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Notation

ξ^t, ξ, ξ^e	Total, self, external electrostatic potentials
$\mathbf{E}^t, \mathbf{E}, \mathbf{E}^e$	Total, self, external electric fields
$\mathbf{D}^t, \mathbf{D}, \mathbf{D}^e$	Total, self, external electric displacements
$\mathbf{P}^t, \mathbf{P}, \mathbf{P}^e$	Total, self (state variable), external polarizations
ρ^t, ρ, ρ^e	Total, self (state variable), external charge densities
ϵ_c, ϵ_0	Permittivity of “comparison” medium and vacuum. $\epsilon_c = \epsilon_0$ up to § 5
V	A connected open regular domain containing the ambient medium and system
Ω	An open (maybe disconnected) domain containing the system of interest. $\Omega = V$ if ϵ_c is different from the ambient permittivity
$\Gamma_D, (\Gamma_R)$	Subset of ∂V on which Dirichlet (Robin) BC is applied
k, ξ_b, σ_0	Functions to prescribe electrostatic boundary conditions, cf., (2.3)-(2.4)
\tilde{F}, F	Free energy functionals, different by a (ρ, \mathbf{P}) -independent constant
U, P	Internal energy functional and potential energy functional
Φ	Internal energy density function

On energy formulations of electrostatics for continuum media

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Abstract

In this paper we present a unified energy formulation of electrostatics for continuum media including conductors, dielectrics, ferroelectrics, etc. The effects of boundary devices, external charges and polarizations are taken into account in formulating the free energy. We further explore the relations between various energy formulations including Landau-Ginzburg-Devonshire's formulation, Toupin's formulation, Ericksen's formulation, formulations with respect to a change of comparison or background medium, a formulation without introducing the quantity of polarization, and the Hashin-Shtrikman variational principle. Finally, we apply the formulation to calculate forces on a charge and a dipole immersed in a smooth polarization (field) and in the proximity of boundary, and to estimate the effective properties of nonlinear dielectric composites. We expect that this formulation and clarification will provide a solid ground for addressing electro-elastics of deformable bodies.

1 Introduction

Consider a continuum body in electrostatics. If the material property of this body is specified, aside from possible metastable states there should be no ambiguity in how this body would respond to mutual interactions and external fields; the state of this body and the electric field in space satisfy a system of *field* equations, i.e., the Maxwell equations:

$$\nabla \times \mathbf{E}^t = 0, \quad \nabla \cdot \mathbf{D}^t = \rho^t, \quad (1.1a)$$

$$\mathbf{D}^t = \epsilon_0 \mathbf{E}^t + \mathbf{P}^t, \quad \mathcal{C}(\mathbf{x}; \mathbf{D}^t, \mathbf{E}^t, \mathbf{P}^t, \rho^t) = 0 \quad (1.1b)$$

on V , where $V \subset \mathbb{R}^3$ is an open connected domain, $\mathbf{E}^t, \mathbf{D}^t, \mathbf{P}^t : V \rightarrow \mathbb{R}^3$ are respectively the (total) electric field, electric displacement, polarization, $\rho^t : V \rightarrow \mathbb{R}$ is the (total) charge density, and $\mathcal{C}(\mathbf{x}; \mathbf{D}^t, \mathbf{E}^t, \mathbf{P}^t, \rho^t) = 0$ represents the constitutive relations of the medium such that the system of (1.1) is well-posed upon specifying suitable boundary conditions on ∂V . From this viewpoint, alternative formulations of electrostatics might appear to be unnecessary or less fundamental for electrostatic analysis.

Nevertheless, an *energy* formulation has proven to be advantageous in addressing a number of difficulties in the Maxwell field formulation (1.1). First, the constitutive relations, describing the medium properties, cannot be derived within the framework of continuum theory but has to be inferred from benchmark experiments or a more fundamental microscopic theory. Moreover, the

constitutive relations must conform to the fundamental laws of thermodynamics, frame indifference and underlying symmetries of the medium. An *energy* formulation, as evident in the classic theory of nonlinear elasticity, has the unique advantage in restricting physically realistic constitutive laws by the fundamental laws of thermodynamics, frame indifference and material symmetries (Gurtin *et al.*, 2010; Dorfmann and Ogden, 2005; Suo *et al.*, 2008). Also, a boundary value problem of (1.1) with a general constitutive law may admit multiple solutions. To analyze the stability/metastability of these solutions, it is in general more convenient to have an energy formulation and conduct the usual stability test (Ericksen, 1991; Dorfmann and Ogden, 2010; Bertoldi and Gei 2011). Moreover, when coupled with deformations and mechanical loadings a well-known difficulty, though not insurmountable, is to introduce the notion of stress, since there are two origins of forces: the local, short-range contact force giving rise to the usual concept of Cauchy stress (Truesdell and Noll, 2003; Gurtin, 1981), and the nonlocal, long-range, electrostatic force giving rise to the notion of Maxwell stress (Toupin, 1956; 1960; Jackson, 1999, p. 261; Truesdell and Toupin, 1960, §542-544; Melcher, 1981, ch. 3; Bustamante *et al.*, 2009; Steigmann 2009). Therefore, the usual free-body-diagram analysis cannot be cleanly carried out¹, not to mention the difficulty in formulating self-consistent realistic constitutive relations of stress, strain, electric field and electric displacement. Finally, in the study of phase transitions and many other physical phenomena for which the body has additional degrees of freedom (or internal variables), e.g., a moving phase boundary or crack tip, an energy formulation is indispensable for calculating the conjugate driving forces and formulating the kinetic laws (Abeyaratne and Knowles, 2001; Attard, 2003; Chen, 2009).

We are therefore motivated to study energy formulations of electrostatics for continuum bodies. At the presence of boundary devices, we consider a domain $V \subset \mathbb{R}^3$ containing the continuum body Ω and ambient medium of permittivity ϵ_c ². For clarity and simplicity, we set a modest goal and assume idealizations: (i) the continuum body and ambient medium is maintained at constant temperature, has constant entropy, do not dissipate energy and all processes are reversible, and (ii) the continuum body does not deform³. For dissipative and/or deformable media, the reader is referred to Shu and Bhattacharya (2001) for deformable ferroelectric crystals, to Fosdick and Tang (2007) for a general continuum framework of electrodynamics and thermomechanics of deformable bodies, to McMeeking and Landis (2005), Suo *et al.* (2008) for deformable dielectrics with or without introducing polarization, Xiao and Bhattacharya (2008) for dissipative semiconducting ferroelectrics, to Bustamante *et al.* (2009) for a variational framework of electro-elasticity, to Miehe *et al.* (2011) for dissipative electro-magneto-elastic composites, and to reviews of Damjanovic (1998) for detailed descriptions of many materials of interest.

Our main interest here is to identify the stable/metastable equilibrium states or in another word, how the continuum bodies interact with each other, how they respond to external sources and boundary devices, and how to analyze the stability of a stationary state. Assuming the above idealizations, we establish a unified framework for addressing various media including conductors, dielectric and ferroelectric media, and the orbital-free model of density functional theory. We also take into account the effects of general boundary conditions (including Dirichlet's, Neumann's and Robin's boundary conditions) on the free energy which were rarely considered in previous treatments. The proposed unified treatment is particularly convenient for addressing interactions

¹For example, it is unclear how to prove the Cauchy theorem from the Cauchy hypothesis (Gurtin, 1981), i.e., the very existence of Cauchy stress is not obvious if one starts from Cauchy hypothesis.

²For the moment, one may think of the ambient medium as vacuum: $\epsilon_c = \epsilon_0 = 8.854 \times 10^{-12} F/m$. However, as far as predicting the stationary electric field, electric displacement and energy, the ambient medium may be any other medium, see discussions in §5.

³Elasticity alone is typically not a source of ambiguity. Coupling with elasticity may be included by letting the internal energy density Φ depend on deformation gradient, cf., (2.10), once issues with electrostatics are clarified.

between bodies of different media, e.g., a conductor and a dielectric/ferroelectric body, and for addressing some unique features of electrostatics, e.g., the existence of mobile charges and conductors (singular in terms of static permittivity) and varieties of laboratory available boundary devices, e.g., capacitors and batteries.

However, as a confusing matter of fact, there are quite a few different energy formulations of continuum electrostatics, particularly when deformations are under consideration as well (Toupin 1956; Eringen 1963; Brown, 1966; Ericksen, 2007). We now understand that the varieties or controversies arise from the freedom in choosing formal state variables, separation of internal energy and total field energy (in the sense defined in § 2.1), and material or spatial descriptions. All of them are undoubtedly consistent with the Maxwell field equations (1.1) and hence equivalent to the extent of determining the fields, but not all of them are physically based in the sense that (i) the variational principle (i.e., minimization or maximization of the energy functional) has no clear and direct thermodynamic interpretation, and (ii) the choices and variations of “state variables” are formal rather than physical. For example, in Toupin’s formulation (cf., § 4.2) the physical meaning of the energy functional is not at all clear, aside from the associated Euler-Lagrange’s equations are consistent with the Maxwell’s equations (1.1). Also, the electrostatic potential is one of the state variables and may vary within some admissible space. If the ambient medium is vacuum, it is rather puzzling why the electrostatic potential in vacuum should be relevant to the thermodynamic state of the system and why it could *respond* to external stimuli so as to reach the *equilibrium state of vacuum* (if there is such a kind in the classic electrostatics).

In regard of these alternative variational formulations, we show in details how the current formulation, formulations of Landau-Ginzburg-Devonshire (Landau 1937; Ginzburg and Landau, 1950; Devonshire, 1951; 1954; Cao, 2008), Toupin (1956) and Ericksen (2007) are related with each other and the Maxwell field equations (1.1). Moreover, it is fairly common that electronic devices work in an ambient medium other than vacuum or air. We are therefore motivated to show a symmetry of the total free energy with respect to the permittivity of the ambient medium, clarifying the impact of ambient medium on some of the fundamental concepts such as polarization, force, stress, etc. We also show a variational formulation without introducing polarization and explain how it is related with the current formulation and the Hashin-Shtrikman variational principles (which has been widely used for bounding effective properties of composites).

In addition, we remark that the proposed energy functional and minimization principle are known and anticipated from thermodynamics, see e.g., Eringen (1963) and Fosdick and Tang (2007), from which ours is different in the form of boundary terms or total field energy. An important purpose here is to sort out mutual relations between various formulations (which motivates us to neglect deformation at this stage), clarifying or justifying (i) the free energy contribution from boundary devices, (ii) the equivalence of various forms of energy associated with external sources, (iii) interactions between conductors and polarizable bodies, and (iv) the equivalence of various forms of total field energy. A particular point we would like to emphasize is that a boundary value problem in the form of partial differential equations like (1.1) may enjoy *infinitely* many different variational formulations; neither the energy functional nor the state variable has to be the same. These variational formulations are equivalent to the extent of determining the relevant fields. If the system, however, has some additional degrees of freedom described by an internal variable and our interest is on, e.g., the dynamics of the internal variable or the stability of the system, the physical free energy and principle of minimum free energy have to be identified among these “equivalent” variational formulations, and one has to decide on which of the energy functionals is the physical free energy and what are the “possible variations” (Ericksen, 1991, p. 7). It is clear that the judgement cannot be made on a mathematical ground; the choice depends on the physical context instead of mathematical form, see detailed discussions and examples in § 6.

As for practical applications, we calculate the explicit formula of minimum free energies for a collection of conductors (cf., (3.41)), for a linear dielectric body (cf., (3.50)), and the effective free energy of a polarizable body interacting with a conductor (cf., (3.65)-(3.66)). These results may serve as the starting points for next level of modelings, e.g., the dynamics, evolution, and statistics of electromagnetic media. In § 6 we recognize the proposed energy functional is closely related with the Hashin-Shtrikman variational principle and generalize an identity (cf., 6.9) between the Hashin-Shtrikman variational principle and classic variational principle for general internal energy density function, boundary conditions and external sources (Milton, 2002, §13.6). By this identity we derive bounds on the effective property of a nonlinear dielectric composite in § 7.3 and anticipate broader applications in the multiscale modeling and analysis of heterogeneous media. The derived force formula in § 7.2 on a point charge or a point dipole immersed in a smooth distribution of charges and polarization is also expected to be useful for modeling field-controlled self-assembly (Sun et al., 2000), separation and concentration (Pankhurst et al., 2003), electric or magnetic suspensions (Odenbach, 2002), electric or magnetic tweezers (Grier, 2003), etc.

The paper is organized as follows. In §2 we formulate the free energy and principle of minimum free energy. In §3 by the energy formulation we recover classic theories of typical media including linear and nonlinear dielectrics, conductors, ferroelectric media, their interactions, and the orbital-free model in the density function theory. In § 4 we select a few variational principles and show their consistence. In § 5 we show a symmetry of total free energy with respect to changes of comparison background media. In § 6 we present the classic variational formulation in terms electrostatic potential, show how it is related with our free energy formulation, and prove a relation between two energies which may be regarded as a generalization of the classic relation permitting the Hashin-Shtrikman’s estimates. In § 7 we present a few applications.

Notation. We will use direct notion in this paper; ∇ is reserved for spatial gradient whereas D is used for differentiating with respect to other variables. Domains are assumed to be open with smooth boundaries. The main trust of this work comes from the need of a consistent theory for modeling electro-elastic materials instead of mathematical analysis. Therefore, the rigor is comprised to some extent that we do not normally state conditions of integrability and differentiability since it is of little interest to applied scientists.

