Application of elastostatic Green function tensor technique to electrostriction in cubic,

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Abstract
The elastostatic Green function tensor approach, which was recently used to
treat electrostriction in the numerical simulation of domain structure formation
in cubic ferroelectrics, is reviewed and extended to the crystals of hexagonal and
orthorhombic symmetry. The tensorial kernels appearing in the expressions for
effective nonlocal interaction of electrostrictive origin are derived explicitly and
their physical meaning is illustrated by simple examples. It is argued that the
bilinear coupling between the polarization gradients and elastic strain should
be systematically included in the Ginzburg–Landau free energy expansion of
electrostrictive materials.

1. Introduction

Technological advancements in ferroelectric materials have triggered interest in the kinetics of
domain pattern formation and its description by the time-dependent Ginzburg–Landau (TDGL)
model. Since the basic TDGL model (with just a few polynomials in homogeneous order
parameter and a single gradient term in its free energy functional) was found useful in many
areas of physics [1–6], its solutions are nowadays known with a remarkable amount of detail
and mathematical rigour [7]. However, the quantitative understanding of ferroelectric domain
structure properties requires the addition of extra terms accounting for the contribution of
long-range interactions of an electric and elastic nature [8–15]. While this extension is quite
straightforward and provides a considerable potential for realistic simulations of domain pattern
evolution, macroscopic ferroelectric and piezoelectric response, impact of defects, finite size
effects and so on, it also brings new technical problems.

The crucial difficulty of this extended TDGL model consists in dealing with the elastic
field controlled by the inhomogeneous polarization due to the electrostrictive coupling.
The full approach would require the simultaneous solution of both coupled equations of motion

(for both elastic and polarization fields). The standard approach to the problem [14–18] consists in the elimination of the elastic degrees of freedom with the help of the mechanical equilibrium conditions. This leads to an effective interaction term F_{het} depending explicitly on the order parameter (polarization $P(x)$) only. Such an effective term is then added to the Landau–Devonshire free energy functional instead of the elastic and the electrostrictive terms and one is left with a single equation of motion for the polarization field only.

A technical drawback of the approach is that the resulting effective energy term is nonlinear and nonlocal. Moreover, if the real space integration is preserved, the elastic properties of the medium come in the formula through the anisotropic elastostatic Green functions for which only complicated integral expressions are known. Nevertheless, at least for some purposes, the explicit expressions for anisotropic elastostatic Green functions can be avoided by expressing the interaction F_{het} in terms of Fourier components of polarization. The Fourier representation is particularly convenient in the case of modulated ferroelectrics, where the polarization has the form of a single plane wave [14], but it is extremely useful even in the case of 3D domain structures [11, 12]. In the Fourier representation, the elastic properties appear in the expression for F_{het} through a tensorial kernel $B_{ijkl}(n)$. This tensorial kernel is a fourth-order tensor angular function comprising all necessary information about the electrostrictive and elastic properties of the material. The elastic properties of the medium are introduced in $B_{ijkl}(n)$ solely via the so-called elastic Green function tensor [17], which is a much more simple object than the (real space) elastic Green function itself.

In some cases, the exact form of the tensorial kernel $B_{ijkl}(n)$ could be reasonably approximated by that of the elastically isotropic medium [17, 18]. Some time ago, however, the components of $B_{ijkl}(n)$ in general cubic crystals were derived explicitly [11] and the fully anisotropic F_{het} was then successfully used in realistic 2D and 3D simulations [11, 12, 19] of domain structure coarsening in perovskite ferroelectrics. The objective of this work is the extension of this technique, which may be called the 'elastostatic Green function tensor technique', to the crystals of lower symmetry.

For the sake of clarity, we have introduced the notation and the approach leading to the expressions for effective energy contribution F_{het} in section 2. The explicit expressions known for cubic crystals [11] are generalized to the case of orthorhombic and hexagonal symmetries in section 3. Section 4 is devoted to the basic electrostriction (without gradient terms). The F_{het} is expressed in terms of a polarization autocorrelation tensor and the physical meaning of the A_{ijkl} tensor introduced in [11] is discussed in detail. Finally, the role of gradient terms in the systematic expansion of electrostrictive energy is elucidated in section 5.

2. Elimination of elastic degrees of freedom

The excess Gibbs free energy functional describing an elastically linear ferroelectric in a general polarization and stress state can be expressed as a sum of three terms:

$$F = F_0\{P_i, P_{i,j}\} + F_1\{P_i, P_{i,j}, u_{ij}\} + F_2\{u_{ij}\}, \tag{1}$$

where $P_i, P_{i,j}$ stands for the ith Cartesian component of the polarization field and for its jth spatial derivative, and u_{ij} is the ij component of the (infinitesimal) strain field.

