Influence of metallic inclusions on the electromechanical response of ferroelectric ceramics

Cristian J. Bottero[1,2] and Martín I. Idiart[1,2,*]

[1]Departamento de Aeronáutica, Facultad de Ingeniería, Universidad Nacional de La Plata,
Avda. 1 esq. 47, La Plata B1900TAG, Argentina.
[2]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), CCT La Plata,
Calle 8 N° 1467, La Plata B1904CMC, Argentina.
[*]email: martin.idiart@ing.unlp.edu.ar

Abstract

Theoretical estimates are given for the overall dissipative response of ferroelectric ceramics with random dispersions of metallic inclusions under arbitrary loading histories. The ferroelectric behavior of the matrix is described via a stored energy density and a dissipation potential in accordance with the theory of generalized standard materials. An implicit time-discretization scheme is used to generate a variational representation of the overall response in terms of a single incremental potential. Estimates are then generated by constructing sequentially laminated microgeometries of particulate type whose overall incremental potential can be computed exactly. Because they are realizable, by construction, these estimates are guaranteed to conform with any material constraints, to satisfy all pertinent bounds, and to exhibit the required convexity properties with no duality gap. Sample results for isotropic composites are reported and discussed.

Keywords: ferroelectrics; composites; homogenization methods; hysteresis

1 Motivation

Ferroelectricity refers to the capacity of certain polar dielectrics to sustain a spontaneous electrical polarization that can be altered by application of an external electric field (Lines and Glass, 1977). Since this change in polarization is usually accompanied by a mechanical deformation, ferroelectrics are electro-deformable materials which find applications as sensors and actuators (e.g., Xu, 1991; Capsal et al., 2012), energy harvesters (e.g., van den Ende et al., 2012), material damping enhancers (e.g., Asare et al., 2012), and other microdevices. Ferroelectric ceramics such as barium titanate and lead zirconate titanate are probably the most prominent examples among this class of materials.

The search for electro-deformable materials with specific combinations of properties not found in monolithic ferroelectrics has recently motivated the development of an increasing variety of two-phase ferroelectric composites, for instance, by dispersing metallic particles in a ferroelectric ceramic matrix (e.g., Duan et al., 2000; Zhang et al., 2010; Ning et al., 2012). However, the influence of metallic inclusions on the overall electrodeformation of the material is not evident a priori for, on the one hand, the resulting concentration of the electric field in the matrix enhances the electromechanical coupling, but on the other hand, the higher elastic stiffness of the inclusions reduces the coupling. The purpose of this work is to estimate theoretically such influence.

The problem calls for a methodology to estimate the overall response of two-phase dielectric materials with complex microstructures and with constituent phases that can simultaneously store and dissipate electrostatic energy. While full-field simulations are certainly an option, the

focus here is on semi-analytical homogenization methods requiring low computational power. In this work we use a variational representation of the problem together with so-called solvable microgeometries.

2 The composite material model

2.1 The material system and field equations

The material system under study is idealized here as a heterogeneous body occupying a domain Ω and made up of a continuous matrix containing a uniform dispersion of inclusions. The matrix phase will be identified with the index $r = 1$ while the inclusions will be collectively identified with the index $r = 2$. Each phase occupies a domain $\Omega^{(r)} \subset \Omega$ ($r = 1, 2$) such that $\Omega = \cup_{r=1}^{2}\Omega^{(r)}$. The domains $\Omega^{(r)}$ can be described by a set of characteristic functions $\chi^{(r)}(\mathbf{x})$, which take the value 1 if the position vector $\mathbf{x}$ is in $\Omega^{(r)}$ and 0 otherwise.