2 Free energy of a continuum body in electrostatics

2.1 Terminologies

Since the literature has no universal agreement on the terminologies such as system, free energy, internal energy, etc, for clarity we define these terminologies below.

1. System and ambient medium. Let $V \subset \mathbb{R}^3$ be a connected open domain containing a finite continuum body Ω (open but may be disconnected) and ambient medium of permittivity ϵ_c on $V \setminus \Omega$. The domain V may be unbounded, but the boundary ∂V is assumed to be bounded. We refer to the continuum body Ω as the system. The state of the continuum body is either described by a distributed charge density $\rho : \Omega \rightarrow \mathbb{R}$ or a distributed polarization $\mathbf{P} : \Omega \rightarrow \mathbb{R}^3$ or both⁴. For ease of notation, below we extend by zero (ρ, \mathbf{P}) to the entire domain V , i.e.,

⁴At the atomistic scale, charge density ρ and polarization \mathbf{P} in a body are not independently assignable and in particular, the definition of polarization \mathbf{P} hinges on the concept of Berry phase in quantum mechanics and is nonlocal (Resta, 1994; King-Smith and Vanderbilt, 1994). Here, we, however, follow the classic viewpoint of polarization and envisage microscopic polarization is associated with individual atoms or molecules in the body and macroscopic polarization is a spatial average of the microscopic one, though this viewpoint clearly does not make much sense for ionic solids.

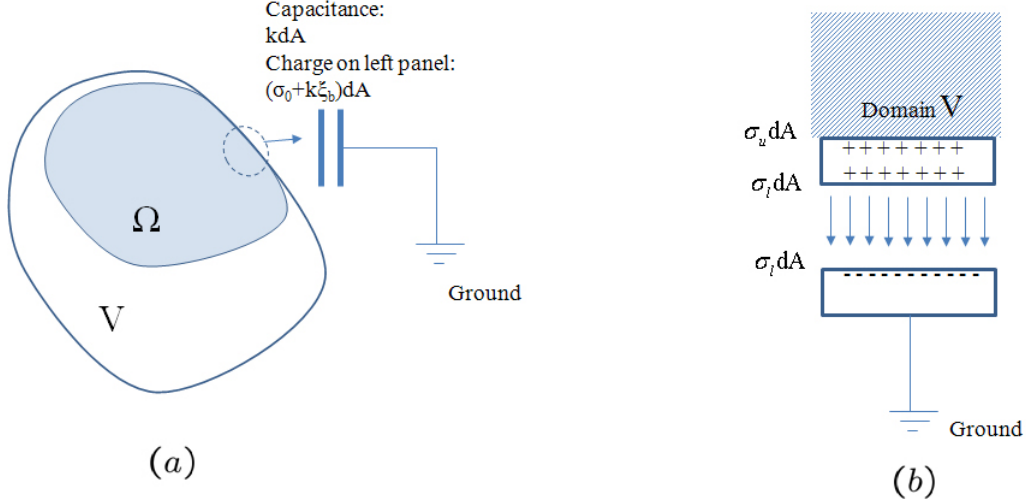


Figure 1: The system, ambient medium and boundary devices: (a) the system Ω with an internal energy density function $\Phi = \Phi(\rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P})$, the linear ambient medium $V \setminus \Omega$ with permittivity ϵ_c and the extended (or combined) system V ; (b) the boundary device (a capacitor) applied on an infinitesimal boundary $dA \subset \partial V$.

$(\rho, \mathbf{P}) = (\rho, \mathbf{P})\chi_\Omega$ and χ_Ω is the characteristic function of Ω . Further, properties of media place some constraint on admissible states of the system which is represented by

$$(\rho, \mathbf{P}) \in \mathcal{S}, \quad (2.1)$$

where \mathcal{S} denotes the collection of all admissible states for the system and will be specified below for typical media.

In the above definition, we have tacitly assumed that the polarization in a medium satisfies $\mathbf{P} = \mathbf{D}^t - \epsilon_c \mathbf{E}^t$, and henceforth the ambient medium is “unpolarizable”. We remark that, as will be shown in §5, one may choose a different “comparison” medium of permittivity ϵ'_c to define polarization. In this case, the system shall include the ambient medium of permittivity ϵ_c since it is now “polarizable”. For this reason, we sometimes refer to the collection of the body and ambient medium, i.e., V , as the *extended system*.

2. External sources. By external sources we refer to a fixed distribution of charge density $\rho^e : \Omega_0 \rightarrow \mathbb{R}$ and polarization $\mathbf{P}^e : \Omega_0 \rightarrow \mathbb{R}^3$, where $\Omega_0 \subset V$ is open and bounded, and $\Omega_0 \cap \Omega = \emptyset$ ⁵. For ease of notation, below we extend (ρ^e, \mathbf{P}^e) by zero to V .
3. Total sources. The sum of (ρ, \mathbf{P}) of the system and the external sources (ρ^e, \mathbf{P}^e) are referred to as the total sources:

$$(\rho^t, \mathbf{P}^t) = (\rho, \mathbf{P}) + (\rho^e, \mathbf{P}^e). \quad (2.2)$$

According to the Maxwell equations (1.1), there exists an electrostatic potential $\xi^t : V \rightarrow \mathbb{R}$ such that the total electric field $\mathbf{E}^t = -\nabla\xi^t$ on V .

⁵Pre-existing charges and dipoles on the system Ω can be handled by choosing appropriate admissible space \mathcal{S} and internal energy density function Φ .

4. Boundary condition and boundary device. Let $\Gamma_D \subset \partial V$ be a subboundary on which the Dirichlet boundary condition

$$\xi^t - \xi_b = 0 \quad \text{on } \Gamma_D \quad (2.3)$$

is applied whereas the Robin boundary condition

$$k(\xi^t - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] - \sigma_0 = 0 \quad \text{on } \Gamma_R \quad (2.4)$$

is applied on $\Gamma_R := \partial V \setminus \Gamma_D$. Here $k \geq 0$, ξ_b , $\sigma_0 : \partial V \rightarrow \mathbb{R}$ are given functions and \mathbf{n} is the outward unit normal on ∂V . The physical devices used to maintain the above boundary conditions (2.3)-(2.4) are referred to as the boundary devices. For an infinitesimal subsurface $dA \subset \partial V$, the boundary condition (2.4) on dA can be realized by a capacitor of capacitance $k dA$ and initial charge $(\sigma_0 + k \xi_b) dA$ as shown in Fig. 1(b), while the boundary condition (2.3) on dA can be realized by the same capacitor in the limit of $k \rightarrow +\infty$. To see this, we consider the infinitesimal capacitor illustrated in Fig. 1(b). Clearly we have

$$\sigma_u + \sigma_l = \sigma_0 + k \xi_b, \quad \sigma_l = k \xi^t, \quad \sigma_u = -\mathbf{n} \cdot \mathbf{D}^t = -\mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e),$$

which, upon eliminating σ_u, σ_l , implies (2.4). Additionally, the energy stored in this infinitesimal capacitor is the field energy between the capacitor and given by $\frac{1}{2} k (\xi^t)^2 dA$, which motivates our subsequent definition of potential energy associated with boundary devices, see equation (2.11).

5. Total electric field. The total electric field $\mathbf{E}^t = -\nabla \xi^t$ in space is clearly determined by the Maxwell's equations:

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] = \rho + \rho^e & \text{on } V, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (2.5)$$

From the classic theory of elliptic equations, we know that the above equation admits a unique (or unique within a constant if $k = 0$ and $\Gamma_D = \emptyset$) solution in

$$\mathbb{W} = \left\{ \zeta : \int_V |\nabla \zeta|^2 < \infty, \zeta(\mathbf{x}) \rightarrow 0 \text{ if } V \text{ is unbounded and } |\mathbf{x}| \rightarrow \infty \right\}. \quad (2.6)$$

6. External electric field. The external electric field $\mathbf{E}^e = -\nabla \xi^e$ is the field when the system is removed and replaced by the ambient medium, determined by

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^e + \mathbf{P}^e] = \rho^e, & \text{on } V, \\ \xi^e - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^e - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^e + \mathbf{P}^e] - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (2.7)$$

Clearly, the external field is independent of the state variables (ρ, \mathbf{P}) of the system.

7. Self electric field, interaction energy and self field energy. The *self* electric field $\mathbf{E} = -\nabla \xi$ is the field induced by the system, satisfying

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi + \mathbf{P}] = \rho & \text{on } V, \\ \xi = 0 & \text{on } \Gamma_D, \\ k \xi - \mathbf{n} \cdot [-\epsilon_c \nabla \xi + \mathbf{P}] = 0 & \text{on } \Gamma_R. \end{cases} \quad (2.8)$$

Clearly, the total electric field is a sum of external field and self field:

$$-\nabla\xi^t = -\nabla\xi^e - \nabla\xi.$$

Further, we refer to

$$\mathcal{E}^{int}[\rho, \mathbf{P}] = \int_V (\rho\xi^e + \mathbf{P} \cdot \nabla\xi^e) \quad \text{and} \quad \mathcal{E}^{self}[\rho, \mathbf{P}] = \frac{\epsilon_c}{2} \int_V |\nabla\xi|^2 \quad (2.9)$$

as the *interaction energy* between the system and external field and the *self field energy* of the system, respectively.

8. Internal energy of the system. We assume the internal energy of the system is an extensive quantity in the sense that the internal energy of the system is equal to the sum of the internal energies of any subdivision of the system. This property entails an internal energy density $\Phi(\mathbf{x}; \rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P})$ such that the internal energy of the system is given by ⁶

$$U[\rho, \mathbf{P}] = \int_{\Omega} \Phi(\mathbf{x}; \rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P}), \quad (2.10)$$

where the explicit \mathbf{x} (position)-dependence of internal energy density Φ reflects that the continuum body may generally be heterogeneous. By the principle of frame indifference and material symmetries, Φ shall satisfy that

$$\begin{aligned} \Phi(\mathbf{x}; \rho, \mathbf{R}\mathbf{P}, \nabla\rho, \mathbf{R}\nabla\mathbf{P}) &= \Phi(\mathbf{x}; \rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P}) \quad \forall \mathbf{R} \in So(3), \\ \Phi(\mathbf{x}; \rho, \mathbf{P}, (\nabla\rho)\mathbf{Q}, (\nabla\mathbf{P})\mathbf{Q}) &= \Phi(\mathbf{x}; \rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P}) \quad \forall \mathbf{Q} \in \mathcal{G}_{\mathbf{x}}, \end{aligned}$$

where $So(3)$ is the group of rigid rotations and $\mathcal{G}_{\mathbf{x}}$ is the material symmetry group at point \mathbf{x} . Below we sometimes drop the explicit \mathbf{x} -dependence of Φ in notation for brevity, unless otherwise indicated.

9. Potential energy or boundary device energy. We refer to

$$P[\rho, \mathbf{P}] = \int_{\Gamma_R} \frac{1}{2}k(\xi^t)^2 + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot [-\epsilon_c \nabla\xi^t + \mathbf{P} + \mathbf{P}^e], \quad (2.11)$$

as the *potential energy* associated with the boundary devices. The first term can be identified as the energy stored in the capacitors shown in Fig. 1 (b) while the second term can be justified as the limit of $k \rightarrow +\infty$, see (2.13).

10. Total field energy. We call

$$\mathcal{E}^t[\rho, \mathbf{P}] = \frac{\epsilon_c}{2} \int_V |\nabla\xi^t|^2 \quad (2.12)$$

the *total field energy* associated with the total electric field ⁷, and

$$U[\rho, \mathbf{P}] + \mathcal{E}^t[\rho, \mathbf{P}]$$

⁶There is no fundamental principle forbidding more sophisticated internal energy functions which will not be considered here. The existence of internal energy density is essentially a constitutive postulation, resulting in a *local* theory.

⁷Some writer may prefer identifying $\frac{1}{2} \int_V \mathbf{E}^t \cdot \mathbf{D}^t$ as the total field energy. The total free energy remains invariant upon transforming $\Phi \rightarrow \Phi + \frac{1}{2}(\mathbf{D}^t - \epsilon_c \mathbf{E}^t) \cdot \mathbf{E}^t$ on Ω for this definition, and hence an equivalent theory is obtained for linear dielectrics, as shown by R. D. James in a private communication. For general nonlinear media, additional technical assumptions are needed to show the equivalence of two theories, cf., § 5. From this viewpoint, there is no unique way to separate the field energy and internal energy, and hence the Maxwell stress and mechanical stress.

the *total internal energy*. Below we reserve the terminology of “internal energy” for U defined by (2.10), and avoid the terminology of *total internal energy* since it is not additive with respect to the system, a property usually assumed for “internal energy”.

We remark that the Neumann boundary condition $\epsilon_c \mathbf{n} \cdot \nabla \xi^t - \sigma_0 = 0$ can be regarded as a special case of the general Robin boundary condition (2.4) by setting $k = 0$ ⁸. The Dirichlet boundary condition (2.3) may also be regarded as the limiting case of (2.4) by sending $k \rightarrow +\infty$. The potential energy contributed by Γ_R in this limit can be calculated as follows. Since $\xi^t = \xi + \xi^e$,

$$\int_{\Gamma_R} \frac{1}{2} k (\xi^t)^2 = \int_{\Gamma_R} [k \xi (\frac{1}{2} \xi + \xi^e) + \frac{1}{2} k (\xi^e)^2].$$

Upon sending $k \rightarrow +\infty$, it can be shown that $\xi \rightarrow 0$, $\xi^e \rightarrow \xi_b$ on Γ_R . Noticing that $k \xi = \mathbf{n} \cdot [-\epsilon_c \nabla \xi + \mathbf{P}]$ on Γ_R , we find that in the limit of $k \rightarrow +\infty$, the above integral is given by

$$\int_{\Gamma_R} \frac{1}{2} k (\xi^t)^2 = \int_{\Gamma_R} \xi_b \mathbf{n} \cdot [-\epsilon_c \nabla \xi + \mathbf{P}] + C_1 = \int_{\Gamma_R} \xi_b \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] + C_2, \quad (2.13)$$

where C_1, C_2 are constants independent of ρ, \mathbf{P} . The above equation verifies the consistence of the two terms in the potential energy (2.11).