The first part $F_0\{P_i, P_{i,j}\}$ may be further divided into an integral of the basic local Landau free energy density f_L, the Ginzburg (gradient) energy density f_G, depending on spatial derivatives of $P(x)$, and the contribution of the dipole–dipole interaction F_{dip}:

$$F_0\{P_i, P_{i,j}\} = F_{\text{dip}} + \int (f_L + f_G) \, dx. \tag{2}$$

The electrostrictive energy $F_1\{P_i, P_{i,j}, u_{ij}\}$ can be expressed as an integral over electrostriction density f_{es}, which is by definition linear in the elastic strain field $u_{ij}(\boldsymbol{x})$:

$$F_1\{P_i, P_{i,j}, u_{ij}\} = \int f_{es}\,\mathrm{d}\boldsymbol{x}, \qquad f_{es} = -g_{ij}u_{ij}, \tag{3}$$

where the leading term in the expansion of coefficient g_{ij}

$$g_{ij} = g_{ij}(P_i, P_{i,j}) = q_{ijkl}P_k P_l + \cdots \tag{4}$$

is just given by the usual electrostriction tensor q_{ijkl}. Note that the Einstein summation rule is assumed in this paper. The last term, the proper elastic energy, is merely a quadratic function of the elastic strain field

$$F_2\{u_{ij}\} = \int (p_{ij}u_{ij} + f_{ela})\,\mathrm{d}\boldsymbol{x}, \qquad f_{ela} = \tfrac{1}{2}C_{ijkl}u_{ij}u_{kl}. \tag{5}$$

In this case the total stress $\sigma_{ij}(\boldsymbol{x})$ can be divided into three contributions—thermal stress p_{ij}, describing for example the common thermal dilatation, purely elastic stress $C_{ijkl}u_{kl}$ and the proper electrostrictive tensile stress field g_{ij} originating from coupling to the polarization field:

$$\sigma_{ij}(\boldsymbol{x}) = \frac{\partial f}{\partial u_{ij}} = p_{ij} + C_{ijkl}u_{kl} - g_{ij}. \tag{6}$$

In static problems or in dealing with slow processes like domain structure formation, the inhomogeneous elastic strain can often be eliminated by means of static equilibrium conditions. The local stress equilibrium condition $\sigma_{ij,j} = 0$ can be considered as a second-order partial differential equation for a displacement field $\boldsymbol{u}(\boldsymbol{x})$:

$$C_{ijkl}\frac{\partial^2 u_k}{\partial x_j \partial x_l} = \frac{\partial g_{ij}}{\partial x_j}. \tag{7}$$

This condition defines $\boldsymbol{u}(\boldsymbol{r})$ up to a linear form (homogeneous strain). Let us first consider a macroscopically clamped crystal with a large volume V, where the homogeneous strain is zero. In principle, the solution to equation (7) satisfying

$$\bar{u}_{ij} \equiv \langle u_{ij}(\boldsymbol{x})\rangle \equiv \frac{1}{V}\int_V u_{ij}(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x} = 0, \tag{8}$$

can be found using the corresponding anisotropic elastostatic Green function $G(\boldsymbol{x})$ defined by

$$C_{ijkl}\frac{\partial^2 G_{km}}{\partial x_j \partial x_l} = \delta(\boldsymbol{x})\delta_{im}, \tag{9}$$

where $\delta(\boldsymbol{x})$ and δ_{ij} are Dirac and Kronecker deltas.

At the same time, the formal solution for $k \neq 0$ Fourier components follows immediately from equation (7):

$$\boldsymbol{u}(\boldsymbol{k}) \equiv \langle \boldsymbol{u}(\boldsymbol{x})\exp(-\mathrm{i}\boldsymbol{k}\boldsymbol{x})\rangle = \frac{\mathrm{i}\Omega(\hat{\boldsymbol{n}})\cdot g(\boldsymbol{k})\cdot \boldsymbol{k}}{k^2}, \tag{10}$$

where $\hat{\boldsymbol{n}}$ is the unit vector such that $\boldsymbol{k} = k\hat{\boldsymbol{n}}$,

$$g_{ij}(\boldsymbol{k}) \equiv \langle g_{ij}(\boldsymbol{x})\exp(-\mathrm{i}\boldsymbol{k}\boldsymbol{x})\rangle \tag{11}$$

are the Fourier components of the electrostrictive tensile stress field $g_{ij}(\boldsymbol{x})$ and the Green function tensor [17] $\Omega(\hat{\boldsymbol{n}})$ is the inverse of the Christoffel (acoustical [20]) tensor $\Gamma(\hat{\boldsymbol{n}})$:

$$(\Omega(\hat{\boldsymbol{n}})^{-1})_{ij} = \Gamma_{ij}(\hat{\boldsymbol{n}}) \equiv C_{ijkl}\hat{n}_k\hat{n}_l. \tag{12}$$

