Flexoelectricity at ferroelectric domain walls: Predicting atomic structures via first-principles macroscopic theory

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(Dated: February 1, 2022)

Ferroelectric domain walls constitute an attractive playground for studying the bulk flexoelectric effect in a context that is free from extrinsic surface contributions. Here we show, by constructing a macroscopic continuum model of the wall as a well-defined approximation of the first-principles crystal Hamiltonian, that the flexocoupling coefficient is plagued by an inherent arbitrariness, which we rationalize as a weight freedom in the definition of the local strain field. Remarkably, such arbitrariness cancels out with an analogous ambiguity in the definition of the polar order parameter, resulting in a well-defined theory overall. This result points to a generalized gauge freedom in the continuum description of inhomogeneous ferroelectric structures: the contributions of flexoelectricity and correlation are individually ill-defined, but their consistent treatment is crucial for guaranteeing that the physically measurable properties (atomic structure and energetics) are correctly represented. We demonstrate our claims with extensive numerical tests on common ferroelectric perovskites, finding excellent agreement between the continuum model and direct first-principles calculations.

I. INTRODUCTION

Flexoelectricity, the polarization response of an insulating material to a strain gradient, has sparked widespread interest in the past few years as a viable route towards novel electromechanical device concepts.\textsuperscript{1} Flexoelectricity is a close relative of piezoelectricity, which describes the coupling between strain and polarization. Unlike the latter, which is present only in crystals that break inversion symmetry, it is a universal property of all insulators. A wealth of interesting functionalities and potential device applications have been demonstrated over the years, including the possibility of rotating\textsuperscript{2} or switching\textsuperscript{3} the ferroelectric polarization by mechanical means, or of engineering a pseudo-piezoelectric effect.\textsuperscript{4} With the recent breakthroughs in the fabrication of oxide membranes via sacrificial layers,\textsuperscript{5} the interest in flexoelectricity will likely increase even faster than it has done to date, calling for reliable theoretical models to support the experimental search.

Since the pioneering works of Resta\textsuperscript{6} and Hong \textit{et al.}\textsuperscript{7} in 2010, the first-principles theory of flexoelectricity has made an impressive progress.\textsuperscript{8} As of early 2020, a complete calculation of the bulk flexoelectric tensor can be carried out\textsuperscript{9} with the latest release of the publicly distributed ABINIT\textsuperscript{10} package. Unfortunately, the availability of a quantitatively accurate theory has hardly improved the situation in regards to the experimental measurements, whose interpretation remain challenging. A major complication in this context stems from the fact that flexoelectricity is not a bulk property in the usual sense. The polarization response to a flexural deformation of a finite sample always contains a contribution that depends on the details of the surface termination,\textsuperscript{11,12} even in the ideal case of an undefected crystal. This implies that the bulk flexoelectric tensor as calculated from first principles is not directly comparable to the experimentally measured (e.g., in a three-point bending setup) flexoelectric current. Of course, first-principles methodologies to calculate the relevant surface terms do exist,\textsuperscript{13} but they are specific to a given surface structure. This means that, for a meaningful comparison to the experiments, a full characterization of the sample termination at the atomic scale is required, and this is impractical in the vast majority of cases.

A possible workaround that has been pointed out recently\textsuperscript{14} consists in benchmarking the results of first-principles theory on phenomena that occur within the bulk of the material, thereby eliminating the surface-related issues at their very root. Spatially inhomogeneous structures in ferroics such as domain walls, vortices, etc. have received growing attention in the past few years,\textsuperscript{15,16} because of their emerging physical properties and nontrivial topology. Nonuniform strain fields are ubiquitous in all these systems, which means that flexoelectricity often plays an important role in the stabilization of the observed patterns.\textsuperscript{17,18} Most importantly, it endows the spatial gradients of the main order parameters with potentially useful functionalities, e.g., a spontaneous polarization at ferroelastic twins,\textsuperscript{19,20} and a spontaneous strain at ferroelectric walls via the converse effect.\textsuperscript{14,21} In the latter case, in particular, the impact of bulk flexoelectricity can be related to the relaxed atomic positions in the vicinity of the wall,\textsuperscript{14}
which in principle provides a means of extracting the flexocoupling coefficients directly from experimental STEM images.\textsuperscript{[17]} For this reason, ferroelectric domain walls appear as a unique playground to gauge the theoretical predictions of the bulk flexoelectric effect, in a context that is \textit{at first sight} free from ambiguities or extrinsic contributions.

From the formal point of view, the central issue for achieving this goal consists in establishing a rigorous two-way mapping between microscopic degrees of freedom and macroscopic order parameters. In the case of spatially homogeneous crystal phases, such a task poses limited conceptual challenges: Building effective low-energy Hamiltonians in terms of the physically relevant lattice distortions (in perovskite crystals these typically include polarization, strain and antiferrodistortive oxygen tilts) is now common practice \textsuperscript{[22–25]} within the \textit{ab initio} community. Whenever these degrees of freedom are no longer constant over space, however, there are a number of subtleties that need to be carefully considered.\textsuperscript{[26]} These concern the definition of the local strain, of the polar distortion pattern and the flexoelectric tensor itself, all of which imply making arbitrary choices along the way. As we shall see, these apparently innocent choices have a drastic impact on both the continuum model parameters and the domain-wall solution as expressed in terms of field variables. The question, then, is: are there specific criteria for ensuring that the result is physically meaningful? And, once we have solved the continuum equations, how can we verify that our solution is consistent with the “training model”, i.e., our first-principles engine?

Here we show, by deriving the continuum equations and parameters as a well-defined approximation to the first-principles lattice Hamiltonian, that the aforementioned ambiguities have a common origin, and can be rationalized as a \textit{weight freedom} in the definition of the local center of mass. Remarkably, the ambiguities cancel out exactly in any physical prediction of the theory, consistent with the arguments of Hong and Vanderbilt,\textsuperscript{[27]} provided that a unique convention choice is made in the calculation of all continuum coefficients. In particular, our multiscale approach to continuum theory yields unique answers for the relaxed atomic structure and energies of a domain wall, which can be directly validated with the results of direct density-functional theory (DFT) calculations. Thus, the arbitrariness in the continuum solution is only apparent: the answer provided by our approach is robust and consistent once the continuum fields are converted back into atomic distortions and total energies.

We demonstrate our claims by calculating 180° ferroelectric walls in six different perovskite materials, finding answers that are within 10–20% of the “exact” result. Given the extreme (one-cell thick) abruptness of the structures, we regard this as a severe test for a continuum approach, and such an accuracy exceptionally good. By calculating domain walls under hydrostatic pressure in BaTiO$_3$ we also demonstrate the exactness of our theory in the limit of smooth domain walls. From our results, a new paradigm emerges in the construction of continuum models of ferroics: the invariance of the Landau-Ginzburg-Devonshire free energy with respect to a number of \textit{generalized gauge transformations} of the parameters and fields. This implies abandoning the widespread belief that such parameters and fields be well-defined (and hence observable) physical properties of the crystal, and emphasizes the need for an intimate connection between microscopics and macroscopics in order to achieve a qualitatively sound physical picture.

This work is organized as follows. In Section II we address the theoretical issues that arise in the design of continuum models, focusing on the aforementioned ambiguities in the definition of local strains, polar distortion patterns, and flexoelectric coefficients. In Section III we present our numerical tests on 180° domain walls in perovskite oxides, alongside with a detailed validation against the results of direct first-principles calculations. In Section IV we discuss the implications of our findings in the context of the relevant literature. We summarize our work and present our conclusions in Section V.
II. THEORY

A. Statement of the problem

Consider a 180° domain wall in a ferroelectric crystal as schematically illustrated in Fig. 1. The outer extremes of both panels correspond to the oppositely oriented ferroelectric domains, where the polarization ($P$) saturates to its bulk value; in the central domain-wall region $P$ transitions from negative to positive values when moving from left to right. The atomic structure far from the wall is well described in terms of a periodically repeated crystalline cell. Such a structure can be readily obtained from a bulk calculation: one typically starts from the reference configuration, breaks the centrosymmetry by hand (e.g. by displacing atom A upwards or atom O downwards by a small amount), and lets the atoms relax to their polar ground state. Note that one can perform the relaxation while fixing either A or O to their original locations; while the resulting distortions, $d_{A,O}$, differ [compare panels (a) and (b) of Fig. 1], the two structures are related by a rigid translation of the whole lattice, and are therefore degenerate.

Once the domain walls forms, the two oppositely oriented domains no longer enjoy translational invariance separately: the wall lifts the indeterminacy modulo a small amount), and lets the atoms relax to their polar ground state. Note that one can perform the relaxation while fixing either A or O to their original locations; while the resulting distortions, $d_{A,O}$ differ [compare panels (a) and (b) of Fig. 1], the two structures are related by a rigid translation of the whole lattice, and are therefore degenerate.

