluster, of the dimensionless potential difference and dimensionless vertical displacements versus $\delta$ are reported. In particular, in Figure 8(a) the dimensionless values of $\Delta \Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{qh})$ where $\beta_{33}$ is the 33 component of the permittivity matrix of the bulk Zinc Oxyde material, are shown versus $\delta$. The blue curve refers to Case 1, while the red curve to Case 2. It is interesting to notice that the optimal behaviour, that maximizes the potential difference of the device, is achieved for different values of $\delta$ considering either Case 1 or Case 2. The maximum values of the curves correspond to small $\delta$ in the range between 0.1 and 0.2. Moreover, in Figure 8(b) the dimensionless values of $U_3 C_{3333}^{ZnO} / (qh)$, are shown as $\delta$ varies. As expected, the vertical displacements of the central cell increase as the density decreases. The sensor with free faces (Case 1) is more flexible than the other. Similarly, the case where the resultant load is kept constant on clusters of variable densities is considered. In Figure 9, the overall response of the sensors in terms of averaged values, referred to the central cell, of $\Delta \Phi$ and $U_3$ versus $\delta$ are plotted. In this case the normalization is performed considering the load resultant $R$. Referring to Figure 9(a), it is confirmed that the sensor with free faces (blue curve) is characterized by higher sensitivity (better performances). Nevertheless, the maximum of the curves is achieved for values of $\delta$ in the range between 0.4 and 0.5, that is shifted to the right with respect to the previous case. Also considering the vertical displacements in Figure 9(b), again the blue curve (sensor with free lateral faces) is always below the red one.

Furthermore, the influence of the height $h$, directly related to the the nanorods length, is investigated.
Fig. 10: Uniform surface load: (a) dimensionless potential difference $\Delta \varphi \sqrt{\beta_{33}}/(\sqrt{qL})$ versus $\alpha$; (b) dimensionless displacement component $U_3 C_{3333}/(qL)$ versus $\delta$. Blue curves refer to the case with free lateral faces, while red curves to the case with fixed lateral faces.

Fig. 11: Load with fixed resultant: (a) dimensionless potential difference $\Delta \varphi \sqrt{\beta_{33}}/(\sqrt{R})$ versus $\alpha$; (b) dimensionless displacement component $U_3 C_{3333}/R$ versus $\delta$. Blue curves refer to the case with free lateral faces, while red curves to the case with fixed lateral faces.
Considering again both the cases with uniform surface load, and load with fixed resultant, the response of the sensors for Case 1 and Case 2 is investigated. For each of the four analysed cases, the density $\delta$ that maximize the corresponding responses in Figures 8(a) and 9(a) is taken into account. Starting with uniform surface load, in Figure 10 the response in terms of averaged values of $\Delta \Phi$ and $U_3$ versus $\alpha$ are reported. The dimensionless value $\alpha$ is let varying between 0.5 and 2 and is equal to the ratio between the actual height of the device $h$ and a reference value of $h^*=1100$ nm. As expected, a nearly linear variation of $\Delta \Phi \sqrt{\beta_{33}}/(\sqrt{qh})$, as $\alpha$ varies, is found, see Figure 10(a). In the case with free faces, blue curves, higher values of both potential difference and vertical displacements are observed. Finally, the results for the load with fixed resultant are shown in Figure 11. Again a linear variation of the dimensionless potential difference versus $\alpha$ is found. On the other hand, concerning the vertical displacements, a nearly linear variation is observed. It is confirmed that the microstructured extension nanogenerators with free faces provide the better response in terms of potential difference, and are more flexible.

7.2 Microstructured bending nanogenerators

A key point of the hybrid flexible nanogenerators is the possibility to exploit flexural mechanisms, related to the bending of the base support, to ensure energy harvesting. This peculiar behaviour is particularly emphasized in such innovative flexible devices, differently from what happen with standard ZnO-nanorods nanogenerator, provided with rigid supports, in which this behaviour is inhibited. Therefore, in this Section, the bending behaviour of such hybrid flexible nanogenerators is investigated and critically commented.

We consider devices made of a cluster of periodic cells topped by a further layer of electroactive polymeric material, see Figure 12(a) where a schematic of the microstructured nanogenerator is depicted. Adopting this particular geometry, we are interested in investigating how the thickness of the top layer influences the overall behaviour of the bending nanogenerator, inspired by the work by Opoku and co-authors, (Opoku et al., 2015). Two electrodes are located at the top and bottom faces of the microstructured device.

This problem is solved via a multi-scale approach, suitable to reduce high computational costs related to the adoption of micromechanical models. In particular, the cluster of periodic cells is preliminary homogenized into an equivalent piezoelectric first order continuum by exploiting the asymptotic homogenization approach. The resulting two-phase composite equivalent material is depicted in Figure 12(a), where the bottom layer is a homogeneous material characterized by overall piezoelectric constitutive tensors equivalent to periodic cells, and the top layer is a homogeneous electroactive polymer. The two-phase device is bent by applying opposite rigid rotations $\Theta$ to the lateral faces (with normal parallel to $x_2$), around the axis $x_1$, that falls at half the height of the device, see Figure 12(a). The qualitative deformed shape of this device is reported in Figure 12(b). Again, two set of boundary conditions are considered, characterized either by free longitudinal faces (with normal parallel to $x_1$) or by longitudinal faces with restricted
displacements in the $x_1$ direction. It results that in this framework, the potential $\Phi$ is only dependent on the $x_3$ axis, i.e. is uniform in $x_1$ and $x_2$, so that the potential difference, measured between two opposite points laying on the top and bottom faces (orthogonal to the $x_3$ axis), is constant.