Assuming a Born–Kármán-like boundary conditions on the volume V, the inverse Fourier transform provides the heterogeneous strain field as [14]

$$\tilde{u}_{ij}(\boldsymbol{x}) = \sum_{k\neq 0} \mathrm{i}k_i u_j(\boldsymbol{k})\exp(\mathrm{i}\boldsymbol{k}\boldsymbol{x}). \tag{13}$$

The k vectors involved in the summation form a discrete set spread homogeneously over the whole Brillouin zone with density $V/(2\pi)^3$. In fact, only the long wave contributions should be essential (theory assumes smooth inhomogeneity or thick enough domain walls) since otherwise the long wavelength elasticity considered in equation (5) is not adequate. By inserting the formal solution equation (13) back into equation (1), we obtain the searched effective interaction term $F_{\text{het}} = F_1 + F_2$ for a macroscopically clamped system in the form [11, 16, 17]

$$F_{\text{het}} = -\frac{V}{2} \sum_{k \neq 0} \sum_{ijkl} \hat{n}_i g_{ij}(\boldsymbol{k}) \Omega_{jk}(\hat{\boldsymbol{n}}) g_{kl}(-\boldsymbol{k}) \hat{n}_l$$

$$= -\frac{V}{2} \sum_{k \neq 0} \hat{\boldsymbol{n}} \cdot g(\boldsymbol{k}) \cdot \Omega(\hat{\boldsymbol{n}}) \cdot g(-\boldsymbol{k}) \cdot \hat{\boldsymbol{n}}, \tag{14}$$

which does not depend on the elastic strain field anymore. The integrand (summand) of equation (14) is a bilinear form in Fourier-transformed tensor components $g_{ij}(\boldsymbol{k})$. It is thus possible to use the Voigt abbreviated subscript notation [21] for C_{ijkl} and for g_{ij}:

$$\begin{aligned} g_1 = g_{11}, &\qquad g_2 = g_{22}, &\qquad g_3 = g_{33}, \\ g_4 = g_{23}, &\qquad g_5 = g_{13}, &\qquad g_6 = g_{12}, \end{aligned} \tag{15}$$

and rewrite equation (14) in a compact form [11] (hereafter the Greek indices go always from 1 to 6):

$$F_{\text{het}} = -\frac{V}{2} \sum_{k \neq 0} g_\alpha(\boldsymbol{k}) B_{\alpha\beta}(\hat{\boldsymbol{n}}) g_\beta(-\boldsymbol{k}). \tag{16}$$

The nonlocal character of this effective interaction is more apparent after returning back to the real space:

$$F_{\text{het}} = -\frac{1}{2} \int_V \int_V \tilde{g}_{ij}(\boldsymbol{x}') \frac{\partial^2 G_{kl}(\boldsymbol{x}' - \boldsymbol{x}'')}{\partial x_j \partial x_m} \tilde{g}_{lm}(\boldsymbol{x}'') \, \mathrm{d}\boldsymbol{x}' \, \mathrm{d}\boldsymbol{x}'' \tag{17}$$

where $\tilde{g}_{ij} = g_{ij} - \langle g_{ij} \rangle$ is the heterogeneous part of the electrostrictive field g_{ij}. This expression shows that the $B_{\alpha\beta}$ tensorial kernel is actually a Fourier-transformed Hessian of the elastostatic Green function $G(\boldsymbol{x})$ defined in equation (9).