The simplest free-energy functional to treat this problem is

$$F(P, \varepsilon) = \frac{C}{2} \varepsilon^2 + \frac{A}{2} P^2 + \frac{B}{4} P^4 + f \varepsilon \frac{\partial P}{\partial x} + \frac{G}{2} \left( \frac{\partial P}{\partial x} \right)^2, \quad (2)$$

where $C$ is the elastic constant ($C_{44}$ component), $A$ and $B$ are the standard parameters of the Landau potential, $f$ is the flexoelectric coefficient, and $G$ is the “correlation” coefficient. Note that the flexoelectric coupling is written here in terms of the converse effect (uniform strain in response to a $P$-gradient); it is related to the direct effect and to the standard Lifshitz-invariant expression via simple integrations by parts,

$$f \varepsilon \frac{\partial P}{\partial x} \simeq -f \frac{\partial \varepsilon}{\partial P} \simeq \frac{f}{2} \left( \varepsilon \frac{\partial P}{\partial x} - \frac{\partial \varepsilon}{\partial P} \right). \quad (3)$$

(The difference between the three expressions consists in surface terms, irrelevant for the present bulk theory.)

It is clear that the strain can be integrated out, by imposing the stationary condition

$$\frac{\partial F}{\partial \varepsilon} = 0. \quad (4)$$

This condition immediately leads to the following result [21] for the strain and the displacement field,

$$\varepsilon = -f \frac{\partial P}{C} \rightarrow u = -f \frac{P}{C}. \quad (5)$$
(We have eliminated a trivial integration constant in $u$ by imposing that $u$ vanishes whenever $P = 0$.) Therefore, the displacement field at a ferroelectric domain wall adopts the exact same spatial profile as the polarization, except for the trivial $-f/C$ scaling factor.

After eliminating the strain, we obtain the following simpler expression for the free energy,

$$F(P) = \frac{A}{2}P^2 + \frac{B}{4}P^4 + \frac{\tilde{G}}{2} \left( \frac{\partial P}{\partial x} \right)^2, \quad \tilde{G} = G - \frac{f^2}{C}. \quad (6)$$

The condition for stability is that the renormalized correlation coefficient be positive, $GC > f^2$. (This condition is well known: if $f$ is large enough, the system becomes unstable and an incommensurate transition to a modulated state may occur. \cite{28, 29}) The equation of state is given by the stationary condition with respect to $P$,

$$AP + BP^3 - \tilde{G} \frac{\partial^2 P}{\partial x^2} = 0. \quad (7)$$

We shall attempt a trial solution of the type

$$P(x) = P_0 \tanh \left( \frac{x}{\xi} \right). \quad (8)$$

After a few steps of straightforward algebra, we arrive at

$$P_0^2 = -\frac{A}{B}, \quad \xi^2 = 2\tilde{G} \frac{1}{|A|}. \quad (9)$$

$P_0$ is trivially determined by the bulk Landau potential, while $\xi$ is a length, and has the obvious physical meaning of domain wall thickness.

The domain-wall energy per unit area can be obtained by integrating the free energy density along the normal to the wall,

$$W = \int dx \left[ F(P(x)) - F_0 \right], \quad (10)$$

where $F_0$ is the energy density of the monodomain ground state. One arrives at

$$W = \frac{A^2}{2B} \xi \int_{-\infty}^{+\infty} dx \text{sech}^4(x) = \frac{A^2}{2B} \xi^4 \frac{4}{3} = \frac{8}{3} F_0 |\xi|, \quad (11)$$

where $F_0 = -A^2/AB$ is the bulk energy density. [Since $F_0$ is an energy per unit volume, Eq. (11) correctly describes $W$ in units of energy per length squared.] One can also extract the net elastic offset, $\Delta u$, that we have introduced in the previous Section as

$$\Delta u = -2P_0f \frac{1}{C}. \quad (12)$$

An obvious consequence of the above derivations is that the relevant physical observables i.e., the domain wall thickness ($\xi$) and energy ($W$), depend on the inhomogeneous coefficients only via the renormalized gradient coupling, $\tilde{G}$. This means that we can replace $f$ and $G$ with arbitrary numbers, provided that $G - f^2/C$ retains the original value, and extract physical answers from our theory that are just as good. This property of Eq. (2) may appear at first sight as a mathematical curiosity, but has profound physical implications in relation to the paradox illustrated in Fig. 1; we shall explore them in the following subsections.

C. Direct mapping to the microscopics

In order to discuss the above results in our specific context, it is important to establish a microscopic interpretation of the continuum fields $u(r)$ and $P(r)$: without a clear mapping between continuum and atomistics we would be unable to test the validity of Eq. (2) on real systems. In full generality, we shall use the following two-step procedure. First, we express the individual atomic displacements as continuum functions of the real-space coordinates $r$ by mapping the order parameters onto a sublattice basis indexed by $\kappa$,

$$u_{\kappa\alpha}(r) = \sum_{\beta} u_{\beta}(r)(\kappa\alpha|\beta) + \sum_{\beta} P_{\beta}(r)(\kappa\alpha|P_{\beta}). \quad (13)$$

Second, we write the displacement of the atom in the $l$-th cell by sampling the atomic displacement fields at the unperturbed lattice sites, $R_{l\kappa}^{(0)}$,

$$u_{\kappa\alpha}^l = u_{\alpha\kappa}(R_{l\kappa}^{(0)}). \quad (14)$$

This means that the atom $l\kappa$ displaces according to the amplitude of the continuum field, $u$ or $P$, at the $R_{l\kappa}^{(0)}$ point, times a sublattice-dependent distortion vector, $(\kappa\alpha|v_{\beta})$ ($v = u, P$). The latter describes the displacement of the sublattice $\kappa$ along $\alpha$ for a unitary $\beta$-component the order parameter $v$.

In the case of $u(r)$, such distortion vector does not depend on the basis index $\kappa$, and corresponds to a unitary rigid shift of the cell along $\alpha$,

$$<\kappa\alpha|u_{\beta}> = \delta_{\alpha\beta}, \quad (15)$$

(Here the scalar products between bras and kets stand for combined sums over an internal sublattice and Cartesian displacement index. \cite{24}) In the case of the polar mode, $<\kappa\alpha|P_{\beta}>$ refers to the ferroelectric distortion of the lattice. In cubic perovskite-structure crystals $\alpha$ and $\beta$ coincide, and $|P_{\beta}|$ reduces then to five independent components,

$$<\kappa\alpha|P_{\beta}> = \delta_{\alpha\beta}P_\kappa, \quad (16)$$

In other words, a uniform domain with the polarization oriented along $\beta$ corresponds to the following distortion pattern,

$$u^l_{\kappa\alpha} = P_0(\kappa\alpha|P_{\beta}) = P_0\delta_{\alpha\beta}P_\kappa. \quad (17)$$

Since the only physical requirement is that the product of $P_0$ and $p_\kappa$ coincide with the spontaneous ferroelectric
distortion, there is some freedom in the choice of the unit in which both \( P(x) \) and \( p_x \) are represented; we shall come back to this point later on. Based on this mapping, we can now proceed to calculating all the coefficients entering \( \text{Eq. } (2) \) in terms of microscopic quantities.

D. Calculation of the coupling coefficients

The homogeneous coefficients \( A \) and \( B \) are easy to extract from a first-principles calculation: they are readily given by a quartic fit of the energy of the primitive cell as a function of the distortion amplitude along the direction (in configuration space) spanned by \( |P_\beta\rangle \). The simplest option consists in requiring that \( F_0 \) coincide with the calculated energy difference between the reference cubic phase and the ferroelectric state, \( \Delta E \), which leads to

\[
A = \frac{4\Delta E}{\Omega P_0^2}, \quad B = \frac{4\Delta E}{\Omega P_0^2}.
\] (18)

The gradient terms (especially \( f \) and \( G \)) are technically more challenging to calculate, in that they are defined in terms of spatially modulated (and hence non cell-periodic) atomic distortion patterns. Recent developments \cite{9, 26, 31} in density-functional perturbation theory have overcome these difficulties by applying the long-wavelength method to the phonon problem; we shall briefly recap the main results, and present a microscopic expression for \( C, f \) and \( G \), in the following.

Since all gradient terms are harmonic, our starting point are the interatomic force constants calculated in the high-symmetry undistorted geometry,

\[
\Phi^{(0)}_{\kappa\alpha,\kappa'\beta} = \frac{\partial^2 E}{\partial u^{(0)}_{\kappa\alpha} \partial u^{(0)}_{\kappa'\beta}}.
\] (19)

These are defined as second derivatives of the total energy with respect to two atomic displacements, respectively of the atom \( \kappa \) along \( \alpha \) and \( \kappa' \) along \( \beta \). We shall introduce a spatial modulation via the Fourier transform of \( \Phi^{(0)}_{\kappa\alpha,\kappa'\beta} \), which we define as \[31\]

\[
\Phi^{\mathbf{q}}_{\kappa\alpha,\kappa'\beta} = \sum_l \Phi^{(l)}_{\kappa\alpha,\kappa'\beta} e^{i\mathbf{q} \cdot (\mathbf{R}_l + \tau_\kappa - \tau_{\kappa'})}.
\] (20)

We perform then a long-wave expansion in powers of \( \mathbf{q} \) as

\[
\Phi^{(l)}_{\kappa\alpha,\kappa'\beta} = \Phi^{(0)}_{\kappa\alpha,\kappa'\beta} - iq_\gamma \Phi^{(1,\gamma)}_{\kappa\alpha,\kappa'\beta} - \frac{q_\gamma q_\delta}{2} \Phi^{(2,\gamma\delta)}_{\kappa\alpha,\kappa'\beta} + \cdots.
\] (21)

