



Electromechanics of Dielectric and Piezoelectric Crystals With Point, Line, and Surface Defects

**by John D. Clayton, Peter W. Chung, Michael A. Grinfeld, and
William D. Nothwang**

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ELECTROMECHANICS OF DIELECTRIC AND PIEZOELECTRIC CRYSTALS WITH POINT, LINE, AND SURFACE DEFECTS

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ABSTRACT

A mathematical continuum theory is developed to describe the electromechanical behavior of dielectric and piezoelectric solids containing imperfections. The macroscopic distortion field consists of recoverable elasticity, deviatoric plasticity arising from dislocation glide, and volumetric deformation from vacancies. A connection on the spatial manifold of deformed lattice vectors describes gradients of stretch and rotation at the microscale caused by various lattice defects. It is shown that parallel transport of a lattice director vector with respect to this connection about a closed loop yields a discontinuity with contributions from the torsion of the connection (physically, from dislocations) and curvature (physically, from domain walls and vacancy gradients). Classical balance laws of electrostatics and mass and momentum conservation are implemented. A free energy function dependent upon lattice distortion, polarization, temperature, and defect densities is suggested. Thermodynamically consistent kinetics relations for dislocation glide and vacancy diffusion are then derived, with the chemical potential for the latter depending upon defect density, electric potential, hydrostatic pressure, and elastic energy density. Vacancy migration and mass rearrangement at the free surface of the substance are also considered explicitly.

Keywords: dielectric, piezoelectric, diffusion, vacancy, dislocation, disclination.

1. INTRODUCTION

Dielectric and piezoelectric solids are used in a great variety of solid state electronic devices owing to their electrical and mechanical properties. In pure dielectric materials, the mechanical and electrostatic behaviors are generally decoupled, whereas in piezoelectric media they are not. In the latter, mechanical strains may induce an electric field, and vice-versa. Ferroelectric media undergo a change in crystal structure with temperature, and may exhibit dielectric or piezoelectric effects as well as spontaneous polarization depending upon crystallographic phase. Examples of ferroelectrics encountered in the semiconductor industry include the crystalline ceramics PZT (Lead Zirconate Titanate) and BST (Barium Strontium Titanate). Defects affect the reliability of many ferroelectric devices, including capacitors, high-frequency sensors, and gate dielectric semiconductors, notably those of thin film geometry [1, 2]. During processing, through heat treatments or addition of doping chemicals, defect densities and excess electric charges may be controlled [3]. Perhaps the most naturally abundant piezoelectric material is crystalline quartz (Silicon Dioxide). Quartz exhibits electromechanical anisotropy, with historic applications in pressure transducers, capacitors, and gate dielectrics [4]. Quartz is also a fundamental constituent of granite, as found in urban construction applications (e.g., buildings) and encountered in geological settings [5, 6].

Physical models are needed in order to predict how existing dielectric and piezoelectric materials respond to new environments, to design engineering systems comprised of such materials, and to tailor new materials (e.g. chemically and/or micro-structurally) with improved combinations of properties. Noteworthy continuum descriptions of electromechanical behavior were set forth in the mid-twentieth century [7-10]. More recently, theories based on thermodynamics of energy minimization have been developed to

predict domain patterning in ferroelectric media [11], and vacancy diffusion and surface rearrangement in dielectric materials [12, 13].

Historically, defects have not been considered explicitly in continuum theories of such materials [7-10], even though their presence may dominate material behavior and hence the performance of the engineering system. In particular, charged vacancies are thought to affect leakage current characteristics of BST thin films [3, 13]. Misoriented, polarized domains are thought to influence the macroscopic dielectric constant of BST, and domain walls may act as a source or sink for charges and point and line defects. Vacancy migration and ion tunneling are important phenomenon in quartz resonators [4]. Dislocations have been found in crystalline quartz [14] and their motion and effects on properties have been reported [5, 6, 15-17]. Such imperfections affect anisotropy, piezoelectric response, and mechanical strength.