2.2 Free energy of the system

As usual, we identify the *free energy of the system* as the total energy of *everything* which, in present context, includes the internal energy of the system, total field energy and potential energy⁹:

$$\begin{aligned} \tilde{F}[\rho, \mathbf{P}] &= U[\rho, \mathbf{P}] + \mathcal{E}^t[\rho, \mathbf{P}] + P[\rho, \mathbf{P}] \\ &= \int_V [\chi_\Omega \Phi(\rho, \mathbf{P}, \nabla \rho, \nabla \mathbf{P}) + \frac{\epsilon_c}{2} |\nabla \xi^t|^2] + \int_{\Gamma_R} \frac{1}{2} k (\xi^t)^2 + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P}^t]. \end{aligned} \quad (2.14)$$

At this stage we do not attempt to justify (2.14) from a more fundamental, microscopic model. In the absence of a boundary device, i.e., $V = \mathbb{R}^3$ and $k = \xi_b = \sigma_0 = 0$, the potential energy $P[\rho, \mathbf{P}]$ associated with the boundary device clearly vanishes. In the presence of boundary device, $P[\rho, \mathbf{P}]$ characterizes the system-dependent energy contributed by the boundary device.

It will be convenient to summarize a few identities which will be repeatedly used subsequently. Consider the total field determined by (2.5). From the first of (2.5), we have that for any $\zeta \in \mathbb{W}$,

$$\begin{aligned} \int_V \zeta (\rho + \rho^e) &= \int_V \zeta \operatorname{div}(-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}) \\ &= \int_V \left\{ \operatorname{div}[\zeta(-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P})] - \nabla \zeta \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}] \right\} \\ &= \int_{\partial V} \zeta \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}) - \int_V \nabla \zeta \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}], \end{aligned}$$

⁸The reader is cautioned that the parallel plate capacitor illustrated in Fig. 1 cannot be used to realize Neumann boundary condition (i.e., $k = 0$) since a plate conductor has a positive *coefficient of capacity* essentially proportional to area, see discussions in §3.1. Then an interesting question is how one can physically realize a Neumann boundary condition in electrostatics.

⁹Recall that entropy and temperature are held constant in our setting. Therefore, the difference between the (internal) energy of *everything* and the Helmholtz free energy is a constant independent of the state variables.

where \mathbf{n} is the unit outward normal on ∂V , and the divergence theorem has been used for the last equality. Similar calculations can be applied to ξ^e and ξ (cf. (2.7) and (2.8)). Therefore, we have that for any $\zeta \in \mathbb{W}$,

$$\begin{aligned}\epsilon_c \int_V \nabla \zeta \cdot \nabla \xi^t &= \int_V [\zeta \rho^t + \mathbf{P}^t \cdot \nabla \zeta] - \int_{\partial V} \zeta \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^t), \\ \epsilon_c \int_V \nabla \zeta \cdot \nabla \xi^e &= \int_V [\zeta \rho^e + \mathbf{P}^e \cdot \nabla \zeta] - \int_{\partial V} \zeta \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e), \\ \epsilon_c \int_V \nabla \zeta \cdot \nabla \xi &= \int_V [\zeta \rho + \mathbf{P} \cdot \nabla \zeta] - \int_{\partial V} \zeta \mathbf{n} \cdot (-\epsilon_c \nabla \xi + \mathbf{P}).\end{aligned}\tag{2.15}$$

It will be convenient to rewrite the free energy (2.14) in a different form. Replacing ζ by ξ^e in the last of (2.15) we obtain

$$\epsilon_c \int_V \nabla \xi^e \cdot \nabla \xi = \int_V [\xi^e \rho + \mathbf{P} \cdot \nabla \xi^e] - \int_{\partial V} \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi + \mathbf{P}).$$

Therefore, the sum of total field energy and potential energy can be rewritten as

$$\begin{aligned}\mathcal{E}^t[\rho, \mathbf{P}] + P[\rho, \mathbf{P}] &= \frac{\epsilon_c}{2} \int_V |\nabla \xi^e|^2 + \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \int_V (\rho \xi^e + \mathbf{P} \cdot \nabla \xi^e) + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e) \\ &\quad + \int_{\Gamma_R} \xi^e \cdot \{ -\mathbf{n} \cdot [-\epsilon_c \nabla \xi + \mathbf{P}] + k \xi \} + \int_{\Gamma_R} \frac{1}{2} k [\xi^2 + (\xi^e)^2] \\ &= T_0 + \int_V (\rho \xi^e + \mathbf{P} \cdot \nabla \xi^e) + \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \frac{1}{2} \int_{\Gamma_R} k \xi^2.\end{aligned}\tag{2.16}$$

where

$$T_0 = \frac{\epsilon_c}{2} \int_V |\nabla \xi^e|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi^e)^2 + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e).$$

It is clear that T_0 defined above is independent of state variables (ρ, \mathbf{P}) of the system, and hence gives no contribution in variations of free energy with respect to changes of states of the system. In particular, it has no effect on the Euler-Lagrange equations and stability analysis. Therefore, we omit this term and call the following expression the free energy of the system as well:

$$F[\rho, \mathbf{P}] = U[\rho, \mathbf{P}] + \int_V (\rho \xi^e + \mathbf{P} \cdot \nabla \xi^e) + \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \int_{\Gamma_R} \frac{1}{2} k \xi^2.\tag{2.17}$$

We remark that the energy is in analogy with the Landau-Lifshitz's energy for micromagnetics (Landau and Lifshitz, 1935), Landau-Ginzburg-Devonshire's energy for ferroelectrics (Devonshire 1951; 1954), or Ginzburg-Landau's energy for superconductivity (Ginzburg and Landau, 1950), except that the boundary effects are explicitly accounted for in (2.17).

We will be interested in variations of free energy for different states of the system. Let $(\rho_1, \mathbf{P}_1) \in \mathcal{S}$ be a new state, $(\rho', \mathbf{P}') = (\rho_1, \mathbf{P}_1) - (\rho, \mathbf{P})$ be the difference between two states. Then the self-field of (ρ_1, \mathbf{P}_1) , denoted by $-\nabla \xi_1$, and the difference between two self field, denoted by $-\nabla \xi' = -\nabla \xi_1 + \nabla \xi$, satisfy (2.8) with (ρ, \mathbf{P}) replaced by (ρ_1, \mathbf{P}_1) and (ρ', \mathbf{P}') , respectively. By (2.17) direct calculations show that

$$\begin{aligned}F[\rho_1, \mathbf{P}_1] - U[\rho_1, \mathbf{P}_1] &= F[\rho, \mathbf{P}] - U[\rho, \mathbf{P}] + \int_V (\rho' \xi^e + \mathbf{P}' \cdot \nabla \xi^e) \\ &\quad + \frac{\epsilon_c}{2} \int_V |\nabla \xi'|^2 + \epsilon_c \int_V \nabla \xi \cdot \nabla \xi' + \int_{\Gamma_R} [\frac{1}{2} k (\xi')^2 + k \xi \xi'].\end{aligned}\tag{2.18}$$

By the last of (2.15) with ξ (ζ) replaced by ξ' (ξ) and the second of (2.8) (with ξ replaced by ξ'), we have

$$\begin{aligned}\epsilon_c \int_V \nabla \xi \cdot \nabla \xi' + \int_{\Gamma_R} k \xi \xi' &= \int_V (\xi \rho' + \mathbf{P}' \cdot \nabla \xi) + \int_{\Gamma_R} \xi [k \xi' - \mathbf{n} \cdot (-\epsilon_c \nabla \xi' + \mathbf{P}')] \\ &= \int_V (\xi \rho' + \mathbf{P}' \cdot \nabla \xi).\end{aligned}$$

Therefore, equation (2.18) can be rewritten as

$$\begin{aligned}F[\rho_1, \mathbf{P}_1] - U[\rho_1, \mathbf{P}_1] &= F[\rho, \mathbf{P}] - U[\rho, \mathbf{P}] + \int_V (\rho' \xi^t + \mathbf{P}' \cdot \nabla \xi^t) \\ &\quad + \frac{\epsilon_c}{2} \int_V |\nabla \xi'|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi')^2.\end{aligned}\quad (2.19)$$

In particular, the first variation contributed by the last three terms in (2.17) is given by

$$\left. \frac{d}{d\delta} \left\{ F[\rho + \delta \rho', \mathbf{P} + \delta \mathbf{P}'] - U[\rho + \delta \rho', \mathbf{P} + \delta \mathbf{P}'] \right\} \right|_{\delta=0} = \int_V (\rho' \xi^t + \mathbf{P}' \cdot \nabla \xi^t), \quad (2.20)$$

and the second variation contributed by the last three terms in (2.17) is given by

$$\left. \frac{d^2}{d\delta^2} \left\{ F[\rho + \delta \rho', \mathbf{P} + \delta \mathbf{P}'] - U[\rho + \delta \rho', \mathbf{P} + \delta \mathbf{P}'] \right\} \right|_{\delta=0} = \frac{\epsilon_c}{2} \int_V |\nabla \xi'|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi')^2. \quad (2.21)$$

2.3 Principle of minimum free energy

We assume the system is at constant temperature and undergoes only reversible processes with constant entropy. We are interested in *equilibrium* states of the system, the stability of equilibrium states and how equilibrium states respond to external sources and boundary devices. To *define* equilibrium states in the energy formulation, we postulate

Principle of minimum free energy. *The (stable) equilibrium state of the system is a pair of $(\rho, \mathbf{P}) \in \mathcal{S}$ such that the free energy (2.14) is minimized among all admissible states \mathcal{S} :*

$$\min_{(\rho, \mathbf{P}) \in \mathcal{S}} F[\rho, \mathbf{P}]. \quad (2.22)$$

We remark that an equilibrium state necessarily satisfies

$$\left. \frac{d}{d\delta} F[\rho + \delta \rho', \mathbf{P} + \delta \mathbf{P}'] \right|_{\delta=0} = 0, \quad \left. \frac{d^2}{d\delta^2} F[\rho + \delta \rho', \mathbf{P} + \delta \mathbf{P}'] \right|_{\delta=0} \geq 0, \quad (2.23)$$

which are also satisfied by metastable states. Here (ρ', \mathbf{P}') are any perturbations such that $(\rho, \mathbf{P}) + \delta(\rho', \mathbf{P}') \in \mathcal{S}$ if $|\delta|$ is small enough. Further, it is tempting to justify the above *principle of minimum free energy* by the fundamental laws of thermodynamics and, in particular, the Second Law, as for the Helmholtz free energy in the classic setting of thermodynamics (Kittel and Kroemer 1980, p. 68; Gibbs, 1878). For a general but different scenario, Fosdick and Tang (2007) presented an elegant proof of the above statement from the Second Law. Besides the fundamental difficulties elucidated in Ericksen (1991, ch. 1), pertaining to electrostatics additional conceptual difficulties are encountered in such an attempt. First, in classic thermodynamics we consider a closed system which can exchange energy with a heat reservoir and undergo irreversible processes, the equilibrium state of the system is defined as the state that satisfies the prescribed macroscopic constraints and

has maximum entropy together with the surroundings (i.e., the most probable state). From this definition, it can be shown that the Helmholtz free energy of the system at a constant temperature is minimized for the equilibrium state (Kittel and Kroemer 1980, p. 68; Ericksen 1991, p. 9). Here it is unclear whether our system can be regarded as “closed” or not since it induces a nonlocal electric field and interacts with external sources and the boundary devices. Second, we have constrained the system such that it has constant temperature and constant entropy, and hence heat exchanges and generations are impossible. Therefore, the Second Law is somewhat irrelevant; the system would behave exactly the same at a finite temperature as at the zero temperature if the internal energy were independent of temperature. Third, even if we assume the internal energy were independent of temperature, the system were at the zero temperature, and hence the system should be at its ground state with minimum total energy, we still have the difficulty in justifying the internal energy of the system can indeed be written in the form of (2.10) in regard of possible “internal variables and fine-scale oscillations” of state variables in a physical non-idealized medium (James and Müller 1994).

Instead of addressing these conceptual obstacles, we regard the above principle of minimum free energy as a *postulation* defining equilibrium states. For modeling physical media we also need to specify the functional form of internal energy density Φ and the admissible states \mathcal{S} , which are again *postulations* based on “good physical judgement” (Ericksen 1991, p. 7). The usefulness and self-consistence of these postulations will be demonstrated by showing that

1. The law of energy conservation takes the form of

$$dF = -dW, \tag{2.24}$$

where dW is work done by the system when the system is mechanically perturbed.

2. The associated Euler-Lagrange equations and boundary conditions are consistent with the Maxwell *field* equations (1.1) upon choosing appropriate and physically *intuitive* internal energy density function Φ and admissible space \mathcal{S} for typical media.