The zero-th order term is the usual zone-center force-constants matrix in short-circuit electrical boundary conditions. The first-order term vanishes in the cubic perovskite reference structure. The second-order term contains the relevant information to describe flexoelectricity, correlation and elasticity. In particular, the coefficients \( C, f \) and \( G \) in Eq. \( (2) \) are readily obtained as projections of \( \Phi^{(2,xx)} \) onto the corresponding acoustic or polar eigendisplacement patterns. By using Eqs. \( (15) \) and \( (16) \) we obtain the following explicit formulas

\[
C = -\frac{1}{2\Omega} (u_y | \Phi^{(2,xx)} | u_y) = -\frac{1}{2\Omega} \sum_{\kappa\kappa'} \Phi^{(2,xx)}_{\kappa\gamma,\kappa'\gamma' y},
\] (22a)

\[
f = -\frac{1}{2\Omega} (u_y | \Phi^{(2,xx)} | p_y) = -\frac{1}{2\Omega} \sum_{\kappa\kappa'} \Phi^{(2,xx)}_{\kappa\gamma,\kappa'\gamma' p},
\] (22b)

\[
G = -\frac{1}{2\Omega} (p_y | \Phi^{(2,xx)} | p_y) = -\frac{1}{2\Omega} \sum_{\kappa\kappa'} \Phi^{(2,xx)}_{\kappa\gamma,\kappa'\gamma' p} p_{\kappa' p}.
\] (22c)

[We assume a (100)-oriented wall, with the polarization oriented along (010)] One can also introduce the flexoelectric force-response tensor,

\[
[yy,xx]^{\kappa'} = -\frac{1}{2} \sum_{\alpha} \Phi^{(2,xx)}_{\kappa\gamma,\kappa'\gamma' y}
\] (23)

as the force on the sublattice \( \kappa' \) produced by a gradient of the shear strain. Thus, the flexocoupling coefficient, \( f \), is simply defined \[30\] as the projection on the polar mode distortion vector of the force-response tensor components, \( f = \sum_{\kappa'} [yy,xx]^{\kappa'} p'_{\kappa'} \).

The fact that we obtain the elastic tensor, which is usually regarded as a homogeneous coupling parameter, via a similar procedure as spatial dispersion coefficients such as \( G \) and \( f \), might come as a surprise to the reader. This is justified by the fact that a uniform strain is a gradient of the elastic displacement field, and therefore it formally enters the long-wave expansion of the dynamical matrix on the same footing as a gradient of the polar modes: elasticity, flexoelectricity and correlation all occur at second order in the wavevector \( \mathbf{q} \). That there exists an intimate connection between flexoelectricity and elasticity is clear from the following trivial consequence of Eq. \( (22) \),

\[
C = \frac{1}{\Omega} \sum_{\kappa'} [yy,xx]^{\kappa'},
\] (24)

which is a special case of the “elastic sum rule” described in Ref. \[31\]. This sum rule generalizes the classic result of Born and Huang \[32\], relating the elastic tensor to the second moment of the dynamical matrix, and provides the formal link between microscopic lattice dynamics and continuum elasticity.

E. Arbitrariness in the gradient-mediated couplings

As expressed via Eqs. \( (22) \), it might appear at first sight that the three dispersion coefficients \( C, f \) and \( G \) are well-defined (and measurable) physical properties of the crystal; most authors have indeed used such an assumption in the past, either implicitly or explicitly. In the following we shall demonstrate that, while \( C \) is indeed
an established and well-defined crystal property, neither $f$ or $G$ are, as they suffer from an unavoidable arbitrariness. We anticipate that such an ambiguity is physical, i.e., it is not specific to the method one uses to calculate the coefficients within microscopic theory, and is directly related to the paradox of Fig. 1.

After a quick glance at Eq. (22), it is not difficult to see where this arbitrariness may come from. Of the two ingredients that enter the definition of $C$, $f$ and $G$, the $\Phi^{(2,xx)}$ matrix is well defined, as it directly emerges from a long-wave expansion of the force constants. The ferroelectric distortion vector $|P_y\rangle$, on the other hand, is only defined modulo a rigid displacement of the whole lattice (Fig. 1). That is, we can always replace $|P_y\rangle$ with any distortion that differs from $|P_y\rangle$ by a constant shift along $y$, or in other words, by an arbitrary constant times $|u_y\rangle$. There is no fundamental symmetry principle that favors one choice over the other—it is entirely a matter of convention. Let’s see what happens if we operate such a transformation, by defining a new polar distortion pattern as

$$|P'_y\rangle = |P_y\rangle + \lambda|u_y\rangle. \quad (25)$$

Evidently, the homogeneous coupling coefficients are unaffected by such a transformation, since the energetics of the uniform phase is insensitive to the choice of the origin. This is not the case for the gradient coefficients, whose transformation rules can be straightforwardly derived by plugging Eq. (25) into Eq. (22).

$$f' = f + \lambda C, \quad (26a)$$

$$G' = G + 2\lambda f + \lambda^2 C. \quad (26b)$$

The fact that both the flexoelectric and gradient coefficients depend on an arbitrary constant, $\lambda$, might appear surprising at first sight, but it’s actually easy to rationalize on elementary physical grounds. Introducing a shift in the polar distortion is harmless in the homogeneous case, but the gradient of $P$ comes with an extra strain field, which contributes to both the elastic and flexoelectric terms in the free energy.

One might wonder, at this point, whether Eq. (2) can be trusted at all, given the aforementioned arbitrariness. To answer this question, it is useful to understand the impact of Eq. (25) and Eq. (26) on the domain wall solution. Remarkably, the renormalized gradient coefficient $G$ remains unchanged, as the respective $\lambda$-dependent contributions to $f$ and $G$ exactly cancel out. This means that all physically measurable properties of the domain wall, i.e., the thickness $\xi$ and the energy $W$, are well defined regardless of the specific convention that we choose for $|P_y\rangle$; the equilibrium solution for $P(x)$ is also unaffected. The only thing that changes with $\lambda$ is the equilibrium solution for the elastic displacement field, and hence the local strain,

$$u'(x) = -\frac{f'}{C}P(x) = -\left(\frac{f}{C} + \lambda\right)P(x). \quad (27)$$

This result looks odd to say the least: by modifying the definition of the polar distortion we have obtained the same profile for $P(x)$, exactly the same energy, but a different solution for the strain field. The solution to this puzzle resides in Eq. (14), which is our gateway from the continuum solution back to the microscopics. And indeed, one can quickly verify that the change in the strain field exactly cancels out with the change in the displacements that are associated with the redefinition of $|P_y\rangle$, leaving the equilibrium solution for the individual atomic displacements well-defined (that is, $\lambda$-independent) and unique. This provides, in a nutshell, the solution to the paradox of Fig. 1 and constitutes one of our main formal results.

F. Converse mapping to the continuum fields

It is ironic, in light of these results, to realize that macroscopic theory is far better suited to predicting equilibrium atomic positions rather than “traditional” macroscopic quantities, such as the strain. To rationalize such an outcome, and get convinced that “it cannot be otherwise”, it is illuminating to consider the converse mapping between continuum fields and microscopics, i.e., the procedure that allows one to extract the values of $P(r)$ and $u(r)$ given a distorted configuration of the crystal. We shall follow the same two-step procedure as in Section II C, but taken in reverse order: (i) transform the discrete sublattice distortions into continuum functions of all space; (ii) perform a local projection of the individual atomic displacements onto the subspace spanned by $|u_\alpha\rangle$ and $|P_\alpha\rangle$.

Step (i) does not involve any ambiguity as long as the atomic displacement pattern is “mesoscopic” in nature (i.e., the distortion amplitudes vary on a length scale that is much larger than the interatomic spacings). Such an assumption implies that, if we express the distortion in reciprocal space, all phonon amplitudes, $u_{\kappa\alpha}(q)$, vanish at the zone boundary. This is a sufficient condition for the Fourier continuation of the atomic displacements from discrete to continuum,

$$u'_{\kappa\alpha} = u_{\kappa\alpha}(R_{ik}^{(0)}) \rightarrow u_{\kappa\alpha}(r) \quad (28)$$

to be uniquely defined. [26] (Whenever the above condition breaks down one can still extract continuum fields from the atomistics by applying standard “macroscopic averaging” [33, 34] techniques. This is, however, a regime where the continuum approximation is no longer justified, and therefore falls outside the scopes of the present discussion.)