Here the kinematic description of defects relies on methods of differential geometry: the purely mathematical basis is given in [18, 19], while recent applications to mechanics of solids can be found in [20, 21]. In the present work, dislocations, disclinations (i.e. rotational discontinuities) and point defects are described via a multiscale continuum framework following [22]. The disclination concept, used previously to describe subgrains in severely deforming metallic crystals [23], is newly applied here to account for lattice rotation across domain walls in polarizable crystals. The description relies on many ideas proposed in early field theories of continuously distributed lattice defects [24-27].

In the present theory, the mechanical deformation is considered from two perspectives. From the macroscopic perspective, the solid deforms according to the displacement gradient or distortion, with contributions from elasticity, plasticity, and porosity. Here, distortions are assumed small, unlike in [22, 23], as fracture is thought likely occur in the relatively brittle materials of interest prior to attainment of large deformations. From the microscopic perspective, however, deformations may be large in the vicinity of defects, including significant rotations across domain walls. A linear connection is defined, accounting for stretch and rotation gradients of the lattice distinct from those induced by the macroscopic distortion. The total discontinuity or burgers vector in the lattice arising from this connection is shown to consist of contributions from dislocations, disclinations, and vacancy gradients. Bulk and surface fluxes of vacancies compatible with mass conservation principles are introduced [12, 13, 28]. Momentum and energy conservation laws are defined, along with standard relations from electrostatics [7]. Thermodynamic dependencies and kinetic relations are then postulated, describing, respectively, the state of the substance and the motion of defects. A proof is given that such relations are consistent with laws of thermodynamics, inspired by procedures of [29-31]. Finally, a specific functional form is suggested for the free energy density of dielectric and piezoelectric bodies, leading to a particular kinetic law for charged vacancy diffusion.

2. KINEMATICS AND BALANCE LAWS

The mechanical and electrical displacement vectors, u^a and D^a , are defined by

$$u^a = x^a - x_0^a, \quad (1)$$

$$D^a = \varepsilon_0 E^a + P^a, \quad (2)$$

where x^a and x_0^a are deformed and initial material coordinates, P^a is the polarization defined only within the solid domain, ε_0 is the permittivity of free space, and E^a is the electric field satisfying

$$E_a = -\phi_{,a}, \quad (3)$$

with ϕ the electric potential [7]. Indices in Roman font span three spatial coordinates, and subscripted commas denote spatial derivatives with respect to these coordinates. Polarization implies a relative displacement among charged ions comprising the primitive unit cell of the lattice. The displacement gradient is decomposed additively as

$$u_{a,b} = \gamma_{ab}^E + \gamma_{ab}^P + \gamma_{ab}^V, \quad (4)$$

with γ_{ab}^E the recoverable lattice distortion, γ_{ab}^P the plastic distortion from dislocation glide, and γ_{ab}^V expansion or contraction from point or volumetric defects, the latter two satisfying

$$(\gamma^P)^a_{,a} = 0, \quad (\gamma^V)^a_{,b} = (\chi/3)\delta^a_b, \quad (5)$$

where χ is the volume fraction of defects and δ^a_b is Kronecker's delta. Plastic flow is dictated by [23, 32, 33]

$$\dot{\gamma}_{ab}^P = \sum_k \nu^{(k)} s_a^{(k)} m_b^{(k)}, \quad (6)$$

where ν is the slip rate on glide system k , with slip direction s_a and slip plane normal m_b . Note that s_a and m_b are orthogonal by definition. Defects, polarization, and slip plane geometry are illustrated in Fig. 1.

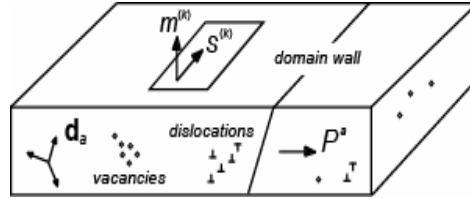


Fig. 1. Material element with point and line defects, polarized domains, and slip plane.

