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Theoretical approach to effective electrostriction in inhomogeneous materials

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An analytical approach is developed for the effective electrostriction, a nonlinearly coupled electromechanical effect, in inhomogeneous materials based on Green's-function method. For an isotropic composite containing randomly oriented ferroelectric crystallites with cubic symmetry, we derive the first effective-medium-like formulas for calculating its effective electrostrictive coefficients. The effects of microstructural features (such as volume fraction, crystallite shape and orientation, and connectivity of phases) on the effective electrostrictive coefficients are illustrated numerically and discussed. The calculations show that it is possible to develop new electrostrictors combining large electrostriction with mechanical flexibility by choosing the best combination of ferroelectric ceramics and polymer.

I. INTRODUCTION

Electrostriction is a nonlinearly coupled electrical-mechanical effect existing in all (dielectric) materials. Recently developed relaxor ferroelectric materials having comparatively large electrostriction and very small hysteresis, such as those from the $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT) family,[1–4] have resulted in a growth of interest in this nonlinear coupling effect. Their strong application potential in electroactive sensor and actuator devices has attracted a worldwide attention of research and development activity in relaxor ferroelectric materials with large electrostriction effect. To the other extreme, design of a material with zero electrostriction effects is also important for applications in areas such as in microelectronic devices where field-induced damage is a significant risk.[2] As a fundamental effect, various microscopic mechanisms have been proposed for understanding the origins of the electrostriction effect.[1,5–8] Since most of the experimental research on relaxor ferroelectric materials has been done and is being done on electrostrictive ceramics (polycrystals), it is highly desirable to link the electrostrictive behavior of the ceramics with the single-crystal properties and ceramic microstructure,[9,10] which itself constitutes an interesting fundamental question.

In recent years *linearly coupled* electromechanical effect (i.e., piezoelectric effect)[11,12] and *uncoupled, pure nonlinear* electrical[13] or mechanical[14,15] effects in inhomogeneous materials have been intensively studied, which results in a few approaches to these effective *linearly coupled* or *nonlinearly uncoupled* properties. However, no such approaches have been developed to treat the *nonlinearly coupled* electromechanical effect in inhomogeneous materials. One principal motivation of the present work is to develop an approach for this *nonlinearly coupled* electromechanical effect in inhomogeneous materials.

In experimental, electrostrictive inhomogeneous materials widely investigated so far have been polycrystalline ferroelectric ceramics, but no electrostrictive composites have been reported in the literature yet. On the other hand, from recently increasing emphasis on the practical development of many new ferroelectric and/or ferromagnetic composites such as piezoelectric ceramic/polymer composites[16] and Terfenol-D/polymer (or metal) composites,[17] one naturally thinks about electrostrictive composites such as relaxor ferroelectric ceramic/polymer composites. The theoretical approach developed in the present work will provide fundamental understanding of the effective electrostrictive behavior of such composites, which answers if it is possible to exploit new electrostrictors based on such possibly new electrostrictive composites, and which is also essential to any technical improvements of such composite electrostrictors.

In this paper, we present a detailed theoretical study of the effective electrostrictive behavior of inhomogeneous materials, and investigate the sensitivity of the effective electrostrictive behavior on the material constants and microstructural scales such as anisotropy, crystallite shape, and orientation. The essence of the present problem is to calculate the strong electroelastic coupling interaction in an inhomogeneous medium. The low-signal, linearly coupled electroelastic (i.e., piezoelectric) response of inhomogeneous media was successfully treated previously by Nan and co-worker[11] using generalized Green's function technique (multiple-scattering method[18] in the sense of Zeller-Dederichs and Gubernatis-Krumhansl[19]). This technique is also valid for nonlinear problems with large fluctuations, although its exact realm of validity is very hard to ascertain.[14,20] More recently, the technique has been developed to successfully treat the nonlinearly coupled magnetic-mechanical strain of magnetostrictive composites.[21,22] In the present work, we shall generalize this approach to address the nonlinearly coupled electromechanical behavior of electrostrictive inhomogeneous materials.

The rest of this article is organized as follows. Section II contains the theoretical framework and the general solution to the effective electrostrictive coefficients of inhomogeneous materials. In Sec. III, without loss of generality, we consider commonly isotropic composites containing randomly-oriented relaxor ferroelectric microcrystallites with cubic symmetry, and give explicit expressions for the effective electrostrictive coefficients of such isotropic composites with randomly-oriented spherical, needle-shaped, or disklike crystallites. For illustrative and quantitative purposes, some numerical results for the effective electrostrictive coefficients of the composites of relaxor ferroelectric ceramics and epoxy are presented for various microstructural features in Sec. IV. The conclusions are summarized in Sec. V.

II. FORMALISM

Consider an electrostrictive inhomogeneous material consisting of microcrystallites having a center of symmetry with perfectly bonded interface. Its nonlinearly coupled electromechanical interaction can be described by the following constitutive equations[2]

$$\sigma = \mathbf{C}\varepsilon - \mathbf{BEE}, \tag{1}$$

$$\mathbf{D} = \kappa\mathbf{E} + 2\mathbf{B}^T\varepsilon\mathbf{E}, \tag{2}$$

where $\sigma, \varepsilon, \mathbf{D}$, and $\mathbf{E}$, are the stress, strain, electric displacement, and electric field, respectively; $\mathbf{C}$ is the elastic stiffness (in the constancy of the electric field), and κ is the permittivity (under the constant-strain conditions), which can depend on $\mathbf{E}$ especially at high electric field. $\mathbf{B} = \mathbf{CM}$ and $\mathbf{M}$ is the electrostrictive coefficient tensor (a fourth-order tensor like $\mathbf{C}$) relating the strain to the electric field. $\mathbf{B}^T$ is the transpose of $\mathbf{B}$. For simplicity, the direct notation of tensors have been used. In the literature on relaxor ferroelectric ceramics, the electrostrictive strain is commonly related to polarization $\mathbf{P}$, namely, Eq. (1) can be written as