A set of numerical analyses is proposed hereafter, where we consider the geometry of the device associated with a cluster of $15 \times 5$ periodic cells and adopting for the top layer the same polymeric material of the matrix, i.e. with Young modulus $E = 535$ MPa and Poisson’s coefficient equal to $\nu = 0.4$. The relative permittivity is $\beta = 3$.

In a first investigation we let the thickness of the top layer $h_t$ vary between 0 nm and 1100 nm (so that the maximum total height is $h + h_t = 2200$ nm). Considering a reference heterogeneous material with nanorods density $\delta = 0.415$, a rigid rotation $\Theta = 1/100$ radians is applied. In Figure 13, the overall response of the
Fig. 13: Bending nanogenerators obtained by homogenizing a cluster of $15 \times 5$ nanorods with $\delta = 0.415$. (a) Dimensionless potential difference $\Delta \Phi \sqrt{\beta_{33}^ZnO} / (\sqrt{C_{3333}^ZnO} (h + h_t))$ versus $h_t$; (b) dimensionless displacement component $U_3 / (h + h_t)$ versus $h_t$.

nanogenerators in terms of the potential difference and of displacement component $U_3$ (measured in the geometric center of the top face) versus $h_t$ are reported. In Figure 13(a), $\Delta \Phi \sqrt{\beta_{33}^ZnO} / (\sqrt{C_{3333}^ZnO} (h + h_t))$ is plotted versus $h_t$ for both the cases with free (blue curve) and prescribed (red curve) lateral displacements. It clearly emerges that when $h_t = 0$ nm, no potential difference is measured, while as soon as the thickness $h_t$ of the top layer is greater than zero, increasingly higher values are found. Better performances are experienced by the device with prescribed displacements. Concerning the dimensionless displacement component $U_3 / (h + h_t)$ shown in Figure 13(b) versus $h_t$, nearly linear trends are observed. The red and blue curves intersect each other around $h_t = 300$ nm, so that below this value the case with fixed longitudinal faces is more flexible than the other. Note that similar trends of both dimensionless $\Delta \Phi$ and $U_3$ are found for different values of $\delta$ referred to the corresponding heterogeneous material.

A principal outcome of this first study is that the nanogenerator exhibits the best performances with maximum values of $h_t$. It follows that the second investigation concerns the analysis of bending nanogenerators with $h_t = 1100$ nm as the density $\delta$ of the corresponding heterogeneous material varies. In Figure 14(a), the dimensionless potential difference $\Delta \Phi \sqrt{\beta_{33}^ZnO} / (\sqrt{C_{3333}^ZnO} (h + h_t))$ is plotted versus the density $\delta$. As before, blue curves refer to the case with free longitudinal faces, while and red curves refer to the case with displacements fixed. An interesting nonlinear behaviour is found, with the potential difference that increases with $\delta$. Also in this case, better performances are provided by the device with prevented lateral displacements (red curve). A nonlinear response is also confirmed in the dimensionless displace-
ment component $U_3/(h + h_t)$. The curves are nearly indistinguishable for low values of $\delta$, while as $\delta > 0.2$ are increasingly far apart. Finally, it can be remarked that the bending nanogenerators show optimal behaviours when designed with very thick top layers, fixed lateral faces and high nanorods densities.

7.3 Microstructured transversal extension nanogenerators

The same devices analysed in Section 7.2 is here investigated adopting a different working principle related to transversal extension mechanism. Similarly to the previous case, the considered devices are made of a cluster of periodic cells topped with a polymeric layer of variable thickness. Again the multi-scale approach is adopted to obtain a two-phase composite equivalent material, see in Figure 12(a). The same geometries and materials as in Section 7.2 are taken into account. The two-phase device undergoes uniform opposite displacements along $x_2$ direction applied to the lateral faces (with normal parallel to $x_2$) inducing an overall extension $\Delta U_2 = 10$ nm of the nanogenerator. Moreover, the displacements of the points on the bottom face are restricted in the $x_3$ direction. The qualitative deformed shape of this device is reported in Figure 12(c). We choose $\Delta U_2$ so that it is comparable with the maximum displacement in the direction $x_2$ induced by the bending (when $h_t = 1100$ nm) in the previous Section. Again, the displacement components along the $x_1$ direction of the longitudinal faces are alternatively free or set equal to zero.

Also in this case, first the influence of the thickness $h_t$ of the top layer (for a fixed corresponding density
δ=0.415) is investigated, and then the response as the corresponding density δ varies (for $h_t=1100\text{ nm}$) is studied. In Figure 15(a), the dimensionless potential difference $\Delta\Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{C_{3333}^{ZnO}} (h + h_t))$ versus $h_t$ is shown for both the cases with free longitudinal faces (blue curve) and restrained faces (red curve). As expected, nearly constant values of potential difference are found, irrespective of the thickness $h_t$. Moreover, the case with fixed longitudinal faces provides higher potential differences. On the other hand, concerning the vertical displacement $U_3/(h + h_t)$, pseudo-linear variations are observed as $h_t$ varies.

