ON VARIATIONAL PRINCIPLES FOR POLARIZATION RESPONSES IN ELECTROMECHANICAL SYSTEMS[*]

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Abstract. Electromechanical systems can be found in many physical and biological applications, such as ion transport in membranes, batteries, and dielectric elastomers. Classical electrodynamics uses a dielectric constant to describe the polarization response of an electromechanical system to charges in an electric field. We generalize that description to include a wide variety of responses to charges in the electric field by a unified, thermodynamically consistent, variational framework. This framework is motivated and developed using the classical energetic variational approach (EnVarA). The coupling between the electrical part and the chemo-mechanical parts of the system is described either by Lagrange multipliers or various energy relaxations. The classical polarization and its dielectrics and dielectric constants appear as outputs of this analysis. The Maxwell equations then become universal conservation laws of charge and current, conjoined to an electromechanical description of the polarization of materials.

Keywords. Electromechanical coupling; Electrodynamics; Energetic Variation Approach.

AMS subject classifications. 35Q49; 70H30; 78A02; 78A30.

1. Introduction

Electromagnetism is often described by Maxwell field equations that form a general and precise description of electrodynamics in the absence of matter, with only two parameters, both of which are true constants that are remarkably constant in a wide range of conditions. In the presence of matter, like dielectrics, things are more complicated, because the field changes things that are charged and the charge changes the field [36]. These interactions depend on the mechanical properties of the system, the distribution of charge and mass, and the Maxwell equations themselves.

Classical electrodynamics included a particularly simple idealized model of electromechanical charge in insulating dielectrics and so, was a constitutive model depending on the properties of materials. In the ideal linear dielectrics, interactions are described by a dielectric constant ε_r, a single real number, in the Maxwell equations. That classical model is, however, unable to adequately describe the complicated interaction between charge and field in most materials [1, 2, 5, 11, 12, 18, 22, 25, 37, 38]. It should not be a surprise that a model adequate to deal with measurements available in the 1850's (typically on a time scale of a tenth of a second) would need revision in the 2020's when time scales of 10^{-9}s are commonplace in experiments and applications.

Other electromechanical systems (beyond insulating dielectrics) are even more complicated because other forces—like diffusion and convection—come into play. One of the most important electro-mechanical systems is the transport of charged particles in dilute solutions, which is often described by a Poisson-Nernst-Planck (PNP) equation [9]. The movement of charged particles is a mechanical process, involving diffusion and convec-

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tion, but the motion of the charges changes their positions, forms an electrical current, and thus changes the electric field in the system, which in turn changes the motion of the charged particles themselves.

In systems involving diffusion, the particles interact through the electric field and use concentration gradients to create a PNP system [13,21]. The classical PNP equation can be written as [21]

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i(\nabla c_i + \frac{qz_i}{k_BT} c_i \nabla \varphi)), \qquad -\Delta \varphi = \frac{1}{\varepsilon}(\sum_{i=1}^{n} qz_i c_i + \rho_0(\boldsymbol{x})), \qquad (1.1)$$

where $c_i(\boldsymbol{x},t)$ is the number density of the i-th species of ions, $\varphi(\boldsymbol{x},t)$ is the electrostatic potential, $\rho_0(\boldsymbol{x})$ represents the density of any immobile background charge, q is the elementary charge, z_i is the electric charge of one molecule of the i-th species, and ε is the permittivity that measures electric polarizability of the solution. Here the effects of magnetic fields are totally neglected, which is only true when there are no time-dependent magnetic fields so $\mathbf{E} = -\nabla \varphi$ is curl-free. The interaction between ions[1] and field is imposed through the Poisson equation not the Maxwell equations.

There exits a large literature developing variational theories for electromechanical and magnetomechanical coupling in a range of systems of this type (excluding diffusion for the most part) [4,7,15–17,24,27,29,31–33,41–43]. Inspired by these, we build a thermodynamically consistent variational description of general electromechanical systems and extend it to include diffusion. The framework is motivated and developed using the classical energetic variational approach (EnVarA) that allows consistent incorporation of other fields, e.g., chemical reactions [44] and even temperature [26]. The key point is to isolate material properties in the Maxwell equations and use the classical theories of continuum mechanics to describe those material properties, using the EnVarA formulation. In this paper, dynamics and fluctuation are imposed in the mechanical part only. The electrical part of electromechanical coupling is imposed through models of the system of interest, or by a Lagrange multiplier in a way less dependent on a specific model. The constitutive properties are separated from the Maxwell equations in this approach, allowing the Maxwell equations to be universal and exact, and the constitutive equations to describe (electro)material properties. As an illustration, we re-derive the classical PNP system in the proposed framework.

