Intrinsic activation energy for twin-wall motion in the ferroelastic perovskite CaTiO$_3$

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Even in a topologically perfect crystal, a moving twin wall will experience forces due to the discrete nature of the lattice. The potential energy landscape can be described in terms of one of two parameters: the Peierls energy, which is the activation energy for domain wall motion in a perfect crystal; and the Peierls stress, the maximum pinning stress that the potential can exert. We investigate these parameters in a one order parameter discrete Landau-Ginzburg model and a classical potential model of the ferroelastic perovskite CaTiO$_3$. Using the one order parameter model we show that the Peierls energy scales with the barrier height of the Landau double well potential and calculate its dependence on the width of the wall numerically. In CaTiO$_3$ we calculate the Peierls energy and stress indirectly from the one order parameter model and directly from the interatomic force field. Despite the simplicity of the one order parameter model, its predictions of the activation energy are in good agreement with calculated values.

I. INTRODUCTION

The motion of ferroelastic or ferroelectric-ferroelastic twin walls plays a significant role in determining the elastic, dielectric, piezoelectric, and ferroelectric properties of a number of materials of scientific and technological interest.[1–6] The lower mantle of the Earth is known to consist mainly of magnesium silicate perovskite, a ferroelastic polymorph of MgSiO$_3$. Recent work has explored the possibility that the seismic properties of the lower mantle, such as attenuation, can be explained in terms of the elastic response of domain walls. The large piezoelectric and dielectric coefficients of barium titanate and lead titanate have been shown to have significant contributions from the motion of twin walls. Finally, ferroelectric switching, which is currently being exploited for computer random access memory applications, is known to be entirely due to the motion of twin walls.

To understand the properties of these materials, and the systems in which they are found, we must understand the factors which affect the motion of twin walls. Unlike magnetic domain walls, with widths of hundreds of nanometers, ferroelastic and ferroelectric walls are atomistically thin, with wall widths of the order of the unit cell parameter.[7] We must understand their behavior from an atomic perspective. In essence this requires an understanding of the energy landscape through which twin walls move.

A schematic of this energy landscape is shown in Fig. 1. As a wall moves through the crystal it experiences a potential which oscillates between E_{minimum} at local minima and E_{saddle} at transition states (saddle points) between two minima. If the motion of the wall is a thermally activated process, then the mobility of the wall depends on the difference between these two energies,

$$\mu_{\text{wall}} = \mu_0 \exp\left(-\frac{E_{\text{saddle}} - E_{\text{minimum}}}{kT}\right). \tag{1}$$

As shown in the figure there are two contributions to the potential energy landscape. These can be labeled *intrinsic* and *extrinsic*. The intrinsic contribution to the energy landscape is present even in a chemically and topologically perfect crystal and is due to the periodicity of the lattice. This contribution is parameterized by the Peierls energy E_{Peierls}, which is the activation energy for twin wall motion far from point defects. The second, extrinsic contribution to the energy landscape is due to defects in the perfect lattice such as vacancies, impurity atoms, dislocations, and other twin walls.

There have been attempts to understand this energy landscape using both experimental and simulation methods. Experimentally, it is clear that extrinsic pinning due to point defects is far more significant than lattice pinning,[2,3,6] which is often too small to detect, except by very sensitive methods.[8] Simulations of oxygen vacancies in ferroelastic calcium titanate[9] and ferroelectric lead zirconate[10] have already been carried out, showing that an oxygen vacancy has an energy approximately 1 eV lower in the wall than in the
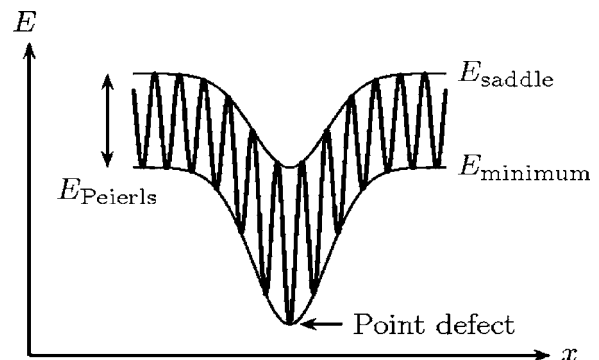