Diffusion of point defects is specialized here to vacancies. Let

$$\chi = \alpha \xi, \quad (7)$$

where ξ is the number of vacancies per unit volume and α is a positive constant. Then vacancy conservation, in the absence of generation or annihilation, requires

$$\dot{\xi} = -Q^a_{,a}, \quad (8)$$

where Q^i is the bulk flux of vacancies. Surface fluxes are also admitted, described by the vector q^α , where Greek indices span two surface coordinates. Let $\dot{a}$ denote the normal velocity of the surface, which may contract as vacancies are released. Denote by M the total mass of the system, with actual and referential (undeformed and defect-free) mass densities ρ and ρ_0 . Conservation at surface s of the system requires a null sum of rates of change in mass from surface expansion/contraction and from bulk and surface fluxes of vacancies:

$$\dot{M} / \rho_0 = \int \dot{a} (1 - \chi - \gamma^E_a) ds + \alpha \int (Q^a n_a + q^\alpha_{, \alpha}) ds = 0, \quad (9)$$

leading to [12, 13]

$$\dot{a} = -\alpha (Q^a n_a + q_{,\alpha}^a) / (1 - \chi - \gamma_{.a}^{Ea}). \quad (10)$$

Bulk and surface coordinates and fluxes are illustrated in Fig. 2.

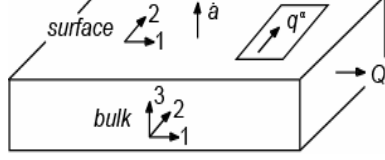


Fig. 2. Defect fluxes and coordinate systems.

The lattice deformation A_b^a is introduced as

$$A_b^a = \delta_b^a + \gamma_{.b}^{Ea} + \gamma_{.b}^{Va}, \quad (11)$$

and includes effects of elasticity and stress-free volumetric expansion, but not dislocation glide, as the latter presumably does not alter the crystal structure once dislocations have convected through the material [22, 23]. Lattice director vectors $\mathbf{d}_a$ (see Fig. 1) are deformed via (11) to the vectors $\mathbf{d}_b A_{.a}^{-1b}$, and the corresponding metric for their change in length is given by the inner product

$$C_{ab} = A_{.a}^{-1c} \mathbf{d}_c \cdot A_{.b}^{-1d} \mathbf{d}_d = A_{.a}^{-1c} \delta_{cd} A_{.b}^{-1d}, \quad (12)$$

where the $\mathbf{d}_a$ constitute an initially orthogonal triad attached to each unit cell of the lattice, and do not necessarily correspond to interatomic bond vectors. Spatial gradients on the manifold of lattice directors are described by the covariant derivative [18, 19, 22]

$$\nabla_b \mathbf{d}_a = \mathbf{d}_{a,b} - \Gamma_{ba}^{..c} \mathbf{d}_c, \quad (13)$$

where Christoffel symbols of the connection

$$\Gamma_{cb}^{..a} = A_{.d}^a A_{.b,c}^{-1d} + \Xi_{cb}^{..a} + \Upsilon_c \delta_b^a. \quad (14)$$

Above, $\Xi_{cb}^{..a}$ and Υ_c are additional degrees of freedom accounting for rotation and stretch gradients, respectively, due to surface and point defects. Covariant versions of these quantities are

$$\Xi_{cba} = \Xi_{cb}^{..d} C_{da} = \Xi_{c[ba]}, \quad \Upsilon_c \delta_b^d C_{da} = \Upsilon_c C_{(ba)}, \quad (15)$$

where bracketed indices are anti-symmetric and indices in parentheses are symmetric. The nonvanishing components of the torsion T and curvature R tensors of the connection (14) are then found as [19, 22, 27]:

$$T_{[cb]}^{..a} = 2A_{.d}^a A_{[b,c]}^{-1d} + 2\Xi_{[cb]}^{..a} + 2\Upsilon_{[c} \delta_{b]}^a, \quad (16)$$

$$R_{[ab][cd]} = 2\nabla_{[c} \Xi_{d]}^{..e} + T_{[cd]}^{..e} \Xi_{e[ba]}, \quad (17)$$

$$R_{(ab)[cd]} = 2\nabla_{[c} \Upsilon_{d]} C_{(ab)} + T_{[cd]}^{..e} \Upsilon_e C_{(ab)}. \quad (18)$$

The microstretch renders the connection (14) non-metric, since $\nabla_c C_{ab} = -2\Upsilon_c C_{ab}$.