Finally, the total strain field under general macroscopic equilibrium conditions is

$$u_{ij}(\boldsymbol{x}) = \bar{u}_{ij} + \tilde{u}_{ij}(\boldsymbol{x}), \tag{18}$$

where $\tilde{u}_{ij}(\boldsymbol{x})$ is given by equation (13) and $\bar{u}_{ij}$ is the homogeneous component defined by the left-hand side of equation (8). For example, the free sample condition $\bar{\sigma}_{ij} = 0$ leads to the equilibrium value (see equation (6))

$$\bar{u}_{ij} = S_{ijkl}(\bar{g}_{kl} - p_{kl}), \tag{19}$$

where $S_{ijkl} = (C^{-1})_{ijkl}$ is the matrix of elastic compliances. Substitution of equation (18) back into the original potential in equation (1) provides $F_1 + F_2 = F_{\text{het}} + F_{\text{hom}}$ where

$$F_{\text{hom}} = -\frac{V}{2}(\bar{g}_\alpha - p_\alpha) S_{\alpha\beta}(\bar{g}_\beta - p_\beta) \tag{20}$$

and F_{het} is just the same as for the case of a clamped crystal (equations (14) and (17)).

3. Elastostatic Green function tensor for cubic, hexagonal and orthorhombic crystals

Provided that the explicit dependence of the electrostrictive tensile stress g_{ij} on polarization field appearing in equation (16) is known, the effective energy term F_{het} can be calculated from equation (14), (16) or (17). Obviously, in some cases [22] it is worth tackling the problem [23] of the calculation of the Green function derivatives appearing in equation (17) explicitly, while in other cases it is possible to avoid it [11, 12, 18, 19] and use equation (14) or (16). For example, it was shown [12, 19] that simulations of domain structure coarsening described by the TDGL equations (including the above effective interaction term F_{het}) can be performed entirely in the Fourier space.

In this paragraph, we will concentrate on properties of the elastic Green function tensor $\Omega_{ij}(\hat{n})$ and the 6×6 matrix of the tensorial kernel $B_{\alpha\beta}(\hat{n})$ appearing in equation (16). In order to avoid numerical inversion of the Christoffel tensor (equation (12)) at each wavevector direction $\hat{n}$, several authors have derived explicit formulae for the cubic symmetry Green function tensor $\Omega_{ij}(\hat{n})$. Among them, the approach of [11] is the most suitable here since it allows for generalization to the case of hexagonal and orthorhombic symmetry. The essential step consists in expressing Γ_{ij} as a sum of a diagonal part $d_j(\hat{n})$ and a tensorial square of a convenient real vector v:

$$\Gamma_{ij}(\hat{n}) = d_j(\hat{n})\delta_{ij} + v_i v_j. \tag{21}$$

This is trivial in cubic crystals where obviously [11]

$$v_i = (C_{12} + C_{44})\hat{n}_i, \tag{22}$$

$$d_i = C_{44} + (C_{11} - C_{12} + C_{44})\hat{n}_i^2. \tag{23}$$

The decomposition is not so straightforward for the crystals of lower symmetry. Nevertheless, for example in the case of an orthorhombic elastic medium with

$$C_{23} > -C_{44}, \qquad C_{13} > -C_{55}, \qquad C_{12} > -C_{66}, \tag{24}$$

(which is a very weak assumption since practically all known crystals have all the off-diagonal elements C_{12}, C_{13} and C_{23} positive), the Christoffel tensor is given by equation (21) with

$$
\begin{aligned}
v_1 &= \hat{n}_1 \sqrt{\frac{(C_{12} + C_{66})(C_{13} + C_{55})}{(C_{23} + C_{44})}}, \\
v_2 &= \hat{n}_2 \sqrt{\frac{(C_{23} + C_{44})(C_{12} + C_{66})}{(C_{13} + C_{55})}}, \\
v_3 &= \hat{n}_3 \sqrt{\frac{(C_{13} + C_{55})(C_{23} + C_{44})}{(C_{12} + C_{66})}},
\end{aligned}
\tag{25}
$$

$$
\begin{aligned}
d_1 &= C_{11}\hat{n}_i^2 + C_{66}\hat{n}_2^2 + C_{55}\hat{n}_3^2 - v_1^2, \\
d_2 &= C_{44}\hat{n}_i^2 + C_{22}\hat{n}_2^2 + C_{44}\hat{n}_3^2 - v_2^2, \\
d_3 &= C_{55}\hat{n}_i^2 + C_{44}\hat{n}_2^2 + C_{33}\hat{n}_3^2 - v_3^2.
\end{aligned}
\tag{26}
$$

Obviously, the above decomposition can be used also for hexagonal crystals; it is sufficient to put $C_{55} = C_{44}$, $C_{22} = C_{11}$, $C_{23} = C_{13}$ and $2C_{66} = C_{11} - C_{12}$.