FIG. 1. The energy landscape experienced by a domain wall moving through a crystal containing a point defect. The bold line shows the potential experienced by the wall while the thin lines show the local equilibrium energy of the wall E_{minimum} and the saddle point energy of the transition state from one local minimum to another E_{saddle}. Far from a defect the difference between these two energies, i.e., the activation energy needed for the wall to move is called the Peierls energy E_{Peierls}.

bulk. These simulations provide information about E_{minimum}, but in order to complete the picture, calculations of E_{saddle} are also necessary.

In this work we only consider intrinsic pinning. We investigate pinning in a one order parameter discrete Landau-Ginzburg model, building on previous work by Ishibashi[11] and Combs and Yip.[12,13] Then we investigate intrinsic pinning in an empirical potential model of orthorhombic calcium titanate $CaTiO_3$ developed by Calleja *et al.*[9] We compare the predictions of the one order parameter model with the results of a transition state calculation and show a good agreement between the two values.

II. A ONE PARAMETER MODEL

In this section we investigate the intrinsic pinning of domain walls in the discrete Landau-Ginzburg or ϕ^4 model.[7] Intrinsic pinning in this model has been investigated by Ishibashi and Combs and Yip.[11–13] We report the results of a numerical calculation of the pinning energy showing, in agreement with previous work, that when the wall width is two lattice spacings the activation energy is practically zero.

The most successful theoretical tool for describing phase transitions in ferroelectric and ferroelastic materials is Landau-Ginzburg theory.[14,15] Through the Landau-Ginzburg free energy the theory provides a framework which can be used to predict both macroscopic behavior, such as the specific heat capacity[17] and elastic constants[18] of a material going through a phase transition, and microstructural details, such as the structure of domain walls.[15,19]

Usually a continuum formulation of the Landau-Ginzburg free energy is used, in which the discrete nature of the lattice is neglected.[7,15] This approach has been very successful even in predicting the structure of twin walls, where the continuum approximation might be expected to break down. It is not possible to calculate the Peierls energy within the continuum limit and so we use a discrete form of the Landau-Ginzburg energy,

$$F = \sum_i \Delta E \left[(Q_i^2 - 1)^2 + \left(\frac{w}{a} \right)^2 (Q_{i+1} - Q_i)^2 \right]. \quad (2)$$

The first term is a double well potential, where ΔE is height of the barrier between the two walls. The second term is the discrete analog of the Ginzburg term, w is the wall width and a is the lattice spacing. These quantities are illustrated in Fig. 2.

Dimensional analysis tells us that the Peierls energy E_{Peierls} must be given by

$$E_{\text{Peierls}} = \Delta E f(w/a), \quad (3)$$

where f is to be determined. It is easy to deduce the limiting values of $f(x)$ in the cases when x is very small or very large.

In the case of $w=0$ the free energy of the discrete Landau-Ginzburg model is

$$F = \sum_i \Delta E (Q_i^2 - 1)^2. \quad (4)$$

The system consists of a collection of independent order parameters Q_i moving in double well potentials. The domain
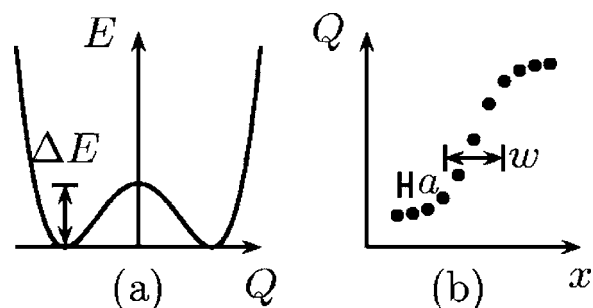