$$\varepsilon = \mathbf{S}\sigma + \mathbf{QPP}, \tag{3}$$

where $\mathbf{S}$ is the elastic compliance tensor at constant polarization and $\mathbf{Q}$ is the polarization-related electrostrictive coefficient tensor. Since the electrostrictively induced strain in the relaxor ferroelectric ceramics is found to be proportional to the square of the polarization not the field due to the nonlinear nature of the $\mathbf{P}$-$\mathbf{E}$ relationship, the $\mathbf{Q}$ coefficient is preferable to and more commonly used than the field-related coefficient $\mathbf{M}$ to cast the electrostriction in the relaxor ferroelectric ceramics.[1–4] However, large $\mathbf{Q}$ coefficient in a material does not imply that it exhibits large electrostrictive strains. The figure of merit used to compare electrostrictive strains generated in a material is $\mathbf{M}$ not $\mathbf{Q}$.[2] Thus Eq. (1) expressed by the field-related $\mathbf{M}$, not Eq. (3) by the polarization-related $\mathbf{Q}$, is used in the present work. The relation between both is expressed by

$$\mathbf{MEE} = \mathbf{Q}\chi\chi\mathbf{EE}, \tag{4}$$

where χ is the dielectric susceptibility. The field dependence of χ at high electric field results in the field dependence of $\mathbf{M}$. For the material with cubic symmetry, $M_{ij} = Q_{ij}\chi^2$ at any given electric field. The figure of merit $\mathbf{M}$ of the inhomogeneous material is emphasized next.

The effective behavior of the inhomogeneous material is defined in terms of macroscopic average (applied) fields (denoted by $\langle\ \rangle$), namely,

$$\langle\sigma\rangle = \mathbf{C}^*\langle\varepsilon\rangle - \mathbf{B}^*\langle\mathbf{E}\rangle\langle\mathbf{E}\rangle, \tag{5}$$

$$\langle\mathbf{D}\rangle = \kappa^*\langle\mathbf{E}\rangle + 2\mathbf{B}^{T*}\langle\varepsilon\rangle\langle\mathbf{E}\rangle. \tag{6}$$

Therefore, the problem of evaluating the effective response of the material essentially consists of the determination of the field variables within it under certain specified boundary conditions, followed by the performance of the averages.

Because of spatial variations in the constitutive behavior in the material with position, the local constitutive coefficients can be written as a variation about a mean value

$$\mathbf{C}(\mathbf{x}) = \mathbf{C}^o + \mathbf{C}'(\mathbf{x}), \quad \kappa(x) = \kappa^o + \kappa'(\mathbf{x}),$$

$$\mathbf{B}(\mathbf{x}) = \mathbf{B}^o + \mathbf{B}'(\mathbf{x}), \tag{7}$$

where the first terms (denoted by superscripts o) represent the constitutive constants of a homogeneous reference medium and the second terms are the spatial fluctuation on the first.

To proceed, let the material be now subjected on its external surface S to homogeneous electric-mechanical boundary conditions, i.e.,

$$u_i(S) = \varepsilon^o_{ij}x_j = u^o_i, \quad \psi(S) = -E^o_i x_i = \psi^o, \tag{8}$$

where u_i and ψ denote elastic displacement and electric potential, respectively. Consider a state of static equilibrium in the absence of body forces and free electric charges so that

$$\sigma_{ij,j}(\mathbf{x}) = 0, \quad D_{j,j}(\mathbf{x}) = 0, \tag{9}$$

where the commas in the subscripts denote partial differentiation with respect to x_j. These are nonlinearly coupling equilibrium equations.

Further by solving the equilibrium equations under the boundary conditions (8) by means of the Green's-function technique,[11] the local strain and electric field within the material can be obtained as

$$\varepsilon = \varepsilon^o + \mathbf{G}^u\mathbf{C}'\varepsilon - \mathbf{G}^u\mathbf{BEE}, \tag{10}$$

$$\mathbf{E} = \mathbf{E}^o + \mathbf{G}^\psi\kappa'\mathbf{E} + 2\mathbf{G}^\psi\mathbf{B}^T\varepsilon\mathbf{E}, \tag{11}$$

where ε^o and $\mathbf{E}^o$ are the strain and electric field in the homogeneous reference medium at equilibrium, and $\mathbf{G}^u$ and $\mathbf{G}^\psi$ are the modified displacement and electric potential Green's functions for the homogeneous medium.[11] After ignoring higher-order electrostriction terms,[2,23] Eqs. (10) and (11) can be rewritten as the following explicit solutions

$$\varepsilon = \mathbf{T}^{66}\varepsilon^o - \mathbf{T}^{66}\mathbf{G}^u\mathbf{B}\mathbf{T}^{33}\mathbf{T}^{33}\mathbf{E}^o\mathbf{E}^o, \tag{12}$$

$$\mathbf{E} = \mathbf{T}^{33}\mathbf{E}^o + 2\mathbf{T}^{33}\mathbf{G}^\psi\mathbf{B}^T\mathbf{T}^{66}\varepsilon^o\mathbf{T}^{33}\mathbf{E}^o, \tag{13}$$