Finally, for the case with $h_t=1100\text{ nm}$, the dimensionless potential difference $\Delta\Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{C_{3333}^{ZnO}} (h + h_t))$ is shown in Figure 16(a), while the dimensionless displacement components $U_3/(h + h_t)$, of the points laying on the top face, is plotted in Figure 16(b) versus the corresponding density δ of the heterogeneous ZnO based hybrid nanogenerator. The plots of the potential difference with δ are almost overlapping with those in Figure 14(a). It is, nevertheless, noted that a qualitative different distribution of the macroscopic electric potential $\Phi$ along the height $(h + h_t)$ of the specimen is observed in the case of bending nanogenerators and transversal extension nanogenerators. In particular, a nonlinear and a linear monotonic trends are observed, along the height of the bottom homogenized layer, in the former and the latter cases, respectively. Moreover, in both cases a nearly constant value is maintained within the polymeric top layer. Concerning the $U_3$ displacement components, as expected, significantly lower values are found (one order of magnitude lower) with respect to the Figure 14(b). It is noteworthy that in the case of
Fig. 16: Uniform traction of an cluster of $15 \times 5$ nanorods with $h_t=1050$ nm. (a) dimensionless potential difference $\Delta \Phi \sqrt{\beta_{33}^{ZnO}} / (\sqrt{C_{3333}^{ZnO}} h_t)$ versus $\delta$; (b) dimensionless vertical displacement $U_3/h$ versus $\delta$.

8 Bloch waves in piezoelectric nanogenerators

This Section is devoted to investigate the dynamic characterization of the piezoelectric periodic nanos- tructured material for the purpose of analysing the Bloch waves propagation. In particular, the frequency spectrum of the heterogeneous material is obtained for different unit vectors of propagation. Moreover the acoustic branches of such frequency spectrum are compared against the dispersion functions obtained by the homogenized model.

Different Periodic Cells $\mathcal{A} = [-d/2, d/2] \times [-d/2, h/2]$ of the microstructured nanogenerators are considered (see Figure 2(a)), characterized by various nanorods densities $\delta$. The ZnO-nanorod has hexagonal section with edge 80 nm, while the height in the polarization direction is $h=1100$ nm. The ZnO nanorod is embedded within a polymeric matrix ($E=535$ MPa, $\nu=0.4$ and $\beta=3$). The same polymeric material is adopted for the top and bottom layers. The mass density of the nanorod is $\rho_{ZnO} = 5680$ kg/m$^3$, while the mass density of the polymeric material is set equal to $\rho=1500$ kg/m$^3$. In this framework, the Periodic Cell $\mathcal{A}$ is associated with the dimensionless first Brillouin zone $\mathcal{B} = [-\pi, \pi] \times [-\pi, \pi] \times [-\pi, \pi]$, defined in the space of the dimensionless wave vectors (whose components are $k_1d$, $k_2d$ and $k_3h$). Such Brillouin zone is characterized by three orthogonal vectors $\pi_i n_i$, parallel to $e_i$, with $i=1,2,3$. 
The influence of the nanorods density $\delta$ on the Floquet-Bloch spectrum, as the unit vector of propagation $\mathbf{n}$ varies, is thus analysed. In particular, the wave vector Main attention is devoted to identifying the existence, the position and the frequency range of full or partial band gaps in the microstructured piezoelectric material. Note that in this case of nanogenerators, the Bloch spectrum analysis is particularly relevant in view of providing design guidelines. Such devices are, indeed, intended to operate under dynamical loadings that can trigger the electrical energy production. A detailed investigation concerning the band gaps is very useful to identify possible frequency ranges in which the device behaves as a filter. It is, thus, clear that a dynamical loading is supposed to be characterized by frequencies falling outside frequency band gaps, in order to be effective.