2. Preliminary

2.1. Mechanics: energetic variational approach.
Mechanical systems can often be described by their energy and the rate of energy dissipation [19]. One of the simplest mechanical systems is a spring-mass system

$$\boldsymbol{x}_t = \boldsymbol{v}, \qquad m\boldsymbol{v}_t = -\gamma \boldsymbol{x}_t - \nabla V(\boldsymbol{x}), \qquad (2.1)$$

where $\boldsymbol{v}$ is the velocity and $V(\boldsymbol{x})$ is the potential energy. For a linear spring, $V(\boldsymbol{x}) = \frac{1}{2}k|\boldsymbol{x}|^2$. It is straightforward to show that the spring-mass system (2.1) satisfies an energy-dissipation identity

$$\frac{\mathrm{d}}{\mathrm{d}t}(\frac{m}{2}|\boldsymbol{x}_t|^2 + V(\boldsymbol{x})) = -\gamma|\boldsymbol{x}_t|^2, \qquad (2.2)$$

where $\mathcal{K} = \frac{m}{2}|\boldsymbol{x}_t|^2$ is the kinetic energy, $\mathcal{U} = V(\boldsymbol{x})$ is the internal energy and $\gamma|\boldsymbol{x}_t|^2$ is the rate of energy dissipation due to the friction. If the system also involves a stochastic

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[1]Holes and electrons in semiconductors share many of the properties of ions in solutions.

force, modeled by a Gaussian white noise, then the dynamics becomes

$$\boldsymbol{x}_t = \boldsymbol{v}, \qquad m\boldsymbol{v}_t = -\gamma v - \nabla V(\boldsymbol{x}) + \boldsymbol{\xi}(t), \tag{2.3}$$

where $\boldsymbol{\xi}(t)$ is a stochastic force satisfying $\langle \boldsymbol{\xi}, \boldsymbol{\xi}' \rangle = 2k_B T m^{-1} \gamma \delta(t - t')$ due to the fluctuation-dissipation theorem (FDT) [28]. The FDT ensures the system admits an energy-dissipation law and reaches the correct equilibrium state [28]. Here we adopt a Langevin representation, understanding fully well that this description is a constitutive model that needs to be confirmed by experiment and simulations of atomic motion. Let $f(\boldsymbol{x}, \boldsymbol{v}, t)$ be the probability of finding the particle in location $\boldsymbol{x}$ with velocity $\boldsymbol{v}$, the Fokker-Planck equation of $f(\boldsymbol{x}, \boldsymbol{v}, t)$ corresponding to the Langevin dynamics (2.3) is given by

$$\partial_t f + \nabla_{\boldsymbol{x}} \cdot (\boldsymbol{v} f) + \nabla_{\boldsymbol{v}} \cdot \left(\left(-\tfrac{\gamma}{m} \boldsymbol{v} - \tfrac{1}{m} \nabla V \right) f \right) = \tfrac{k_B T \gamma}{m^2} \Delta_v f. \tag{2.4}$$

Note that this is the full Langevin equation including the acceleration term. Direct calculation reveals that the Fokker-Planck Equation (2.4) for the full Langevin equation satisfies an energy-dissipation identity

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \frac{m}{2} f |v|^2 + k_B T f \ln f + V f \, \mathrm{d}v \mathrm{d}\boldsymbol{x} = \int -\gamma f |\boldsymbol{v} + k_B T m^{-1} \nabla_v \ln f|^2 \mathrm{d}v \mathrm{d}\boldsymbol{x} \le 0. \tag{2.5}$$

The $(k_B T)(f \ln f)$ mixing term comes from the noise, which corresponds to the entropy $-T\mathcal{S}$ in classical thermodynamics.

In an overdamped region ($\gamma \gg m$), the inertial term in (2.3) can be ignored and the dynamics can be reduced to an overdamped Langevin equation (after rescaling but keeping the same notation) [14, 20, 39, 40, 45]

$$\gamma \boldsymbol{x}_t = -\nabla V(\boldsymbol{x}) + \boldsymbol{\xi}(t), \tag{2.6}$$

where $\langle \boldsymbol{\xi}, \boldsymbol{\xi}' \rangle = 2k_B T \gamma \delta(t - t')$. The corresponding Fokker-Planck equation of $\rho(\boldsymbol{x}, t)$ is

$$\rho_t = \nabla \cdot \left(\tfrac{1}{\gamma} (k_B T \nabla \rho + \rho \nabla V) \right), \tag{2.7}$$

where $\rho(\boldsymbol{x}, t)$ is the probability distribution of finding the particle at location $\boldsymbol{x}$. If we define the average velocity as $\mathbf{u} = \tfrac{1}{\gamma} \nabla (k_B T (\ln \rho + 1) + V)$, then the energy-dissipation law of the Fokker-Planck Equation (2.7) can be formulated as

$$\frac{\mathrm{d}}{\mathrm{d}t} \int (k_B T \rho \ln \rho + V(\boldsymbol{x})) \, \mathrm{d}\boldsymbol{x} = -\int \gamma \rho |\mathbf{u}|^2 \, \mathrm{d}\boldsymbol{x}. \tag{2.8}$$

Again, the mixing term $k_B T \rho \ln \rho$ term corresponds to $-T\mathcal{S}$ with $\mathcal{S} = -\rho \ln \rho$ being the entropy [8].