We restrict attention to isothermal processes produced by quasistatic electromechanical loadings. These interactions are represented by a fixed electrostatic potential $\hat{\phi}$ applied via a surface electrode occupying the portion $\partial\Omega_v$ of the body boundary $\partial\Omega$ or by a displacement $\hat{\mathbf{u}}$ imposed in a portion $\partial\Omega_u$ of the body boundary $\partial\Omega$. For simplicity, we disregard the possible presence of free charges within the material. The governing field equations are then given by

$$\nabla \cdot \mathbf{D} = 0 \quad \text{and} \quad \mathbf{E} = -\nabla\phi \quad \text{in } \mathbb{R}^3, \tag{1}$$

$$\phi = \hat{\phi} \quad \text{on } \partial\Omega_v \quad \text{and} \quad [\mathbf{D} \cdot \mathbf{n}] = 0 \quad \text{on } \partial\Omega \backslash \partial\Omega_v, \tag{2}$$

$$\nabla \cdot \boldsymbol{\sigma} = 0 \quad \text{and} \quad \boldsymbol{\varepsilon} = \nabla \otimes_s \mathbf{u} \quad \text{in } \Omega, \tag{3}$$

$$\mathbf{u} = \hat{\mathbf{u}} \quad \text{on } \partial\Omega_u \quad \text{and} \quad [\boldsymbol{\sigma}\mathbf{n}] = \mathbf{0} \quad \text{on } \partial\Omega \backslash \partial\Omega_u \tag{4}$$

with

$$\mathbf{D} = \begin{cases} \epsilon_0 \mathbf{E} & \text{in } \mathbb{R}^3 \backslash \Omega \\ \epsilon_0 \mathbf{E} + \mathbf{P} & \text{in } \Omega. \end{cases} \tag{5}$$

In these expressions, ϕ is the electrostatic potential, $\mathbf{D}$, $\mathbf{E}$, $\mathbf{P}$, $\mathbf{u}$, $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$ are the electric displacement, the electric field, the material polarization, the displacement, the stress field and the material strain respectively, $[\cdot]$ denotes the jump across $\partial\Omega$, $\mathbf{n}$ is the outward normal vector to $\partial\Omega$, and ϵ_0 denotes the electric permittivity of vacuum. In addition, the electrostatic potential must vanish at infinity, i.e., $\phi \to 0$ as $|\mathbf{x}| \to \infty$.

The above field equations must be supplemented with constitutive relations describing the dielectric response of each phase. Given our interest on ferroelectric composites, we follow the thermodynamic approach of Bassiouny et al. (1988) wherein dissipative processes can be characterized by an irreversible polarization $\mathbf{p}$ playing the role of an internal variable. This framework is general enough to characterize simple responses such as linear polarizability as well as complex responses such as rate-dependent ferroelectricity —see, for instance, Kamlah (2001) and Miehe and Rosato (2011).

The total energy and dissipation of the material system and its surroundings are thus written as

$$\mathcal{E} = \int_{\Omega} \varepsilon(\mathbf{x}, \boldsymbol{\varepsilon}, \mathbf{P}, \mathbf{p}) \, \mathrm{d}V + \int_{\mathbb{R}^3} \frac{1}{2}\epsilon_0 \mathbf{E}^2 \, \mathrm{d}V, \qquad \mathcal{D} = \int_{\Omega} \frac{\partial\varphi}{\partial\dot{\mathbf{p}}}(\mathbf{x}, \dot{\mathbf{p}}) \cdot \dot{\mathbf{p}} \, \mathrm{d}V, \tag{6}$$

where the first term in the energy expression corresponds to the energy stored in the composite material while the second term is the electrostatic energy associated with the electric field. The function φ is a convex, positive function of the irreversible polarization rate $\dot{\mathbf{p}}$ such that $\varphi(\cdot, \mathbf{0}) = 0$. Thermodynamic arguments then imply that the constitutive relations of the material

are given by (see Bassiouny et al., 1988)

$$\mathbf{E} = \frac{\partial \varepsilon}{\partial \mathbf{P}}(\mathbf{x}, \varepsilon, \mathbf{P}, \mathbf{p}), \quad \boldsymbol{\sigma} = \frac{\partial \varepsilon}{\partial \varepsilon}(\mathbf{x}, \varepsilon, \mathbf{P}, \mathbf{p}) \quad \text{and} \quad \frac{\partial \varepsilon}{\partial \mathbf{p}}(\mathbf{x}, \varepsilon, \mathbf{P}, \mathbf{p}) + \frac{\partial \varphi}{\partial \dot{\mathbf{p}}}(\mathbf{x}, \dot{\mathbf{p}}) = \mathbf{0}. \tag{7}$$

The field equations and boundary conditions (1)-(5), together with the constitutive relations (7) and appropriate initial conditions, completely define the electrostatic response of the system under consideration.