For arbitrary crystal symmetry, once the explicit expressions for v_i and d_i are known, the Green function tensor Ω_{ij} is obtained directly using the lemma from the appendix:

$$\Omega_{ij}(\hat{n}) = \frac{\delta_{ij}}{d_j} - \frac{v_i v_j}{d_i d_j}\left(1 + \sum_{k=1}^{3} \frac{v_k^2}{d_k}\right)^{-1}. \tag{27}$$

The tensorial kernel $B_{\alpha\beta}$ then is

$$B_{\alpha\beta}(\hat{n}) = \beta_{\alpha\beta} - \theta_\alpha\theta_\beta \left(1 + \sum_{k=1}^{3} \frac{v_k^2}{d_k}\right)^{-1}, \tag{28}$$

where

$$\begin{aligned}
\theta_1 &= \hat{n}_1 v_1/d_1, & \theta_2 &= \hat{n}_2 v_2/d_2, & \theta_3 &= \hat{n}_3 v_3/d_3, \\
\theta_4 &= \hat{n}_2 v_3/d_3 + \hat{n}_3 v_2/d_2, & \theta_5 &= \hat{n}_1 v_3/d_3 + \hat{n}_3 v_1/d_1, \\
\theta_6 &= \hat{n}_2 v_1/d_1 + \hat{n}_1 v_2/d_2,
\end{aligned} \tag{29}$$

modifies equation (4.16) used in [11] for cubic crystals and the components of the $\{\beta_{\alpha\beta}\}$ tensor:

$$\begin{pmatrix}
\frac{\hat{n}_1^2}{d_1} & 0 & 0 & 0 & \frac{\hat{n}_3\hat{n}_1}{d_1} & \frac{\hat{n}_2\hat{n}_1}{d_1} \\
0 & \frac{\hat{n}_2^2}{d_2} & 0 & \frac{\hat{n}_3\hat{n}_2}{d_2} & 0 & \frac{\hat{n}_1\hat{n}_2}{d_2} \\
0 & 0 & \frac{\hat{n}_3^2}{d_3} & \frac{\hat{n}_2\hat{n}_3}{d_3} & \frac{\hat{n}_1\hat{n}_3}{d_3} & 0 \\
0 & \frac{\hat{n}_3\hat{n}_2}{d_2} & \frac{\hat{n}_2\hat{n}_3}{d_3} & \frac{\hat{n}_2^2}{d_3} + \frac{\hat{n}_3^2}{d_2} & \frac{\hat{n}_1\hat{n}_2}{d_3} & \frac{\hat{n}_1\hat{n}_3}{d_2} \\
\frac{\hat{n}_3\hat{n}_1}{d_1} & 0 & \frac{\hat{n}_1\hat{n}_3}{d_3} & \frac{\hat{n}_1\hat{n}_2}{d_3} & \frac{\hat{n}_1^2}{d_3} + \frac{\hat{n}_3^2}{d_1} & \frac{\hat{n}_3\hat{n}_2}{d_1} \\
\frac{\hat{n}_2\hat{n}_1}{d_1} & \frac{\hat{n}_1\hat{n}_2}{d_2} & 0 & \frac{\hat{n}_1\hat{n}_3}{d_2} & \frac{\hat{n}_2\hat{n}_3}{d_1} & \frac{\hat{n}_2^2}{d_1} + \frac{\hat{n}_1^2}{d_2}
\end{pmatrix} \tag{30}$$

as a function of d_i simply coincide with those given previously for cubic crystals in equation (4.15) of [11].

Let us note that, in the rare cases when some of the denominators in equation (25) would become zero [20] or negative, the method works equally well. It is sufficient to modify these equations in order to express the Christoffel matrix in the form assumed in the appendix.

4. Basic electrostriction in crystal of arbitrary symmetry class

In this section, we will assume that the electrostrictive tensile stress g_{ij} is a bilinear form of polarization components:

$$g_{ij}(\boldsymbol{x}) = q_{ijkl} P_k(\boldsymbol{x}) P_l(\boldsymbol{x}), \tag{31}$$

where q_{ijkl} is the usual electrostrictive tensor, symmetric both in the first and second pair of indexes. In all crystal symmetry classes, at least some of the components are nonzero. Since it is also the lowest-order term in non-piezoelectric materials, most of the phenomenological models are limited just to that term [11, 12, 14, 18, 22]. In this case, it is convenient to introduce [11] an autocorrelation tensor $Y_{ij}(\boldsymbol{k})$:

$$Y_{ij}(\boldsymbol{k}) \equiv \langle P_i(\boldsymbol{x}) P_j(\boldsymbol{x}) \exp(-\mathrm{i}\boldsymbol{k}\boldsymbol{x}) \rangle, \tag{32}$$

which is nothing else but a convolution of corresponding Fourier components of the polarization field:

$$Y_{ij}(\boldsymbol{k}) = \sum_{\boldsymbol{k}'} P_i(\boldsymbol{k}') P_j(\boldsymbol{k} - \boldsymbol{k}'). \tag{33}$$