In general, as in previous examples, an isothermal mechanical system can be well defined through an energy-dissipation law

$$\frac{\mathrm{d}}{\mathrm{d}t} (\mathcal{K} + \mathcal{F}) = -\triangle, \tag{2.9}$$

along with the kinematics of the employed variables. Here $\mathcal{K}$ is the kinetic energy, $\mathcal{F} = \mathcal{U} - T\mathcal{S}$ is the Helmholtz free energy, and $\triangle$ is the rate of the energy dissipation, which is the rate of entropy production in the system [19]. From the energy-dissipation law (2.13), the corresponding evolution equation can be derived by the energetic variational approach (EnVarA). In more detail: EnVarA consists of two distinct variational

processes: the Least Action Principle (LAP) and the Maximum Dissipation Principle (MDP) [19]. The LAP states that the dynamics of a Hamiltonian system are determined as a critical point of the action functional $\mathcal{A}(\boldsymbol{x}) = \int_0^T (\mathcal{K} - \mathcal{F}) \, \mathrm{d}t$ with respect to $\boldsymbol{x}(\mathbf{X}, t)$ (the trajectory for mechanical systems, where $\mathbf{X}$ are Lagrangian coordinates) [19], i.e., $\delta \mathcal{A} = \int_0^T \int_{\Omega(t)} (f_{\text{inertial}} - f_{\text{conv}}) \cdot \delta \boldsymbol{x} \, \mathrm{d}\boldsymbol{x} \mathrm{d}t$. The dissipative force in such a system can be determined by minimizing the dissipation functional $\mathcal{D} = \frac{1}{2}\triangle$ with respect to the "rate" $\boldsymbol{x}_t$ in the linear response regime [6], i.e., $\delta \mathcal{D} = \int_{\Omega(t)} f_{\text{diss}} \cdot \delta \boldsymbol{x}_t \, \mathrm{d}\boldsymbol{x}$. This principle is known as Onsager's MDP [34,35]. According to force balance, we have, in Eulerian coordinates,

$$\frac{\delta A}{\delta \boldsymbol{x}} = \frac{\delta \mathcal{D}}{\delta \boldsymbol{x}_t}. \tag{2.10}$$

This describes the dynamics of the system. It is worth mentioning that in principle, mechanical systems are totally determined by the trajectory or the flow map $\boldsymbol{x}(\mathbf{X}, t)$, as indicated by the above variational procedure.

The PNP Equation (1.1) can be derived from the energy-dissipation law [9]

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \sum_{i=1}^n k_B T c_i (\ln c_i - 1) + \frac{\varepsilon}{2} |\nabla \varphi|^2 = -\int \frac{k_B T}{D_i} c_i |\mathbf{u}_i|^2 \mathrm{d}\boldsymbol{x} \tag{2.11}$$

with the constraint $-\nabla \cdot (\varepsilon(\nabla \varphi)) = (\sum_{i=1}^n q z_i c_i + \rho_0(\boldsymbol{x}))$, which is a differential form of the Gauss's law. We refer the interested readers to [9] for detailed derivation.

2.2. Electricity: Maxwell field equations in vacuum. The fundamental equations in classical electromagnetism are Maxwell's field equations,

$$\begin{aligned} \nabla \cdot (\varepsilon_0 \mathbf{E}) &= 0, & \nabla \cdot \mathbf{B} &= 0 \\ \frac{\partial \mathbf{B}}{\partial t} &= -(\nabla \times \mathbf{E}), & \nabla \times \mathbf{B} &= \mu_0 \left(\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right), \end{aligned} \tag{2.12}$$

in vacuum, where $\mathbf{E}$ and $\mathbf{B}$ are electric and magnetic fields, ε_0 is the electrical constant, also called the permittivity of free space and μ_0 is the magnetic constant, also called the permeability of free space. Direct calculations show the Maxwell Equations (2.12) satisfy the energy-dissipation identity