Definition 2.1 Dislocation tensor. The dislocation density tensor is defined in component form as

$$2\bar{\alpha}^{ab} = \varepsilon^{bcd} T_{dc}^{..a}. \quad (19)$$

Remark. When the microrotation and microstretch vanish, $\bar{\alpha}^{ab}$ in (19) agrees with the form given in [33] in the absence of volumetric defects:

$$\bar{\alpha}^{ab} = \varepsilon^{bcd} A_e^a A_{..c,d}^{-1e} = -\varepsilon^{bcd} A_{e,d}^a A_{..c}^{-1e} \approx -\varepsilon^{bcd} \gamma_{..c,d}^{Ea}, \quad (20)$$

and vanishes when the elastic distortion is integrable, i.e. when $\gamma_{..b}^{Ea} = u_{..b}^{Ea}$, where u^E is an elastic displacement. In (19) and (20), ε^{abc} denotes the permutation operator.

Definition 2.2 Disclination tensor. The rank two disclination density is defined as

$$4\bar{\theta}^{gd} = \varepsilon^{gba} \varepsilon^{dce} R_{abce}. \quad (21)$$

Remark. The disclination density vanishes when the microrotation $\mathcal{E}_{cba} = 0$.

Definition 2.3 Point defect vector. This quantity is defined by

$$\bar{\mathcal{G}}^e = C^{-1ab} \varepsilon^{ecd} R_{(ab)cd} = 2\varepsilon^{ecd} \nabla_{[c} \mathcal{Y}_{d]} + \varepsilon^{ecd} T_{cd}^{..f} \mathcal{Y}_f. \quad (22)$$

Remark. The point defect vector vanishes when the microstretch $\mathcal{Y}_c = 0$.

Definition 2.4 Total burgers vector. The total burgers vector over oriented lattice plane a from defect fields represented in (14) is given by

$$b^a = \int_a \left(\bar{\alpha}^{ad} + C^{-1af} \varepsilon_{f gb} \bar{\theta}^{gd} x^b + \bar{\mathcal{G}}^d x^a \right) n_d da. \quad (23)$$

Remark. In the absence of microstretch and microrotation, $\bar{\alpha}/b$ can be interpreted as the number of parallel dislocation lines per unit area with constant burgers vector b perpendicular to oriented differential area element nda .

Proposition 2.5 The total burgers vector is equivalent to the following discontinuity induced by parallel transport of a lattice vector about an infinitesimal closed circuit c :

$$b^a = \frac{1}{2} \oint_c \left(T_{bc}^{..a} - R_{ecb}^{..a} x^e \right) dx^b \wedge dx^c. \quad (24)$$

Proof. The contribution from torsion and curvature to the closure failure upon parallel transport with respect to a connection of the form (13) is derived in Eqs. (2.19) and (4.1) and accompanying discussion of [19], neglecting terms of third and higher order in dx . Then, from the skew-symmetry of the differential two-form $dx^b \wedge dx^c = \varepsilon^{dbc} n_d da$, and substituting definitions (19)-(22) into (24), expression (23) is recovered.

The remaining conservation laws are now introduced and are used in the thermodynamic description that follows. Bulk mass conservation is described by

$$\dot{\rho} + \rho \dot{u}_{..a}^a = 0. \quad (25)$$

Linear and angular momentum conservation are written

$$\sigma_{..b}^{ab} = 0, \quad \sigma^{[ab]} = 0, \quad (26)$$

and the mechanical traction vector $t^a = \sigma^{ab} n_b$ is introduced. Maxwell's equation of electrostatics is

$$\hat{\rho} = D_{..a}^a, \quad (27)$$

with the charge density related to volumetric defects (i.e., charged vacancies) as follows:

$$\hat{\rho} = ez\xi, \quad (28)$$

where e is the charge of an electron and z is the valence contribution of each defect.

3. THERMODYNAMICS AND KINETICS

Two energy balances are introduced. The first is the local balance of electrostatic energy [7, 30]:

$$-(\varepsilon_0 E^a + P^a) \phi_{,a} = \phi \hat{\rho} \leftrightarrow D^a E_a = \phi \hat{\rho}. \quad (29)$$