2.4 Conservation of energy

To justify our definition of free energy of the system, we show the law of conservation of energy can be expressed as (2.24) when the system is *mechanically* perturbed, i.e., a subbody $\mathcal{P} \subset \Omega$ is translated by an external mechanical force. For simplicity we assume ρ is piecewise smooth and \mathbf{P} is continuous, piecewise smooth such that $\nabla \nabla \xi^t$ is bounded and piecewise smooth on V as well (i.e., $\xi^t \in W^{2,\infty}$, see Evans, 1998), and postpone cases of more singular (ρ, \mathbf{P}) to §7.2.

First, the classic electrostatics asserts that in an electric field $\tilde{\mathbf{E}}$ the force on a point charge q and a point dipole \mathbf{p} is given by

$$q\tilde{\mathbf{E}} \quad \text{and} \quad (\nabla \tilde{\mathbf{E}})\mathbf{p}, \tag{2.25}$$

respectively, see, e.g., Jackson (1999, (1.1) and (5.69)). We emphasize that the above force formulas hold only if the charge or dipole does not affect their *experienced* electric field so that there is no ambiguity in the electric field $\tilde{\mathbf{E}}$ used in (2.25). At the proximity of boundary devices, the above electric field is not just the *external* electric field; it should also include the change of field due to the presence of the point charge or dipole, as one will see in §7.2.

To calculate the electrostatic force on a subbody $\mathcal{P} \subset \Omega$, we divide the subbody \mathcal{P} into infinitesimal parts. Then the field experienced by each infinitesimal part, to the leading order, is

unambiguously given by the local total electric field $\mathbf{E}^t = -\nabla\xi^t$. Therefore, upon summing over all infinitesimal parts, we obtain that the force on the subbody \mathcal{P} is given by

$$\mathbf{f} = \int_{\mathcal{P}} [-\rho\nabla\xi^t - (\nabla\nabla\xi^t)\mathbf{P}]. \quad (2.26)$$

Here, we stress that the above formula is valid for any boundary device as long as the charge and polarization distributions are such that the above integral is finite, e.g., ρ is piecewise smooth and \mathbf{P} is continuous, piecewise smooth restricted to \mathcal{P} . The reader is cautioned that in the presence of a boundary device, the argument to recover (2.25) from (2.26) by sending a smooth sequence (ρ, \mathbf{P}) to a point charge or a point dipole demands particular care since the local field $-\nabla\xi^t$ goes to infinity as well in the limit.

Moreover, we consider a process of shifting the subbody \mathcal{P} to a new position $\mathbf{x} \rightarrow \mathbf{x} + \delta\mathbf{e}$ in the direction of \mathbf{e} for some positive $\delta \ll 1$, and denote the new configuration of the subbody by

$$\mathcal{P}_\delta = \{\mathbf{x}_\delta : \mathbf{x}_\delta = \mathbf{x} + \delta\mathbf{e}, \mathbf{x} \in \mathcal{P}\}.$$

For simplicity we assume \mathcal{P}_δ does not penetrate into the rest of the body $\Omega \setminus \mathcal{P}$ ¹⁰. Then the new charge density ρ_δ and polarization \mathbf{P}_δ is given by¹¹

$$\begin{cases} \rho \rightarrow \rho_\delta(\mathbf{x}) = \rho(\mathbf{x}) - \rho(\mathbf{x})\chi_{\mathcal{P}} + \rho(\mathbf{x} - \delta\mathbf{e})\chi_{\mathcal{P}_\delta}, \\ \mathbf{P} \rightarrow \mathbf{P}_\delta(\mathbf{x}) = \mathbf{P}(\mathbf{x}) - \mathbf{P}(\mathbf{x})\chi_{\mathcal{P}} + \mathbf{P}(\mathbf{x} - \delta\mathbf{e})\chi_{\mathcal{P}_\delta}, \end{cases} \quad (2.27)$$

where $\chi_{\mathcal{P}}$ ($\chi_{\mathcal{P}_\delta}$) denotes the characteristic function of \mathcal{P} (\mathcal{P}_δ). From (2.26), an external mechanical force $\mathbf{f}^e = -\mathbf{f}$ is needed to maintain the force balance on \mathcal{P}_δ and the *mechanical* work done by the system in this process, to the leading order of δ , is given by

$$dW = -\delta\mathbf{f}^e \cdot \mathbf{e} = \delta\mathbf{f} \cdot \mathbf{e}. \quad (2.28)$$

We now calculate the change of free energy in this process. Clearly, the new state $(\rho_\delta, \mathbf{P}_\delta)$ has the same internal energy as the original state (ρ, \mathbf{P}) by the assumed additive property, i.e., (2.10)¹². By (2.19) we find that the change of free energy is given by

$$\begin{aligned} dF &= F[\rho_\delta, \mathbf{P}_\delta] - F[\rho, \mathbf{P}] = \int_V \left[\xi^t(\rho(\mathbf{x} - \delta\mathbf{e})\chi_{\mathcal{P}_\delta} - \rho\chi_{\mathcal{P}}) + \nabla\xi^t \cdot (\mathbf{P}(\mathbf{x} - \delta\mathbf{e})\chi_{\mathcal{P}_\delta} - \mathbf{P}\chi_{\mathcal{P}}) \right] \\ &= \int_{\mathcal{P}} [(\xi^t(\mathbf{x} + \delta\mathbf{e}) - \xi^t(\mathbf{x}))\rho + \nabla(\xi^t(\mathbf{x} + \delta\mathbf{e}) - \xi^t(\mathbf{x})) \cdot \mathbf{P}]. \end{aligned} \quad (2.29)$$

Recall that \mathbf{P} and ρ are bounded on \mathcal{P} and $\nabla\nabla\xi^t$ are well-defined on \mathcal{P} almost everywhere. Comparing (2.26) with (2.29) we obtain identity (2.24), as one expects from conservation of energy¹³.

¹⁰In general we may divide the overall body Ω into N subbodies and shift each subbody independently in directions such that they do not penetrate into each other. A similar but more complicate calculation will enable us to withdraw identity (2.24) for all such processes.

¹¹Here it is tacitly assumed that the gap between the perturbed subbody \mathcal{P}_δ and the rest of body $\Omega \setminus \mathcal{P}$ has zero polarization, i.e., is filled with the “unpolarizable” ambient medium with zero internal energy. This is of critical importance since the force depends on the ambient medium.

¹²If the internal energy depends on spatial gradients of state variables, e.g., $\nabla\rho$ or $\nabla\mathbf{P}$, it would cost energy to create new surfaces in the new state $(\rho_\delta, \mathbf{P}_\delta)$. This energy is independent of δ , and hence does not affect our results.

¹³Some writer may prefer starting from (2.24), and regarding (2.28) as the definition of the force on the subbody \mathcal{P} , equation (2.26) as the consequence.

At the presence of boundary devices, it is worthwhile noticing that the work done to the system is not all stored as internal energy of the system and field energy. To see this, by (2.14) we have

$$dF = d\tilde{F} = dU + d\mathcal{E}^t + dP,$$

where

$$dP = \int_{\Gamma_R} k\xi^t d\xi + \int_{\Gamma_D} \xi_b d[\mathbf{n} \cdot (-\epsilon_c \nabla \xi + \mathbf{P})] \quad (2.30)$$

represents the work absorbed by the boundary device in this process and is of practical importance for energy harvesting.

2.5 Euler-Lagrange equations

We now derive the Euler-Lagrange equations associated with the principle of minimum free energy (2.22). For clarity we consider a generic situation, assuming that the body Ω is open, bounded, connected, and the admissible space for charge density and polarization (ρ, \mathbf{P}) is given by

$$\mathcal{S} = \mathcal{C}_q \times \mathcal{P}, \quad \mathcal{C}_q := \{\rho : \int_{\Omega} \rho = q\}, \quad \mathcal{P} := \{\mathbf{P} : \int_{\Omega} |\mathbf{P}|^2 < +\infty\}, \quad (2.31)$$

where q is the total charge on Ω . We again emphasize that the admissible space is a material property; it shall be chosen based on “good physical judgement” or experiments instead of the well-posedness of the mathematical problem (Ericksen 1975), and one choice may be reasonable for one material but fail for a different material. Moreover, for a specified medium, we may have more constraints on state variables. For example, we shall assume $\mathbf{P} = 0$ for conductors and set $\rho = 0$ for uncharged dielectrics.

Further, the internal energy density function $\Phi(\rho, \mathbf{P}, \nabla \rho, \nabla \mathbf{P})$ is a mapping from $\mathbb{R} \times \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbb{R}^{3 \times 3}$ to \mathbb{R} . We rewrite this function as

$$\Phi = \Phi(\rho, \mathbf{P}, \mathbf{g}, \mathbf{G}),$$

assume it is smooth with respect to arguments $(\rho, \mathbf{P}, \mathbf{g}, \mathbf{G})$, and denote its differentiations with respect to its arguments by

$$D_{\rho}\Phi = \frac{\partial \Phi}{\partial \rho}, \quad D_{\mathbf{P}}\Phi = \frac{\partial \Phi}{\partial \mathbf{P}}, \quad D_{\mathbf{g}}\Phi = \frac{\partial \Phi}{\partial \mathbf{g}}, \quad D_{\mathbf{G}}\Phi = \frac{\partial \Phi}{\partial \mathbf{G}}.$$

To calculate the first variation of free energy, we consider a smooth perturbation of state variables (ρ, \mathbf{P}) for $|\delta| \ll 1$,

$$(\rho, \mathbf{P}) \rightarrow (\rho + \delta\rho', \mathbf{P} + \delta\mathbf{P}'),$$

where (ρ', \mathbf{P}') and all their derivatives are assumed to vanish on $\partial\Omega$. The first variation contributed by the internal energy is given by

$$\left. \frac{d}{d\delta} U[\rho + \delta\rho', \mathbf{P} + \delta\mathbf{P}'] \right|_{\delta=0} = \int_{\Omega} \left\{ [D_{\rho}\Phi - \operatorname{div} D_{\mathbf{g}}\Phi] \rho' + [D_{\mathbf{P}}\Phi - \operatorname{div} D_{\mathbf{G}}\Phi] \cdot \mathbf{P}' \right\}.$$

Recall that the first variation contributed by the field energy and boundary potential energy is given by (2.20). Therefore, for a stationary point $(\rho, \mathbf{P}) \in \mathcal{S}$ of the free energy $F[\mathbf{P}, \rho]$, it necessarily satisfies

$$\begin{cases} D_{\rho}\Phi - \operatorname{div} D_{\mathbf{g}}\Phi + \xi^t = \phi_0 & \text{on } \Omega, \\ D_{\mathbf{P}}\Phi - \operatorname{div} D_{\mathbf{G}}\Phi + \nabla \xi^t = 0 & \text{on } \Omega, \end{cases} \quad (2.32)$$

where the constant $\phi_0 \in \mathbb{R}$ is the Lagrangian multiplier associated with the constraint in (2.31).

We remark that the physical interpretations of the Euler-Lagrange equations (2.32) are versatile. If the internal energy density function Φ is independent of $\nabla\rho$ and $\nabla\mathbf{P}$, equations in (2.32) can be regarded as constitutive laws between (ρ, \mathbf{P}) and $(-\xi^t, -\nabla\xi^t)$. Inserting (2.32) into (2.5), we obtain a boundary value problem which can be used to determine the total electric field $-\nabla\xi^t$ and state variables (ρ, \mathbf{P}) . Media that can be described by $(\nabla\rho, \nabla\mathbf{P})$ -independent internal energy density functions include conductors and dielectrics. If the internal energy density function Φ is allowed to depend on $\nabla\rho$ or $\nabla\mathbf{P}$, we need to specify boundary conditions on (ρ, \mathbf{P}) for (2.32) which, together with (2.5), can be used to determine state variables (ρ, \mathbf{P}) . Such $(\nabla\rho, \nabla\mathbf{P})$ -dependent internal energy density functions are necessary for ferroelectrics and the model of orbital-free density functional theory. Below we describe these media or models in details. For brevity and with an abuse of notation, we omit in notation trivial arguments of which the internal energy density is independent, e.g., $\Phi = \Phi(\rho)$, $\Phi = \Phi(\rho, \nabla\rho)$, $\Phi = \Phi(\mathbf{P})$ or $\Phi = \Phi(\mathbf{P}, \nabla\mathbf{P})$.

3 Theories for typical media

In this section we postulate internal energy density functions Φ based on physical intuitions and experiments, and recover the classic theories for typical media including conductors, dielectrics and ferroelectrics.