FIG. 2. Dimensional quantities of the general model. (a) The Landau double well potential is characterized by an energy barrier ΔE. (b) The discrete nature of the lattice means the model contains two length scales: a the lattice parameter and w the wall width.

wall moves when one order parameter flips from one state to another. The activation energy for this process is ΔE and thus

$$\lim_{x \to 0} f(x) = 1. \quad (5)$$

If w is very large, then the discrete nature of the lattice is irrelevant and a continuum approximation may be used. In the continuum theory the energy of a domain wall is independent of its position, and thus there is no activation energy for domain wall motion

$$\lim_{x \to \infty} f(x) = 0. \quad (6)$$

For intermediate cases we calculate $f(x)$ numerically. We calculate the energy of a single wall in a 200 site system, both without constraints (E_{minimum}) and with the constraint that $Q_{100}=0$ (E_{saddle}). The difference between the two energies divided by ΔE gives us $f(x)$, shown in Fig. 3. The figure shows that when the wall width is twice the lattice parameter the Peierls energy is already practically zero. The free energies were minimized using a conjugate gradient minimizer.[16] This calculation is susceptible to rounding error since as the wall width w increases, E_{minimum} and E_{saddle} increase, while the difference between them, ΔE, decreases. To minimize the rounding error we simulated the constrained and unconstrained systems together, allowing us to calculate ΔE on a term by term basis and used the double precision arithmetic.
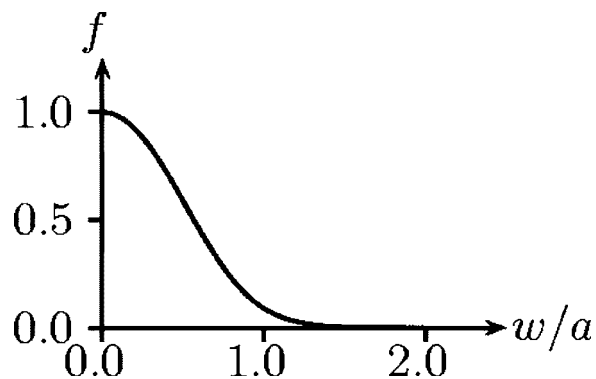

FIG. 3. Dependence of the activation energy on the ratio between wall width and lattice parameter.
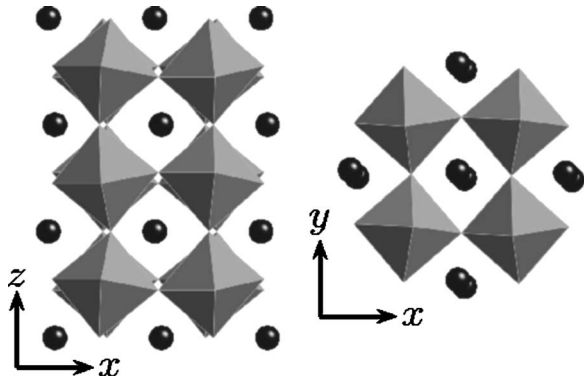
FIG. 4. Crystal structure of CaTiO$_3$, showing the coordinate system used in this work. Ca atoms are shown in black, the octahedra have O atoms at their vertices, and Ti atoms are at the centers.

In a crystal the width of a twin wall can be affected by two parameters: temperature and velocity. Elementary Landau-Ginzburg theory predicts that the twin wall width should diverge as T approaches T_c.[15] This prediction has been confirmed experimentally.[20] As the temperature approaches T_c the activation energy for wall motion will decrease. The second factor which can affect the wall width is the velocity of the wall. If the speed of the wall v approaches the velocity of sound in the material c, then the width of the wall is "Lorentz contracted" by a factor of

$$\sqrt{1 - v^2/c^2}. \qquad (7)$$

As a wall accelerates, the forces it experiences due to the lattice potential increases.

III. TWIN WALL MOTION IN CaTiO$_3$

To test the validity of the above approach we compared the value of the activation energy calculated by the method described above with a direct transition state energy calculation. We used an empirical potentials model to investigate twin walls in CaTiO$_3$. We calculate the structure of the twin walls of the system and calculate the Peierls energy and stress.