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\frac{\varepsilon_0}{2} |\mathbf{E}|^2 + \frac{1}{2\mu_0} |\mathbf{B}|^2) \, \mathrm{d}x = -\int_\Omega \frac{1}{\mu_0} \nabla \cdot (\mathbf{E} \times \mathbf{B}) \, \mathrm{d}\boldsymbol{x} = -\int_{\partial \Omega} \frac{1}{\mu_0} (\mathbf{E} \times \mathbf{B}) \cdot \boldsymbol{\nu} \, \mathrm{d}S, \tag{2.13}$$

where $\boldsymbol{\nu}$ is the outward normal of Ω. Motivated by the above calculation, we can define the electromagnetic field energy density $e_F(\mathbf{E}, \mathbf{B})$ as

$$e_F(\mathbf{E}, \mathbf{B}) = \frac{\varepsilon_0}{2} |\mathbf{E}|^2 + \frac{1}{2\mu_0} |\mathbf{B}|^2. \tag{2.14}$$

The vector $\frac{1}{\mu_0} \mathbf{E} \times \mathbf{B}$ is the Poynting vector that represents the directional energy flux (the energy transfer per unit area per unit time) of an electromagnetic field.

Conventionally, one introduces the electric and magnetic displacement vectors $\mathbf{D}$ and $\mathbf{H}$, defined by $\mathbf{D} = \varepsilon_0 \mathbf{E}$, $\mathbf{H} = \frac{1}{\mu_0} \mathbf{B}$, which are known as Lorentz-Maxwell æther relations. Note that

$$\mathbf{D} = \frac{\partial e_F}{\partial \mathbf{E}}, \quad \mathbf{H} = \frac{\partial e_F}{\partial \mathbf{B}}, \tag{2.15}$$

which provides an energetic variational formulation for $\mathbf{D}$ and $\mathbf{E}$ connecting the energies and these classic fields.

REMARK 2.1. The field energy e_F per unit volume can be formulated with different primitive variables. For instance, in [16], the field energy e_F is defined as

$$e_F(\mathbf{B}, \mathbf{D}) = \frac{|\mathbf{B}|^2}{2\mu_0} + \frac{|\mathbf{D}|^2}{2\varepsilon_0} \tag{2.16}$$

by using $\mathbf{B}$ and $\mathbf{D}$ as independent variables. The electric and magnetic fields $\mathbf{E}$ and $\mathbf{H}$ can be defined as

$$\mathbf{E} = \frac{\partial e_F}{\partial \mathbf{D}} = \frac{1}{\varepsilon_0}\mathbf{D}, \quad \mathbf{H} = \frac{\partial e_F}{\partial \mathbf{B}} = \frac{1}{\mu_0}\mathbf{H}. \tag{2.17}$$

We refer the interested readers to [4] for detailed discussions of different variational formulations.

REMARK 2.2. The classical case describes an idealized dielectric $\mathbf{D} = \epsilon_0\epsilon_r\mathbf{E}$ in which the dielectric constant ϵ_r is a single real number. Small magnetic fields are described by a single real number the permeability μ giving $\mathbf{H} = \mathbf{B}/\mu$ in some types of matter (diamagnetic and paramagnetic). When nothing is known about the actual behavior of a dielectric or a dia- or paramagnetic material, it is customary and reasonable to use the classical approximation, even today.

For a particle of charge q_k and velocity $\boldsymbol{v}_k$, the *Lorentz* force on the particle is

$$f = q_k(\mathbf{E} + \boldsymbol{v}_k \times \mathbf{B}). \tag{2.18}$$

Then the movement of the particle can be described by

$$m\ddot{\boldsymbol{x}}_k = q_k(\mathbf{E} + \boldsymbol{v}_k \times \mathbf{B}), \tag{2.19}$$

where $\boldsymbol{v}_k = \dot{\boldsymbol{x}}_k$ is the velocity of the particle. Notice that $(\boldsymbol{v}_k \times \mathbf{B}) \cdot \boldsymbol{v}_k = 0$, it is straightforward to show that (2.19) satisfies the energy identity

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{1}{2}m\boldsymbol{v}_k^2\right) = q_k\mathbf{E} \cdot \boldsymbol{v}_k. \tag{2.20}$$

The Maxwell field equation in this case can be formulated as

$$\nabla \cdot (\varepsilon_0\mathbf{E}) = \rho, \qquad \nabla \cdot \mathbf{B} = 0$$
$$\frac{\partial \mathbf{B}}{\partial t} = -(\nabla \times \mathbf{E}), \quad \nabla \times \mathbf{B} = \mu_0\left(\varepsilon_0\frac{\partial \mathbf{E}}{\partial t} + \mathbf{j}\right), \tag{2.21}$$

where the charge density ρ and the (particle) current density $\boldsymbol{j}$ [10,25] is defined by $\rho = q_k\delta(\boldsymbol{x} - \boldsymbol{x}_k)$ and $\boldsymbol{j} = q_k v_k\delta(\boldsymbol{x} - \boldsymbol{x}_k) = \rho\boldsymbol{v}_k$, with δ being the Dirac delta function. Here, we assume that placing a charged particle in a vacuum does not change the permittivity.