3.1 Conductors

We first consider a collection of mutually disconnected conductors Ω_a with charge q_a ($a = 1, \dots, N$; $\Omega = \cup_{a=1}^N \Omega_a$), as illustrated in Fig. 2(a). The classic theory of electrostatics implies that the total electric fields are determined by

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^t + \mathbf{P}^e] = \rho + \rho^e & \text{on } V, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^e) - \sigma_0 = 0 & \text{on } \Gamma_R, \\ \xi^t = \phi_a & \text{on } \Omega_a, a = 1, \dots, N, \end{cases} \quad (3.33)$$

where ϕ_a ($a = 1, \dots, N$) are constants to be determined by

$$\int_{\partial\Omega_a^+} \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^e) = \int_{\partial\Omega_a^+} \mathbf{n} \cdot (-\epsilon_c \nabla \xi) = q_a, \quad (3.34)$$

and $\partial\Omega_a^+$ represents exterior boundary values on $\partial\Omega_a$ and \mathbf{n} is the outward normal on $\partial\Omega_a$. The first equality in the above equation follows by applying the divergence theorem to external electric displacement on Ω_a^+ : $\int_{\partial\Omega_a^+} \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e) = \int_{\Omega_a^+} \operatorname{div}(-\epsilon_c \nabla \xi^e + \mathbf{P}^e) = 0$. Equations (3.33) and (3.34) completely determine the electric fields in space and charge distributions on the conductors. In particular, there is no free charge inside conductors (i.e., $\rho = 0$ inside Ω_a) and the surface charge density on $\partial\Omega$ are given by

$$\sigma_n = \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^e) \quad \text{on } \partial\Omega. \quad (3.35)$$

To recover predictions of (3.33)-(3.35) in our energy formulation, we only need charge density $\rho: \Omega \rightarrow \mathbb{R}$ to describe states of conductors and postulate the admissible space as

$$\mathcal{S} := \{(\rho, \mathbf{P}) : \int_{\Omega_a} \rho = q_a (a = 1, \dots, N), \mathbf{P} = 0\}. \quad (3.36)$$

Since charges in conductors are “free”, we choose the internal energy density function as

$$\Phi(\rho) \equiv 0. \quad (3.37)$$

Then the first of (2.32) implies the last of (3.33) while the rest of (3.33) coincide with (2.5). Further, we observe that by (2.21) the second variation of the free energy is positive, and hence the stationary state (ρ, \mathbf{P}) satisfying (2.32) and (2.5) (i.e., (3.33)) is indeed the global minimizer. Therefore, we conclude that the principle of minimum free energy in current formulation implies the same equilibrium state as the classic theory for conductors. We remark that the variational principle (2.22) with the internal energy density (3.37) for conductors are well-known and referred to as *Thomson’s Theorem*, see Landau *et al.* (1995, p. 6) and Kovetz (2000, p. 115).

The presence of conductors result in the free energy $F[\rho, \mathbf{P}]$ changes from zero (obtained by evaluating (2.17) at $\rho = \mathbf{P} = 0$) to

$$F_{\min}[\rho, 0] = \int_V \rho \xi^e + \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \int_{\Gamma_R} \frac{1}{2} k \xi^2, \quad (3.38)$$

where the self potential $\xi = \xi^t - \xi^e$ and charge density ρ (more precisely, surface charge density) are determined by (3.33), (3.34) and (3.35). By the divergence theorem we have

$$\epsilon_c \int_{V \setminus \Omega} |\nabla \xi|^2 = - \int_{\Gamma_R} k \xi^2 + \sum_{a=1}^N \int_{\partial \Omega_a^+} \xi \mathbf{n} \cdot (-\epsilon_c \nabla \xi), \quad (3.39)$$

where \mathbf{n} is the outward normal on $\partial \Omega_a$ and the last two of (2.8) has been used to rewrite the integral on ∂V . Noticing that $\xi^e = \phi_a - \xi$ on $\partial \Omega_a^+$, the surface charge density on conductor $\sigma_n = \mathbf{n} \cdot (-\epsilon_c \nabla \xi) + \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e)$ on $\partial \Omega_a^+$, and $\int_{\partial \Omega_a^+} \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e) = 0$, by (3.39) we obtain

$$\begin{aligned} \int_V \rho \xi^e &= \sum_{a=1}^N \int_{\partial \Omega_a^+} [(\phi_a - \xi) \mathbf{n} \cdot (-\epsilon_c \nabla \xi) + \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e)] \\ &= \sum_{a=1}^N \phi_a q_a + \sum_{a=1}^N \int_{\partial \Omega_a^+} \xi \mathbf{n} \cdot (\epsilon_c \nabla \xi) + \sum_{a=1}^N \int_{\partial \Omega_a^+} \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e) \\ &= \sum_{a=1}^N \phi_a q_a - \epsilon_c \int_V |\nabla \xi|^2 - \int_{\Gamma_R} k \xi^2, \end{aligned} \quad (3.40)$$

where the identity $\int_{\partial \Omega_a^+} \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e) = -\epsilon_c \int_{\Omega_a} |\nabla \xi^e|^2 = -\epsilon_c \int_{\Omega_a} |\nabla \xi|^2$ has been used in the last equality. Inserting (3.40) into (3.38) we find the minimum free energy of a collection of conductors is given by

$$F_{\min}[\rho, 0] = \sum_{a=1}^N \phi_a q_a - \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 - \int_{\Gamma_R} \frac{1}{2} k \xi^2. \quad (3.41)$$

The above formula of minimum free energy will be useful for studying mutual interactions between conductors and with external sources. For example, if the conductor ($N = 1$) is neutral ($q_1 = 0$), by (3.41) we have $F_{\min}[\rho, 0] = -\frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 - \int_{\Gamma_R} \frac{1}{2} k \xi^2$, and hence conclude that the conductor is roughly attracted to high external field since $|\nabla \xi| \sim |\nabla \xi^e|$. If the conductor is small, the left hand side of (3.40), to the leading order, can be rewritten as

$$\int_V \rho \xi^e = \int_V \rho (\xi^e(\mathbf{x}_0) + (\mathbf{x} - \mathbf{x}_0) \cdot \nabla \xi^e) \approx \mathbf{p} \cdot \nabla \xi^e(\mathbf{x}_0), \quad \mathbf{p} = \int_V \rho \mathbf{x},$$

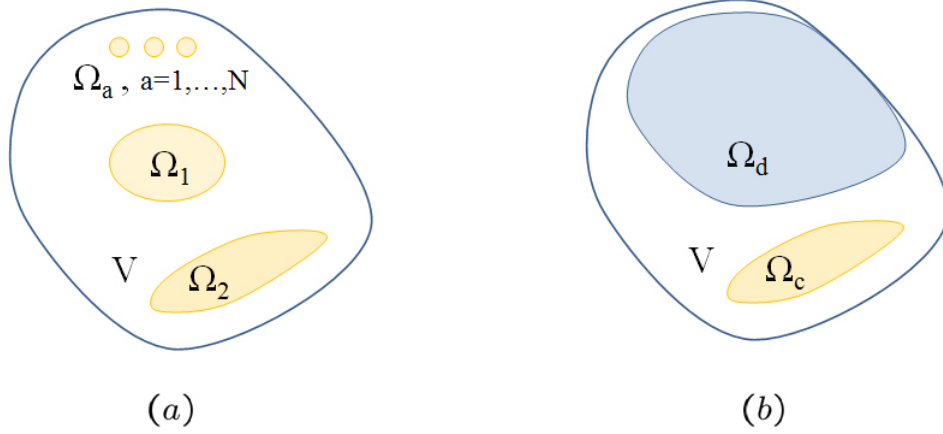


Figure 2: System of various media: (a) Ω_a ($a = 1, \dots, N$) represent disconnected conductors in V ; (b) Ω_c represents an isolated conducting body whereas Ω_d represents a polarizable dielectric body.

where \mathbf{x}_0 is typically chosen as the center of domain Ω_1 . Therefore, the minimum free energy is approximately given by

$$F_{\min}[\rho, 0] = \frac{1}{2} \int_V \rho \xi^e = \frac{1}{2} \mathbf{p} \cdot \nabla \xi^e(\mathbf{x}_0), \quad (3.42)$$

which has been used by Landau *et al.* (1995, p. 6) for deriving the “free energy” associated with a dipole. Further, if there is no external field ($-\nabla \xi^e = 0$), then by (3.40) and within a constant we have $F_{\min}[\rho, 0] = \frac{1}{2} \sum_{a=1}^N \phi_a q_a = \frac{1}{2} \sum_{a,b=1}^N C_{ab} q_a q_b$, where C_{ab} are referred to as the *coefficients of capacity* if $a = b$ and *coefficients of electrostatic induction* if $a \neq b$, see Landau *et al.* (1995, §2).

3.2 Dielectrics

3.2.1 Nonlinear dielectric media

We only need polarization $\mathbf{P} : \Omega \rightarrow \mathbb{R}^3$ to describe states of dielectrics and postulate the admissible space for state variables as

$$\mathcal{S} := \{(\rho, \mathbf{P}) : \rho = 0 \text{ in } \Omega, \int_{\Omega} |\mathbf{P}|^2 < +\infty\}. \quad (3.43)$$

For dielectric media, a constitutive relation $\mathbf{E}^t = \hat{\mathbf{E}}(\mathbf{P})$ between the total electric field and polarization can be postulated or measured by experiments, which in general may be a nonlinear function. Then the Maxwell’s equations imply

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] = \rho^e & \text{in } V, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}] - \sigma_0 = 0 & \text{on } \Gamma_R, \\ \mathbf{E}^t = -\nabla \xi^t = \hat{\mathbf{E}}(\mathbf{P}) & \text{in } \Omega. \end{cases} \quad (3.44)$$

To recover the last of the above equation as the Euler-Lagrange equation associated with the principle of minimum free energy, by the second of (2.32) we define an internal function $\Phi : \mathbb{R}^3 \rightarrow \mathbb{R}$

such that

$$D_{\mathbf{P}}\Phi(\mathbf{P}) = \hat{\mathbf{E}}(\mathbf{P}). \quad (3.45)$$

Therefore, for a given constitutive law specifying the functional dependence of total electric field on polarization $\mathbf{E}^t = \hat{\mathbf{E}}(\mathbf{P})$, we can construct the proper internal energy density function as

$$\Phi(\mathbf{P}) = \int_{\gamma(0, \mathbf{P})} \hat{\mathbf{E}}(\mathbf{P}_1) \cdot d\mathbf{P}_1, \quad (3.46)$$

where $\gamma(0, \mathbf{P})$ is any smooth integration path with initial point 0 and final point \mathbf{P} . From the hypothesis that the medium is non-dissipative, we infer that the above integral depends only on its initial and final points, i.e., no hysteresis. Conversely, if the internal energy density function $\Phi = \Phi(\mathbf{P})$ is specified, we infer the above constitutive law (3.45) by the last of (2.32), which relates the local total electric field and polarization.

3.2.2 Linear dielectric media

For a linear dielectric body Ω with permittivity tensor ϵ , the polarization and total electric field are determined by the Maxwell's equations:

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] = \rho^e & \text{in } V, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}] - \sigma_0 = 0 & \text{on } \Gamma_R, \\ \mathbf{P} = -\epsilon_c \chi \nabla \xi^t & \text{in } \Omega. \end{cases} \quad (3.47)$$

where $\chi = \epsilon/\epsilon_c - \mathbf{I}$ is the dimensionless susceptibility tensor. To recover the linear relation between polarization and local total electric field, by (3.46) the internal energy density function shall be given as

$$\Phi(\mathbf{P}) = \frac{1}{2} \mathbf{P} \cdot \mathbf{A} \mathbf{P}, \quad \mathbf{A} = \frac{1}{\epsilon_c} \chi^{-1}. \quad (3.48)$$

Then the last of (2.32) implies

$$\mathbf{A} \mathbf{P} = -\nabla \xi^t \quad \text{on } \Omega, \quad (3.49)$$

which, together with (2.5), is exactly the same problem as (3.47).

Further, by (2.21) we find that the second variation of free energy is given by

$$\frac{d^2}{d\delta^2} F[0, \mathbf{P} + \delta \mathbf{P}'] \Big|_{\delta=0} = \frac{1}{2} \int_{\Omega} \mathbf{P}' \cdot (\epsilon - \epsilon_c \mathbf{I})^{-1} \mathbf{P}' + \frac{\epsilon_c}{2} \int_V |\nabla \xi'|^2 + \int_{\Gamma_R} \frac{1}{2} k(\xi')^2$$

Therefore, if $\epsilon - \epsilon_c \mathbf{I}$ is semi-positive definite, the above second variation is positive and hence the stationary state satisfying (3.47) (i.e., (2.32) and (2.5)) is the (in fact, global by convexity) minimizing state. We conclude that the principle of minimum free energy implies the same equilibrium state as the classic theory for linear dielectric media. If, however, $\epsilon - \epsilon_c \mathbf{I}$ has a negative eigenvalue, the equilibrium state determine by (3.47) is unstable. We can construct polarization states with lower free energy than the stationary state satisfying (2.32), though the boundary value problem (3.47) is still strictly elliptic and well-posed for positive definite ϵ . From this viewpoint, we may conclude

that dielectric materials shall always have permittivity larger than that of vacuum, which, to our best knowledge, is indeed so ^{14,15}.

Additionally, it is worthwhile noticing that the minimum free energy (i.e., when the Euler-Lagrange equation (3.49) is satisfied) is given by (cf., (11.7) in Landau *et al.* 1995)

$$F_{\min}[0, \mathbf{P}] = \frac{1}{2} \int_V \mathbf{P} \cdot \nabla \xi^e. \quad (3.50)$$

To see this, inserting (3.49) into (2.17) we obtain

$$F[0, \mathbf{P}] = -\frac{1}{2} \int_V \mathbf{P} \cdot \nabla \xi^t + \int_V \mathbf{P} \cdot \nabla \xi^e + \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \int_{\Gamma_R} \frac{1}{2} k \xi^2. \quad (3.51)$$

Moreover, by the last of (2.8), i.e., $\mathbf{n} \cdot (-\epsilon_c \nabla \xi + \mathbf{P}) = k \xi$ on Γ_R , and the last of (2.15) with ζ replaced by ξ and $\rho = 0$, we have

$$\frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 = \frac{1}{2} \int_V \mathbf{P} \cdot \nabla \xi - \frac{1}{2} \int_{\Gamma_R} k \xi^2.$$

Inserting the above equation into (3.51) we obtain (3.50).