Regarding step (ii), in full generality we shall define the continuum fields as follows,

$$u_{\alpha}(r) = \sum_{\kappa\beta}(\tilde{v}_{\alpha}|\kappa\beta)u_{\beta\kappa}(r), \quad (29)$$

where $v$ stands for $u$ or $P$, and $(\tilde{v}_{\alpha}|\kappa\beta)$ are the duals to the eigendisplacement vectors $|u_\alpha\rangle$ and $|P_\alpha\rangle$ that we have
The basic requirement on the direct and dual vectors is that they form an orthonormal set,

\[
\begin{align*}
    \langle \tilde{u}_\alpha | u_\beta \rangle &= \delta_{\alpha\beta}, \\
    \langle \tilde{P}_\alpha | P_\beta \rangle &= \delta_{\alpha\beta}.
\end{align*}
\]  

(30)

This is a necessary condition to ensure consistency, e.g., that a subsequent application of the direct and converse mapping recovers the initial values of the continuum fields. The most general choice that satisfies these constraints consists in introducing a set of sublattice-dependent weights, \(w_\kappa\), whose sum is unity, \(\sum_\kappa w_\kappa = 1\). Then, we define the duals as

\[
\begin{align*}
    \langle \tilde{u}_\alpha | \kappa \beta \rangle &= w_\kappa \delta_{\alpha\beta}, \\
    \langle \tilde{P}_\alpha | \kappa \beta \rangle &= w_\kappa P_\kappa \delta_{\alpha\beta}.
\end{align*}
\]  

(31a)

(31b)

This way, the orthonormality of the elastic displacement vectors is enforced by construction, while the remainder of Eq. (30) leads to the following two conditions on \(P_\kappa\),

\[
\begin{align*}
    \sum_\kappa w_\kappa P_\kappa &= 0, \\
    \sum_\kappa w_\kappa P_\kappa^2 &= 1.
\end{align*}
\]  

(32a)

(32b)

Eq. (32a) is a “hard” requirement on \(P_\kappa\), and must always be enforced after some choice of weights is made. This condition lifts the indeterminacy of the polar distortion vector that we illustrated in Fig. 1, and clarifies the role of \(w_\kappa\) in subtracting the (weighted) average displacement of the cell from the polar mode. Doing so is consistent with physical intuition: the polarization, by its nature, is a distortion of the lattice that does not move the unit cell of the crystal as a whole.

Eq. (32b), on the other hand, is a consequence of Eq. (31b), which is to some extent arbitrary. Indeed, one can always multiply Eq. (31b) by a constant factor; such freedom boils down to the choice of units that we use to measure the polar distortion amplitude. (For example, one could require \(P_0\) to coincide with the spontaneous polarization of the ferroelectric crystal, as customary in macroscopic theories.) The present convention, which consists in measuring \(P(x)\) in length units, has the drawback that the normalization condition [Eq. (32b)], and hence the values of all coefficients of Eq. (2), depends on the choice of weights. Still, we shall prefer it here because it bears a direct formal link to the eigenvectors of the dynamical matrix (see Appendix A), and for consistency with earlier works [19, 26, 30].

Eq. (32a) and (32b), together with the prescriptions of Section II C, yield a well-defined procedure to construct the eigendisplacement vectors, and hence the model parameters, given a set of weights \(w_\kappa\). Starting from the atomic distortions of the ferroelectric state, \(d_\kappa\), we first of all enforce Eq. (32a) via

\[
\tilde{d}_\kappa = d_\kappa - \sum_\kappa w_\kappa d_\kappa.
\]  

(33)

Then, we define the amplitude of the spontaneous distortion as

\[
P_0 = \sqrt{\sum_\kappa w_\kappa d_\kappa^2}.
\]  

(34)

Finally, we enforce Eq. (32b) by defining the dimensionless eigendisplacement vector as \(p_\kappa = \tilde{d}_\kappa / P_0\). The result manifestly depends on the (arbitrary) choice of the weights; we shall discuss the physical implications of this outcome in the following subsection.

### G. Arbitrariness of the strain field

With the above derivations, we have established the continuum displacement field as a weighted average over all sublattices,

\[
u(r) = \sum_\kappa w_\kappa u_\kappa(r).
\]  

(35)

The issue with this formula, which is otherwise rather trivial, is the fact that the weights are completely arbitrary. There may be, of course, some choices that are preferable over others, for different reasons. Several authors [14, 26], for example, advocate the use of the physical masses of the atoms as weights; this is convenient for dynamical problems, where masses indeed play a role, and provides the physically intuitive interpretation of the displacement field as the displacement of the local center of mass. Then, microscopists routinely use the positions of the heaviest ions to define the local strain, as they correspond to the brightest spots in the images; this implies setting their weight to unity, and the others to zero. Simply taking the average displacement of the cell (with equal weights) is not uncommon, either.

The key point is that there is no fundamentally right (or wrong) choice: since spatial inversion is broken in the polar structure, within the bulk domains the relation between the cell origin and the atomic positions cannot be fixed by symmetry (see Fig. 1). Yet, the “covariance” of Eq. (2) with respect to the weight arbitrariness guarantees that the physics is uniquely described, even if the strain field (and hence the net elastic offset across the wall, \(\Delta u\)) depends on such choice. Note that this result, which has been established here for a static domain-wall structure, holds in full generality: In Appendix 3 we generalize it to the time-dependent regime, and use it to reconcile the existing controversies around the so-called “dynamical flexoelectric effect”.

An important consequence of the formalism developed here is that the definition of strain and polarization are intimately related: they are both bound, respectively via Eq. (35) and Eq. (32a), to the same weight choice ambiguity. And indeed, one can show that \(\nu(r)\) is ambiguous only if either the strain or the polarization are nonuniform in space, and is uniquely defined otherwise. To see this, recall Eq. (16) and Eq. (17) in absence of \(P(r)\), the
TABLE I. Data computed using DFT for six perovskite oxides: simple-cubic lattice parameter, $a_0$ (in Å); displacements (in a.u.) of the atoms from their high-symmetry positions in the distorted tetragonal structure at fixed lattice constants $a_0$, $d_e$, for the $A$ cation ($d_A$), $B$ cation ($d_B$), apical anion ($d_{O_1}$), and equatorial anions ($d_{O_{2,3}}$); energy of this relaxed tetragonal configuration with respect to the simple cubic one (in meV/f.u.); and polarization of the tetragonal phase (in C/m$^2$). (*): calculations of BaTiO$_3$ under hydrostatic pressure, see Sec. III D.

| Compound      | $a_0$  | $d_A$  | $d_B$  | $d_{O_1}$ | $d_{O_{2,3}}$ | $\Delta E$ (meV/f.u.) | $P$ (C/m$^2$) |
|---------------|--------|--------|--------|------------|---------------|------------------------|--------------|
| BaTiO$_3$     | 3.935  | +0.0186| +0.538 | -0.0359    | -0.0183      | -2.87                  | 0.188        |
| BaTiO$_3^{(*)}$| 3.904  | +0.0087| +0.0237| -0.0117    | -0.0064      | -0.083                 | 0.078        |
| CaTiO$_3$     | 3.799  | +0.2369| +0.0584| -0.0432    | -0.1261      | -36.72                 | 0.508        |
| KNbO$_3$      | 3.947  | +0.0244| +0.0553| -0.0229    | -0.0287      | -3.77                  | 0.205        |
| NaNbO$_3$     | 3.907  | +0.2097| +0.0498| -0.0480    | -0.1057      | -18.75                 | 0.359        |
| PbTiO$_3$     | 3.879  | +0.1894| +0.0793| -0.0524    | -0.1081      | -30.56                 | 0.578        |
| PbZrO$_3$     | 4.102  | +0.3674| +0.0716| -0.0241    | -0.2075      | -187.50                | 0.647        |

III. RESULTS

A. Computational parameters

Our calculations are performed in the framework of DFT as implemented in the “in-house” Lautrec code [35]. We use the local-density approximation [36], the projector augmented wave method (PAW) [37], and a plane-wave basis set with a kinetic energy cutoff of 50 Ry in all our calculations. The PAW datasets are generated by treating the following orbitals as valence electrons: $s$ for $A$, $B$, and $O$; $d$ for $A$, $B$, and $O$; and $p$ for $A$, $B$, and $O$. We use the real-space supercell approach of Ref. 27. This implies calculating the second-order moments of the interatomic force constants according to

$$\Phi_{\kappa,y',x'}^{(2,xx)} = \sum_l \Phi_{\kappa,y',x'}^l (R_l + \tau_{x'} - \tau_{x})_x^2.$$  (36)

[Due to inversion symmetry, displacements of the atoms along $y$ do not generate electric fields along $x$; this implies that the interatomic forces decay exponentially with distance, and the lattice sums in Eq. (36) converge to a unique, well defined value.] To compute $\Phi_{\kappa,y',x'}$, we carry out calculations in which we displace one atom at the time by 0.005 a.u. along $y$ and extract the resulting forces. In practice, we use a $8a_0 \times 8a_0 \times a_0$ supercell, with the same geometry as in Figure 2 except that we use the centrosymmetric paraelectric structure as reference. (The resulting matrix elements are given in Appendix A.)
Finally, to validate the model results against full DFT calculations we prepare two domains with opposite polarization in a long (100)-oriented supercell (as in Figure 2) for different values of $N$, and we allow the atoms to relax along $y$ till the forces on them are negligible. We consider both AO-centered and BO$_2$-centered wall types. Note that we neglect octahedra rotations, strain relaxations, or other wall orientations that might result in energetically more favorable structures. Our main goal here is testing the continuum approximation on a minimal Landau model of a ferroelectric wall, and discussing the subtleties related to the incorporation of flexoelectric effects. In this sense, incorporating additional degrees of freedom to achieve a more realistic picture would have constituted an unnecessary complication. In some members of our materials set such a simplified model does not yield a physically meaningful description of the bulk or domain wall structure (or both). For this reason, we shall primarily focus our attention on BaTiO$_3$, PbTiO$_3$ and KNbO$_3$, and present the data on other materials for comparison purposes and future reference.