with

$$\mathbf{T}^{66} = (\mathbf{I} - \mathbf{G}^u\mathbf{C}')^{-1},$$

$$\mathbf{T}^{33} = (\mathbf{I} - \mathbf{G}^\psi\kappa')^{-1},$$

where $\mathbf{I}$ is the unit tensor. By averaging these equations and eliminating ε^o and $\mathbf{E}^o$ from them, we get the solutions to the effective properties of the material

$$\mathbf{C}^* = \langle \mathbf{C}\mathbf{T}^{66} \rangle \langle \mathbf{T}^{66} \rangle^{-1}, \tag{14}$$

$$\kappa^* = \langle \kappa \mathbf{T}^{33} \rangle \langle \mathbf{T}^{33} \rangle^{-1}, \tag{15}$$

$$\mathbf{M}^* \langle \mathbf{T}^{33} \rangle \langle \mathbf{T}^{33} \rangle = \mathbf{C}^{*-1} \langle [(\mathbf{C}-\mathbf{C}^*)\mathbf{T}^{66}\mathbf{G}^u + \mathbf{I}]\mathbf{C}\mathbf{M}\mathbf{T}^{33}\mathbf{T}^{33} \rangle. \tag{16}$$

In the present treatment all higher-order electrostriction terms are ignored.[2,23] Equations (14) and (15) are the commonly used expressions for the effective stiffness and permeability tensors. Equation (16) is the first formula for the effective electrostrictive coefficient tensor. These results are independent of the models assumed for the material and contain the effects of material constants and microstructural features. As in the linearly uncoupled[18,19] or coupled[11] response cases, this approach involves an exact calculation of the nonlinearly coupled fields induced in the homogeneous reference medium by a single spherical or ellipsoidal crystallite and an approximate treatment of the interaction between the effects of various crystallites. For simplicity, we consider only dipolar interaction as did in common Bruggeman-Landauer effective-medium (EM) approach[13,18] for the uncoupled linear response cases. Accordingly, this approximate treatment will give a self-consistent EM-like approximation in which each phase is exposed to the effective medium of yet unknown moduli that are dependent in detail on the nature of the interactions between phases. Next we derive the explicit EM-like approximation for the effective electrostrictive coefficients from the general equations.

III. ISOTROPIC COMPOSITES AND POLYCRYSTALS CONTAINING CRYSTALLITES WITH CUBIC SYMMETRY

In an isotropic electrostrictive composite containing randomly oriented crystallites having cubic symmetry (such as cubic PMN-PT having the point group *m3m),* the cubic crystallite has electrostrictive and elastic anisotropy but no dielectric anisotropy, which are characterized by three independent electrostrictive coefficients (M_{11}, M_{12}, and M_{44}) and elastic constants (c_{11}, c_{12}, and c_{44}), namely,

$$M_{ij} = \begin{pmatrix} M_{11} & M_{12} & M_{12} & 0 & 0 & 0 \\ M_{12} & M_{11} & M_{12} & 0 & 0 & 0 \\ M_{12} & M_{12} & M_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & M_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & M_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & M_{44} \end{pmatrix}. \tag{17}$$

The hydrostatic electrostrictive coefficient and bulk modulus are defined as $M_h = M_{11} + 2M_{12}$ and $K = (c_{11} + 2c_{12})/3$, respectively. The isotropic composite has only two independent electrostrictive coefficients, i.e., the effective hydrostatic electrostrictive coefficient $M_h^* = M_{11}^* + 2M_{12}^*$ and shearlike electrostrictive coefficient $M_{44}^* = 2(M_{11}^* - M_{12}^*)$, as for the effective elastic constants [the effective bulk modulus $K^* = (c_{11}^* + 2c_{12}^*)/3$ and shear modulus $G^* = (c_{11}^* - c_{12}^*)/2$]. For illustrative purposes, next we consider such electrostrictive composites with different crystallite geometries: (a) spherical crystallites and (b) ellipsoidal crystallites.

A. Spherical ferroelectric crystallites

Let us first consider a commonly isotropic two-phase composite consisting of randomly oriented, spherical relaxor ferroelectric crystallites having cubic symmetry. In this case, Eq. (16) directly yields explicit effective-medium-like approximate results for the two independent effective electrostrictive coefficients

$$M_h^* = M_{11}^* + 2M_{12}^* = \sum_{i=1}^{2} f_i (A_{11}^{(i)} + 2A_{12}^{(i)}) \left(\frac{3\kappa^*}{\kappa_i + 2\kappa^*} \right)^2, \tag{18}$$

$$M_{44}^* = 2(M_{11}^* - M_{12}^*) = \sum_{i=1}^{2} f_i \frac{4(A_{11}^{(i)} - A_{12}^{(i)}) + 6A_{44}^{(i)}}{5} \left(\frac{3\kappa^*}{\kappa_i + 2\kappa^*} \right)^2, \tag{19}$$

where $A_{ij}^{(i)}$ are the components of the tensor $\mathbf{A} = [\mathbf{I} - \mathbf{G}^u(\mathbf{C} - \mathbf{C}^*)]^{-1}(\mathbf{C}^*)^{-1}\mathbf{C}\mathbf{M}$ of the ith phase and

$$A_{11}^{(i)} + 2A_{12}^{(i)} = M_h^{(i)} \frac{1 + 4G^*/3K^*}{1 + 4G^*/3K_i}, \tag{20}$$