Polycrystalline polar solids exhibiting isotropic ferroelectricity are commonly characterized by potentials of the form —see, for instance, Kamlah (2001) and Miehe and Rosato (2011)—

$$\varepsilon(\varepsilon, \mathbf{P}, \mathbf{p}) = \frac{1}{2}(\varepsilon - \hat{\varepsilon}) \cdot \mathbf{C}(\varepsilon - \hat{\varepsilon}) + \frac{1}{2}\kappa(\mathbf{P} - \mathbf{p})^2 + (\mathbf{P} - \mathbf{p}) \cdot \mathbf{h}(\mathbf{p})(\varepsilon - \hat{\varepsilon}) + \varepsilon_{st}(\mathbf{p})$$

$$\varphi(\dot{\mathbf{p}}) = e_c|\dot{\mathbf{p}}| + \frac{e_0 \dot{p}_0}{1 + m^{(r)}} \left(\frac{|\dot{\mathbf{p}}|}{\dot{p}_0}\right)^{1+m} \tag{8}$$

with

$$\varepsilon_{st}(\mathbf{p}) = -h_0 p_s^2 \left[\ln\left(1 - \frac{|\mathbf{p}|}{p_s}\right) + \frac{|\mathbf{p}|}{p_s}\right], \tag{9}$$

$$\hat{\varepsilon}(\mathbf{p}) = \frac{3}{2}\varepsilon_s \left(\frac{|\mathbf{p}|}{p_s}\right)^2 \frac{\mathbf{p}}{|\mathbf{p}|} \otimes_d \frac{\mathbf{p}}{|\mathbf{p}|}, \tag{10}$$

$$\mathbf{h}(\mathbf{p}) = \left(\alpha_0 \frac{\mathbf{p}}{|\mathbf{p}|} \otimes \frac{\mathbf{p}}{|\mathbf{p}|} \otimes \frac{\mathbf{p}}{|\mathbf{p}|} + \alpha_\perp \mathbf{I} \otimes \frac{\mathbf{p}}{|\mathbf{p}|} + \alpha_\parallel \frac{\mathbf{p}}{|\mathbf{p}|} \otimes_s \mathbf{I}\right) \frac{|\mathbf{p}|}{p_s}, \tag{11}$$

where ε_{st} and φ represent the energy stored and dissipated via microdomain switching and $\hat{\varepsilon}$ is the remanent strain induced by this switching. In the energy potential $(8)_1$, $\mathbf{C}$ is the material stiffness tensor, κ is a positive material parameter characterizing the polarizability of the material and $\mathbf{h}$ represents the piezoelectric coupling tensor. In the dissipation potential $(8)_2$, e_c is the coercive field strength of the material —i.e., the electric field level above which domain switching is triggered—, e_0 and $\dot{p}_0$ are reference electric field and polarization rate characterizing the rate-dependence of the switching process, and m is a rate sensitivity exponent. In the stored energy density (9), in turn, p_s is the saturation polarization and h_0 is a material parameter characterizing the hysteresis slope. In the remanent strain (10), ε_s is the saturation strain at the saturation polarization $p_s^{(r)}$.

The focus of this work is on material systems where the characteristic size of the microstructural heterogeneities —e.g., particles— is much smaller than the characteristic size of the composite body. In this case, we can define an overall response of the composite material as the relation between conjugate fields averaged over a 'representative volume element' (RVE) which contains a sufficient number of heterogeneities for the overall response to be effectively independent of the prevalent conditions on its boundary. The determination of the overall response thus requires the solution to the above field equations for some suitable choice of boundary conditions on the surface of the RVE. The problem can be cast in variational form by discretizing in time following an implicit Euler scheme as in Idiart (2014). This problem is solved for a special, yet quite general, class of composite microstructures known as sequential laminates —see Idiart (2014) for details in the context of purely dielectric systems.