The second is the global balance of the rate of external work, internal energy, and electrostatic field energy [13, 30]:

$$W = \int \rho \dot{U} dv + \frac{d}{dt} \int \frac{\varepsilon_0}{2} E^a E_a dv + \frac{d}{dt} \int \hat{\sigma} \phi ds, \quad (30)$$

where U is the internal energy per unit mass, $\hat{\sigma}$ is the surface charge density, and the rate of external work W is given by

$$W = \frac{d}{dt} \int \hat{\sigma} \phi ds + \int t^a \dot{u}_a ds - \int \mu Q^a n_a ds, \quad (31)$$

with μ the chemical potential for vacancy diffusion. The Helmholtz free energy ψ , specific entropy η , and absolute temperature θ are related by

$$\psi = U - \eta \theta. \quad (32)$$

Neglecting heat conduction, the global entropy inequality is written

$$\int \theta \rho \dot{\eta} dv \geq 0 \rightarrow \int \rho (\dot{U} - \dot{\psi} - \dot{\theta} \eta) dv \geq 0, \quad (33)$$

and can be expressed compactly as

$$\Phi = W - \dot{\Omega} \geq 0, \quad (34)$$

where the rate of system energy

$$\dot{\Omega} = \int \rho (\dot{\psi} + \dot{\theta} \eta) dv + \frac{d}{dt} \int \frac{\varepsilon_0}{2} |\phi_{,a}|^2 dv + \frac{d}{dt} \int \hat{\sigma} \phi ds. \quad (35)$$

The Helmholtz free energy is assumed to exhibit the following functional dependencies:

$$\psi = \psi(\gamma_{ab}^E, P^a, \xi, h, \theta), \quad (36)$$

with the generic scalar-valued function $h = h(\bar{\alpha}^{ab}, \bar{\theta}^{ab}, \bar{g}^a)$ accounting for energetic contributions from defects apart from ξ .

Proposition 3.1 A set of bulk thermodynamic and kinetic relations simultaneously satisfying (29), (34), and constitutive assumption (36) and neglecting electrostatic terms of second order is

$$\sigma^{ab} = \rho \frac{\partial \psi}{\partial \gamma_{ab}^E}, \quad (37)$$

$$E_a = \rho \frac{\partial \psi}{\partial P^a}, \quad (38)$$

$$\eta = -\frac{\partial \psi}{\partial \theta}, \quad (39)$$

$$Q^a = -d^{ab} \mu_{,b} \quad |d^{ab}| > 0, \quad (40)$$

$$\mu = \rho \frac{\partial \psi}{\partial \xi} + ez\phi + \alpha p, \quad (41)$$

$$\nu^{(k)} = \nu_0 \left| \tau^{(k)} / \sigma_0 \right|^n \text{sgn}(\tau^{(k)}), \quad \nu_0 > 0, \quad (42)$$

$$\sum_k \tau^{(k)} \nu^{(k)} \geq \rho \frac{\partial \psi}{\partial h} \dot{h}. \quad (43)$$

Above, d^{ab} is the diffusivity, $\tau^{(k)} = \sigma^{ab} s_a^{(k)} m_b^{(k)}$ is the resolved shear stress on slip system k , ν_0 is a reference shearing rate, n denotes rate hardening, and σ_0 is the slip resistance. The notation $\text{sgn } x = x/|x|$.

Proof. Expanding the internal energy rate using (36) gives

$$\rho(\dot{\psi} + \dot{\theta}\eta) = \rho \frac{\partial \psi}{\partial \gamma_{ab}^E} \dot{\gamma}_{ab}^E + \rho \frac{\partial \psi}{\partial P^a} \dot{P}^a + \rho \frac{\partial \psi}{\partial \xi} \dot{\xi} + \rho \frac{\partial \psi}{\partial h} \dot{h} + \rho \left(\frac{\partial \psi}{\partial \theta} + \eta \right) \dot{\theta}, \quad (44)$$

from which assuming that $\dot{\Omega} = 0$ for purely thermal processes gives (39). Expanding the electric field energy by using Eq. (29),

$$\frac{d}{dt} \left(\frac{\epsilon_0}{2} \int E^a E_a dv \right) = - \int E_a \dot{P}^a dv + \int \phi \dot{\rho} dv + \int \dot{u}^a \Sigma_{a,b}^b dv - \int \Sigma^{ab} n_a \dot{u}_b ds, \quad (45)$$