We remark that the minimum free energy (3.50) shall not be confused with the interaction field energy defined in the first of (2.9) for their similarity in appearance. Above all, the polarization \mathbf{P} in the minimum free energy (3.50) is the minimizing state, satisfies the Euler-Lagrange equation (3.49), and hence is completely determined by (3.47), whereas the interaction field energy in (2.9) is defined for all polarization states. Also, the expression (3.50) applies *only to linear dielectric media* and is convenient for modeling phase transitions (i.e., the domain Ω of the system is changing) where the system has additional degrees of freedom and the minimizing polarization can be a priori determined, see, e.g., Cheng and Chaddock (1984).

3.2.3 Conductors as a linear dielectric medium with infinite permittivity

The conductor can also be characterized as a linear dielectric medium with an infinite permittivity or a dielectric medium with internal energy density function given by $\Phi(\mathbf{P}) \equiv 0$. To see this, we assume isotropic permittivity tensor $\epsilon = \epsilon_1 \mathbf{I}$. As $\epsilon_1 \rightarrow +\infty$ equation (3.48) implies that $\mathbf{A} = 0$ and $\Phi(\mathbf{P}) = 0$. Also, by the last of (3.47), we see that ξ^t necessarily remains constant on each connected component of Ω , and henceforth, equation (3.47) is equivalent to (3.33). In addition, the minimum free energy formula (3.50) is consistent with (3.42) for a small conductor.

3.3 Ferroelectric media

Ferroelectric crystals may be described by postulating the internal energy density as

$$\Phi(\mathbf{P}, \nabla \mathbf{P}) = \frac{\alpha}{2} |\nabla \mathbf{P}|^2 + \psi(\mathbf{P}), \quad (3.52)$$

where $\alpha > 0$ is the exchange constant and $\psi : \mathbb{R}^3 \rightarrow \mathbb{R}$ is the part of internal energy density depending only on local polarization. To reflect that the crystal has certain preferred directions

¹⁴An argument for this fact is presented in §14 of Landau *et al.* (1995) from the viewpoint of quantum mechanics. We also note that in this stability argument, ϵ_c must be chosen as that of vacuum since other choices would make the admissible space (3.43) unphysical, see more detailed discussions in § 5.

¹⁵It is worthwhile noticing that there exist diamagnetic materials with magnetic permeability smaller than that of vacuum, e.g., water. This arises from microscopic orbital currents instead of magnetic dipoles (Ashcroft and Mermin, 1976, §31).

and magnitude of polarization, ψ is postulated to be nonconvex and have a multi-well structure, attains its minimum at those preferred directions and magnitude of polarization, and is also referred to as the anisotropy energy. By (2.5) and (2.32), the boundary value problem for (ξ^t, \mathbf{P}) is as follows:

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] = \rho^e & \text{on } V, \\ -\alpha \Delta \mathbf{P} + D_{\mathbf{P}} \psi(\mathbf{P}) + \nabla \xi^t = 0 & \text{on } \Omega, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e] - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (3.53)$$

We remark that the above problem is not yet closed; a boundary condition shall be provided for \mathbf{P} , which is typically chosen as $(\nabla \mathbf{P})\mathbf{n} = 0$ on $\partial\Omega$. The physical meaning/justification of this boundary condition, however, appears to be elusive. Also, the variational principle (2.22), together with the free energy functional (2.17) and internal energy density (3.52), is referred to as the Landau-Ginzburg-Devonshire theory of ferroelectrics (Landau, 1937; Ginzburg and Landau, 1950; Devonshire, 1949; 1954; Cao 2008).

Though it can be shown that the above boundary value problem admits a solution (in a suitable Sobolev space $W^{1,p}$ with some moderate growth assumption on ψ at the infinity), the solution is in general complicated. Nevertheless, when the ferroelectric body Ω is a single-crystal ellipsoid, the external field $-\nabla \xi^e$ is uniform on Ω , and the boundary ∂V is far away and can be neglected for problem (2.8), closed-form solutions to (3.53) can be found (i) in the small-body limit where the exchange term forces the crystal to be a single domain, and (ii) in the large-body limit where the exchange term has no influence on the macroscopic domain structures and may be neglected (DeSimone, 1993). The solution in the small-body limit is the foundation of the well-known Stoner-Wohlfarth model for hysteresis in the context of ferromagnetics (Stoner and Wohlfarth, 1948); the solution in the large-body limit has been analyzed in Shu and Bhattacharya (2001) and Desimone and James (2002) where the effects of strain have also been taken into account.

3.4 Effects of a conductor on a polarizable body

A great conceptual advantage offered by our energy formulation lies in that the internal energy is additive. Therefore, if two bodies of different properties are placed together, the total free energy can be easily identified. For example, we consider a collection of a conductor Ω_c and a polarizable body Ω_p as illustrated in Fig. 2(b). Recall that $\mathbf{P}^e = \rho^e = 0$ on $\Omega = \Omega_c \cup \Omega_p$, and for simplicity assume that Ω_c is connected. The admissible space for (ρ, \mathbf{P}) is prescribed as

$$\mathcal{S} = \{(\rho, \mathbf{P}) : \int_{\Omega_c} \rho = q_0; \rho = 0 \text{ on } V \setminus \Omega_c; \mathbf{P} = 0 \text{ on } V \setminus \Omega_p\}. \quad (3.54)$$

From discussions in §3.1-3.2, we infer that the total free energy of the system including both the conductor Ω_c and polarizable body Ω_p is given by

$$F[\rho, \mathbf{P}] = \int_{\Omega_p} \Phi(\mathbf{P}, \nabla \mathbf{P}) + \int_V (\rho \xi^e + \mathbf{P} \cdot \nabla \xi^e) + \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \int_{\Gamma_R} \frac{1}{2} k \xi^2, \quad (3.55)$$

where the self field is determined by (2.8).

In applications, our interest usually lies in the polarizable body Ω_p instead of the conductor. We therefore introduce an effective free energy for the polarizable body alone:

$$F_p[\mathbf{P}] = \min_{\rho} F[\rho, \mathbf{P}], \quad (3.56)$$

where the admissible space for charge density ρ is still specified by (3.54). By the first of (2.32), the self potential satisfies that, in addition to (2.8),

$$\xi + \xi^e = \phi_0 \quad \text{on } \Omega_c, \quad (3.57)$$

where ϕ_0 is the potential of the conductor determined by

$$\int_{\partial\Omega_c^+} \mathbf{n} \cdot [-\epsilon_c \nabla(\xi + \xi^e) + \mathbf{P} + \mathbf{P}^e] = \int_{\partial\Omega_c^+} \mathbf{n} \cdot (-\epsilon_c \nabla\xi + \mathbf{P}) = q_0. \quad (3.58)$$

Further, it is desirable to separate the contribution to the self field of the polarizable body Ω_p from that of the conductor Ω_c . To this end, we introduce ξ^p and ξ^c by

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^p + \mathbf{P}] = 0 & \text{on } V \setminus \Omega_c, \\ \xi^p = -\xi^c & \text{on } \Omega_c, \\ \xi^p = 0 & \text{on } \Gamma_D, \\ k\xi^p - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^p + \mathbf{P}] = 0 & \text{on } \Gamma_R, \end{cases} \quad (3.59)$$

$$\begin{cases} \Delta \xi^c = 0 & \text{on } V \setminus \Omega_c, \\ \xi^c = 1 & \text{on } \Omega_c, \\ \xi^c = 0 & \text{on } \Gamma_D, \\ k\xi^c + \epsilon_c \mathbf{n} \cdot \nabla \xi^c = 0 & \text{on } \Gamma_R, \end{cases} \quad (3.60)$$

and denote by

$$\hat{q} = - \int_{\partial\Omega_c^+} \epsilon_c \mathbf{n} \cdot \nabla \xi^c, \quad \sigma_p = \mathbf{n} \cdot [-\epsilon_c \nabla \xi^p + \mathbf{P}] \quad \text{on } \partial\Omega_c^+. \quad (3.61)$$

We remark that \hat{q} , independent of polarization on Ω_p , may be interpreted as the capacity of the conductor Ω_c (cf., (3.62)) whereas σ_p , depending on the polarization \mathbf{P} , may be interpreted as the surface charge density on $\partial\Omega_c^+$ induced by the polarization on Ω_p . Direct calculations verify that

$$\xi = \xi^p + \phi_0 \xi^c, \quad \phi_0 = \frac{1}{\hat{q}}(q_0 - q_p), \quad q_p := \int_{\partial\Omega_c^+} \mathbf{n} \cdot (-\epsilon_c \nabla \xi^p + \mathbf{P}) = \int_{\partial\Omega_c^+} \sigma_p$$

satisfies (2.8), (3.57) and (3.58), and hence $-\nabla\xi = -\nabla\xi^p - \phi_0 \nabla\xi^c$ is the self field. By (3.59), (3.60), (3.61) and the divergence theorem, we have

$$\begin{aligned} \int_{V \setminus \Omega_c} \epsilon_c \nabla \xi^c \cdot \nabla \xi^p &= \int_{V \setminus \Omega_c} \left[\operatorname{div}(\epsilon_c \xi^p \nabla \xi^c) - \xi^p \operatorname{div}(\epsilon_c \nabla \xi^c) \right] \\ &= \int_{\partial V} \epsilon_c \xi^p \mathbf{n} \cdot \nabla \xi^c - \int_{\partial\Omega_c^+} \epsilon_c \xi^p \mathbf{n} \cdot \nabla \xi^c, \\ \frac{\epsilon_c}{2} \int_{V \setminus \Omega_c} |\nabla \xi^c|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi^c)^2 &= -\frac{\epsilon_c}{2} \int_{\partial\Omega_c^+} \xi^c \mathbf{n} \cdot \nabla \xi^c = \frac{\hat{q}}{2}. \end{aligned} \quad (3.62)$$

Therefore, the last two terms on the right hand side of (3.55) can be written as

$$\begin{aligned} \frac{\epsilon_c}{2} \int_V |\nabla \xi|^2 + \int_{\Gamma_R} \frac{1}{2} k \xi^2 &= \frac{\epsilon_c}{2} \int_V |\nabla \xi^p|^2 - \phi_0 \int_{\partial\Omega_c^+} \epsilon_c \xi^p \mathbf{n} \cdot \nabla \xi^c + \frac{\hat{q}}{2} \phi_0^2 \\ &\quad + \phi_0 \int_{\Gamma_R} \{ \epsilon_c \xi^p \mathbf{n} \cdot \nabla \xi^c + k \xi^c \xi^p \} + \int_{\Gamma_R} \frac{1}{2} k (\xi^p)^2 \\ &= \frac{\epsilon_c}{2} \int_V |\nabla \xi^p|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi^p)^2 + \frac{\hat{q}}{2} \phi_0^2 - \phi_0 \int_{\partial\Omega_c^+} \epsilon_c \xi^p \mathbf{n} \cdot \nabla \xi^c. \end{aligned} \quad (3.63)$$

Additionally, the (surface) charge density ρ on the conductor is given by $\sigma_n = \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^t) = \mathbf{n} \cdot [-\epsilon_c \nabla (\xi^p + \xi^e) + \mathbf{P} + \mathbf{P}^e] + \phi_0 \mathbf{n} \cdot (-\epsilon_c \nabla \xi^c)$ on $\partial\Omega_c^+$, and hence (cf., (3.61))

$$\int_V \rho \xi^e = \int_{\partial\Omega_c^+} [\xi^e \sigma_p + \phi_0 \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi^c) + \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e)]. \quad (3.64)$$

The effective free energy for the polarizable body Ω_p , defined as (3.56), follows by evaluating (3.55) at the equilibrium charge density. Inserting (3.63)-(3.64) into (3.55), and noticing that $\xi^p = -\xi^e$ on $\partial\Omega_c^+$ and that $\int_{\partial\Omega_c^+} \xi^e \mathbf{n} \cdot (-\epsilon_c \nabla \xi^e + \mathbf{P}^e) = -\epsilon_c \int_{\Omega_c} |\nabla \xi^e|^2$, we find that the effective free energy of the polarizable body is given by

$$F_p[\mathbf{P}] = \int_{\Omega_p} \Phi(\mathbf{P}, \nabla \mathbf{P}) + \int_{V \setminus \Omega_c} \frac{\epsilon_c}{2} |\nabla \xi^p|^2 + \int_{\Omega_p} \mathbf{P} \cdot \nabla \xi^e + \int_{\Gamma_R} \frac{1}{2} k (\xi^p)^2 + \int_{\partial\Omega_c^+} \xi^e \sigma_p + \frac{\hat{q}}{2} \phi_0^2. \quad (3.65)$$

In particular, if $V = \mathbb{R}^3$ ($k = 0$) and $\xi^e = 0$, the above expression can be rewritten as

$$F_p[\mathbf{P}] = \frac{(q_0 - q_p)^2}{2\hat{q}} + \int_{\Omega_p} \Phi(\mathbf{P}, \nabla \mathbf{P}) + \frac{\epsilon_c}{2} \int_{\mathbb{R}^3 \setminus \Omega_c} |\nabla \xi^p|^2. \quad (3.66)$$

Comparing (3.65) and (3.66) with (2.17), we observe that a conductor influences the polarizable body in two aspects: (i) there are additional energy cost associated with polarization on Ω_p since it induces redistribution of charges on the conductor, i.e., the last two terms in (3.65); (ii) the definition of “self field” $-\nabla \xi^p$ now depends on the external potential ξ^e and domain Ω_c , see (3.59). The effective free energies obtained in (3.65) and (3.66) may serve as the starting point for modeling interactions between conductors and polarizable/ferroelectric bodies.