CaTiO$_3$ is a ferroelastic, but not ferroelectric, perovskite. The crystal structure consists of corner linked TiO$_6$ octahedra with Ca atoms distributed between the octahedra. At high temperatures the crystal structure is cubic but at room temperature the crystal structure is orthorhombic, with a space group of *Pbnm* and a Glazer octahedral tilt system of $a^-a^-c^+$.[21,22] The crystal structure and the coordinate system used in this work is shown in Fig. 4. When measurements of wall widths are given below they are given in units of the pseudocubic unit cell, containing a single formula unit.

A. Structure of static twin walls

In this work we consider a ferroelastic wall perpendicular to the x axis. The structure of the wall can be described in terms of order parameters and strains. The Glazer tilt system allows us to define order parameters (Q_x, Q_y, Q_z) associated with rotations of octahedra about the x, y, and z axes
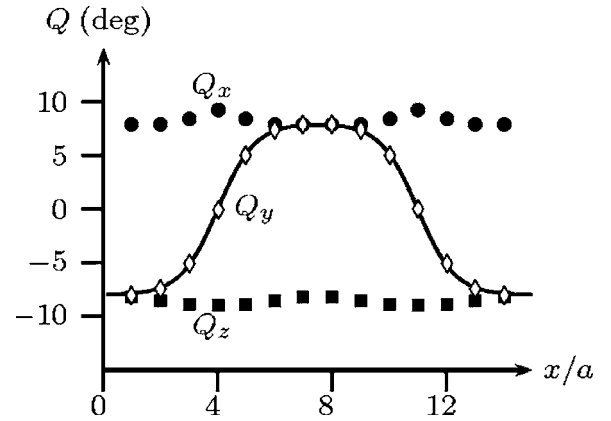

FIG. 5. The behavior of the order parameters across the wall. The order parameters are described in Eq. (8). Q_y shows a hyperbolic tangent variation across the wall, and Q_x and Q_y show anomalies at the wall.

$(\theta_x, \theta_y, \theta_z)$. If the position of an octahedron in the crystal is labeled by integers (i_x, i_y, i_z), then the order parameters are defined by

$$\theta_x = Q_x(-1)^{i_x+i_y+i_z}, \qquad (8)$$

$$\theta_y = Q_y(-1)^{i_x+i_y+i_z}, \qquad (9)$$

$$\theta_z = Q_z(-1)^{i_x+i_y}. \qquad (10)$$

The compatibility conditions limit the strains which can vary across an interface. For an interface perpendicular to the x axis only the strains ϵ_{xx}, ϵ_{xy}, and ϵ_{zx} can be nonzero. Furthermore the symmetry of the crystal constrains the strain ϵ_{zx} to be zero. The strain ϵ_{xy} is the ferroelastic strain. This changes sign across a ferroelastic wall. The strain ϵ_{xx} is a secondary strain, which only takes nonzero values within the wall.