where the divergence of the Maxwell stress [9, 30],

$$\Sigma_{a,b}^{,b} = -\phi_{,ab} P^b - \phi_{,a} \hat{\rho} = (E_a D^b - \epsilon_0 E^c E_c \delta_a^b / 2)_{,b}, \quad (46)$$

as well as the value of the stress itself, Σ^{ab} , are both set to zero henceforth by the assumption of small electrostatic terms. The net dissipation of (34) then becomes

$$\begin{aligned} \Phi &= \int t^a \dot{u}_a ds - \int \mu_{,a} Q^a dv - \int \rho \frac{\partial \psi}{\partial \gamma_{ab}^E} \dot{\gamma}_{ab}^E dv - \dots \\ &\quad \int \left(E_a - \rho \frac{\partial \psi}{\partial P^a} \right) \dot{P}^a dv - \int \left(\rho \frac{\partial \psi}{\partial \xi} + ez\phi - \mu \right) \dot{\xi} dv - \int \rho \frac{\partial \psi}{\partial h} \dot{h} dv. \end{aligned} \quad (47)$$

Expanding the stress power using the divergence theorem, (4), and (5),

$$\int t^a \dot{u}_a ds = \int \underbrace{\sigma_{,b}^{ab}}_0 + \sigma^{ab} (\dot{\gamma}_{ab}^E + \dot{\gamma}_{ab}^P + \alpha \dot{\xi} \delta_{ab} / 3) dv = \int (\sigma^{ab} \dot{\gamma}_{ab}^E + \hat{\sigma}^{ab} \dot{\gamma}_{ab}^P - p \alpha \dot{\xi}) dv, \quad (48)$$

where the deviatoric stress $\hat{\sigma}^{ab} = \sigma^{ab} + p \delta^{ab}$ and the hydrostatic pressure $-3p = \sigma_{,a}^a$. Then

$$\begin{aligned} \Phi = & \int \hat{\sigma}^{ab} \dot{\gamma}_{ab}^P dv - \int \mu_{,a} Q^a dv - \int \rho \frac{\partial \psi}{\partial h} \dot{h} dv + \dots \\ & \int \left(\sigma^{ab} - \rho \frac{\partial \psi}{\partial \gamma_{ab}^E} \right) \dot{\gamma}_{ab}^E dv - \int \left(E_a - \rho \frac{\partial \psi}{\partial P^a} \right) \dot{P}^a dv - \int \left(\rho \frac{\partial \psi}{\partial \xi} + e z \phi - \mu + p \alpha \right) \dot{\xi} dv. \end{aligned} \quad (49)$$

The final three volume integrals on the right of (49) vanish when (37), (38), and (41) apply. From (40), dissipation is always non-negative from vacancy flux:

$$-\mu_{,a} Q^a = \mu_{,a} d^{ab} \mu_{,b} \geq 0. \quad (50)$$

This leaves the local requirement

$$\hat{\sigma}^{ab} \dot{\gamma}_{ab}^P - \rho \frac{\partial \psi}{\partial h} \dot{h} \geq 0. \quad (51)$$

From (42), plastic work is always non-negative:

$$\hat{\sigma}^{ij} \dot{\gamma}_{ij}^P = \sum_k \tau^{(k)} \nu_0 \left| \tau^{(k)} / \sigma_0 \right|^n \text{sgn}(\tau^{(k)}) \geq 0, \quad (52)$$

meaning that the energy storage rate from generation, annihilation, and/or interaction of lattice defects, $\dot{h}$, cannot exceed the rate of dissipation from dislocation glide, as required by (43).

Corollary 3.2 Thermodynamically consistent boundary conditions on bulk vacancy flux, and an admissible kinetic equation for surface flux, compatible with Proposition 3.1, are

$$Q^i n_i = \beta \left[\alpha (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) + \mu \right], \quad \beta \geq 0, \quad (53)$$

$$q^\alpha = -\hat{A}^{\alpha\beta} \left[(\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) \right]_{,\beta}, \quad |\hat{A}^{\alpha\beta}| \geq 0, \quad (54)$$

assuming that

$$(\rho \psi + \phi \hat{\rho}) \geq 0, \quad \hat{A}^{\alpha\beta} \left[(\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) \right]_{,\beta\alpha} \geq 0, \quad (55)$$

and subject to the boundary restrictions of constant (in time) charge and electric potential on s , and traction-free or quasi-static surface s .