$$A_{11}^{(i)} - A_{12}^{(i)} = (M_{11}^{(i)} - M_{12}^{(i)}) \frac{1 + F^*/G^*}{1 + F^*/G_i}, \tag{21}$$

$$A_{44}^{(i)} = \frac{M_{44}^{(i)}}{2} \frac{1 + F^*/G^*}{1 + F^*/c_{44}^{(i)}}, \tag{22}$$

with

$$F^* = \frac{G^*(9K^* + 8G^*)}{6(K^* + 2G^*)}, \tag{23}$$

$$G_i = (c_{11}^{(i)} - c_{12}^{(i)})/2, \tag{24}$$

here K^* and G^*, and κ^* are, respectively, the effective bulk and shear moduli, and the effective dielectric constant of the composite, which are given by Eqs. (14) and (15) and determined self-consistently by

$$\sum_{i=1}^{2} f_i \frac{K_i - K^*}{3K_i + 4G^*} = \sum_{i=1}^{2} f_i \left[\frac{2(G_i - G^*)}{G_i + F^*} + \frac{3(c_{44}^{(i)} - G^*)}{c_{44}^{(i)} + F^*} \right] = 0, \tag{25}$$

$$\sum_{i=1}^{2} f_i \frac{\kappa_i - \kappa^*}{\kappa_i + 2\kappa^*} = 0, \tag{26}$$

where f_i, κ_i, $c_{ij}^{(i)}$, and $M_{ij}^{(i)}$ are the volume fraction, dielectric constant, elastic constants, and electrostrictive coefficients of the ith phase, respectively. Equation (26) is obviously the commonly used Bruggeman-Landauer EM expression for the effective dielectric constant, and Eq. (25) is the self-consistent EM expressions for the effective elastic constants in this case and reduces to the commonly used

Hill-Budiansky self-consistent expression for the case of isotropic crystallites [i.e., $c_{44}^{(i)}=G_i=(c_{11}^{(i)}-c_{12}^{(i)})/2$]. Equations (18) and (19) are the first explicit EM-like expressions for the effective electrostrictive coefficients of such an isotropic composites and contain the volume fraction and all related material constants.

Further for a single-phase isotropic polycrystalline ceramic of such cubic crystallites (such as a PMN-PT ceramic), these explicit EM-like formulas reduce to

$$M_h^*=M_h, \tag{27}$$

$$M_{44}^*=2(M_{11}^*-M_{12}^*)$$
$$=\frac{3(1+F^*/G^*)}{5(1+F^*/c_{44})}\left[M_{44}-\frac{2(M_{11}-M_{12})(G^*/c_{44}-1)}{2G^*/(c_{11}-c_{12})-1}\right], \tag{28}$$

with

$$K^*=(c_{11}+2c_{12})/3,$$

$$\frac{2(c_{11}-c_{12})-4G^*}{(c_{11}-c_{12})+2F^*}=\frac{3(G^*-c_{44})}{c_{44}+F^*},$$

which relate the ceramic electrostrictive coefficients with the ceramic elastic constants and single crystal constants. It must be pointed out here that the electrostrictive coefficients Q_{ij}^* commonly used for relaxor ferroelectric ceramics have the same form expressions [i.e., just replacing M_{ij}^* and M_{ij} in Eq. (27) and Eq. (28), respectively, with Q_{ij}^* and Q_{ij}] in this case of the single-phase relaxor ferroelectric ceramic composed of crystallites with a center of symmetry. It is also evident from Eq. (27) that such an isotropic ceramic exhibits the same hydrostatic electrostrictive coefficient as the cubic crystallites composed of this ceramic, though $M_{11}^*\neq M_{11}$ and $M_{12}^*\neq M_{12}$. Furthermore, in the simplest case of the isotropic crystallites, i.e., $c_{11}-c_{12}=2c_{44}$ and $2(M_{11}-M_{12})=M_{44}$, the ceramic just has the same electrostriction as the crystallites.

B. Ellipsoidal ferroelectric crystallites

We now consider randomly oriented disklike or needle-shaped ferroelectric crystallites for simplicity of formulas. For disklike ferroelectric crystallites, the two independent effective electrostrictive coefficients can be obtained as

$$M_h^*=\sum_{i=1}^{2}\frac{f_iM_h^{(i)}(2+\kappa^*/\kappa_i)^2}{\left(2+\sum_{i=1}^{2}f_i\kappa^*/\kappa_i\right)^2}\,\frac{1+4G_i/3K^*}{1+4G_i/3K_i}, \tag{29}$$

$$M_{44}^*=\sum_{i=1}^{2}\frac{f_i(2+\kappa^*/\kappa_i)^2}{5\left(2+\sum_{i=1}^{2}f_i\kappa^*/\kappa_i\right)^2}\left[4(M_{11}^{(i)}-M_{12}^{(i)})\times\frac{G_i[1+2(G_i+G^*)/3K_i]}{G^*(1+4G_i/3K_i)}+M_{44}^{(i)}\left(1+\frac{c_{44}^{(i)}}{2G^*}\right)\right], \tag{30}$$

where the effective bulk and shear moduli, and the effective dielectric constant are determined by

$$\sum_{i=1}^{2}f_i\frac{(K_i-K^*)(3K^*+4G_i)}{(3K_i+4G_i)}=0, \tag{31}$$

$$\sum_{i=1}^{2}f_i\left[4(G_i-G^*)\frac{3K_i+2G_i+2G^*}{3K_i+4G_i}+(c_{44}^{(i)}-G^*)\frac{2G^*+c_{44}^{(i)}}{2c_{44}^{(i)}}\right]=0, \tag{32}$$

$$\sum_{i=1}^{2}f_i(\kappa_i-\kappa^*)(2+\kappa^*/\kappa_i)=0. \tag{33}$$

Equation (33) is the Bruggeman-Landauer EM expression for the effective dielectric constant in this case; Eq. (31) is the self-consistent EM expression for the effective bulk modulus, which is the same for the case of isotropic crystallites,[14] and Eq. (32) reduces to the known self-consistent expression[14] for the case of isotropic crystallites as $c_{44}^{(i)}=G_i=(c_{11}^{(i)}-c_{12}^{(i)})/2$.