Calleja *et al.*[9] developed an empirical potential set for this mineral, based on electrostatic interactions due to formal charges on ions, and Buckingham potentials describing the interactions between nearest neighbor ions and three body potentials describing the rigidity of the TiO$_6$ octahedra. They used this model to investigate the interaction between oxygen vacancies and twin walls in a configuration containing $26 \times 10 \times 6$ cells. The authors simulated a single domain structure and then rotated part of their configuration through 90° to generate twin walls. This procedure generates an interface consisting of the combination of a ferroelastic twin wall (with an order parameter Q_y) with an antiphase boundary (with an order parameter Q_z). These two types of walls can exist independently so in this work we consider simple ferroelastic twin walls in a system of $14 \times 6 \times 4$ octahedra implemented in DL_POLY (Ref. 23) using Calleja *et al.*'s potential set. Periodic boundary conditions make it impossible to simulate a single twin wall so instead we simulate a system with two walls. The order parameters and strains in the walls relaxed at absolute zero are shown in Figs. 5 and 6. The order parameter Q_y and the shear strain ϵ_{xy} change sign across the walls. Fitting Q_y to a hyperbolic tangent profile gives a wall width $w = 1.3a$. Q_x, Q_z, and ϵ_{xx} show anomalies
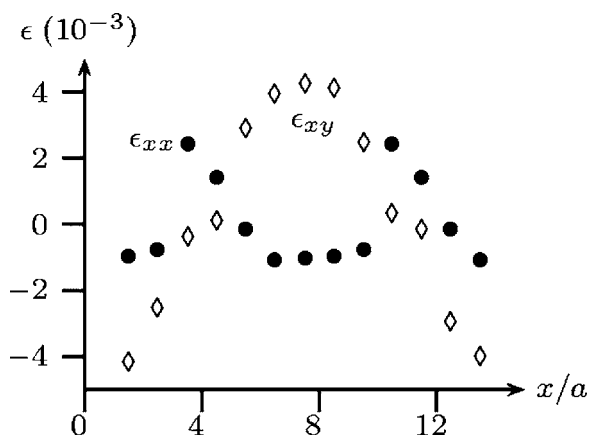
FIG. 6. Strain behavior across the twin wall. The ferroelastic strain ϵ_{xy} follows the order parameter Q_y, while the secondary strain ϵ_{xx} shows an anomaly within the wall.

across the wall. This is the behavior expected from secondary order parameters.[19]

B. Activation energy for twin wall motion in CaTiO$_3$

We compare two methods of calculating the Peierls energy $E_{Peierls}$. The first method is an indirect calculation using Eq. (3). Secondly, we perform a direct calculation of the transition state energy. These two energies are in good agreement. We also calculate the Peierls stress $\sigma_{Peierls}$ which is the maximum restoring stress the wall can exert.

To calculate the Peierls energy $E_{Peierls}$ using Eq. (3), we first calculate ΔE from the interfacial energy γ of the twin walls. From ΔE and the value of the function f for $w/a = 1.3$ we can calculate $E_{Peierls}$. Finally, assuming a sinusoidal variation of the energy as the wall moves through the lattice we can calculate the Peierls stress $\sigma_{Peierls}$. The stages of the calculation are summarized in Table I.

To calculate the Peierls energy directly we perform a transition state calculation on our system. We start with initial and final states which differ in that the two twin walls of the system are each translated by one lattice parameter in the

TABLE I. Indirect and direct calculation of the activation energy and Peierls stress. The results of the calculations are in good agreement.

Indirect calculation	
γ	0.116 J m^{-2}
ΔE	0.034 J m^{-2}
w/a	1.13
$f(w/a)$	0.016
$E_{Peierls}$	0.530 mJ m^{-2}
$\sigma_{Peierls}$	4.35 MPa
Direct calculation	
$E_{Peierls}$	0.313 mJ m^{-2}
$\sigma_{Peierls}$	2.57 MPa

same direction. The difference in atomic coordinates between these two states defines the reaction coordinate. We moved the system from the initial to the final state in 100 steps, relaxing all the degrees of freedom perpendicular to the reaction coordinate. At each step we calculated the force along the reaction coordinate and, by numerical integration of the work done by that force, the Peierls energy and stress. (This approach was necessary because DL_POLY cannot directly resolve the energy differences involved.) Again the results of these calculations are summarized in Table I.

The agreement between our two results is very good—less than a factor of 2—especially given the small value of the Peierls energy compared with the interaction energy of a twin wall with an oxygen vacancy, which, as noted above, is of the order of 1 eV. The residual discrepancy may be due to the complexity of the system. Equation (3) was developed for a domain wall which can be described by a single order parameter. As shown in Figs. 5 and 6 at least five parameters show anomalies across the wall. The energies of these anomalies may lead to an overestimation of ΔE calculated from the interfacial energy γ of the wall.