Proof. The system's total energy rate with a moving boundary is written using (35) and (45):

$$\dot{\Omega} = \int \rho (\dot{\psi} + \dot{\theta} \eta) dv - \int E_i \dot{P}^i dv + \int \phi \dot{\hat{\rho}} dv + \frac{d}{dt} \int \hat{\sigma} \phi ds + \int \dot{a} (\rho \psi + e z \phi \xi) ds, \quad (56)$$

assuming Maxwell stress $\Sigma^{ab} = 0$. This is expanded using (36) and (48) as

$$\dot{\Omega} = \int t^a \dot{u}_a ds - \int \hat{\sigma}^{ab} \dot{\gamma}_{ab}^P dv + \int \rho \frac{\partial \psi}{\partial h} \dot{h} dv + \int \left(\rho \frac{\partial \psi}{\partial \xi} + e z \phi + \alpha p \right) \dot{\xi} dv + \int \dot{a} (\rho \psi + e z \phi \xi) ds. \quad (57)$$

For a traction-free or quasi-static surface, $t^a \dot{u}_a = 0$, and with dissipative plastic work and plastic variables, (51) applies. Then using the divergence theorem,

$$\dot{\mathcal{Q}} = -\int \mu Q^a n_a ds + \int \mu_{,a} Q^a dv + \int \dot{a} (\rho \psi + ez \phi \xi) ds. \quad (58)$$

Since $\mu_{,a} Q^a = -d^{ab} \mu_{,a} \mu_{,b} \leq 0$, the following requirement arises in order to satisfy (34) in the absence of external working:

$$\dot{a} (\rho \psi + \phi \hat{\rho}) - \mu Q^a n_a \leq 0. \quad (59)$$

Substituting from mass conservation requirement (10) gives

$$-Q^a n_a \left[\alpha (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) + \mu \right] + q_{,a}^\alpha (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) \leq 0. \quad (60)$$

Then, from (53),

$$-Q^a n_a \left[\alpha (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) + \mu \right] = -\beta \left[\alpha (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) + \mu \right]^2 \leq 0. \quad (61)$$

Finally, from (54) and (55), the following inequality remains:

$$q_{,a}^\alpha (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) = -\hat{A}^{\alpha\beta} \left[(\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) \right]_{,\beta\alpha} (\rho \psi + \phi \hat{\rho}) / (1 - \chi - \gamma_{,a}^{Ea}) \leq 0. \quad (62)$$

Remark. Since $0 \leq \chi < 1$, (55) and (62) suggest that the sum of the free energy per unit volume and electrostatic energy per unit volume should be non-negative and convex when elastic volume changes are small.

4. CONSTITUTIVE FUNCTIONS FOR PIEZOELECTRICS AND DIELECTRICS

The following more specific form of (36) is proposed for single crystalline electromechanical solids, in the absence of phase changes or spontaneous polarization:

$$\rho \psi = (1/2) \mathbb{C}^{abcd} (1 - \alpha \xi) \gamma_{(ab)}^E \gamma_{(cd)}^E + (1/2) \Lambda_{ab} P^a P^b + \Delta_{..c}^{ab} \gamma_{(ab)}^E P^c + \varphi(\xi, \theta) + h, \quad (63)$$

where $\mathbb{C}$ and Λ are, respectively, the anisotropic elastic moduli and inverse dielectric susceptibility, and Δ are piezoelectric constants. For a dielectric material such as BST in the paraelectric state [3, 13], $\Delta_{..c}^{ab} = 0$, and (2), (37), and (38) lead to

$$D^a = \varepsilon_0 \varepsilon_R^{ab} E_b, \quad (64)$$

$$\sigma^{ab} = \mathbb{C}^{abcd} (1 - \chi) \gamma_{(cd)}^E, \quad (65)$$

$$E_a = \Lambda_{ab} P^b, \quad (66)$$

with $\varepsilon_R^{ab} = \delta^{ab} + \varepsilon_0^{-1} \Lambda^{-1ab}$ the relative permittivity. For a piezoelectric material such as pure α -quartz,

$$D^a = \varepsilon_0 \varepsilon_R^{ab} E_b - \Pi^{abc} \gamma_{(bc)}^E, \quad (67)$$