The heterogeneous effective energy term F_{het} then is [11]

$$F_{\text{het}} = -\frac{V}{2} \sum_{\boldsymbol{k}\neq\boldsymbol{0}} Y_\alpha(\boldsymbol{k}) A_{\alpha\beta}(\hat{\boldsymbol{n}}) Y_\beta(-\boldsymbol{k}). \tag{34}$$

where $A_{\alpha\delta}(\hat{\boldsymbol{n}}) = q_{\alpha\beta} B_{\beta\gamma}(\hat{\boldsymbol{n}}) q_{\gamma\delta}$ now depends on both elastic and electrostrictive material constants.

Let us now assume that the sample contains a single planar domain wall perpendicular to a fixed direction $\hat{n}_0$. Then we can keep only $P(k)$ and $Y_\alpha(k)$ with $k \parallel \hat{n}_0$ so that $A_{\alpha\beta}(\hat{n}) = A_{\alpha\beta}(\hat{n}_0)$ can be taken in front of the summation symbol in equation (34):

$$F_{\text{het}} = -\frac{V}{2} A_{\alpha\beta}(\hat{n}_0)\left[\sum_k Y_\alpha(k) Y_\beta(k) - Y_\alpha(0) Y_\beta(0) \right]. \tag{35}$$

Let us further assume, for example, a 180° domain wall with P_1, $P_3 = 0$, so that only $Y_2(k)$ contributes. The Einstein summation in the above expression then reduces to a single term:

$$F_{\text{het}} = -\frac{V}{2} A_{22}(\hat{n}_0)[\langle P_1^4 \rangle - \langle P_1^2 \rangle^2], \tag{36}$$

where $\langle \ \rangle$ stands for the spatial average as defined in equation (8).

Since the polarization field comes in equation (36) via the spatial mean square deviation of P_2^2, it is apparent that the nonzero contributions to F_{het} comes only from the region in the vicinity of the domain wall. Our example thus allows us to give a clear interpretation to the $A_{\alpha\beta}(\hat{n}_0)$ tensor function. For a fixed domain wall profile, its angular dependence defines how the electrostrictive reduction of the domain wall energy varies with domain wall orientation $\hat{n}_0$ and its tensorial components distinguish various types of domain walls according to the associated change in polarization direction. Obviously, in a well-coarsened domain pattern, where the polarization inhomogeneities are limited to the domain wall regions, the F_{het} again become effectively *local* functionals, but depending on density, *type* and *orientation* of domain walls.

Incommensurate structures with modulated polarization represent another transparent case of 1D inhomogeneity where equation (35) holds. Actually, it was shown [14] that the F_{rel} term is essential for explanation of the dielectric anomalies of incommensurate ferroelectric $NaNO_2$. In the ideal case of uniaxial sinusoidal modulation with P_1, $P_3 = 0$ and wavevector $k_0 \parallel \hat{n}_0$, there is only a single nonzero pair of Fourier components of polarization $\{P_2(k_0), P_2(-k_0)\}$ so that

$$F_{\text{het}} = -V A_{2,2}(\hat{n}_0)[P_1(k_0) P_1(-k_0)]^2, \tag{37}$$

As noted previously [14], this expression does not depend explicitly on the modulation wavevector and thus it does not vanish in the $k_0 \to 0$ limit. In fact, this observation is not so surprising in the present context, since it follows from the fact that the volume ratio between 'domain walls' and 'domains' is fixed by the sinusoidal profile of the modulation. Naturally, if one assumes that, with decreasing k_0, the modulation becomes of a more and more 'rectangular' shape, the 'gap' between the energy of a homogeneous and modulated ferroelectric would vanish in the $k_0 \to 0$ limit.

Finally, let us note that, in the case of 1D inhomogeneity with a fixed direction $\hat{n}_0$, the first term on the right-hand side of equations (35) and (36) can actually be interpreted as a local term, merely renormalizing fourth-order terms in the Landau–Devonshire potential F_L. At the same time, the second term, although nonlocal, depends on polarization in the same way as the F_{hom}.