### B. DFT calculations of domain walls

We start by discussing our direct DFT calculation of the domain-wall structures. Figure 2 shows the resulting atomic displacements from the high symmetry positions. Two features are common to all materials: the domain walls are atomically thin, and the atomic positions at the center of each domain depend only on the material, and not on the type of wall (AO or BO$_2$). The six oxides considered here can be roughly classified into two categories: those for which the relative displacement between $A$ cations in adjacent domains is significantly larger than the one between $B$ cations (CaTiO$_3$, NaNbO$_3$, PbTiO$_3$, and PbZrO$_3$), and those for which this is not so (BaTiO$_3$ and KNbO$_3$). This is just a reflection of the tetragonal distortion pattern quoted in Table I which indeed shows that BaTiO$_3$ and KNbO$_3$ have similar properties, and in particular small displacements of their $A$ cations. This classification also applies regarding domain wall energies, listed in Table II for BaTiO$_3$ and KNbO$_3$ the domain wall energy of the BO$_2$ wall type is small, but around 50% higher than the one of the AO domain wall; for the other oxides the energies are larger, but for both types of wall they are within 25% of each other (the BO$_2$ type becomes favored for CaTiO$_3$ and PbZrO$_3$; previous calculations in PbTiO$_3$ agree with this, but those were carried out allowing for cell parameter optimization). In line with the previous literature, we find that the domain wall energy in PbTiO$_3$ is around one order of magnitude larger than in BaTiO$_3$.

The atomic configurations and energies of some perovskite oxide domain walls have been studied in the past using DFT-based methods. Padilla, Zhong, and Vanderbilt carried out a pioneering study on 180° domain walls in BaTiO$_3$ using an effective Hamiltonian built from DFT results; they reported that the walls are atomically thin and centered at the Ba atoms, consistent with our results, and that the domain wall energies are of the order of 10 mJ/m$^2$. Full DFT studies of 180° domain walls in PbTiO$_3$, first by Pöykkö and Chadi and later by

![FIG. 2. (Color online.) Example of unit cell used in some of our full-DFT calculations (here, $N = 8$, and domains with opposite orientations give rise to an AO-type domain wall).](image-url)

| Material     | $A$   | $B$   | $C$   | $f$   | $G$   |
|--------------|-------|-------|-------|-------|-------|
| BaTiO$_3$    | −0.276| 74.6  | 4.81  | −0.560| 2.47  |
| BaTiO$_3^{(c)}$| −0.0503| 83.3  | 4.77  | −0.590| 2.66  |
| CaTiO$_3$    | −0.219| 3.29  | 3.47  | −0.861| 2.59  |
| KNbO$_3$     | −0.322| 77.8  | 3.27  | −1.62 | 3.86  |
| NaNbO$_3$    | −0.135| 2.65  | 2.56  | −1.36 | 2.30  |
| PbTiO$_3$    | −0.234| 4.79  | 3.45  | −1.06 | 3.73  |
| PbZrO$_3$    | −0.365| 2.26  | 2.09  | −0.386| 3.14  |
| BaTiO$_3$    | −0.448| 195   | 4.61  | −3.82 | 7.04  |
| BaTiO$_3^{(c)}$| −0.0801| 212   | 4.77  | −3.86 | 7.35  |
| CaTiO$_3$    | −0.219| 3.30  | 3.47  | −2.28 | 3.87  |
| KNbO$_3$     | −0.316| 74.9  | 3.27  | −4.15 | 8.26  |
| NaNbO$_3$    | −0.215| 6.72  | 2.56  | −2.60 | 5.14  |
| PbTiO$_3$    | −0.302| 8.02  | 3.45  | −5.49 | 13.1  |
| PbZrO$_3$    | −0.431| 3.14  | 2.09  | −2.75 | 7.24  |

**TABLE II.** Coefficients of the Landau model of Eq. (2) computed from DFT calculations. The values are calculated by expressing both $u$ and $P$ fields in Bohr units of length. Then, $A$ is in $10^{-13}$ Ha bohr$^{-1}$; $B$ in $10^{-15}$ Ha bohr$^{-3}$; $f$, $G$ and $C$ are all in atomic units of pressure, i.e., $10^{-3}$ Ha bohr$^{-3}$. Top block: unit weights are used. Bottom block: physical atomic masses are used as weights.
Meyer and Vanderbilt[40] reached the same conclusion regarding thickness, and predicted domain wall energies of 100 to 200 mJ/m². In this case, the most favorable domain walls are found to be centered on the Pb atoms, which is again consistent with our findings. To the best of our knowledge, Ref. [40] was the first to point out the geometrical offset of the atomic rows between the oppositely polarized domains; we shall discuss this point extensively in the next Section.

Regarding perovskite oxides where O₆ octahedra rotations are important, DFT-based studies[43, 44] have shown that the walls are still one or two unit cells in width, and that the matching of the octahedra at the wall strongly affects the value of the wall energy. Although experimental probing of the structure and energetics of ferroelectric domain walls is still challenging, by now there is enough experimental evidence showing that domain walls in perovskite oxides can indeed be atomically thin (see, for example, Ref. 45 and other references therein).

C. Landau model calculations of domain walls

In this Section we develop Landau models for each of our six perovskite oxides according to the guidelines specified earlier. We start from the calculated distortion pattern (δκ) and energy gain (∆E) of the tetragonal ferroelectric phase, as reported in Table II. After processing the latter values via the procedure described in Sec. II C and Sec. II F, we readily obtain the values of A, B and pκ for each bulk material. The gradient-mediated coefficients of the model (C, f, G) are then computed from pκ and the calculated Φ²(2xx′y′) via Eq. (22). To illustrate our arguments, we shall use two different choices of weights for defining pκ (and hence the A, B, f and G parameters of the model), by setting wκ either to equal values or to the physical masses of the atoms. We shall compare the results and demonstrate their mutual consistency in the following.

In Table III we summarize our results for the calculated model parameters depending on the weight choice. As expected, all parameters (with the exception of the elastic coefficient) considerably differ between the equal-mass and the standard-mass convention. Recall that this difference is twofold. First, there is a trivial scale factor (proportional to some power of P₀) that is due to the normalization of the polar eigendisplacements pκ. The present choice of measuring the polar order parameter via the norm (in length units) of the atomic distortion amplitude differs from the usual convention of macroscopic theories. To connect with the latter we provide in Table V the same coefficients in SI units, where we have set P₀ to the spontaneous polarization of the bulk crystal, in C/m². In this case, the A and B coefficients agree between different choices of the weights, while a discrep-
Elastic displacement field $u$ (Å)

-0.04 -0.02 0 0.02 0.04

Distance from wall ($a_0$)

-0.2 -0.1 0 0.1 0.2

Combined elastic fields for

- BaTiO$_3$
- KNbO$_3$
- PbTiO$_3$

FIG. 4. (Color online.) Value of the elastic displacement field as a function of distance to the domain wall, for three perovskite oxides. The lines correspond to Landau model predictions using unit weights (broken lines) or atomic weights (continuous lines). The symbols correspond to local center of mass calculations computed with full DFT, for different cells centered on AO or BO$_2$ layers, and for those two different weights.

As a first test of such claim, we use the calculated values of the coefficients to compute the energy and the width of the domain walls following Equations 9 and 11. We find that the results are indeed consistent (to machine precision) between the two weight choices. Table III shows that the domain-wall energies extracted from the model are also consistent with the results of our full DFT calculations; the level of agreement is remarkable considering the simplicity of the Landau model. The wall width, in particular, is of the order of the cubic lattice periodicity.) Note that the direct DFT calculations yield a marked dependence of the domain wall energy on the wall location respect to the underlying atomic structure; such a dependence is obviously missing within the continuum description.

Next, we compute the elastic displacement field by combining Eqs. 11 and 8,

$$u(x) = -\frac{f}{C} P(x) = -\frac{f}{C} P_0 \tanh \frac{x}{\xi} \quad (37)$$

The resulting profile, shown in Fig. 3, drastically differs depending on the weight choice, but is in excellent agreement with the “local center of mass” that we extract from our explicit domain-wall calculations by using the same weight convention. (For an AO wall, we compute this by considering the positions of the A and O atoms in a AO layer together with an average of the B and O atoms in adjacent BO$_2$ layers—we follow an equivalent procedure for the BO$_2$ walls.) In all materials considered here, taking unit weights (discontinuous lines) leads to flatter profiles than taking atomic weights (continuous lines), but with neither choice the centers of mass is fully aligned across the wall. Any choice of weights, on the other hand, leads to the same values of atomic displacements predicted by the Landau model via Eq. 13. The resulting curves are plotted as continuous lines next to the full DFT results for the domain-wall structures in Fig. 3. The agreement between the displacements predicted by the Landau model and those from full DFT calculations is obvious.

For a more quantitative analysis, we extract the overall displacement of the center of mass across the wall, $\Delta u$, from the relaxed domain-wall structures, and use it to estimate the effective flexocoupling coefficient by inverting Eq. 12.

$$f_{\text{eff}} = -\frac{C \Delta u}{2P_0} \quad (38)$$

The results for both choices of weights are compared in Table IV to the values predicted by the macroscopic model. One can note that the equal-weight convention yields values of $f$ and $f_{\text{eff}}$ that are systematically smaller than those obtained by setting $w_A$ to the physical atomic masses. Overall, the values of $f_{\text{eff}}$ and $f$ nicely agree, differing at most by few tenths of a volt in all cases.