For needle-shaped ferroelectric crystallites, we can also obtain a bit more complex explicit formulas of the two independent effective electrostrictive coefficients of the composite

$$M_h^*=\sum_{i=1}^{2}f_iM_h^{(i)}\left(\frac{\kappa_i+5\kappa^*}{\kappa_i+\kappa^*}\right)^2\times\frac{1+(3G^*+G_i)/3K^*}{1+(3G^*+G_i)/3K_i}\left(\sum_{i=1}^{2}f_i\frac{\kappa_i+5\kappa^*}{\kappa_i+\kappa^*}\right)^{-2}, \tag{34}$$

$$M_{44}^*=\sum_{i=1}^{2}\frac{f_i}{5}\left(\frac{\kappa_i+5\kappa^*}{\kappa_i+\kappa^*}\right)^2\left[\frac{G_i(M_{11}^{(i)}-M_{12}^{(i)})(F_{11}+F_{12})}{G^*}+M_{44}^{(i)}\left(1+\frac{c_{44}^{(i)}}{G^*}F_{44}\right)\right]\left(\sum_{i=1}^{2}f_i\frac{\kappa_i+5\kappa^*}{\kappa_i+\kappa^*}\right)^{-2} \tag{35}$$

with

$$F_{11}=\frac{3K^*+4G^*}{3K^*+G_i+3G^*}, \tag{36}$$

$$F_{12}=\frac{2G^*(3K^*+4G^*)}{G^*(3K^*+G^*)+G_i(3K^*+7G^*)}, \tag{37}$$

$$F_{44}=\frac{G^*(3K^*+4G^*)}{G^*(3K^*+G^*)+c_{44}^{(i)}(3K^*+7G^*)}, \tag{38}$$

where the effective bulk and shear moduli, and the effective dielectric constant are determined by

$$\sum_{i=1}^{2} f_i\frac{(K_i-K^*)(3K^*+3G^*+G_i)}{3K_i+3G^*+G_i}=0, \tag{39}$$

$$\sum_{i=1}^{2} f_i\Bigg[2(G_i-G^*)\frac{3K_i+4G^*}{3K^*+4G^*}(F_{11}+F_{12})+(c_{44}^{(i)}-G^*)\times\left(\frac{G^*}{c_{44}^{(i)}}+F_{44}\right)\Bigg]=0, \tag{40}$$

$$\sum_{i=1}^{2} f_i(\kappa_i-\kappa^*)\frac{\kappa_i+5\kappa^*}{\kappa_i+\kappa^*}=0. \tag{41}$$

Similarly, Eq. (41) is the Bruggeman-Landauer EM expression for the effective dielectric constant in this case; Eqs. (39) and (40) are self-consistent EM expressions for the effective elastic constants in this case and reduce to the known self-consistent expressions[14] for the case of isotropic crystallites [i.e., $c_{44}^{(i)}=G_i=(c_{11}^{(i)}-c_{12}^{(i)})/2$]. These explicit EM-like formulas give the effective electrostrictive coefficients from the volume fraction and all related material constants and also constitute interrelationships between these five effective coefficients for the isotropic composite with randomly oriented disklike or needle-shaped ferroelectric crystallites whose aspect ratio approaches zero or infinite.

IV. NUMERICAL RESULTS AND DISCUSSIONS

Now for numerically illustrative purpose, let us consider a possibly new flexible electrostrictive composite consisting of a volume fraction f of relaxor ferroelectric crystallites and an isotropic, flexible epoxy. The properties of the constituent phases used for the calculations are taken as: $c_{11}=130$, $c_{12}=65$, and $c_{44}=25$ GPa, $\kappa/\kappa_o=10^4$, $M_{11}=1.96\times10^{-16}$, $M_{12}=-7.84\times10^{-17}$, and $M_{44}=5.10\times10^{-16}\mathrm{m}^2/\mathrm{V}^2$ ($Q_{11}=0.025$, $Q_{12}=-0.01$, and $Q_{44}=0.065$ $\mathrm{m}^4/\mathrm{C}^2$)[2,24] for the relaxor ferroelectric phase; $c_{11}=6$ and $c_{12}=3$ GPa, $\kappa/\kappa_o=10$, $M_{11}=1.587\times10^{-20}$, and $M_{12}=-1.27\times10^{-20}$ $\mathrm{m}^2/\mathrm{V}^2$ ($Q_{11}=2.5$ and $Q_{12}=-2$ $\mathrm{m}^4/\mathrm{C}^2$)[2,25] for the epoxy. Although there are no electrostrictive composites reported in the literature and thus no experimental data of the effective electrostrictive coefficients are available for comparison with the present theory, our theoretical trends of evaluating influences of microstructural features on the effective electrostrictive coefficients of the composites based on the EM-like method, which has been successful for the magnetostriction problem (one analogue of the electrostriction problem) of composites should be reasonable. These interesting consequences predicted theoretically remain to be experimentally verified.