One important question is whether interactions between the two walls of the simulated system could affect the results. While the complexity of the transition state energy calculation forced us to use a smaller system than that simulated by Calleja *et al.*[9] the separation between the twin walls is still much greater than the wall width w, which is the parameter describing the length scale of the interaction between parallel walls.[15] Furthermore, since the walls move synchronously during the transition state calculation any interaction between them will remain approximately constant during the calculation and thus not influence the final result.

C. Simulation of a moving domain wall

Our results suggest that if a pressure greater than $\sigma_{Peierls} \approx 3$ MPa is applied to a twin wall it will move freely, rather than as a thermally activated process. In this section we demonstrate that this is the case by molecular dynamics simulation. Working in an *NVT* ensemble we shear the system to generate a force on the walls and observe their motion.

In order to calculate the force on the wall generated by a shear stress we need to calculate the Eshelby force on the wall.[24] The stress on a wall σ_{Wall} generated by an externally applied shear stress σ_{xy} is given by

$$\sigma_{Wall} = 4\sigma_{xy}\epsilon_{xy}, \quad (11)$$

where ϵ_{xy} is the spontaneous strain of the transition. For CaTiO$_3$, $\epsilon_{xy} = 4 \times 10^{-3}$ (see Fig. 6).

We started with a configuration of $26 \times 10 \times 6$ octahedra from the simulation of Calleja *et al.*, containing, as noted above, both ferroelastic walls and antiphase boundaries. On annealing at 10 K using DL_POLY the antiphase boundaries spontaneously moved together and annihilated each other, leaving only the ferroelastic walls. DL_POLY does not allow the direct imposition of a constant shear stress so instead we sheared the whole system (both coordinates and velocities) through an angle of 0.3°, generating an initial shear stress. (The *NVT* ensemble prevents the relaxation of this stress by

TABLE II. Parameters used in the simulation of a moving twin wall. The stresses acting on the system and the wall are only initial values. As the walls move in response to the forces these stresses will relax.

Time step	1.0 fs
Thermostat relaxation time	0.5 ps
Simulation duration	10.0 ps
Initial shear stress on crystal	6.0 GPa
Initial pressure on walls	100.0 MPa
Peierls stress	3.0 MPa

a macroscopic shear of the system.) The Eshelby force on the wall exceeded the Peierls stress and so motion of the wall was observed. The parameters of the simulation are summarized in Table II. In response to these forces the walls move as shown in Fig. 7. Initially the walls accelerate because the pressure acting on them is higher than the Peierls stress. The walls traverse several unit cells and then decelerate, as the stress acting on them decreases.

IV. CONCLUSIONS

A complete picture of twin wall motion in ferroelastic and ferroelectric materials would shed light on questions such as the fatigue problem in ferroelectric memories and the contri-
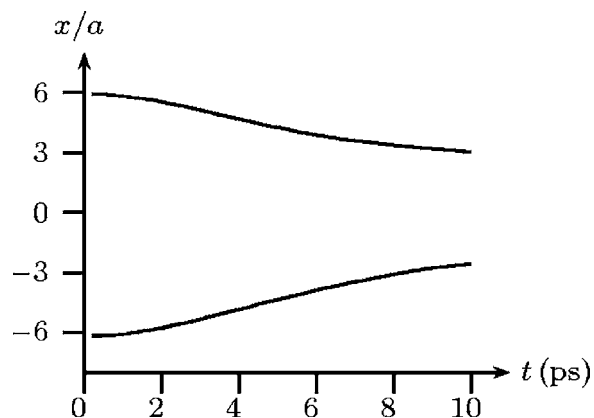

FIG. 7. Observed motion of the two twin walls of the simulated system.

bution of twin wall motion to the seismic properties of the Earth's lower mantle. Such a picture requires an understanding of the energy landscape through which the twin wall moves in the presence and absence of point defects. We have shown that the Peierls energy and stress of a ferroic material can be accurately estimated using an indirect approach by mapping the system onto a one order parameter model.

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