5. Gradient electrostriction

Since the elastostatic Green function tensor technique described in section 2 was developed for dealing with inhomogeneous polarization configurations, it is natural to include in the free energy expansion terms depending on the spatial derivations of polarization. In principle, consistent free energy expansion may require such terms not only in the expansion of F_0,

but also in the expansion of F_1. Thus, instead of equation (31), one may need to assume (in a crystal with a centrosymmetric paraelectric phase)

$$g_{ij} = q_{ijkl} P_k P_l + r_{ijkl} \frac{\partial P_k}{\partial x_l} + s_{ijklmn} \frac{\partial P_k}{\partial x_l} \frac{\partial P_m}{\partial x_n} + \cdots . \tag{38}$$

Let us demonstrate the role of this gradient electrostriction term in the case of a uniaxial ($P_1, P_3 = 0$) ferroelectric with orthorhombic paraelectric phase. Due to the choice of easy polarization direction and the obvious symmetry constraints, all nonzero terms in the $g_\alpha(\boldsymbol{x})$ expansion up to the second order in $P = P_2$ and $P_{,j} = \partial P/\partial x_j$ can be easily enumerated and conveniently expressed using Voigt notation:

$$
\begin{aligned}
g_1 &= q_{12} P^2 + r_{12} P_{,2} + s_{12i} P_{,i}^2, \\
g_2 &= q_{22} P^2 + r_{22} P_{,2} + s_{22i} P_{,i}^2, \\
g_3 &= q_{32} P^2 + r_{32} P_{,2} + s_{32i} P_{,i}^2, \\
g_4 &= r_{44} P_{,3} + s_{442} P_{,3} P_{,2}, \\
g_5 &= s_{564} P_{,1} P_{,3}, \\
g_6 &= r_{66} P_{,1} + s_{662} P_{,1} P_{,2}.
\end{aligned}
\tag{39}
$$

The Fourier components $g_\alpha(\boldsymbol{k})$ are then

$$
\begin{aligned}
g_1(\boldsymbol{k}) &= (q_{12} - s_{12i} k_i^2) Y(\boldsymbol{k}) - i r_{12} k_2 P(\boldsymbol{k}), \\
g_2(\boldsymbol{k}) &= (q_{22} - s_{22i} k_i^2) Y(\boldsymbol{k}) - i r_{22} k_2 P(\boldsymbol{k}), \\
g_3(\boldsymbol{k}) &= (q_{32} - s_{32i} k_i^2) Y(\boldsymbol{k}) - i r_{32} k_2 P(\boldsymbol{k}), \\
g_4(\boldsymbol{k}) &= -i r_{44} k_3 P(\boldsymbol{k}) - s_{442} k_3 k_2 Y(\boldsymbol{k}), \\
g_5(\boldsymbol{k}) &= -s_{564} k_1 k_3 Y(\boldsymbol{k}), \\
g_6(\boldsymbol{k}) &= -i r_{66} k_1 P(\boldsymbol{k}) - s_{662} k_1 k_2 Y(\boldsymbol{k}),
\end{aligned}
\tag{40}
$$

where we have used the autocorrelation tensor component $Y(\boldsymbol{k}) = Y_2(\boldsymbol{k})$ defined previously in equation (32).

The effective interaction F_{het} can now be evaluated from equation (16). Let us examine the case of 1D inhomogeneity where only $P(\boldsymbol{k})$ with $\boldsymbol{k} \parallel \hat{\boldsymbol{n}}_1$ parallel to the crystallographic axis x_1 is nonzero. Then, the only nonzero components of the $B_{\alpha\beta}(\hat{\boldsymbol{n}}_1)$ tensorial kernel (equation (28)) are

$$B_{11}(\hat{\boldsymbol{n}}_1) = \frac{1}{C_{11}}, \qquad B_{55}(\hat{\boldsymbol{n}}_1) = \frac{1}{C_{55}}, \qquad B_{66}(\hat{\boldsymbol{n}}_1) = \frac{1}{C_{66}}, \tag{41}$$

and the F_{het} then reduces to a sum of two terms:

$$F_{\text{het1}} = -\frac{V}{2} \sum_{k_1 \neq 0} \frac{(q_{12} - s_{12i} k_i^2)^2}{C_{11}} Y(k_1) Y(-k_1), \tag{42}$$

and

$$F_{\text{het2}} = -\frac{V}{2} \sum_{k_1 \neq 0} \frac{r_{66}^2 k_1^2}{C_{66}} P(k_1) P(-k_1). \tag{43}$$

The first term has the same form as the expression in equation (34), except for the fact that the $s_{\alpha\beta\gamma}$ coupling makes the generalized $A_{\alpha\beta}$ tensor dependent also on the modulus of the $\boldsymbol{k}$ vector. Therefore, the $s_{\alpha\beta\gamma}$ tensor terms in equation (38) can be safely neglected (unless the problem under study is drastically sensitive to the inhomogeneity length scale, as for example at the lock-in phase transition in type-II incommensurate systems [14]).