A. Isotropic particulate composites

Figure 1 presents some numerical results for the effective electrostrictive coefficients of the isotropic two-phase composites with randomly oriented spheroidal relaxor ferroelectric crystallites. As expected, the effective electrostrictive coefficients M_{ij}^* [Fig. 1(a)] increase with the increase in the volume fraction f of the relaxor ferroelectric crystallites. For illustration and comparison, corresponding numerical results for the polarization-related coefficients Q_{ij}^* are also shown in Fig. 1(b). Contrary to M_{ij}^*, the Q_{ij}^* values decrease with the volume fraction, as the Q_{ij} values of the relaxor ferroelectric crystallites are more than 100 times lower than those of the epoxy. Although Q_{ij}^* at low-volume fractions is about two orders of magnitude higher than Q_{ij}^* at high-volume fractions, the electrostrictively induced strains at high-volume fraction are expected to be larger than those at low-volume fractions. As such, M_{ij}^* is more preferably used to evaluate the electrostrictive response of the inhomogeneous materials. Hence our following numerical results and discussions are focused upon M_{ij}^*, the figure of merit of the electrostriction.

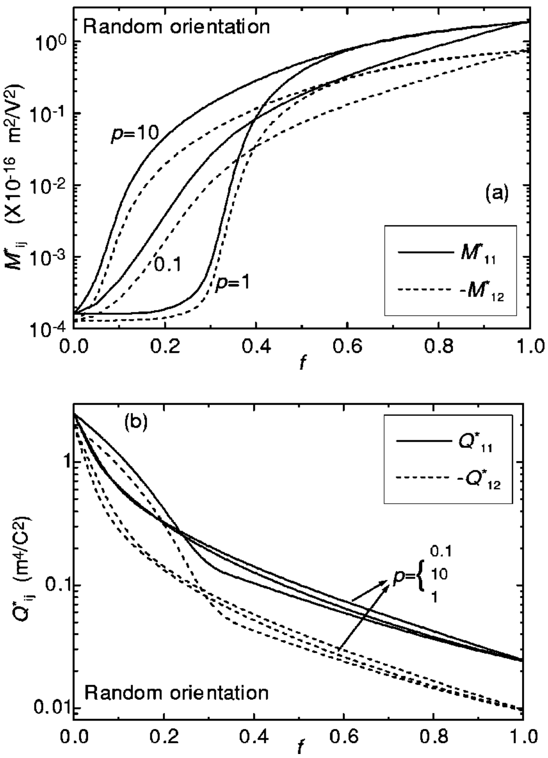

FIG. 1. (a) The effective electrostrictive coefficients M_{ij}^* (the figure of merit) and (b) effective polarization-related electrostrictive coefficients Q_{ij}^* of an isotropic two-phase composite of an isotropic epoxy and the randomly-oriented spheroidal relaxor ferroelectric crystallites.

As shown in Fig. 1, at low-volume fraction, where the relaxor crystallites are surrounded by the epoxy, this type of matrix-based particulate composite has rather low M_{ij}^*. When the volume fraction of the crystallite particles increases and the particles can agglomerate to form large clusters or an interpenetrating phase above a critical volume fraction, i.e., percolation threshold, the M_{ij}^* values of the particulate composites increase. Only above the percolation thresholds, do such particulate composites exhibit larger effective electrostrictive coefficients M_{ij}^*.

The aspect ratio p of the spheroidal relaxor crystallites has a pronounced effect on the effective electrostrictive coeffi-

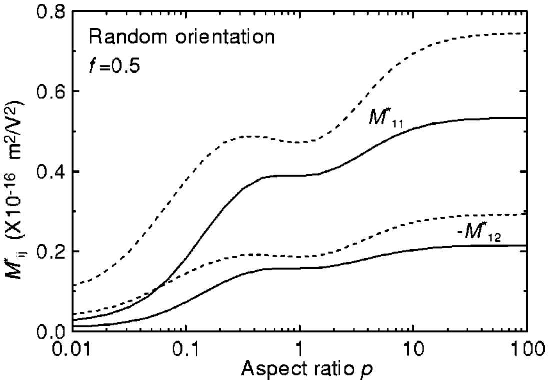

FIG. 2. Effect of the aspect ratio p of the relaxor crystallites on the effective electrostrictive coefficients of the isotropic composites with 50 vol % relaxor crystallites. The dashed lines are corresponding to the predictions for the porous relaxor ferroelectric ceramic (see text).

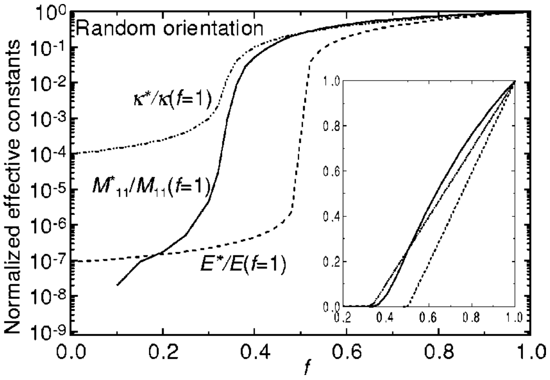

FIG. 3. The normalized effective electrostrictive coefficient $[M^*_{11}/M_{11}(f=1)]$, Young's modulus $[E^*/E(f=1)]$, and dielectric constant $[\kappa^*/\kappa(f=1)]$ of the isotropic composite with spherical relaxor crystallites.