The Equation (2.21) satisfies the following energy identity

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \frac{\varepsilon_0}{2}|\mathbf{E}|^2 + \frac{1}{2\mu_0}|\mathbf{B}|^2\,\mathrm{d}x = \int_\Omega -\mathbf{E}\cdot\boldsymbol{j}\,\mathrm{d}\boldsymbol{x} - \int_{\partial\Omega}\frac{1}{\mu_0}(\mathbf{E}\times\mathbf{B})\cdot\boldsymbol{\nu}\,\mathrm{d}S. \tag{2.22}$$

Combining (2.20) with (2.22), we obtain the energy-dissipation law of the total electromechanical system

$$\frac{\mathrm{d}}{\mathrm{d}t}\int \frac{m}{2}|\boldsymbol{v}_k|^2\delta(\boldsymbol{x} - \boldsymbol{x}_k) + \frac{\varepsilon_0}{2}|\mathbf{E}|^2 + \frac{1}{2\mu_0}|\mathbf{B}|^2 = 0. \tag{2.23}$$

We can define $c = \delta(\boldsymbol{x} - \boldsymbol{x}_k)$ as the **number density** of the charged particles. Then formally, the energy-dissipation law can be written as (using $u(\boldsymbol{x}_k) = \boldsymbol{v}_k$)

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \left(\frac{m}{2} c |\boldsymbol{u}|^2 + \frac{\varepsilon_0}{2} |\mathbf{E}|^2 + \frac{1}{2\mu_0} |\mathbf{B}|^2 \right) \mathrm{d}\boldsymbol{x} = 0. \tag{2.24}$$

REMARK 2.3.   Similarly, if a charged particle is placed in a medium and satisfies the ordinary differential equation (the force balance between mechanical and Lorentz forces)

$$m\ddot{\boldsymbol{x}}_k + \gamma\dot{\boldsymbol{x}}_k + \nabla V(\boldsymbol{x}_k) = q_k(\mathbf{E} + \dot{\boldsymbol{x}}_k \times \mathbf{B}), \tag{2.25}$$

then the energy-dissipation law is formally given by

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \left(\frac{mc(\boldsymbol{x})}{2} |\boldsymbol{u}|^2 + c(\boldsymbol{x})V(\boldsymbol{x}) + W(\mathbf{E}, \mathbf{B}) \right) \mathrm{d}\boldsymbol{x} = -\int \gamma c(\boldsymbol{x}) |\boldsymbol{u}|^2 \mathrm{d}\boldsymbol{x}, \tag{2.26}$$

where $c(\boldsymbol{x}) = \delta(\boldsymbol{x} - \boldsymbol{x}_k)$, $u(\boldsymbol{x}_k) = \boldsymbol{v}_k$, $V(\boldsymbol{x})$ is the potential energy, and $W(\mathbf{E}, \mathbf{B})$ is the electromagnetic field energy. The formulation also works for the case with N-particles although one must be careful in evaluating interactions.

3. Variational treatment of general electro-mechanical systems

The EnVarA framework allows a general treatment of the response of a dielectric to a change of the electric field. It includes classical polarization of an ideal dielectric and electromechanical systems that involve diffusion and translation, and other energy sources not present in the classical Maxwell equations. Throughout this section, we assume that $\nabla \times \mathbf{E} = 0$. The approach starts with a general electromechanical free energy

$$\mathcal{F}(\mathbf{E}, \boldsymbol{\zeta}) = \int W(\mathbf{E}, \boldsymbol{\zeta}) \mathrm{d}\boldsymbol{x}, \tag{3.1}$$

where $W(\mathbf{E}, \boldsymbol{\zeta})$ is the electromechanical free energy per unit volume, $\mathbf{E}$ is the electric field, and $\boldsymbol{\zeta}$ represents other mechanical variables, such as densities of ions, the deformation tensor, and order parameters in liquid crystals. We can generalize the definition of electric displacement field $\mathbf{D}$ in vacuum (2.15) and define $\mathbf{D}$ as [4, 25, 27, 42]

$$\mathbf{D} = \frac{\partial W(\mathbf{E}, \boldsymbol{\zeta})}{\partial \mathbf{E}}. \tag{3.2}$$