The values of the dimensionless angular frequency $\omega h \sqrt{\rho_{\text{ZnO}}} / \sqrt{C_{3333}^{\text{ZnO}}}$, against the dimensionless wave number $k_3 h$, related to the unit vector of propagation $\mathbf{n}_3$ parallel to $\mathbf{e}_3$, are shown in Figure 17 for three densities $\delta$ equal to 0.57, 0.415 and 0.10, respectively. The piezoelectric nanogenerator exhibits a high spectral density for all the densities. The first 15 branches of the spectrum are plotted in dark blue, while the other ones in light blue. In particular, in Figure 17(a) the Floquet-Bloch spectrum for density $\delta=0.57$ is plotted. Only ten curves are visible, since multiple roots are found by virtue of material symmetry characterizing the Periodic Cell. As expected, three acoustic branches departs from zero angular frequency (in the Figure only two are distinguishable, since two of them are coincident). The remaining 8 curves are the
optical branches. The Floquet-Bloch spectrum exhibits one point of crossing between acoustic and optical branches and also a point of crossing between different optical branches. Four partial band gaps are detected. In Figure 17(b), instead, the Floquet-Bloch spectrum for the material with density $\delta=0.415$ is plotted. The spectrum is qualitatively similar to the previous one, in Figure 17(a). The first three acoustic branches and the first two optical branches (two coincident curves) are very similar to the corresponding ones for $\delta=0.57$. On the other hand all the remaining branches are pulled down, resulting in curves closer together (more dense spectrum) and partial band gaps basically characterized by lower amplitudes. As a consequence, the relative position of the band gaps is shifted towards lower frequencies. Moreover, in Figure 17(c) the Floquet-Bloch spectrum for the material with density $\delta=0.1$ is shown. The same trend of Figure 17(b) is confirmed and emphasized. Again the first three acoustic branches and the first two optical branches remain almost unchanged, but all the others are shifted towards smaller angular frequencies. A very dense spectrum is observed. This analysis suggests that, by focusing on a given frequency interval, for instance $0 < \omega \sqrt{\rho_{ZnO}} / \sqrt{C_{3333}^{ZnO}} < 1$, as the density $\delta$ decreases, the microstructured piezoelectric device exhibits better performances, since the spectrum is more dense. A considerably broader passband width is, indeed, found. The acoustic branches of the Floquet-Bloch spectrum that characterize the heterogeneous material are compared against the dispersion curves obtained adopting the first order homogenization theory (red curves in Figure 17). A good agreement is found, confirming the capability of the first order homogenization theory to satisfactorily reproducing the lowest (acoustic) branches of the Bloch spectrum for a wide range of wavelengths. As expected, the model at the first order only describes non-dispersive waves exhibiting a linear dependence between the angular frequency and the wave-number.

A further investigation concerns the Floquet-Bloch spectrum for waves characterized by unit vector of propagation $\textbf{n}_3$, studying the influence of the height of the nanorods, considering the parameter $\alpha = h/h^*$, as the height $h$ varies with $h^*=1100$ nm. A density $\delta=0.415$ is considered. In this case, the dimensionless angular frequency $\omega \sqrt{\rho_{ZnO}} / \sqrt{C_{3333}^{ZnO}}$, against the dimensionless wave number $k_3 h$, are shown in Figure 18 for three heights $h$ equal to 550 nm, 1650 nm and 2200 nm, respectively. The first 15 branches of the spectrum are plotted in dark blue, while the others are plotted in light blue. It is remarked that, in the considered frequency range, the spectral density tends to increase as the height $h$ increases. In Figure 18(a), the case with $h=0.5 h^*$ is taken into account. A wide partial band gap is found with central dimensionless frequency around 1.2, while a second partial band gap is characterized by lower amplitude and higher central angular frequency. Again various crossing points are observed. Figures 18(b), and 18(c) shows the cases with $h=1.5 h^*$ and $h=2 h^*$, respectively. As the height increases, a higher number of partial band gaps, characterized by lower frequencies, are observed. The acoustic and optical branches tend to be shifted towards lower angular frequencies. Also in this case, the red curves represent the acoustic branches of the Floquet-Bloch spectrum obtained via a first order homogenization approach. Such linear dispersion functions are in good agreement with the the lowest (acoustic) branches of the Bloch spec-
Fig. 18: Floquet-Bloch spectra for unit vector of propagation \( \mathbf{n}_3 \) for different ratios between the height \( h \) of the ZnO nanorod and the reference height \( h^* = 1100 \) nm. The dimensionless angular frequency \( \omega h^* \sqrt{\rho_{ZnO}} / \sqrt{C_{3333}} \) is plotted versus versus the dimensionless wave number \( k_3 h \). (a) \( h = 0.5 h^* \); (b) \( h = 1.5 h^* \); (c) \( h = 2 h^* \).

A similar investigation, concerning both the influence of the density \( \delta \) and of the height \( h \), is performed considering the unit vector of propagation \( \mathbf{n}_1 \) parallel to \( \mathbf{e}_1 \). Also in this case, the first 15 branches of the spectrum are plotted in dark blue, while the others are plotted in light blue. In Figure 19, three densities \( \delta \) equal to 0.57, 0.415 and 0.10, respectively, are taken into account. Very dense spectra are here observed, where no partial band gaps are detected irrespective of the considered density. It is confirmed that the spectrum density increases as the density \( \delta \) decreases. Focusing on Figure 19(a), various crossing points and a veering point (with dimensionless frequency about 2) are found. Three distinct acoustic branches are observed, well approximated by the dispersion functions (red linear curves) obtained by the first order piezoelectric continuum. It is, moreover, noted that the first two acoustic branches tend to overlap each other as the density \( \delta \) decreases. It is noteworthy that in the long wave regime the phase and group velocity, associated with the acoustic branches, tend to decrease as the density \( \delta \) decreases.