TABLE III. Domain wall properties for six perovskite oxides: domain wall energy $W$ as computed using DFT (for the two possible AO and BO$_2$ domain walls) and as computed using the Landau model; and domain wall thickness $\xi$ as computed using the Landau model.

| Material       | DFT (AO) | DFT (BO$_2$) | Eq. 11 | Eq. 7 |
|----------------|----------|--------------|--------|-------|
| BaTiO$_3$      | 2.95     | 4.59         | 4.43   | 2.201 |
| KNbO$_3$       | 0.321    | 0.322        | 0.324  | 5.441 |
| CaTiO$_3$      | 63.2     | 60.8         | 70.5   | 2.463 |
| NaNbO$_3$      | 4.46     | 6.61         | 6.03   | 2.303 |
| NaTiO$_3$      | 26.6     | 32.7         | 34.3   | 2.557 |
| PbTiO$_3$      | 54.9     | 58.1         | 63.8   | 2.855 |
| PbZrO$_3$      | 200      | 133          | 252    | 2.170 |
Interestingly, the continuum approach yields a slight overestimation of the converse flexoelectric effect at the wall; such a feature appears to be systematic across all the materials set and irrespective of the weight convention being used. A possible explanation might lie in the atomically sharp nature of the domain-wall structures, which clearly challenges the continuum description. The estimated values of \( f^{\text{eff}} \), however, appear to be largely insensitive to the atomistic details of the wall (AO- and \( \text{BO}_2 \)-type walls yield very similar values for most materials); therefore, it is unlikely that the aforementioned discrepancy originate from the continuum approximation itself. We suspect that such an effect may depend on higher-order terms (either in the gradient expansion or in the polar distortion amplitude) that we neglect in Eq. (2). In any case, the accuracy of the present theory is more than sufficient for a quantitative comparison of first-principles calculations and experiments, e.g., along the lines of Ref. [14].

### D. “Soft” ferroelectric walls: \( \text{BaTiO}_3 \) under pressure

The values of \( \xi \) in Table III are smaller than one lattice parameter in all cases, which agrees with the usual perception that 180° ferroelectric domain walls are very thin. In order to evaluate the accuracy of the polarization profile of Equation 8, it would be desirable to study thicker ferroelectric domain walls with a smaller distortion amplitude; in such a limit we expect the free energy functional of Eq. (2) to match the results of direct DFT calculations exactly. One way to access this regime consists in using an external parameter to bring the material closer to the phase transition. The domain wall thickness, also known as correlation length, diverges in a vicinity of a ferroelectric phase transition, because of the vanishing \( A \) coefficient at the denominator of Eq. (9). Temperature is the most obvious choice in an experimental context; this is, however, impractical in the context of direct DFT simulations. A simpler alternative consists in applying a hydrostatic pressure \( \rho \) to our simulation cells; in many ferroelectrics, this results in a suppression of the ferroelectric instability already at moderate values of \( \rho \), thus mimicking the effect of increasing temperature in real experiments.

We shall apply this strategy to \( \text{BaTiO}_3 \) by repeating all the calculations under hydrostatic pressure; the corresponding results are indicated in the tables with a (*) symbol. We find that, at a lattice constant of 99.2% of the equilibrium \( a_0 \) (see Table I), the \( A \) parameter is still negative, but its magnitude is about an order of magnitude smaller (see Table I) than in standard conditions. Consistently, as the soft mode eigenvalue approaches zero the atomic displacements around the wall become smoother, and the value of \( \xi \) increases to 5.441 Å. The profile of atomic displacements for these walls is shown in Figure 5; the results of the Landau model (continuous lines, parameters are reported in Table II) are essentially in perfect agreement with the full DFT results in a \( 20a_0 \times a_0 \times a_0 \) unit cell (symbols), both for the AO and for the \( \text{BO}_2 \) types of domain wall. The agreement regarding domain wall energy is also extremely good (see Table III). Equation (11) yields 0.324 mJ/m², while from full DFT calculations we obtain 0.321 mJ/m² (for the AO

### TABLE IV. Value of \( f^{\text{eff}} = -C\Delta u/2P_0 \), in V, as computed with DFT and with our Landau model. Top block: unit masses are used. Bottom block: actual atomic masses are used.

| Material          | DFT (AO) | DFT (BO₂) | Landau Model |
|-------------------|----------|-----------|--------------|
| \( \text{BaTiO}_3 \) | -0.203   | -0.198    | -0.283       |
| \( \text{BaTiO}_3^* \) | -0.279   | -0.279    | -0.288       |
| \( \text{CaTiO}_3 \)  | -0.409   | -0.454    | -0.681       |
| \( \text{KNbO}_3 \)   | -0.676   | -0.670    | -0.793       |
| \( \text{NaNbO}_3 \)  | -1.07    | -1.09     | -1.33        |
| \( \text{PbTiO}_3 \)  | -0.395   | -0.400    | -0.628       |
| \( \text{PbZrO}_3 \)  | 0.038    | -0.124    | -0.373       |

The table shows the values of \( f^{\text{eff}} \) for different materials, comparing DFT calculations and Landau model predictions. The top block uses unit masses, while the bottom block uses actual atomic masses.
type) and 0.322 mJ/m² (for the BO₂ type).

Note that the direct DFT calculations of the domain wall energies and atomic structures are numerically much more challenging than in the zero pressure case, because of the extreme softness of the ferroelectric instability. To achieve a reasonable level of accuracy, and hence allow for a meaningful comparison to the model results, we had to be unusually careful with the usual computational parameters: (i) the domain-wall calculations were performed with a larger 20a₀ × a₀ × a₀ unit cell, to accommodate the thicker wall structure; (ii) the five-atom unit cell calculations were done using a 20 × 8 × 8 Monkhorst-Pack grid, exactly reproducing the folded Brillouin zone of the supercell (the ferroelectric distortion amplitude and double-well potential depth is remarkably sensitive to the k-point mesh); (iii) the tolerance on residual forces were set to 0.0001 eV/Å, approaching the inherent precision limits of the numerical algorithms. On the other hand, the calculation of the Landau model parameters required a similar computational effort as in the zero-pressure case, highlighting the obvious advantages of our multiscale approach in softer ferroelectric materials.

IV. DISCUSSION

The impact of flexoelectricity on the properties of ferroelectric domain walls was studied in several recent works. [14, 21, 46–48] Yudin and Tagantsev [21] established the role of flexoelectricity in determining the elastic offset at the wall, as well as its impact on domain wall energy and thickness via the renormalization of the polarization gradient coefficient, G. These formal results, which we have largely built upon in our present work, were applied by Wang et al. [14] to domain-wall structures in PbTiO₃ that were obtained either via first-principles calculations or experimental microscopy images. These authors, however, assumed that an “authentic” [14] definition of the strain exists, and overlooked (as did earlier works on this topic) the inherent arbitrariness that we highlight here. The definition used by Ref. [14] corresponds to using physical masses as weights within our formalism. Within such a convention, however, our result of f₁₁ = −2.87 V (or f₁₁ = −2.64 V as extracted from the direct calculation of the BO₂-centered domain-wall structure) in PbTiO₃ disagrees with the value of f₁₁ = −5.4 V quoted by Wang et al. by a factor of two. We believe that the source of the disagreement lies in Eq. (9b) of Wang et al. [14], where a spurious factor of two is indeed present compared to our Eq. (38). Such a factor of two is likely wrong in Ref. [14]; our calculated C = 101 GPa is in excellent agreement with the value of C₁₁ = 100.8 GPa quoted therein, ruling out possible issues in the definition of the shear elastic constant. Once the result of Ref. [14] is divided by two, it is in excellent agreement with ours.

From the point of view of the physics, the main conceptual advance of our work can be summarized as follows: The contribution of flexoelectricity to the domain-wall properties is ill-defined; however, the contribution of the polarization gradient energy is ill-defined as well, and including both terms is essential for for guaranteeing that their respective arbitrariness cancels out. The obvious question then is: Is it really necessary to consider both terms explicitly? Or can we choose the weights in such a way that the contribution of flexoelectricity vanishes identically, leaving only the gradient terms? A quick glance at Fig. 4 suggests, at first sight, that the answer to the latter question be “yes”: for the equal-weights case, the elastic offset between the domains is already small — by weighing the cations slightly less than the oxygens, one could certainly make ∆u to vanish exactly. However, this would “renormalize out” flexoelectricity only for a [100]-oriented wall; the same choice of weights would not yield a vanishing ∆u for a different (say, [110]) orientation. This means that, for a truly isotropic material, flexoelectricity can be reabsorbed into the polarization gradient energy, while anisotropic crystals generally require its explicit treatment. Similar conclusions were reached in Ref. [20] via a consideration of the electrostatic energy in presence of an inhomogeneous deformation of the crystal.