3.5 Model of orbital-free density functional theory

It is interesting to notice that the present framework may include the orbital-free model in density functional theory. In this model, the state variable is the charge density or electron density ρ and the internal energy density is given by (Parr and Yang, 1989)

$$\Phi(\rho, \nabla \rho) = \frac{\lambda}{8\rho} |\nabla \rho|^2 + C_F \rho^{5/3} + \mathcal{E}_{xc}(\rho) = \frac{\lambda}{8\rho} |\nabla \rho|^2 + \psi(\rho),$$

where λ, C_F are constants, $\mathcal{E}_{xc}(\rho)$ is referred to as the exchange and correlation energy, the first two term terms describe the kinetic energy of electrons, and $\psi(\rho) = C_F \rho^{5/3} + \mathcal{E}_{xc}(\rho)$ is introduced for ease of notation. Also, the external sources consist only of nuclei charges at the lattice points (i.e., $\mathbf{P}^e = 0$). By (2.5) and (2.32), the boundary value problem for (ξ^t, ρ) is given by

$$\begin{cases} \operatorname{div}(-\epsilon_c \nabla \xi^t) = \rho + \rho^e & \text{on } V, \\ -\frac{\lambda}{8\rho} \operatorname{div}(\frac{1}{\rho} \nabla \rho) + D_\rho \psi(\rho) + \xi^t = \phi_0 & \text{on } \Omega, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t) - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (3.67)$$

Again, a boundary condition on ρ shall be provided on $\partial\Omega$ to close the problem, which is typically chosen as $\rho = 0$ on $\partial\Omega$. Since ρ^e oscillates at the atomistic lengthscale, a local variational formulation in terms of both electrostatic potential and charge density (ξ^t, ρ) would be convenient for numerical simulations, which has been developed in Gavini *et al.* (2007), also see discussions in §4.2.

4 Alternative variational formulations and their equivalence

Because of the freedom in choosing formal state variables and separation between internal energy and field energy, one can construct *infinitely* many variational principles that are consistent with the Maxwell field equations (1.1). Below we select three typical formulations and explore their mutual relations. The reader is referred to Bustamante *et al.* (2009) for other alternative formulations.

4.1 Landau's formulation

As shown in § 2.2, the free energy functional (2.17) different from the original free energy functional (2.14) by a constant independent of the state variables (ρ, \mathbf{P}) . In the absence of boundary devices, i.e., $V = \mathbb{R}^3$ and $k = 0$, we recover the familiar Landau-Ginzburg-Devonshire's energy functional¹⁶

$$F[\rho, \mathbf{P}] = \int_{\Omega} \Phi(\rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P}) + \int_{\Omega} (\rho\xi^e + \mathbf{P} \cdot \nabla\xi^e) + \frac{\epsilon_c}{2} \int_{\mathbb{R}^3} |\nabla\xi|^2, \quad (4.1)$$

where the self field $-\nabla\xi$ satisfies

$$\begin{cases} \operatorname{div}(-\epsilon_c \nabla\xi + \mathbf{P}) = \rho & \text{on } \mathbb{R}^3, \\ |\nabla\xi| \rightarrow 0 & \text{as } |\mathbf{x}| \rightarrow +\infty. \end{cases} \quad (4.2)$$

For simplicity it is frequently assumed that the external field $-\nabla\xi^e$ is uniform on Ω . From the procedure of arriving at (4.1) from (2.14) and the definitions (2.7) and (2.8), one sees that this simplification, in addition to a uniform external field, requires that Ω is far away from the physical boundary ∂V such that the solution to (4.2) is indeed a good approximation of the solution to (2.8).

4.2 Toupin's formulation

From a practical viewpoint, the postulated free energy (2.14) or (2.17) suffers from the disadvantage that the total electric field or self field energy depends on state variables (ρ, \mathbf{P}) nonlocally which gives rise to the difficulty of, e.g., deriving the first order and second order variations of the free energy. We overcome this difficulty by using divergence theorem in (2.20) and (2.21). In the absence of charges, i.e., $\rho \equiv 0$, an alternative way of addressing this issue is to rewrite the last two terms on the right hand side of (2.17) as

$$\frac{\epsilon_c}{2} \int_V |\nabla\xi|^2 + \int_{\Gamma_R} \frac{1}{2} k \xi^2 = \frac{1}{2} \int_{\Omega} \int_{\Omega} \mathbf{K}(\mathbf{x}, \mathbf{x}') \mathbf{P}(\mathbf{x}) \mathbf{P}(\mathbf{x}'), \quad (4.3)$$

where the matrix kernel $\mathbf{K}(\mathbf{x}, \mathbf{x}')$ is such that

$$\nabla\xi(\mathbf{x}) = \int_V \mathbf{K}(\mathbf{x}, \mathbf{x}') \mathbf{P}(\mathbf{x}') d\mathbf{x}'$$

is the solution to (2.8). The explicit form of this kernel can be found for simple domains V , e.g., a unit ball, and simple boundary conditions, e.g., $\Gamma_R = \emptyset$.

Moreover, for the same disadvantage the energy formulation based on (2.17) and (2.22) implies no clear numerical method. If one attempts to discretize the problem by, e.g., the finite element

¹⁶This type of energy functional is referred to as the Landau-Lifshitz energy in micromagnetics (Landau and Lifshitz, 1935; Brown, 1966, p. 73) and the Ginzburg-Landau energy in superconductivity (Ginzburg and Landau, 1950).

method, one immediately sees that the last two terms in (2.17), i.e., the left hand side of (4.3), give rise to a non-sparse matrix because of the nonlocal interaction between the polarizations as demonstrated by the right hand side of (4.3). These issues may be remedied by Toupin's formulation in which the energy functional is given by ¹⁷

$$\begin{aligned} \tilde{E}_T[\rho, \mathbf{P}, \zeta] &= U[\rho, \mathbf{P}] + \int_V [(\mathbf{P} + \mathbf{P}^e) \cdot \nabla \zeta + (\rho + \rho^e) \zeta] \\ &\quad - \frac{\epsilon_c}{2} \int_V |\nabla \zeta|^2 - \int_{\Gamma_R} \left[\frac{1}{2} k \zeta^2 - \zeta (k \xi_b + \sigma_0) \right], \end{aligned} \quad (4.4)$$

and the state variables and total electric field is determined by the min-max problem:

$$\min_{(\rho, \mathbf{P}) \in \mathcal{S}} \max_{\zeta \in \mathbb{W}_{\xi_b}} \tilde{E}_T[\rho, \mathbf{P}, \zeta], \quad (4.5)$$

where $\mathbb{W}_{\xi_b} := \{\zeta \in \mathbb{W} : \zeta = \xi_b \text{ on } \Gamma_D\}$ (cf., (2.6)). The predictions of (2.22) and (4.5) will be the same if it holds that

$$\tilde{F}[\rho, \mathbf{P}] - \max_{\zeta \in \mathbb{W}_{\xi_b}} \tilde{E}_T[\rho, \mathbf{P}, \zeta] = \text{a constant independent of state variables } (\rho, \mathbf{P}). \quad (4.6)$$

Indeed, by the standard first-variation calculation we find the Euler-Lagrange equation for a maximizer ξ^t of the inner maximization problem in (4.5) is precisely (2.5). Therefore, by (2.5) and the first of (2.15) with ζ being replaced by ξ^t we obtain

$$\begin{aligned} \max_{\zeta \in \mathbb{W}_{\xi_b}} \tilde{E}_T[\rho, \mathbf{P}, \zeta] &= \tilde{E}_T[\rho, \mathbf{P}, \xi^t] = U[\rho, \mathbf{P}] + \frac{\epsilon_c}{2} \int_V |\nabla \xi^t|^2 \\ &\quad + \int_{\partial V} \xi^t \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e) + \int_{\Gamma_R} \left[-\frac{1}{2} k (\xi^t)^2 + \xi^t (k \xi_b + \sigma_0) \right] \\ &= U[\rho, \mathbf{P}] + \frac{\epsilon_c}{2} \int_V |\nabla \xi^t|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi^t)^2 + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e). \end{aligned}$$

Comparing the right hand side of the above equation with (2.14) we conclude (4.6) and hence the equivalence of two formulations: (2.22) and (4.5).

Moreover, in analogy with (2.17) and within a constant independent of state variables (ρ, \mathbf{P}) we can rewrite Toupin's energy functional (4.4) as

$$E_T[\rho, \mathbf{P}, \zeta] = U[\rho, \mathbf{P}] + \int_V [\mathbf{P} \cdot \nabla (\zeta + \xi^e) + \rho (\zeta + \xi^e)] - \frac{\epsilon_c}{2} \int_V |\nabla \zeta|^2 - \int_{\Gamma_R} \frac{1}{2} k \zeta^2, \quad (4.7)$$

and claim the state variables (ρ, \mathbf{P}) and self electric field are determined by the min-max problem

$$\min_{(\rho, \mathbf{P}) \in \mathcal{S}} \max_{\zeta \in \mathbb{W}_0} E_T[\rho, \mathbf{P}, \zeta], \quad \mathbb{W}_0 := \{\zeta \in \mathbb{W} : \zeta = 0 \text{ on } \Gamma_D\} \text{ (cf., (2.6)).} \quad (4.8)$$

¹⁷This energy functional is sometimes referred to as ‘‘enthalpy’’ of the system in the literature. The implication of this terminology is, however, substantially different from what enthalpy means in the standard setting of thermodynamics (Kittel and Kroemer 1980, p. 68, p. 246, p. 262). In particular, the equilibrium state in the setting of Kittel and Kroemer (1980) is always determined by minimizing a proper energy functional instead of a min-max problem. The proper energy functional, i.e., one of the internal energy, Helmholtz free energy, enthalpy, Gibbs free energy, is determined by the constraints on the system: internal energy for closed and isolated systems, Helholtz free energy for closed systems at constant temperature, enthalpy for closed systems at constant pressure, and Gibbs free energy for systems at constant temperature and constant chemical potential.

To see this, we first notice that the Euler-Lagrange equation for a maximizer ξ of the inner maximization problem in (4.8) is precisely (2.8). Therefore, by (2.8) and the last of (2.15) with ζ being replaced by ξ we find that (cf., (2.17))

$$F[\rho, \mathbf{P}] = \max_{\zeta \in \mathbb{W}_0} E_T[\rho, \mathbf{P}, \zeta].$$

The Toupin's energy functional depends on its state variables locally and implies a standard finite element method to determine both the charge density, polarization and field simultaneously (Yang and Dayal, 2011). However, it is unclear in this formulation how to analyze the stability of a stationary state (ρ, \mathbf{P}) and field $-\nabla\xi^t$ (or $-\nabla\xi$) since it is a saddle point of the energy functional, as remarked by Brown (1966, p. 78) and Ericksen (2007). Also, numerical schemes based on a minimization principle are typically more robust than schemes based on min-max principle. It is therefore of interest to reformulate the problem as a local minimization problem, which is proposed by Ericksen (2007) ¹⁸.

4.3 Ericksen's formulation

In the absence of charges and boundary devices, i.e., $\rho = \rho^e \equiv 0$ on $V = \mathbb{R}^3$, Ericksen (2007) proposed the following energy functional

$$E_E[\rho, \mathbf{P}, \mathbf{A}] = U[\rho, \mathbf{P}] + \frac{1}{2\epsilon_c} \int_{\mathbb{R}^3} |\nabla \times \mathbf{A} - \mathbf{P}|^2 - \int_{\mathbb{R}^3} (\nabla \times \mathbf{A} - \mathbf{P}) \cdot \nabla \xi^e, \quad (4.9)$$

such that the the vector potential and polarization are determined by minimizing the energy functional:

$$\min_{(\rho, \mathbf{P}) \in \mathcal{S} \cap \{\rho=0\}} \min\{E_E[\rho, \mathbf{P}, \mathbf{A}] : \mathbf{A} \in \mathcal{A}\}, \quad (4.10)$$

where \mathcal{A} denotes the admissible space for the vector potential \mathbf{A} which may be assumed as $\mathcal{A} = \{\mathbf{A} : \int_{\mathbb{R}^3} |\nabla \times \mathbf{A}|^2 < +\infty\}$. Again, the above variation problem is equivalent to (2.22) since

$$F[\rho, \mathbf{P}] - \min_{\mathbf{A} \in \mathcal{A}} E_E[\rho, \mathbf{P}, \mathbf{A}] = \text{a constant independent of } \mathbf{P} \ (\rho \equiv 0).$$

To see this, we denote by $\mathbf{A}^* \in \mathcal{A}$ the minimizing vector potential. By the first variational calculations we find that \mathbf{A}^* satisfies

$$\int_{\mathbb{R}^3} \left[\frac{1}{\epsilon_c} (\nabla \times \mathbf{A}^* - \mathbf{P}) - \nabla \xi^e \right] \cdot \nabla \times \mathbf{A}_1 = 0 \quad \forall \mathbf{A}_1 \in \mathcal{A}. \quad (4.11)$$

Let

$$\mathbf{g}(\mathbf{x}) = \frac{1}{\epsilon_c} (\nabla \times \mathbf{A}^* - \mathbf{P}) - \nabla \xi^e = \begin{cases} \frac{1}{\epsilon_c} \nabla \times \mathbf{A}^* - \nabla \xi^e & \text{on } \mathbb{R}^3 \setminus \Omega, \\ \frac{1}{\epsilon_c} (\nabla \times \mathbf{A}^* - \mathbf{P}) - \nabla \xi^e & \text{on } \Omega. \end{cases} \quad (4.12)$$

Then (4.11) can be rewritten as

$$\int_{\mathbb{R}^3} \mathbf{g} \cdot \nabla \times \mathbf{A}_1 = 0 \quad \forall \mathbf{A}_1 \in \mathcal{A},$$

¹⁸This formulation is to some extent parallel to the Ginzburg-Landau theory in the context of superconductivity.

which implies that $\mathbf{g} : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ is necessarily the gradient of a scalar field. We denote this gradient field by $-\nabla\xi^t$, let $\xi = \xi^t - \xi^e$, and by (4.12) obtain

$$\nabla \times \mathbf{A}^* = -\epsilon_c \nabla \xi + \mathbf{P} \chi_\Omega \quad \text{on } \mathbb{R}^3. \quad (4.13)$$

Since $\text{div}[\nabla \times \mathbf{A}^*] = 0$ on \mathbb{R}^3 , we identify $-\nabla\xi$ as the self electric field induced by the polarization $\mathbf{P} \chi_\Omega$ (cf., (2.8) or (4.2)) and the field $\mathbf{g} = -\nabla\xi^t$ as the total electric field. Replacing $\nabla \times \mathbf{A}$ in (4.9) by the right hand side of (4.13), we find that

$$\min_{\mathbf{A} \in \mathcal{A}} E_E[\rho, \mathbf{P}, \mathbf{A}] = U[\rho, \mathbf{P}] + \frac{\epsilon_c}{2} \int_{\mathbb{R}^3} |\nabla \xi|^2 + \int_{\Omega} \mathbf{P} \cdot \nabla \xi^e,$$

which is identical with (2.17) since $V = \mathbb{R}^3$ and $k = 0$, also see (4.1) with $\rho \equiv 0$.