Analogous considerations are valid for the Figure 20, in which the dimensionless angular frequency \( \omega h \sqrt{\rho_{ZnO}} / \sqrt{C_{3333}} \), against the dimensionless wave number \( k_1 d \), are shown, for three heights \( h \) equal to 550 nm, 1650 nm and 2200 nm, respectively, adopting \( \delta = 0.415 \). Also in this case, indeed, no partial band gaps are detected, and the spectrum density increases as the height \( h \) increases. Various crossing and points are found. Finally, three distinct acoustic branches are observed, well approximated by the red
Fig. 19: Floquet-Bloch spectra for unit vector of propagation $\mathbf{n}_1$ and different densities $\delta$ of the piezoelectric composite material. The dimensionless angular frequency $\omega h \sqrt{\rho_{\text{ZnO}}/C_{\text{ZnO}3333}^*}$ is plotted versus the dimensionless wave number $k_1d$. (a) $\delta=0.57$; (b) $\delta=0.415$; (c) $\delta=0.10$.

Fig. 20: Floquet-Bloch spectra for unit vector of propagation $\mathbf{n}_1$ for different ratios between the height $h$ of the ZnO nanorod and the reference height $h^*=1100$ nm. The dimensionless angular frequency $\omega h^* \sqrt{\rho_{\text{ZnO}}/C_{\text{ZnO}3333}^*}$ is plotted versus the dimensionless wave number $k_1d$. (a) $h=0.5~h^*$; (b) $h=1.5~h^*$; (c) $h=2~h^*$. 

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linear curves, representing the dispersion functions of a first order homogeneous equivalent continuum. A more comprehensive description of the acoustic characteristics of the piezoelectric nanoscopic mate-

![Image](image.png)

Fig. 21: Axonometric view of the Floquet-Bloch spectra for unit vector of propagation \( \mathbf{n} \) laying on the plane with normal \( \mathbf{n}_3 \). (a) First 15 surfaces; (b) zoomed view of the partial band gap.

rial is given by the dispersion surfaces in the Brillouin zone, representing the dimensionless angular frequency \( \omega h \sqrt{\rho Z_{n0}} / \sqrt{C_{3333} Z_{n0}} \) of waves characterized by unit vector of propagation \( \mathbf{n} = \cos \theta \mathbf{n}_1 + \sin \theta \mathbf{n}_2 \), with \( 0 \leq \theta \leq \pi/2 \). In Figure 21(a), an axonometric view is show for the case with density \( \delta = 0.415 \). In the domain of considered wave vectors, a high spectral density is observed, since the acoustic surfaces intersect the first optical ones and, moreover, the optical surfaces at higher frequencies intersect each other over and over. One partial band gap is detected between the eight and ninth surfaces.

In particular, in Figure 21(a) a zoomed view of the surfaces defining the partial band gap is shown. As a consequence, in this range the propagation of waves characterized by \( k_3 = 0 \) is inhibited.
9 Final Remarks

Hybrid piezoelectric nanogenerators, made of Zinc Oxide nanorods, embedded into a polymeric matrix and growth on a flexible polymeric supports, are investigated. Due to the high density and nearly regular distribution of the nanorods an equivalent periodic topology can be considered. The resulting device is made of a microstructured composite material, whose global response is strongly influenced by the microstructure, i.e. by the geometry and materials properties of each constituents and by their collaborative behaviour.

In such case, a very detailed description could be obtained via micromechanical approaches, resulting in often too cumbersome analyses. For this reason, multi-scale techniques can be alternatively used, being a very valuable tool to gather the overall behaviour. In this framework, a dynamic asymptotic homogenization approach, for periodic piezoelectric composites, is proposed. By exploiting this homogenization approach, a rigorous constitutive characterization of the periodic piezoelectric microstructured material is carried out, with the aim of optimizing their performances by analysing the behaviour of the material/device in the space of the physical-mechanical parameters. Among different parameters, focus is on the influence of both the height of the nanorods and of the density (defined as ratio between the volume occupied by the nanorods and the volume of the Periodic Cell), since during the synthesis process of the samples it is possible to directly modify those parameters. Under the assumption of considering an equivalent homogenized material at the macroscopic scale, also analytical solutions are found, providing benchmark comparative solutions. Almost perfect match is found by comparing the macroscopic analytic results with those obtained by the heterogeneous model via up-scaling relations, by confirming the optimal accuracy of the proposed homogenization scheme.

The behaviour of three piezoelectric microstructured nanogenerators, characterized by different working principles, is studied as a set of geometrical parameters changes. Both extension and bending nanogenerators are taken into account, considering either extension along the nanorods axis, or orthogonally to it. The influence of either the height of nanorods and their density on the overall behaviour of such devices is analysed. Concerning the microstructured extension nanogenerators, both cases of uniform surface load and load with fixed resultant have been investigated. In the first case, maximum values of the potential differences are observed for low values of the density, in the range 0.1-0.2. In the second case, instead, the maximum potential differences correspond to higher values of 0.4-0.5. As expected, the variation of the nanorods height determine a grossly linear variation of the potential difference in the considered nanogenerator. In all the analysed case, it is noted that devices with free lateral faces exhibit better performances in terms of potential difference, with respect to the corresponding ones with constrained faces. With reference to microstructured bending nanogenerators, it is noted that an improved response is achieved by adding a further top layer, of increasing thickness, on the initial composite material made of two equal layers sandwiching the periodically distributed nanorods, embedded into the polymeric matrix. Moreover, for a fixed thickness of the additional top layer, the best response in terms of potential differ-
ence is observed for the highest values of the nanorods density. As regards the microstructured transversal extension nanogenerators, it emerges that the response, in terms of potential difference, is not affected by the thickness of the additional top layer. Moreover, for a fixed thickness, again the best response is observed for the highest values of the nanorods density.