Before closing, it is useful to place the methodology that we have developed here in the context of the existing literature. Our strategy differs in spirit from Landau-Ginzburg-Devonshire (LGD) theories in that the latter have been traditionally approached with a phenomenological mindset. Granted, combining first-principles techniques with LGD theories is not new: the former are being increasingly used [49] to estimate a subset, or even the entirety of the LGD model coefficients. However, such a practice is seldom supported by a formal link between the macroscopic and microscopic degrees of freedom, which has thwarted so far a quantitative validation of LGD models against the ab initio results. (At the qualitative level, successful comparisons do exist, see Ref. [47] for an example that is relevant to the topics of this work.) The conceptual novelty of our approach consists in deriving the macroscopic field equations as a rigorous long-wave approximation to the discrete lattice Hamiltonian. This constitutes a much more intimate synergy between the two levels of theory, which allows for quantitatively accurate predictions (compared to the “training” first-principles model) of the relevant physical properties. Most importantly, our approach leads to a deeper awareness of the internal structure of the theory, the mutual relation between the many physical quantities involved, and their potential dependence on some arbitrary choices that are inevitable in the mapping of the problem onto continuum fields.

For the above reasons, our “first-principles macroscopic theory” belongs to the class of methods that are commonly known as second-principles. The latter are obtained via an appropriate coarse-graining of the first-principles Hamiltonian, whose physically relevant low-energy degrees of freedom are treated explicitly, while
most of the original complexity is integrated out. In the case of ferroelectrics, the reference in this context is the “effective Hamiltonian” approach, pioneered by Zhong, Rabe and Vanderbilt. \[23\] Performing a fair comparison of the virtues and shortcomings of either strategy would require substantial additional work, and will be best carried out in the framework of a separate publication. Here we will limit ourselves to observe that, once the continuum differential equations are discretized on a regular mesh corresponding to the unit cells of the original perovskite lattice, our approach essentially reduces to an effective Hamiltonian – at least for the simple domain-wall geometry considered here. [A generalization to the full three-dimensional case appears feasible, too, by writing all the couplings of Eq. 2 in a tensorial form and by explicitly treating the electrostatic energy.] From this point of view, the present method effectively bridges the gap between atomistic and continuum approaches, while preserving an exact limit at length scales that are large compared to the interatomic spacings.

V. CONCLUSIONS

We have established a formal mapping between continuum fields and atomistics, and demonstrated its predictive power in the study of spatially inhomogeneous structures (e.g., domain walls) in ferroics. Our formalism demonstrates the necessity of abandoning some widespread beliefs in continuum theory, for example that the local strain field be a physically well-defined degree of freedom of the crystal. While the arbitrariness in the definition of the elastic strain has a profound impact on the continuum model coefficients, we demonstrate that the physical answers derived from the model are robust against the specific convention that is being used.

On one hand, this results in a fundamental principle of invariance that we deem of great practical utility in validating the internal consistency of the continuum equations. On the other hand, and most importantly, our results provide a stringent benchmark to determine what are the physically sound questions that one can ask, and what are not. As illustrated by our practical tests, examples of well-posed questions concern the domain wall energy, or the atomic positions; we show that macroscopic theory (within the validity range of the continuum approximation) can be an excellent tool to predict both – with comparable accuracy to the full first-principles “training model”. Conversely, questions of the type “what is the contribution of flexoelectricity to the domain wall energy?”, or “what is the impact of the dynamic flexoelectric effect on the acoustic phonon dispersion?” are physically meaningless, as the answer can be about “anything”, depending on some (necessarily) arbitrary choices that one makes along the way.

In the present work we have voluntarily chosen, for the sake of clarity, a minimal model of macroscopic phenomena where the above ideas have a nontrivial impact. (For example, we have neglected most components of the strain tensor, as well as competing antiferrodistortive modes.) This choice has inevitably limited the predictive power of our study in some materials. An obvious future development of this work consists in extending the scopes of our first-principles continuum approach to more complex structures, e.g., involving a higher dimensionality or a broader range of degrees of freedom. For example, it will be interesting to clarify whether the principle of invariance established here also applies to the bichiral domain-wall structures described in Refs. 46, 47. Also, incorporating the effect of octahedral tilts appears especially promising, in light of the results of Ref. 49. Generalizing the ideas developed here in such directions will be an exciting avenue for further study.

ACKNOWLEDGMENTS

O.D. acknowledges funding from the Israel Science Foundation under Grants No. 1814/14 and No. 2143/14. M.S. acknowledges the support of Ministerio de Economía, Industria y Competitividad (MINECO-Spain) through Grant No. PID2019-108573GB-C22 and Severo Ochoa FUNFUTURE center of excellence (CEX2019-000917-S); of Generalitat de Catalunya (Grant No. 2017 SGR1506); and of the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (Grant Agreement No. 724529).

Appendix A: Relation to the eigenmode representation

In this Appendix we shall link the formalism developed in the main text to the prescriptions of Ref. 26 for the construction of the continuum Hamiltonian. Their proposed strategy consists in identifying the distortion patterns associated with the mechanical displacement and polarization fields with, respectively, the acoustic and “soft” polar eigenmodes of the zone-center dynamical matrix, \(D\). We shall adopt here a slightly more general definition by introducing the following operator,

\[
\tilde{D}_{\kappa,\alpha,\kappa',\beta} = \frac{1}{\sqrt{w_{\kappa}w_{\kappa'}}} \Phi_{\kappa,\alpha,\kappa',\beta}(0),
\]

which reduces to the standard definition of \(D\) when the weights are set to the physical atomic masses, \(m_{\alpha}\). Following Ref. 26 we shall define the displacement pattern \(u_{\alpha}^{(i)}\) associated to a given eigenmode \(\alpha\) (\(i\) runs over the transverse polar modes – acoustic and TO\(_1\)–TO\(_3\) in a perovskite, \(\alpha\) is a Cartesian direction) as

\[
\langle \kappa|\beta|u_{\alpha}^{(i)}\rangle = \sqrt{\sum_{\kappa} \frac{w_{\kappa}}{w_{\kappa'}}} \langle \kappa|\beta|v_{\alpha}^{(i)}\rangle,
\]

where \(v_{\alpha}^{(i)}\) are the normalized eigenvectors of \(\tilde{D}\). This definition results in a generalized orthonormality condi-
tion for the eigendisplacements,
\[ \langle u^{(i)}_{\alpha}|W|u^{(j)}_{\beta}\rangle = \delta_{ij}\delta_{\alpha\beta}, \]  
(A3)

where the “overlap operator” \( W \) is defined as
\[ W_{\kappa\alpha,\kappa'\beta} = \frac{w_{\kappa}}{w_{\kappa}}\delta_{\kappa\kappa'}\delta_{\alpha\beta}. \]  
(A4)

One can show that, within such prescriptions, the eigendisplacements associated to the acoustic mode \((i = A)\) are independent of the weights, thus recovering Eq. (15). Then, by setting \( i = A \) and \( j = \text{TO} \) in Eq. (A3), we find that both Eq. (32a) and Eq. (32b) are automatically satisfied by all polar modes. We can, thus, identify
\[ |u_{\alpha}\rangle = |u_{\alpha}^{\text{TO}}\rangle, \quad |P_{\alpha}\rangle = |u_{\alpha}^{\text{TO}1}\rangle, \]  
(A5)

where we have assumed that \( \text{TO}1 \) corresponds to the ferroelectric “soft mode”.

There is a slight drawback with such a procedure: different conventions for the weights lead to definitions of \(|P_{\alpha}\rangle\) that are generally not related via Eq. (25). Indeed, the configuration space spanned by \(|P_{\alpha}\rangle\) changes depending on the weights, as the three polar optical modes of the perovskite structure can mix. (This is a well-known issue in the construction of effective Hamiltonian for ferroelectrics, where typically the lowest eigenvector of the force-constant matrix is used for \(|P_{\alpha}\rangle\); this corresponds to choosing equal weights in the context of our formalism.) In practical cases, \(|P_{\alpha}\rangle\) might not reproduce the correct distortion pattern (and energetics) of the bulk ferroelectric ground state, which is undesirable in the study of a domain wall. To avoid this issue, in this work we followed the prescriptions of Section II F and defined \( p_{\kappa} \) starting from the relaxed distortion pattern of the bulk ferroelectric crystal instead. In the limit of a weak ferroelectric instability, one can show that this definition of \(|P_{\alpha}\rangle\) exactly matches the eigenvector representation provided by Eq. (A3) regardless of the choice of the weights.

**Appendix B: Dynamical equations of motion**

Tagantsev [50] and Kvasov and Tagantsev [51] claimed that there are two well-defined contribution to the bulk flexoelectric tensor, static and dynamic in nature, and that they are, in principle, separately measurable. Later works [21] clarified that such a partition is arbitrary, and that: (i) the total flexoelectric coefficient is meaningful for dynamical problems; (ii) either the total or the “static” flexoelectric tensor yield identical answers at mechanical equilibrium. To firm up our arguments, we shall revisit this long-standing debate on the static versus dynamical contribution to the flexoelectric tensor in light of the results presented so far. We shall see that it bears strong connections to the aforementioned ambiguities in the definitions of the continuum fields, and that our formalism resolves once and for all the existing confusion around this topic. The coupled dynamics of the polar and acoustic degrees of freedom is, of course, irrelevant to the study of static structures, such as the domain walls that we consider in this work. Still, it is interesting to discuss this topic here, as it provides an additional proof of the internal consistency of our arguments.