$$\sigma^{ab} = \mathbb{C}^{abcd} (1 - \chi) \gamma_{(cd)}^E + \Delta_{..c}^{ab} P^c, \quad (68)$$

$$E_a = \Lambda_{ab} P^b + \Delta_{..a}^{bc} \gamma_{(bc)}^E, \quad (69)$$

where $\Pi^{abc} = \Lambda^{-1ad} \Delta_{..d}^{bc}$. The scalar function ϕ is assumed to follow the universal relation for the chemical potential of an ideal mixture [13, 34]:

$$\phi N_A = N_T (G_0(\theta) + N_A k_B \theta \hat{v} \ln \hat{v}), \quad (70)$$

where N_A is Avagadro's number, k_B is Boltzmann's constant, $N_T = 1/\alpha$ is the number of atomic sites per unit volume, $\hat{v} = \xi / N_T$ is the mole fraction of vacancies, and $G_0(\theta)$ is the bulk Gibbs free energy of the unstressed, defect-free crystal. Note that for constant temperature applications, each atom (or missing atom) occupies a fixed reference volume, such that $N_T = 1/\alpha$ and $\hat{v} = \chi$. From (41), the chemical potential for vacancy diffusion is then

$$\mu = k_B \theta (1 + \ln \chi) + e z \phi - \alpha \left[(1 - \chi) \mathbb{C}_a^{abc} \gamma_{(bc)}^E / 3 + (1/2) \mathbb{C}^{abcd} \gamma_{(ab)}^E \gamma_{(cd)}^E \right]. \quad (71)$$

The kinetic equation for bulk flux follows from (40) as

$$Q^a = d^{ab} \left[e z E_b - \frac{k_B \theta}{\chi} \chi_{,b} + \frac{\alpha(1 - \chi)}{3} \left(\mathbb{C}_e^{edc} \gamma_{(dc),b}^E - \mathbb{C}_e^{edc} \gamma_{(dc)}^E \chi_{,b} \right) + \alpha \mathbb{C}^{efcd} \gamma_{(ef)}^E \gamma_{(cd),b}^E \right]. \quad (72)$$

Consider now a one-dimensional reduction of (72), where uniaxial strain conditions hold for the x -direction, i.e. $\sigma = \mathbb{C}(1 - \chi) \gamma^E$, where $\mathbb{C}$ is an elastic constant:

$$Q/d = e z E - \frac{k_B \theta}{\chi} \frac{d\chi}{dx} + \frac{\alpha(1 - \chi)}{3} \left(\mathbb{C}(1 + 3\gamma^E) \frac{d\gamma^E}{dx} - \mathbb{C} \gamma^E \frac{d\chi}{dx} \right). \quad (73)$$

This can also be written as follows, neglecting terms of second order in elastic strain and porosity:

$$Q/d = - \left[\frac{2\alpha \mathbb{C} \gamma^E}{3} + \frac{k_B \theta}{\chi} \right] \frac{d\chi}{dx} - [e z] \frac{d\phi}{dx} - \left[\alpha(1 - \chi)(1 + 3\gamma^E) \right] \frac{dp}{dx}, \quad (74)$$

where the first term on the right causes vacancies to move to areas of lower concentration, the second term causes charged vacancies to move to areas of lower electric potential, and the third term accounts for the elastic strain energy density, causing vacancies to move to areas of lower hydrostatic pressure. While the final term vanishes under static stress equilibrium in the one dimensional case (i.e., the first of (26) gives $dp/dx = 0$), analogous terms containing stress or pressure gradients do not generally vanish in the three dimensional Eq. (72).

5. CONCLUSIONS

A continuum framework for the electromechanical behavior of dielectric and piezoelectric solids has been developed. The kinematic description accounts for the contributions of dislocations, disclinations (i.e., domain walls), and point defects to covariant derivatives and discontinuities in the field of lattice director vectors on their spatial manifold. Thermodynamically admissible relationships for recoverable elasticity, polarization, dislocation glide, and bulk and surface diffusion of charged vacancies have been derived. Specific constitutive functions have been postulated for dielectric and piezoelectric single crystals, with particular emphasis given to the form of the governing equation for bulk diffusion kinetics.

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