With reference to the study in the dynamic regime, the free wave propagation in such a periodic material is analysed. Considering waves travelling along the nanorods axis, it turns out that as the material density decreases and the height of nanorods increases, more dense spectra are found. Moreover, various partial partial band gaps are detected for higher values of density, suggesting that lower values of the density enables better functioning as nanogenerators. As the nanorods height increases, a higher number of partial band gaps, characterized by lower frequencies, are observed. The acoustic and optical branches tend to be shifted towards lower angular frequencies. Finally, with reference to waves travelling in the plane normal to the nanorods axis, very dense spectra are here observed, where no partial band gaps, in the low frequency range, are detected irrespective of the considered density and height (few partial band gaps are found in the high frequency and characterized by small amplitudes). It is confirmed that the spectrum density increases as the density decreases and the height increases. The acoustic branches of the Floquet-Bloch spectrum, characterizing the heterogeneous material, are compared against the dispersion curves obtained adopting the first order homogenization theory. A good agreement is found, confirming the capability of the first order homogenization theory to satisfactorily reproducing the lowest (acoustic) branches of the Bloch spectrum for a wide range of wavelengths.

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Appendix A: Solutions of the hierarchical differential problems

The following hierarchical differential problems, expressed in terms of the sensitivities \( u_k^{(j)}, \phi^{(j)} \) of both microscopic displacement \( u_k \) and potential \( \phi \) fields, can be obtained from the asymptotic expansion of the field equations (6) by collecting the terms at the same order of \( \varepsilon \).

More specifically, the recursive problem the at the order \( \varepsilon^{-2} \) reads

\[
\begin{align*}
&C_{ijkl}^{m} u_{k,l}^{(0)}_{i,j} + \left( e_{ijk}^{m} \phi_{k}^{(0)} \right)_{i,j} = f_{i}^{(0)}(x, t), \\
&e_{kli}^{m} u_{k,l}^{(0)}_{i} - \left( \beta_{il}^{m} \phi_{l}^{(0)} \right)_{i} = g^{(0)}(x, t).
\end{align*}
\]  

(43)

The solvability condition in the class of the \( Q \)-periodic functions implies that both source terms vanish, i.e. \( f_{i}^{(0)}(x, t) = 0 \) and \( g^{(0)}(x, t) = 0 \). It follows that the solution of the differential problem is independent on the fast variable \( \xi \) and it takes the form reported in (7).

Analogously, by exploiting the solution of the differential problem (43), the recursive problem the at the order \( \varepsilon^{-1} \) is

\[
\begin{align*}
&C_{ijkl}^{m} u_{k,l}^{(1)}_{i,j} + C_{ijkl}^{m} \frac{\partial U_{k}}{\partial x_{l}} + \left( e_{ijk}^{m} \phi_{k}^{(1)} \right)_{i,j} + e_{ijk,l}^{m} \frac{\partial \phi}{\partial x_{k}} = f_{i}^{(1)}(x, t), \\
&e_{kli}^{m} u_{k,l}^{(1)}_{i} + e_{kli,l}^{m} \frac{\partial U_{k}}{\partial x_{l}} - \left( \beta_{il}^{m} \phi_{l}^{(1)} \right)_{i} - \beta_{il}^{m} \frac{\partial \phi}{\partial x_{l}} = g^{(1)}(x, t).
\end{align*}
\]  

(44)

Here, the solvability condition in the class of the \( Q \)-periodic functions implies that

\[
\begin{align*}
&f_{i}^{(1)}(x, t) = \langle C_{ijkl}^{m} \frac{\partial U_{k}}{\partial x_{l}} + \left( e_{ijk}^{m} \phi_{k}^{(1)} \right)_{i,j} + e_{ijk,l}^{m} \frac{\partial \phi}{\partial x_{k}} \rangle = 0, \\
g^{(1)}(x, t) = \langle e_{kli}^{m} \frac{\partial U_{k}}{\partial x_{l}} - \left( \beta_{il}^{m} \phi_{l}^{(1)} \right)_{i} \rangle = 0,
\end{align*}
\]  

(45)

since the components of the constitutive tensors at the microscopic scale are \( Q \)-periodic. In this case, the solution of the differential problem takes the form reported in (8).