Consequently, the electric polarization field $\mathbf{P}$ is defined by [17], $\mathbf{P} = \mathbf{D} - \varepsilon_0 \mathbf{E}$, so both $\mathbf{D}$ and $\mathbf{P}$ are derived from the electromechanical free energy $W(\mathbf{E}, \boldsymbol{\zeta})$. The different $W(\mathbf{E}, \boldsymbol{\zeta})$ correspond to different constitutive relations between $\mathbf{D}$ and $\mathbf{E}$. For a 'linear' dielectric, we have $W(\mathbf{E}, \boldsymbol{\zeta}) = \omega(\boldsymbol{\zeta}) + \frac{\varepsilon(\boldsymbol{\zeta})}{2} |\mathbf{E}|^2$. Then $\mathbf{D} = \varepsilon(\boldsymbol{\zeta})\mathbf{E}$ and $\varepsilon(\boldsymbol{\zeta}) = \varepsilon_0 \varepsilon_r(\boldsymbol{\zeta})$ is the conventional permittivity and $\varepsilon_r(\boldsymbol{\zeta})$ is the dielectric constant. The form of free energy $W(\mathbf{E}, \boldsymbol{\zeta})$ can be obtained from experiments by solving some inverse problems or from a more-detailed model [30, 46]. In general, the relation between $\mathbf{D}$ and $\mathbf{E}$ can be fully nonlinear and nonlocal.

As an illustration, let us first consider dielectric fluids. We can take ρ and $\mathbf{E}$ as the state variables, and assume the free energy is given by [41]

$$\mathcal{F}(\rho, \mathbf{E}) = \mathcal{F}_M(\rho) + \mathcal{F}_{\text{elec}}(\rho, \mathbf{E}), \tag{3.3}$$

where $\mathcal{F}_M(\rho) = \int \omega(\rho)\mathrm{d}\boldsymbol{x}$ is the purely mechanical component of the free energy, i.e., the free energy of the system in the absence of the electric field $\mathbf{E}$. $\mathcal{F}_{\mathrm{elec}}(\rho, \mathbf{E})$ is the electromechanical energy, which is assumed to be $\mathcal{F}_{\mathrm{elec}}(\rho, \mathbf{E}) = \frac{\varepsilon(\rho)}{2}|\mathbf{E}|^2$ for linear dielectrics. Then, the variational procedure (3.2) leads to $\mathbf{D} = \varepsilon(\rho)\mathbf{E}$ and $\mathbf{P} = \mathbf{D} - \varepsilon_0\mathbf{E}$. For the pure dielectric case without any free charges, we have

$$\nabla \cdot \mathbf{D} = 0, \quad \nabla \times \mathbf{E} = 0, \tag{3.4}$$

which indicates that there exists an electrostatic potential φ such that $\mathbf{E} = -\nabla\varphi$ and φ satisfies the Poisson equation $-\nabla \cdot (\varepsilon(\rho)\nabla\varphi) = 0$.

The electrostatic potential φ can be viewed as a Lagrange multiplier for the constraint $\nabla \cdot \mathbf{D} = 0$, along with the quasi-equilibrium condition, i.e., $\mathbf{E}$ minimize the free energy (3.3) without delay [25]. Indeed, we can introduce a Lagrange multiplier φ for the constraint $\nabla \cdot \mathbf{D} = 0$, which leads to

$$\mathcal{F}(\rho, \mathbf{E}; \varphi) = \mathcal{F}_M(\rho) + \frac{\varepsilon(\rho)}{2}|\mathbf{E}|^2 - \varphi(\nabla \cdot (\varepsilon(\rho)\mathbf{E})). \tag{3.5}$$

By assuming that the electric field reaches equilibrium without delay, we have

$$0 = \frac{\delta\mathcal{F}(\rho, \mathbf{E}; \varphi)}{\delta\mathbf{E}} = \varepsilon(\rho)\mathbf{E} + \varepsilon(\rho)\nabla\varphi, \tag{3.6}$$

which leads to $\mathbf{E} = -\nabla\varphi$, and $\nabla \times \mathbf{E} = 0$. In the delay case, one can impose a dynamics $\eta\mathbf{E}_t = -(\varepsilon(\rho)\mathbf{E} + \varepsilon(\rho)\nabla\varphi)$, then $\mathbf{E}$ may not be curl-free and one has to consider the full Maxwell equations. We will explore this case in future work.

Next, we discuss the dynamics of the system, which is described by a suitable dissipation functional on the mechanical part. A simple choice of the dissipation is $\triangle = 2\mathcal{D} = \int \eta(\rho)|\mathbf{u}|^2\mathrm{d}\boldsymbol{x}$, where $\eta(\rho)$ is the friction coefficient. By a standard variational procedure [19], we have $-\eta(\rho)\mathbf{u} = \rho\nabla(\omega'(\rho) + \frac{1}{2}\varepsilon'(\rho)|\mathbf{E}|^2)$, which is equivalent to the results in [25] [page 68, Equation (15.12)].