2.2 Results and discussion

The model presented above is used in this section to explore the effects of a random dispersion of perfectly conducting particles on the response of three-dimensional ferroelectric composites exhibiting overall isotropic symmetry. Table 1 shows the numerical values employed in the

Symbol	Parameter	Units	Value
	Ferroelectric matrix		
ϵ	electric permittivity	C/(V · m)	$1800\epsilon_0$
p_s	saturation polarization	C/m^2	0.25
h_0	hysteresis slope	MV·m/C	0.1
m	rate-sensitivity exponent	—	0.2
$\dot{p}_0$	reference polarization rate	C/(m^2· s)	100
e_c	coercive electric field	MV/m	0.35
e_0	reference electric field	MV/m	0.35
μ	Lamé parameter	GPa	45
λ	Lamé parameter	GPa	70
ϵ_s	saturation strain	—	10^{-3}
α_0	axial piezoelectric expansion	MN/C	12.6
$\alpha_\perp$	lateral piezoelectric expansion	MN/C	276.2
$\alpha_=$	piezoelectric shearing	MN/C	-1460
	Metallic inclusions		
ϵ	electric permittivity	C/(V · m)	∞
μ	Lamé parameter	GPa	60
λ	Lamé parameter	GPa	225

Table 1: Parameters for the ferroelectric material ($r = 1$) and the conductive inclusion ($r = 2$). These values roughly reproduce the rate-dependent behavior of a polycrystalline lead zirconate titanate at low frequencies (e.g., Zhou et al., 2001; Miehe and Rosato, 2011) and platinum.

simulations for the various material parameters of the ferroelectric phase and the conductive inclusion. These values roughly reproduce the rate-dependent behavior of a polycrystalline lead zirconate titanate at low frequencies (e.g., Zhou et al., 2001; Miehe and Rosato, 2011) and platinum. In the following, overbars are used to denote macroscopic quantities.

Figure 1 shows predictions for various volume fractions of metallic inclusions. These results correspond to initially unpoled composites subjected to a triangular electric signal with a peak amplitude of $4e_c$ and a frequency f_0 of 1Hz.

In part (a) we observe that the addition of conducting inclusions reduces the macroscopic coercive strength —i.e., the value of $\overline{E}$ for which $\overline{D} = 0$— but produces minimal changes in the macroscopic residual polarization —i.e., the value of $\overline{D}$ at $\overline{E} = 0$. This is indeed consistent with the experimental measurements of Duan et al. (2000) on PZT composites containing a dispersion of Pt particles. The predictions also show that, unlike the monolithic ferroelectric matrix, the composite exhibits a two-stage saturation. This phenomena fades out with decreasing volume fraction of particles. Additional results —not provided here for brevity— show the same tendency with increasing loading rate. The two-stage saturation is a consequence of the fact that metallic particles induce a bimodal distribution of the electric field in the matrix. A more detailed discussion of this phenomenon is given in Bottero & Idiart (2014).

More importantly, however, we observe in part (b) that the addition of metallic inclusions actually results in a composite material with *lower* electrodeformability. This indicates that the higher elastic stiffness of the inclusions wins over the concomitant localization of the electric field in the matrix phase. It is also interesting to note that, unlike the monolithic phase, the composite does not recover a strain-free configuration during cyclic loading. This is, once again, a consequence of the underlying bimodal distribution of the electric field.