Similarly, the recursive problem the at the order \( \varepsilon^{0} \) is obtained by exploiting the solution of both the differential problems (43) and (44), and it reads

\[
\begin{align*}
&C_{ijkl}^{m} u_{k,l}^{(2)}_{i,j} + \left[ C_{ijkl}^{m} N_{kplt}^{(1)} + C_{ijkl}^{m} N_{kplt}^{(1)} + e_{ijpq}^{m} \tilde{W}_{pq}^{(1)}(x, t) \right] \frac{\partial^{2} U_{p}}{\partial x_{q_{1}} \partial x_{q_{2}}} + \frac{\partial^{2} \phi}{\partial x_{q_{1}} \partial x_{q_{2}}} + \\
&+ \left( e_{ijk}^{m} \phi_{k}^{(2)} \right)_{i,j} + \left[ C_{ijkl}^{m} \tilde{N}_{kq}^{(1)} + C_{ijkl}^{m} \tilde{N}_{kq}^{(1)} + e_{ijpq}^{m} W_{pq}^{(1)}(x, t) \right] \frac{\partial^{2} \phi}{\partial x_{q_{1}} \partial x_{q_{2}}} + \\
&- \rho^{m} \tilde{U}_{i} = f_{i}^{(2)}(x, t),
\end{align*}
\]  

(46)
Finally, the solvability condition in the class of the $Q$-periodic functions implies that

\[
\begin{align*}
\left( c_{klq}^{(2)} \right)_{i} & + \left[ c_{kq1}^{(2)} N_{kq1,1}^{(1)} + e_{kq2}^{m} N_{kq1,1}^{(1)} - \left( \beta_{q2}^{m} \tilde{W}_{pq1}^{(1)} \right)_{i} - \beta_{q2}^{m} \tilde{W}_{pq1,1}^{(1)} \right] \frac{\partial^2 U_p}{\partial x_{q1} \partial x_{q2}} + \\
& - \left( \beta_{q2}^{m} \varphi_{l}^{(2)} \right)_{i} + \left[ c_{kq1}^{(2)} \tilde{N}_{kq1}^{(1)} + e_{kq2}^{m} \tilde{N}_{kq1,1}^{(1)} - \left( \beta_{q2}^{m} W_{q1,1}^{(1)} \right)_{i} - \beta_{q2}^{m} \tilde{W}_{q1,1}^{(1)} \right] \frac{\partial^2 \Phi}{\partial x_{q1} \partial x_{q2}} = g^{(2)}(x, t).
\end{align*}
\]

The solution of the differential problem takes the form reported in (9).

**Appendix B: Average field equation of infinite order**

By plugging the down-scaling relations (15) in the field equations (1), i.e. by reassembling the recursive differential problems at different $\varepsilon$ orders (43), (44) and (46), the following average field equation of infinite order are obtained as

\[
\begin{align*}
\left( n_{ipq1q2}^{(2,0)} \right) \frac{\partial^2 U_p}{\partial x_{q1} \partial x_{q2}} + \left( n_{iq1q2}^{(2,0)} \right) \frac{\partial^2 \Phi}{\partial x_{q1} \partial x_{q2}} - n_{ip}^{(2,0)} \tilde{U}_p + O(\varepsilon) + b_{i}(x) &= 0, \\
\left( \tilde{w}_{pq1q2}^{(2,0)} \right) \frac{\partial^2 U_p}{\partial x_{q1} \partial x_{q2}} - \left( w_{q1q2}^{(2,0)} \right) \frac{\partial^2 \Phi}{\partial x_{q1} \partial x_{q2}} + O(\varepsilon) - \rho_{e}(x) &= 0, \tag{48}
\end{align*}
\]

where the components of the constant global constitutive tensors, involved in the governing equations, take the form

\[
\begin{align*}
n_{ipq1q2}^{(2,0)} &= \frac{1}{2} \left( c_{iq1q2}^{m} + c_{iq2q1}^{m} N_{kq1,1}^{(1)} + e_{iq2q1}^{m} \tilde{W}_{k}^{(1)} + c_{iq1k}^{m} N_{kq1,1}^{(1)} + e_{iq1k}^{m} \tilde{W}_{k}^{(1)} \right), \\
\tilde{n}_{iq1q2}^{(2,0)} &= \frac{1}{2} \left( c_{iq2q1}^{m} \tilde{N}_{kq1,1}^{(1)} + e_{iq2q1}^{m} W_{q1,k}^{(1)} + c_{iq1k}^{m} \tilde{N}_{kq1,1}^{(1)} + e_{iq1k}^{m} W_{q1,k}^{(1)} \right), \\
n_{ip}^{(2,0)} &= \left( \rho_{e}^{m} \right) \delta_{ip}, \tag{49}
\end{align*}
\]

\[
\begin{align*}
\tilde{w}_{pq1q2}^{(2,0)} &= \frac{1}{2} \left( e_{klq2}^{m} N_{kq1,1}^{(1)} + e_{pq2q1}^{m} - \beta_{q2}^{m} W_{pq1,1}^{(1)} + e_{klq1}^{m} N_{kq1,1}^{(1)} + e_{pq1q2}^{m} - \beta_{q2}^{m} \tilde{W}_{pq1,1}^{(1)} \right), \\
w_{q1q2}^{(2,0)} &= \frac{1}{2} \left( \beta_{q1q2}^{m} W_{q1,1}^{(1)} - e_{klq2}^{m} \tilde{N}_{kq1,1}^{(1)} + \beta_{q2}^{m} W_{q2,1}^{(1)} - e_{klq1}^{m} \tilde{N}_{kq1,1}^{(1)} \right).
\end{align*}
\]
In order to obtain a formal solution of equations (48), the macroscopic variables $U_k$ and $\Phi$ are asymptotically expanded as follows

$$U_k(x, t) = \sum_{j=0}^{+\infty} \varepsilon^j U_k^{(j)}(x, t),$$

$$\Phi(x, t) = \sum_{j=0}^{+\infty} \varepsilon^j \Phi^{(j)}(x, t).$$

(50)