To describe the dynamical evolution of the mechanical and acoustic degrees of freedom, we need to work out the kinetic energy density in terms of the mode velocities. We shall write it as
\[ \mathcal{T} = \frac{1}{2} \sum_{ij} \dot{u}^{(i)}_{\alpha}M_{ij}\dot{u}^{(j)}_{\beta}, \]  
(B1)

where the Latin indices run over the acoustic and polar modes, and the matrix \( M_{ij} \), of the dimension of a mass density, is given by
\[ M_{ij} = \frac{1}{\Omega} \langle u^{(i)}|M|u^{(j)}\rangle, \quad M = m_{\kappa}\delta_{\kappa\kappa'}\delta_{\alpha\beta}. \]  
(B2)

The off-diagonal kinetic term, coupling the acoustic and optical mode velocities, has been identified as a dynamical contribution to the bulk flexoelectric tensor by Tagantsev and coworkers [21, 50, 51].

Based on the arguments of the earlier Sections, it is clear that the magnitude of such contribution, and even whether it exists at all, depends on the choice we make for the weights, \( w_{\kappa} \). The definition given by Tagantsev of the “static” flexoelectric tensor corresponds, within our formalism, to using equal weights in the construction of our free energy functional coefficients. If we do so, the matrix element \( M_{\kappa\kappa} \) then reduces to his definition of the “dynamic” contribution. If we made a different choice, the partition between the two would change arbitrarily – and yet both the dynamical (phonon frequencies and dispersions) and static properties (domain wall energy, equilibrium atomic positions) predicted by our Lagrangian would be exactly the same. Remarkably, if we set the weights to the physical masses of the atoms, \( w_{\kappa} = m_{\kappa} \), the orthogonality condition Eq. (A3) immediately leads to \( M_{\kappa\kappa} = 0 \), i.e., the “dynamical flexoelectric effect” disappears altogether. Given that the magnitude, and even the very existence, of such an effect depends on some arbitrary convention we have made along the way in order to map our lattice-dynamical problem onto a continuum Lagrangian density, we are forced to conclude that such an effect is not measurable. Still, we find that incorporating a mass cross-term, as suggested in Ref. 21 is necessary to guarantee that the physical predictions of the theory are unaffected by such ambiguities.

**Appendix C: Supporting numerical data**

In Table V we provide the complete list of the calculated model coefficients for all materials. This is essentially the same data as in Table III only expressed in SI units while setting \( P_0 \) to the spontaneous ferroelectric polarization of the bulk crystal. This conversion
Table V. Coefficients (in SI units) of the Landau model of Eq. (2) computed from DFT calculations, when $P_0$ is the spontaneous polarization of the bulk crystal (measured in C/m$^2$). Top block: unit weights are used. Bottom block: physical atomic masses are used.

| Material | $A$ (10$^3$m/F) | $B$ (10$^{15}$m$^2$/kg) | $C$ (10$^{11}$Pa) | $f$ (V) | $G$ (10$^{-13}$m$^3$/F) | $G$ (10$^{-13}$m$^3$/F) |
|----------|----------------|--------------------------|-------------------|--------|-------------------------|-------------------------|
| BaTiO$_3$ | −0.857 | 2.43 | 1.36 | −0.283 | 0.214 | 0.208 |
| BaTiO$_3$ | −0.145 | 2.36 | 1.40 | −0.288 | 0.221 | 0.215 |
| CaTiO$_3$ | −1.66 | 0.645 | 1.02 | −0.681 | 0.550 | 0.505 |
| KNbO$_3$ | −0.934 | 2.22 | 0.961 | −0.793 | 0.313 | 0.248 |
| NaNbO$_3$ | −1.56 | 1.21 | 0.755 | −1.33 | 0.746 | 0.510 |
| PbTiO$_3$ | −1.00 | 0.299 | 1.01 | −0.628 | 0.447 | 0.409 |
| PbZrO$_3$ | −4.15 | 0.991 | 0.616 | −0.373 | 1.00 | 0.979 |

is useful for two purposes. First, it shows that the $A$ and $B$ coefficients are consistent between different weight choices, provided that the respective distortion vectors, $p_{\alpha}$, are related via Eq. (25), i.e., they only differ by a sublattice-independent constant. This is obviously the case if the electrical polarization is chosen as a measure of the atomic distortion, but not when the total norm of the distortion is used; in the latter case there is generally an overall scaling factor that originates from Eq. (32b). Second, the coefficients are now expressed in the same units as in conventional macroscopic theory, allowing for a direct comparison. In the case of BaTiO$_3$, for example, our calculated polarization gradient coefficient, $G$, is in good agreement with the phenomenological value of $G = 0.2 \times 10^{-13}$ m$^3$/F reported in Ref. [7].

The elements of the second-moment interatomic force-constant matrix, calculated via Eq. (36), are reported in Table VI for reference.

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|     | \( q^{(2,xx)} \)   |
|-----|---------------------|
| BaTiO\(_3\) | 0.0920 \(-0.5561\) \(-0.2022\) \(-0.0383\) \(-0.1299\) |
|       | \(-0.5561\) \(-0.0191\) 0.0539 \(-0.0259\) \(-0.0202\) |
|       | \(-0.2022\) 0.0539 \(-0.0847\) 0.7573 0.0142 |
|       | \(-0.0383\) \(-0.0258\) \(-0.7573\) \(-0.4640\) 0.1104 |
|       | \(-0.1299\) \(-0.0202\) \(-0.0214\) \(-0.1104\) \(-0.2174\) |
| BaTiO\(_3^{(3)}\) | 0.0915 \(-0.5773\) \(-0.1854\) \(-0.0319\) \(-0.1605\) |
|       | \(-0.5773\) \(-0.0230\) 0.0580 0.0177 \(-0.0231\) |
|       | \(-0.1854\) 0.0580 \(-0.0799\) \(-0.7699\) 0.0142 |
|       | \(-0.0319\) \(-0.0178\) 0.0769 \(-0.4921\) \(-0.1121\) |
|       | \(-0.1605\) \(-0.0231\) \(-0.0142\) \(-0.1119\) \(-0.2326\) |
| CaTiO\(_3\) | 0.0082 \(-0.3563\) \(-0.1531\) \(-0.0596\) \(-0.1967\) |
|       | \(-0.3563\) \(-0.0374\) 0.1251 0.2363 \(-0.0124\) |
|       | \(-0.1531\) 0.1252 \(-0.1968\) \(-0.9531\) 0.0092 |
|       | \(-0.0596\) 0.2363 \(-0.9531\) \(-0.7121\) \(-0.1863\) |
|       | \(-0.1967\) \(-0.0124\) 0.0092 0.1835 \(-0.0636\) |
| KNbO\(_3\) | 0.0195 \(-0.3345\) \(-0.1154\) \(-0.0530\) \(-0.2348\) |
|       | \(-0.3345\) \(-0.0671\) 0.1619 0.2763 \(-0.0124\) |
|       | \(-0.1154\) 0.1619 \(-0.1782\) \(-0.9074\) 0.0163 |
|       | \(-0.0194\) 0.2763 \(-0.9075\) \(-0.7123\) \(-0.1230\) |
|       | \(-0.0530\) \(-0.0216\) 0.0163 0.1230 \(-0.0259\) |
| NaNO\(_3\) | 0.0022 \(-0.2023\) \(-0.0782\) \(-0.0274\) \(-0.0196\) |
|       | \(-0.2023\) \(-0.0821\) 0.2043 0.3915 \(-0.0237\) |
|       | \(-0.0782\) 0.2043 \(-0.2783\) \(-0.9913\) 0.0250 |
|       | \(-0.0274\) 0.3916 \(-0.9913\) \(-0.8334\) 0.1769 |
|       | \(-0.0916\) \(-0.0237\) 0.2950 0.1769 \(-0.0633\) |
| PbTiO\(_3\) | \(-0.0529\) \(-0.3944\) \(-0.0856\) \(-0.0003\) \(-0.1969\) |
|       | \(-0.3944\) \(-0.0254\) 0.0977 0.1092 \(-0.0240\) |
|       | \(-0.0856\) 0.0978 \(-0.1416\) \(-0.7698\) \(-0.0030\) |
|       | \(-0.0003\) 0.1092 \(-0.7698\) \(-0.4886\) 0.0226 |
|       | \(-0.1969\) \(-0.0240\) 0.0300 0.0226 \(-0.2507\) |
| PbZrO\(_3\) | \(-0.1344\) \(-0.3815\) \(-0.1047\) \(-0.0158\) \(-0.3713\) |
|       | \(-0.3815\) \(-0.0260\) 0.0573 0.1440 \(-0.0367\) |
|       | \(-0.1047\) 0.0573 \(-0.1189\) \(-0.5866\) 0.0543 |
|       | \(-0.0015\) 0.1440 \(-0.5866\) \(-0.5552\) \(-0.0543\) |
|       | \(-0.3713\) \(-0.0367\) \(-0.0134\) 0.0543 \(-0.2071\) |

**TABLE VI.** Elements of the second-moment interatomic force-constant matrix (in atomic units), as computed using DFT calculations in forty-atom \( a_0 \times a_0 \times a_0 \) unit cells, for six perovskite oxides.
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