The variation in the electrodeformation of the specimen can be summarized by analyzing the maximum strain variation, $\Delta\overline{\varepsilon}$, defined as the difference between the maximum and minimum
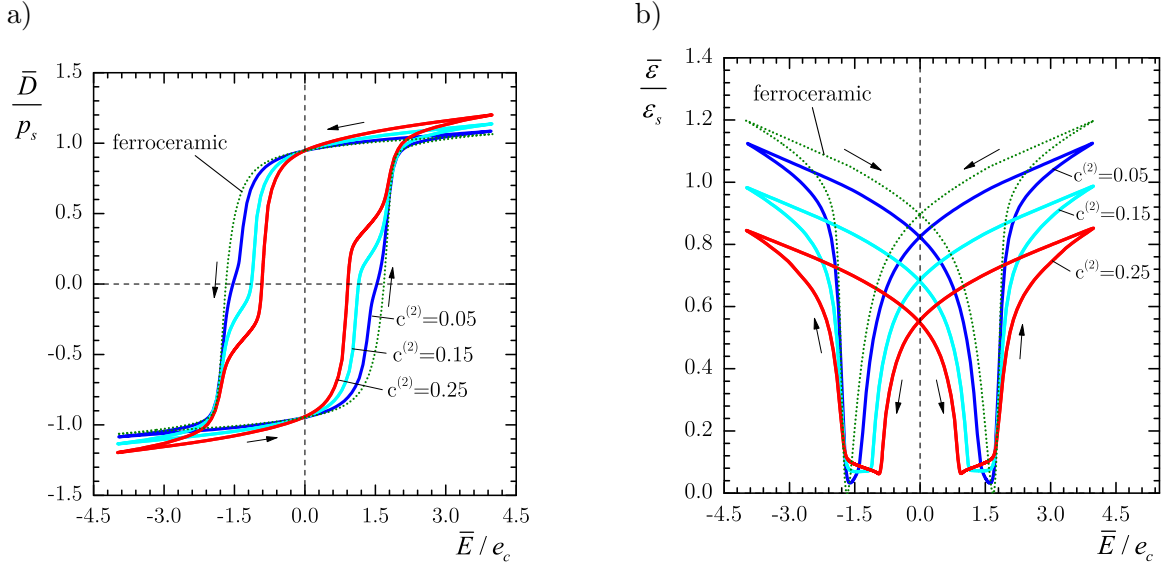
a)

b)

Figure 1: Predictions for various volume fractions ($c = 0.05; 0.15; 0.25$). The composite is subjected to a triangular electric signal with a peak amplitude of $4e_c$ and a frequency of 1Hz. Normalized vector components along the direction of applied electric field: (a) overall dielectric displacement, (b) overall longitudinal strain.

strains in the cycle. These results are presented in figure 2(a) as a function of the peak amplitude of the applied electric signal for several inclusion concentrations. It can be observed that when cycled with a maximum amplitude above roughly $1.6e_c$, the electrodeformation of the specimen is reduced by the addition of conductive inclusions. However, for fields below that value, an improvement in the electrodeformation is actually obtained. Figure 2(b) shows the predicted piezoelectric coefficient $\overline{d}_{33}$ —i.e. the slope of the strain-electric field diagram at $\overline{E} = 0$— for the composites as a function of peak amplitude. It is observed that for the whole range of amplitudes considered, the addition of metallic inclusions increases the piezoelectric coupling of the material. Thus, the predictions suggest that, on one hand, the addition of metallic particles can prove beneficial or detrimental for the electromechanical coupling of the material depending on the loading history imposed.

We conclude this discussion by noting that in the course of this study we have found that the model (7)-(10) may actually lead to numerical instabilities related to the non-convexity of the stored energy function. This problem is being assessed and its consequences will be reported in due time.

Acknowledgements

References

[1] Asare, T.A., Poquette, B.D., Shultz, J.P., Kampe, S.L., 2012. Investigating the vibration damping behavior of barium titanate ($BaTiO_3$) ceramics for use as a high damping reinforcement in metal matrix composites. J. Mater. Sci. 47, 2573–2582.