For systems involving free charges, the electric displacement field $\mathbf{D}$ satisfies a differential version of Gauss's law $\nabla \cdot \mathbf{D} = \rho_f(\boldsymbol{x})$, where $\rho_f(\boldsymbol{x})$ is the total (electric) free charge density at $\boldsymbol{x}$. From the mechanical part of the system, one can calculate the (mechanical) charge density $\hat{\rho}_f(\boldsymbol{\zeta})$. However, in general, $\widehat{\rho}_f(\boldsymbol{\zeta})$ may not be exactly the same as ρ_f in the Gauss's law. For instance, polarization arises from the separation of the centers of positive and negative charges, which produces a difference between the mechanical charge density $\hat{\rho}_f(\boldsymbol{\zeta})$ and the electric charge density $\rho_f(\boldsymbol{x})$. In the energetic variational formulation, $\rho_f(\boldsymbol{x})$ and $\hat{\rho}_f(\boldsymbol{\zeta})$ can be linked by either a Lagrange multiplier or various energy relaxations. Energy relaxations are a general way of describing electromechanical coupling.

In the following, we illustrate both approaches by modeling the transportation of charged particles in dilute solutions. We assume the free energy is given by

$$\mathcal{F}(c, \mathbf{E}) = \int \sum_{i=1}^{n} K_B T c_i(\ln c_i - 1) + W_{\mathrm{elec}}(\boldsymbol{c}, \mathbf{E})\mathrm{d}\boldsymbol{x}, \tag{3.7}$$

and $\mathbf{D} = \frac{\partial W_{\mathrm{elec}}}{\partial \mathbf{E}}$. From the mechanical part of the system, one can calculate the (mechanical) charge density as

$$\widehat{\rho}_f(\boldsymbol{c}) = \sum_{i=1}^{n} q z_i c_i + \rho_0(\boldsymbol{x}), \tag{3.8}$$

$\rho_0(\boldsymbol{x})$ is the density of any immobile background charge, z_i is the electric variance of i-th species, and q is the elementary charge. Both approaches can lead to PNP-type systems with suitable dissipations.

3.1. PNP equation with a Lagrange multiplier. In the first approach, we can introduce a Lagrange multiplier to link $\widehat{\rho}_f(\boldsymbol{c})$ and $\rho_f(\boldsymbol{x})$ [3, 23, 25, 29], i.e.,

$$\mathcal{F}(\boldsymbol{\rho},\boldsymbol{E};\varphi) = \int_\Omega \sum_{i=1}^n K_B T c_i(\ln c_i - 1) + W_{\mathrm{elec}}(\boldsymbol{c},\mathbf{E}) - \varphi(\nabla\cdot(\tfrac{\partial W_{\mathrm{elec}}}{\partial\mathbf{E}}) - \sum_{i=1}^n q z_i c_i - \rho_0(\boldsymbol{x}))\mathrm{d}\boldsymbol{x}, \tag{3.9}$$

where φ is the Lagrange multiplier. To derive the classical PNP Equation (1.1), we take $W_{\mathrm{elec}}(\mathbf{E})$ as $W_{\mathrm{elec}} = \frac{\varepsilon}{2}|\mathbf{E}|^2$, with ε being a constant, and $\mathbf{D} = \varepsilon\mathbf{E}$. In the situation when the electric part can reach equilibrium without delay, we will have $\frac{\delta\mathcal{F}}{\delta\mathbf{E}} = 0$, which leads to $\mathbf{E} = -\nabla\varphi$. The Lagrange multiplier φ is the usual electrostatic potential φ.

Next, we look at the dynamics of the system, which are on the mechanical part only. As we did in Equation (2.11), we can impose the dissipation as $\triangle = 2\mathcal{D} = \int \sum_{i=1}^n \frac{k_B T}{D_i} c_i |\mathbf{u}_i|^2 \mathrm{d}\boldsymbol{x}$, where $\mathbf{u}_i$ is the average velocity of i-th species. By a standard energetic variational approach, we obtain $\frac{k_B T}{D_i} c_i \mathbf{u} = -c_i \nabla\mu_i$, where $\mu_i = \frac{\delta\mathcal{F}}{\delta c_i} = k_B T \ln c_i + \varphi c_i q$. The final PNP equation can be written as

$$\partial_t c_i = \nabla\cdot(D_i(\nabla c_i + \frac{q z_i}{k_B T} c_i \nabla\varphi)), \qquad -\nabla\cdot(\varepsilon\nabla\varphi) = \sum_{i=1}^n q z_i c_i + \rho_0(\boldsymbol{x}). \tag{3.10}$$