By plugging (50) into the (48), the asymptotic expansion of the average field equation of infinite order takes the form

$$n_{ipq1q2}^{(2,0)} \left( \frac{\partial^2 U_p^{(0)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon \frac{\partial^2 U_p^{(1)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon^2 \frac{\partial^2 U_p^{(2)}}{\partial x_{q_1} \partial x_{q_2}} + \ldots \right) + \tilde{n}_{ipq1q2}^{(2,0)} \left( \frac{\partial^2 \Phi^{(0)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon \frac{\partial^2 \Phi^{(1)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon^2 \frac{\partial^2 \Phi^{(2)}}{\partial x_{q_1} \partial x_{q_2}} + \ldots \right) + b_i(x) = 0,$$

$$w_{ipq1q2}^{(2,0)} \left( \frac{\partial^2 U_p^{(0)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon \frac{\partial^2 U_p^{(1)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon^2 \frac{\partial^2 U_p^{(2)}}{\partial x_{q_1} \partial x_{q_2}} + \ldots \right) - w_{ipq1q2}^{(2,0)} \left( \frac{\partial^2 \Phi^{(0)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon \frac{\partial^2 \Phi^{(1)}}{\partial x_{q_1} \partial x_{q_2}} + \varepsilon^2 \frac{\partial^2 \Phi^{(2)}}{\partial x_{q_1} \partial x_{q_2}} + \ldots \right) - \rho_e(x) = 0.$$

(51)

In particular, by collecting the terms in (51) at the same order of $\varepsilon$, an infinite set of macroscopic hierarchical differential problems, expressed in terms of the sensitivities $U_p^{(j)}$, $\Phi^{(j)}$ of both macroscopic displacement $U_p$ and potential $\Phi$ fields can be determined. Namely, the recursive problem at the macroscopic scale of order $\varepsilon^0$ reads

$$n_{ipq1q2}^{(2,0)} \frac{\partial^2 U_p^{(0)}}{\partial x_{q_1} \partial x_{q_2}} + \tilde{n}_{ipq1q2}^{(2,0)} \frac{\partial^2 \Phi^{(0)}}{\partial x_{q_1} \partial x_{q_2}} - n_{ip}^{(2,0)} \hat{U}_p^{(0)} + b_1(x) = 0,$$

$$w_{ipq1q2}^{(2,0)} \frac{\partial^2 U_p^{(0)}}{\partial x_{q_1} \partial x_{q_2}} - w_{ipq1q2}^{(2,0)} \frac{\partial^2 \Phi^{(0)}}{\partial x_{q_1} \partial x_{q_2}} - \rho_e(x) = 0,$$

(52)

while the generic recursive problem at the macroscopic scale of order $\varepsilon^m$ with $m \in \mathbb{Z}$, $m \geq 1$, is found as

$$n_{ipq1q2}^{(2,0)} \frac{\partial^2 U_p^{(m)}}{\partial x_{q_1} \partial x_{q_2}} + \tilde{n}_{ipq1q2}^{(2,0)} \frac{\partial^2 \Phi^{(m)}}{\partial x_{q_1} \partial x_{q_2}} - n_{ip}^{(2,0)} \hat{U}_p^{(m)} + s_i^{(m)}(x, t) = 0,$$

$$w_{ipq1q2}^{(2,0)} \frac{\partial^2 U_p^{(m)}}{\partial x_{q_1} \partial x_{q_2}} - w_{ipq1q2}^{(2,0)} \frac{\partial^2 \Phi^{(m)}}{\partial x_{q_1} \partial x_{q_2}} - \psi^{(m)}(x, t) = 0,$$

(53)
where $s_i^{(m)}$ and $v^{(m)}$ are known $\mathcal{L}$-periodic fields, playing the role of source terms. Such fields depend both on higher order constant tensors, that appear in the terms at orders equal or higher than $\varepsilon^m$ of the average field equation of infinite order (48), and on sensitivities $U_k^{(j)}$ and $\Phi^{(j)}$ descending from macroscopic hierarchical differential problems of order lower than $\varepsilon^m$.

Due to the $\mathcal{L}$-periodicity of the source terms, the solution of equations (52) and (53) are in turn $\mathcal{L}$-periodic. More specifically, the uniqueness of such solution is guaranteed by the fulfilment of the following normalization conditions:

$$\frac{1}{|\mathcal{L}|} \int_{\mathcal{L}} U^{(m)} dx = 0$$

$$\frac{1}{|\mathcal{L}|} \int_{\mathcal{L}} \Phi^{(m)} dx = 0$$

where $|\mathcal{L}| = \eta L^3$.

It is worth noting that the formal structure of equation (53) is the same as the one of (52), i.e. the governing equation of a first order piezoelectric continuum (Mindlin, 1974). Nevertheless, while the source terms in (52) are body forces and free charge densities acting on the heterogeneous medium, the terms in (53) are auxiliary source terms that take into account nonlocal effects occurring in equation (48), that asymptotically approximate the governing equations of the heterogeneous piezoelectric material, i.e. equation (1).