[2] Bassiouny, E., Ghaleb, A.F., Maugin, G.A., 1988. Thermodynamical formulation for coupled electromechanical hysteresis effects. I. Basic equations. Int. J. Eng. Sci. 26, 1279–1295.
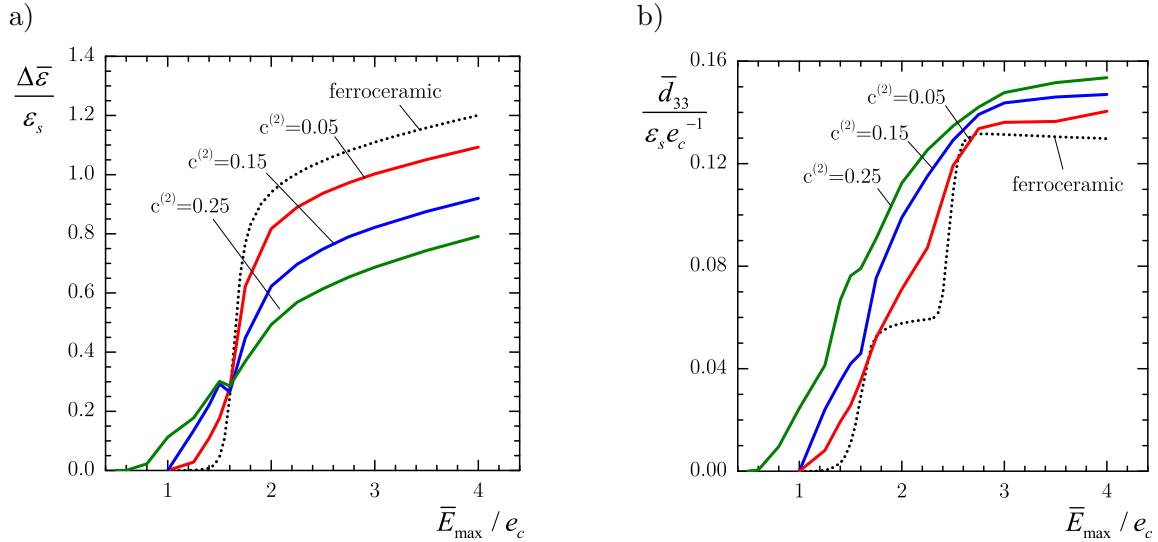
a)

b)

Figure 2: Variation as a function of the inclusion concentration for various peak amplitudes of the applied electric signal of: (a) the maximum strain variation $\Delta\overline{\varepsilon}$, (b) the piezoelectric coefficient $\overline{d}_{33}$.

[3] Bottero, C.J., Idiart, M.I., 2015. The influence of second-phase inclusions on the electro-deformation of ferroelectric ceramics. In preparation.

[4] Damjanovic, D., 2006. Hysteresis in piezoelectric and ferroelectric materials. In: The Science of Hysteresis Vol. 3, I. Mayergoyz and G. Bertotti (Eds.), Elsevier.

[5] Duan, N., ten Elshof, J.E., Verweij, H., 2000. Enhancement of dielectric and ferroelectric properties by addition of Pt particles to a lead zirconate titanate matrix. App. Phys. Lett. 77, 3263–3565.

[6] van den Ende, D.A., van de Wiel, H.J., Groen, W.A., van der Zwaag, S., 2012. Direct strain energy harvesting in automobile tires using piezoelectric PZT-polymer composites. Smart Mater. Struct. 21, 015011.

[7] Idiart, M.I., 2014. Modeling two-phase ferroelectric composites by sequential laminates. J. Modelling Simul. Mater. Sci. Eng. 22, 025010

[8] Kamlah, M., 2001. Ferroelectric and ferroelastic piezoceramics – modelling of electromechanical hysteresis phenomena. Continuum Mech. Thermodyn. 13, 219–268.

[9] Lines, M.E., Glass, A.M., 1977. Principles and Applications of Ferroelectrics and Related Materials. Oxford University Press, Oxford, U.K.

[10] Miehe, C., Rosato, D., 2011. A rate-dependent incremental variational formulation of ferroelectricity. Int. J. Eng. Sci. 49, 466–496.

[11] Xu, Y., 1991. Ferroelectric Materials and their applications. North-Holland Elsevier Science, Amsterdam.

[12] Zhou, D., Kamlah, M., Munz, D., 2001. Rate dependence of soft PZT ceramics under electric field loading. Proc. SPIE 4333: Smart Struct. Mater., C.S. Lynch (Ed.), 64–70.