The second term given by equation (43) can be straightforwardly transformed to

$$F_{\text{het2}} = -\frac{1}{2} \frac{r_{66}^2}{C_{66}} \int_V \left(\frac{\partial P(\boldsymbol{x})}{\partial x_1} \right)^2 d\boldsymbol{x}, \tag{44}$$

so that it is apparent that this term renormalizes the coefficient of the lowest order gradient term in the 'Ginzburg part' f_{G} of the free-energy expansion (equation (1)). The experimental studies of bilinear coupling between soft mode and acoustic branches by Brillouin and inelastic neutron scattering techniques show that the r_{ijkl} coupling term in equation (38) may indeed cause an important renormalization of the Ginzburg term. Probably, more pronounced effects are expected in crystals with a small Ginzburg term. It is even believed that in some crystals this gradient electrostriction compensates the Ginzburg term completely, which leads to the appearance of incommensurate modulated structure [24, 25]. Unfortunately, in the general 3D case, the effect of the r_{ijkl} coupling term does not reduce to a simple renormalization of coefficients in the Ginzburg free energy and the full anisotropy of $B_{\alpha\beta}(\hat{\boldsymbol{n}})$ tensorial kernel should be taken into account.

6. Conclusion

The elastostatic Green function tensor technique presented here is concerned with the simulation of the ferroelectric domain pattern, being a cutting edge problem both in the theory of phase transitions and technological applications. We have found that this technique, applied recently to electrostriction in ferroelectrics with a cubic paraelectric phase, can be straightforwardly generalized to hexagonal and orthorhombic crystals. The contribution of this approach is most valuable for orthorhombic crystals since they are far from isotropy and the closed formulas for elastostatic Green functions are known only for a few very special limit cases [20]. Unfortunately, the method outlined here is not very convenient for tetragonal, trigonal and monoclinic symmetries since the $\boldsymbol{v}$ vector used in decomposition of the Christoffel matrix would have a nontrivial angular dependence. We are not aware of any elegant method for the inversion of a Christoffel matrix in such cases.

The essential effect of the nonlocal, nonlinear and anisotropic effective interaction term F_{het} consists in reduction of domain wall energies as a function of their orientation and the associated change of polarization vector. This information is conveniently contained in the tensor $A_{\alpha\beta}(\hat{\boldsymbol{n}})$ introduced in equation (34). Polar diagrams of the $A_{\alpha\beta}(\hat{\boldsymbol{n}})$ tensorial components may thus be quite instructive for understanding the behaviour of a particular system.

Finally, the bilinear coupling between the polarization gradients and elastic strain should not be overlooked in the realistic simulations. The values of the corresponding tensorial coefficients r_{ijkl} can be determined, for example, with the help of Brillouin and inelastic neutron scattering techniques.

Acknowledgments

Appendix

Let us suppose that a finite regular real symmetrical matrix A can be written as a sum of a diagonal part D and a real multiple of a tensorial (dyadic) square $\boldsymbol{v} \otimes \boldsymbol{v}$ of a real vector $\boldsymbol{v}$ as

$$A_{ij} = (D + \lambda \boldsymbol{v} \otimes \boldsymbol{v})_{ij} = d_j \delta_{ij} + \lambda v_i v_j, \tag{45}$$

where λ is real. Let $w_i \equiv v_i/d_i$. Then the matrix inverse to A is

$$A^{-1} = D^{-1} - \frac{\lambda \boldsymbol{w} \otimes \boldsymbol{w}}{1 + \lambda \boldsymbol{v} \cdot \boldsymbol{w}}, \tag{46}$$

provided that the right-hand side of equation (46) exists. This can be easily proven by multiplication of the expressions in equations (45) and (46).

In the case of orthorhombic, hexagonal and cubic crystals, the above result allows us to find compact explicit expressions for the corresponding elastostatic Green function tensors. For example, in equations (21) and (27), we have applied equation (46) with $\lambda = 1$.

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