cients M^*_{ij}. The ellipsoidal crystallites lead to larger increase in the numerical values of the effective electrostrictive coefficients at the low-volume fractions than the spherical crystallites [Fig. 1(a)], since they exhibit lower percolation thresholds than the spherical crystallites.[18] The M^*_{ij} values at the high-volume fractions increase with the increase in the aspect ratio p of the relaxor crystallites, as shown in Fig. 2. The randomly oriented disklike crystallites with $p<0.2$ lead to lower M^*_{ij} values of the composites than the spherical crystallites. As the aspect ratio is less than about 0.2, the numerical values of M^*_{ij} of the composites rapidly decrease with decreasing p. As $10>p>1$ the numerical values of the effective electrostrictive coefficients, especially M^*_{11}, gradually increase with increasing p. As $p>10$, the numerical values of M^*_{ij} slightly change with p and finally approach the values in the limit case of fibers $(p\rightarrow\infty)$, predicted by Eqs. (34) and (35).

The effective electrostrictive properties are also influenced by the elastic stiffness of the epoxy. For convenience and comparison, Fig. 2 also shows predictions by taking $c_{11}=10^{-5}$ and $c_{12}=5\times10^{-6}$ GPa and $\kappa/\kappa_o=1$ and $M_{ij}=0$ for the isotropic epoxy phase, which corresponds to the predictions for the porous relaxor ferroelectric ceramics. The effective electrostrictive coefficients of the composites can increase through the use of softer polymer phases, which is directly attributed to the improved displacement transfer capability of the more flexible polymers. In this case of a big difference between the material constants of two phases, it has been well recognized that the dielectric and elastic constants separately present different scaling behaviors in the vicinity of the percolation threshold.[18] Figure 3 shows the critical behavior of this composite with randomly oriented spherical crystallites. Like the general EM theory,[13,18] the critical exponents for the elastic and dielectric constants are about 1, that is less than their expected scaling values. The difference between the connectivity threshold $(f_c=1/3)$ for dielectric constant and the rigidity threshold $(f_c=1/2)$ for elastic constant is attributed to inherent feature of the EM approach. The rigidity threshold is generally above the connectivity percolation threshold because simple connectivity does not insure the rigidity of the structure since many single bonds can ‘‘buckle’’ without costing any energy. Above the rigidity threshold, the dielectric and elastic constants linearly decrease with decreasing f (see the inset in Fig. 3). The effective electrostrictive coefficients (nonlinearly) decrease more slowly than the elastic and dielectric constants above the rigidity threshold, and drop down sharply near an intermediate threshold between the connectivity and rigidity thresholds, which is due mainly to the mechanical-electrical interaction. From Fig. 3 it seems that the effective electrostrictive coefficients also have the critical behavior near the intermediate threshold. It is unknown yet that the effective electrostrictive coefficients really exhibit such critical behavior or it is just due to the inherent feature of the EM-like approach. But the predictions definitely demonstrate that the effective electrostrictive coefficients will present different scaling behavior from both the effective dielectric and elastic constants if the critical behavior is real for the effective electrostrictive coefficients, as in the case of the (linear coupling) piezoelectric effect.[11,26] This remains to be an interesting fundamental question.

B. Anisotropic composites

The effective electrostriction of the composite is also dependent upon the relaxor crystallite orientation. Figure 4 shows the orientation effect of the spherical and prolate crystallites by considering a uniform orientation distribution be-

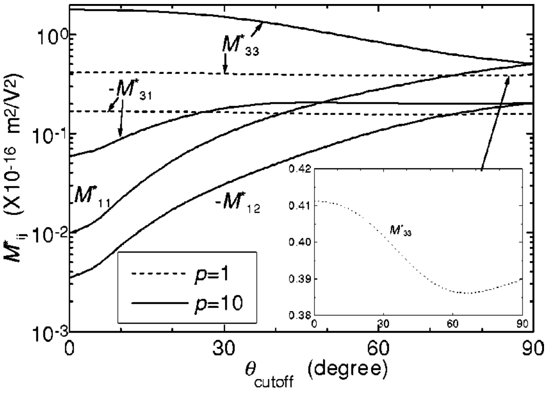

FIG. 4. Effect of a uniform orientation distribution of spherical or prolate relaxor crystallites on the effective electrostrictive coefficients of 50 vol % relaxor crystallites/epoxy composites.

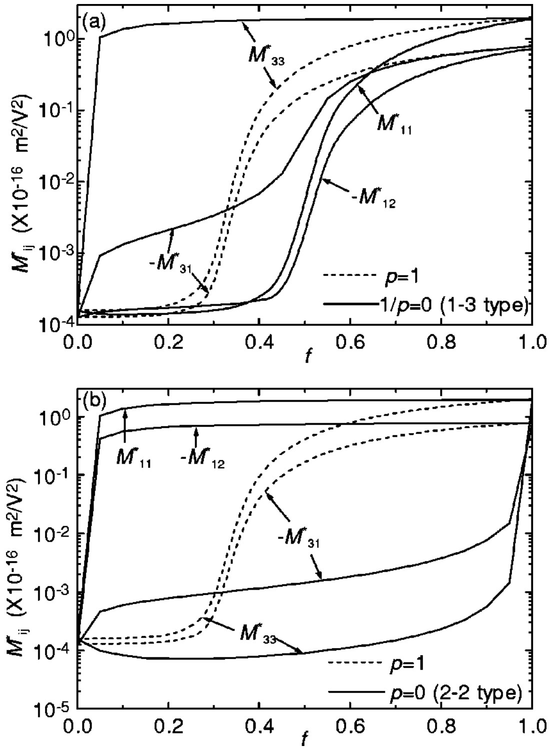

FIG. 5. The effective electrostrictive coefficients of (a) 1-3 type and (b) 2-2 type relaxor crystallites/epoxy composites. The predictions for the 0-3 type composite containing spherical crystallites with their ⟨001⟩ directions parallel to the sample X_3 axis are also shown for comparison.