3.2. PNP equation with an energy relaxation. As mentioned earlier, $\rho_f(\boldsymbol{x})$ may not be exactly the same as the mechanical charge $\hat{\rho}_f(\boldsymbol{c})$. Instead of using a Lagrange multiplier, which forces $\rho_f(\boldsymbol{x})$ to be the same to $\hat{\rho}_f(\boldsymbol{c})$, we can use the following form of the free energy

$$\mathcal{F}(\boldsymbol{c},\boldsymbol{E}) = \int_\Omega k_B T \sum_{i=1}^n c_i(\ln c_i - 1) + W_{\mathrm{elec}}(\mathbf{E}) + \tfrac{M}{2}(\nabla\cdot(\tfrac{\partial W_{\mathrm{elec}}}{\partial\mathbf{E}}) - \sum_{i=1}^n z_i c_i q - \rho_0(\boldsymbol{x}))^2 \mathrm{d}\boldsymbol{x}, \tag{3.11}$$

where the last term is the energy cost for the difference between mechanical charge density $\hat{\rho}_f(\boldsymbol{c})$ and the electric charge density $\rho_f(\boldsymbol{x})$ and M is a phenomenological parameter.

Again, we take $W_{\mathrm{elec}}(\mathbf{E})$ as $W_{\mathrm{elec}}(\mathbf{E}) = \frac{\varepsilon}{2}|\mathbf{E}|^2$ to illustrate the idea. Similar to the previous calculations, in the case when the electrical part can immediately go to equilibrium, we have

$$\frac{\delta\mathcal{F}(\boldsymbol{c},\boldsymbol{E})}{\delta\mathbf{E}} = \varepsilon\mathbf{E} - \varepsilon\nabla(M(\nabla\cdot(\varepsilon\mathbf{E}) - \sum_{i=1}^n z_i c_i q - \rho_0(\boldsymbol{x}))) = 0, \tag{3.12}$$

which leads to $\mathbf{E} = \nabla(M(\nabla\cdot(\varepsilon\mathbf{E}) - \sum_{i=1}^n z_i c_i q - \rho(\boldsymbol{x})))$. According to (3.2), we take

$$\varphi = -(M(\nabla\cdot(\varepsilon\mathbf{E}) - \sum_{i=1}^n z_i c_i q - \rho_0(\boldsymbol{x}))), \tag{3.13}$$

which corresponds to usual definition of electrostatic potential formulations. From (3.13), we can then obtain an equation for φ, given by

$$-\nabla\cdot(\varepsilon\nabla\varphi) - \sum_{i=1}^n z_i c_i q - \rho_0(\boldsymbol{x}) = \frac{-\varphi - C}{M} \tag{3.14}$$

for any constant C that can be taken as 0. Formally, we can recover the Poisson equation $-\nabla\cdot(\varepsilon\nabla\varphi) = \sum_{i=1}^n z_i c_i q + \rho(\boldsymbol{x})$ for the limit $M \to \infty$.

For the mechanical part, the chemical potential of each species can be computed as $\mu_i = k_B T \ln c_i - M(\nabla\cdot(\varepsilon\mathbf{E}) - \sum_{i=1}^n c_i z_i q - \rho_0(\boldsymbol{x}))z_i q = \ln c_i + \varphi z_i q$, which is exactly the same as that in the classical PNP case. The final PNP system is given by

$$\partial_t c_i = \nabla \cdot (D_i(\nabla c_i + \frac{qz_i}{k_B T} c_i \nabla \varphi)), \qquad -\nabla \cdot (\varepsilon \nabla \varphi) = \sum_{i=1}^{n} z_i c_i q + \rho(\boldsymbol{x}) + \frac{-\varphi}{M}, \qquad (3.15)$$

with the dissipation in (2.11).

It is worth mentioning that the energy relaxation is not unique. Here we choose the simplest form for an illustration. In general, energy relaxation will depend on the structure of the system, including the measurement apparatus, and the boundary properties of the structure.

REMARK 3.1. We focus on $\nabla \times \mathbf{E} = 0$ in this section. For general systems with $\nabla \times \mathbf{E} \neq 0$, one can introduce another Lagrange multiplier or a penalization for the constraint $\partial_t \mathbf{B} = -(\nabla \times \mathbf{E})$. We will study this in future work.

4. Conclusion

In this paper, we develop a new electric-field based variational formulation of the polarization response of dieletrics to changes in the electric field. We view the polarization response as a general electromechanical system and include diffusion processes. This framework is motivated and developed using the classical EnVarA. The dynamics and fluctuation are imposed in the mechanical part only. As an illustration, we re-derive the classical PNP system by two approaches and show consistency with previous formulations. The variational formulation can be applied to more general electromechanical systems and opens a new door for developing structure-preserving numerical methods.

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