tween $\theta=0$ and θ_{cutoff} of their local crystallographic axis X'_3 with respect to the sample axis X_3 but random orientation in the X_1X_2 plane, i.e., the composite being transversely isotropic and exhibiting ∞mm symmetry. For the spherical crystallites, the effective electrostrictive coefficients of the composite only slightly vary with the orientation, and the anisotropy is very small. However, the effective electrostrictive coefficients of the composite containing prolate crystallites are very sensitive to the crystallite orientation. As $\theta_{cutoff}=0°$, i.e., X'_3 directions (symmetric axis) of all prolate crystallites are identically aligned parallel to the sample X_3 axis, the composite exhibits maximum anisotropy and larger M^*_{33} value, which is only a little bit lower than the M_{11} value of the relaxor crystallites. With increasing θ_{cutoff}, the M^*_{33} value decreases and the values of the other components of M^*_{ij} increase to the values for the random orientation case at $\theta_{cutoff}=90°$.

As shown in Fig. 4, the composite exhibits larger M^*_{33} when all crystallites are aligned parallel to the sample X_3 axis. For further illustration for this case of $\theta_{cutoff}=0°$, we consider special but technologically important composites having the so-called 1-3 or 2-2 connectivity of phases (in the terminology introduced by Newnham, Skinner, and Cross[16]), in which cylindrical relaxor rods embedded in the matrix are aligned parallel to the sample axis X_3 or the relaxor/epoxy phases are laminated with the sample axis X_3 perpendicular to the layers. Figures 5(a) and 5(b) show, respectively, the effective electrostrictive coefficients for the 1-3– and 2-2–type composites. It can be seen that the 1-3–type composite has larger M^*_{33} values and the 2-2–type composite has larger M^*_{11} values even at the low volume fractions. The explicit expressions of these two electrostrictive coefficients can easily be obtained as

$$M^*_{33}=\sum_{i=1}^{2} f_i\{s^*_{33}(M^{(i)}_{11}c^{(i)}_{11}+2M^{(i)}_{12}c^{(i)}_{12}) + 2h^{(i)}_{13}[M^{(i)}_{11}c^{(i)}_{12}+M^{(i)}_{12}(c^{(i)}_{11}+c^{(i)}_{12})]\}, \qquad (42)$$

for the 1-3–type composite; and

$$M^*_{11}=\sum_{i=1}^{2} f_i\{s^*_{11}(M^{(i)}_{11}c^{(i)}_{11}+2M^{(i)}_{12}c^{(i)}_{12}) + h^{(i)}_{22}[M^{(i)}_{11}c^{(i)}_{12}+M^{(i)}_{12}(c^{(i)}_{11}+c^{(i)}_{12})]\}, \qquad (43)$$

for the 2-2–type composite, where

$$h^{(i)}_{13}=\frac{2s^*_{13}c^*_{11}+s^*_{33}(c^*_{13}-c^{(i)}_{12})}{c^{(i)}_{11}+c^{(i)}_{12}+c^*_{11}-c^*_{12}}, \qquad (44)$$

$$h^{(i)}_{22}=\frac{s^*_{12}c^{(i)}_{11}+s^*_{33}c^*_{33}+(s^*_{11}+s^*_{12})(c^*_{13}-c^{(i)}_{12})}{c^{(i)}_{11}}, \qquad (45)$$

and s^*_{ij} are the effective compliance constants of the composites. They depend on the elastic constants and electrostrictive coefficients of the two phases and the effective elastic constants. The predictions demonstrate that such 1-3– and 2-2–type composites can be good for electrostrictors, as in the piezoceramic/polymer composites already widely investigated. The flexible relaxor ceramic/polymer composites may be important smart composites for electrostrictive devices that can be mechanically flexible with desired electrostriction.

V. CONCLUSIONS

An effective-medium-like approach has been developed for the effective electrostriction in inhomogeneous materials by utilizing Green's-function technique. For the isotropic composites containing randomly oriented spheroidal relaxor ferroelectric crystallites, and 1-3–type fibrous composite and 2-2–type laminated composite, explicit approximate expressions for the effective electrostrictive coefficients have been given. Numerical calculations for the effective electrostrictive coefficients in a flexible relaxor ferroelectric crystallites/epoxy composite have demonstrated that the effective electrostrictive coefficients of the composite can be strongly influenced by the material constants, the volume fraction, phase connectivity, particle shape, and orientation of the relaxor crystallites. These numerical results have shown the interesting behavior of the composites; they can provide a general guideline for the evaluation of more composite systems and thereby be used to develop criteria for choosing the best combination of different constituent materials for the electrostrictors. Although such electrostrictive composites have not yet been reported in the literature, our theoretical results indicate that by choosing the best combination of different constituent materials and microstructural features it is possible to develop electrostrictors combining large electrostriction with mechanical flexibility, which may open up promising territory in the quest for practical electrostrictive materials. The present theoretical framework can also be extended to modeling other macroscopic properties, such as strain versus *E*-field behavior, hysteresis, stress and thermal effect, of the inhomogeneous electrostrictive materials.

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