5 Transformation of free energy for different comparison media

Before proceeding to detailed derivations, a few remarks are in order here regarding the general form of internal energy density $\Phi = \Phi(\rho, \mathbf{P}, \nabla\rho, \nabla\mathbf{P})$. On one hand the general dependence of internal energy on $\rho, \nabla\rho, \nabla\mathbf{P}$ is convenient; it allows us to study different media including conductors, dielectrics and ferroelectrics in a unified framework. On the other hand, it unnecessarily complicates calculations if one's interest is mainly on a body with polarization \mathbf{P} being the only state variable. Further, the dependence of internal energy on $\nabla\mathbf{P}$, such as the first term in (3.52), referred to as the exchange term, is *phenomenological*. The effects of this term include favoring long-range ordering of polarization, penalizing domain walls, giving rise to an intrinsic lengthscale of domain patterns and domain walls, etc.

With the above mentioned, we subsequently focus on dielectric media and, with an abuse of notation, assume that the internal energy density function is simply given by

$$\Phi = \Phi(\mathbf{x}, \mathbf{P}), \quad (5.14)$$

where the $\nabla\mathbf{P}$ -dependence is neglected. In this section, we will use ϵ_c different from the permittivity of the ambient medium in our definition of free energy (cf., (2.14)). It is therefore necessary to extend spatial definition of Φ to the entire domain V and assume the convention that $1/0 = +\infty$, $0 \cdot \infty = 0$ for ease of notation. Again we sometimes drop the \mathbf{x} (position)-dependence of Φ for brevity and the stated properties for Φ such as convexity, invertibility, etc apply pointwisely to every $\mathbf{x} \in V$ unless otherwise stated.

As a dielectric medium, vacuum plays a special role in the sense that it cannot be polarized according to the conventional definition, i.e., $\mathbf{P} = \mathbf{D}^t - \epsilon_0 \mathbf{E}^t \equiv 0$. The physical reason of singling out vacuum as the ambient ‘‘comparison’’ medium is self-evident. It is also convenient since systems of interest are usually in air with permittivity negligibly different from that of vacuum. Then the standard definition of polarization $\mathbf{P} = \mathbf{D}^t - \epsilon_0 \mathbf{E}^t$ enables us to focus on the polarizable body, in spite of complications arising from the nonlocal electrostatic field in the ambient medium.

So far the ϵ_c in the free energy (2.14) is chosen as that of the ambient medium¹⁹, which is tacitly understood as vacuum, i.e., $\epsilon_c = \epsilon_0 = 8.854 \times 10^{-12} F/m$. We denote the functional dependence of the free energy on $(\epsilon_c, \mathbf{P}, \Phi)$ by

$$\hat{F} = \hat{F}[\Pi], \quad \Pi = (\epsilon_c, \mathbf{P}, \Phi),$$

¹⁹In this case, the internal energy density function at $\mathbf{x} \in V \setminus \Omega$ is defined as $\Phi(\mathbf{x}, \mathbf{P}) = +\infty$ if $\mathbf{P} \neq 0$; $= 0$ if $\mathbf{P} = 0$.

where the dependence of free energy on other parameters such as $\rho, \rho^e, \mathbf{P}^e, \Phi, k, \xi_b, \sigma_0$, etc, is omitted since they will remain unchanged in the following calculations.

We now consider a dielectric body immersed in a linear dielectric medium with permittivity ϵ_1 , e.g., water. If vacuum is again used as the comparison medium, our system shall include the dielectric body Ω and ambient medium $V \setminus \Omega$ — the very scenario one would like to avoid by introducing the concept of polarization. In analogy with a dielectric body in air (or vacuum), we expect that it would be more convenient to use the actual ambient medium of ϵ_1 as the comparison medium in our energy formulation. Unquestionably, the physics of the body and ambient medium shall not depend on the choice of comparison medium. We are therefore motivated to seek a general transformation of $\Pi \rightarrow \Pi' = T(\Pi)$ such that the free energy of the system remains invariant:

$$\hat{F}[T(\Pi)] = \hat{F}[\Pi]. \quad (5.15)$$

To find the transformation, we require that the total electric field $\mathbf{E}^t = -\nabla\xi^t$ remain invariant and satisfy the same equations as (2.5) with the permittivity $\epsilon_c = \epsilon_0$ being replaced by $\epsilon_c = \epsilon_1$. This determines

$$\epsilon_c = \epsilon_0 \rightarrow \epsilon_c = \epsilon_1, \quad \mathbf{P} \rightarrow \mathbf{P}' = \mathbf{P} + (\epsilon_0 - \epsilon_1)\mathbf{E}^t, \quad (5.16)$$

which also guarantees the invariance of electric displacement and potential energy $P[\rho, \mathbf{P}]$ (cf., (2.11)). In addition, we require the total field energy is again given by (2.12) but with ϵ_0 replaced by ϵ_1 :

$$\mathcal{E}^t[\rho, \mathbf{P}] \rightarrow \mathcal{E}^{t'}[\rho, \mathbf{P}'] = \frac{\epsilon_1}{2} \int_V |\nabla\xi^t|^2.$$

Finally, the invariance of free energy requires that

$$U[\rho, \mathbf{P}] \rightarrow U'[\rho, \mathbf{P}'] = \int_V \Phi(\mathbf{P}) + \frac{\epsilon_0 - \epsilon_1}{2} \int_V |\nabla\xi^t|^2. \quad (5.17)$$

Recall that by the constitutive law, i.e., the last of (3.44) and (3.45), and (5.16) we have

$$\mathbf{P}' = \mathbf{P} + (\epsilon_0 - \epsilon_1)\hat{\mathbf{E}}(\mathbf{P}) \quad \text{on } V. \quad (5.18)$$

Assume the above mapping $\mathbf{P} \mapsto \mathbf{P}'$ is invertible and denote by the inverse mapping by $\mathbf{P}' \mapsto \mathbf{P} = \mathbf{q}(\mathbf{P}')$. Then equation (5.17) determines the transformation of the internal energy density function as

$$\Phi(\mathbf{P}) \rightarrow \Phi'(\mathbf{P}') = \Phi(\mathbf{q}(\mathbf{P}')) + \frac{\epsilon_0 - \epsilon_1}{2} |\hat{\mathbf{E}}(\mathbf{q}(\mathbf{P}'))|^2 \quad \text{on } V. \quad (5.19)$$

We henceforth obtain the transformation

$$T(\Pi) = \Pi', \quad \Pi' = (\epsilon_1, \mathbf{P}', \Phi') \quad (\text{defined by (5.16) and (5.19)}), \quad (5.20)$$

which may be regarded as a symmetry group of the free energy functional with one continuous parameter ϵ_1 . From this viewpoint, it makes more physical sense to directly postulate the existence of an ϵ_c -dependent internal energy density $\tilde{\Phi}(\mathbf{P}, \epsilon_c)$, e.g., $\tilde{\Phi}(\mathbf{P}, \epsilon_c) = \frac{1}{2}\mathbf{P} \cdot (\boldsymbol{\epsilon} - \epsilon_c\mathbf{I})^{-1}\mathbf{P}$ for a linear dielectric medium with permittivity tensor $\boldsymbol{\epsilon}$ ²⁰. In particular, we may choose $\epsilon_c = 0$. Then at the absence of Robin boundary (i.e., $\Gamma_R = \emptyset$), by (2.14) the free energy is given by

$$\tilde{F}[\mathbf{P}] = \int_V \tilde{\Phi}(\mathbf{P}, 0) + \int_{\partial V} \xi_b \mathbf{n} \cdot [\mathbf{P} + \mathbf{P}^e], \quad (5.21)$$

²⁰The internal energy function $\tilde{\Phi}(\mathbf{P}, \epsilon_c)$ shall be such that the free energy (total electric field and electric displacement) remain invariant with respect to transformations (5.20). It will be interesting to have a simple explicit characterization of such energy functions without assuming the invertibility of the mapping in (5.18).

which appears to be exceptionally simple. The trade-off is that, by (2.5), the polarization now has to satisfy a differential constraint

$$\operatorname{div}(\mathbf{P} + \mathbf{P}^e) = \rho^e \quad \text{on } V. \quad (5.22)$$

In spite of the above differential constraint, we anticipate that the free energy functional (5.21) will be convenient for analysis of ferroelectric media for which $\mathbf{P} \mapsto \tilde{\Phi}(\mathbf{P}, 0)$ is nonconvex.

On the other hand, if the extended system consist of an inhomogeneous inclusion Ω immersed in an ambient medium of isotropic linear permittivity ϵ_1 on $V \setminus \Omega$, by sending $\epsilon_c \rightarrow \epsilon_1$ we obtain that the free energy is given by

$$\tilde{F}[\mathbf{P}] = \int_{\Omega} \Phi(\mathbf{P}, \epsilon_1) + \int_V \frac{\epsilon_1}{2} |\nabla \xi^t|^2 + \int_{\Gamma_R} \frac{1}{2} k (\xi^t)^2 + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot [-\epsilon_1 \nabla \xi^t + \mathbf{P} + \mathbf{P}^e],$$

where we necessarily require the matrix $V \setminus \Omega$ be unpolarizable, i.e., $\mathbf{P} = 0$ on $V \setminus \Omega$ to keep the free energy finite. If we further increase the comparison medium such that $\epsilon_c > \epsilon_1$, then by (2.21) it can be shown that a stationary polarization (i.e., polarization determined by (2.5) and (2.32)) cannot be a local minimizer of $\tilde{F}[\mathbf{P}]$ in the admissible space \mathcal{P} (cf., (2.31)). This of course does not mean our free energy formula or the principle of minimum free energy fails; the paradox arises from that \mathcal{P} is now no longer a “physical” admissible space for the state variable.

We remark that the above symmetry of free energy functional with respect to the comparison medium (cf. (5.20)) is not entirely new. It has been briefly mentioned in Landau *et al* (1995, §12) and tacitly used in many calculations concerning electrostatic forces on a subbody immersed in a fluid, etc. Moreover, general transformations for which the ambient or background medium is non-uniform can be similarly found. In this case, the total field energy is given by $\int_V \frac{\epsilon_c(\mathbf{x})}{2} |\nabla \xi^t|^2$ which can be identified as $\int_V \frac{1}{2} \mathbf{E}^t \cdot \mathbf{D}^t$ for a linear dielectric medium upon choosing $\epsilon_c(\mathbf{x})$ being the actual permittivity in V .

6 A variational formulation without introducing polarization

As mentioned above, the second of the Euler-Lagrange equations (2.32) associated with the principle of minimum free energy can be interpreted as a constitutive relation between the (local) polarization and total electric field if the internal energy density $\Phi = \Phi(\mathbf{P})$ is independent of $\nabla \mathbf{P}$:

$$\mathbf{E} = -\nabla \xi^t = \hat{\mathbf{E}}(\mathbf{P}) := D_{\mathbf{P}} \Phi(\mathbf{P}). \quad (6.1)$$

Suppose that the above mapping $\mathbf{P} \mapsto \hat{\mathbf{E}}(\mathbf{P})$ is invertible^{21,22}, and denote the inverse mapping by $\hat{\mathbf{P}} : \mathbb{R}^3 \rightarrow \mathbb{R}^3$, i.e.,

$$\hat{\mathbf{P}}(\mathbf{E}) = \mathbf{P} \quad \text{if} \quad \mathbf{E} = \hat{\mathbf{E}}(\mathbf{P}) \quad \forall \mathbf{P} \in \mathbb{R}^3. \quad (6.2)$$

Inserting the above constitutive equation into (2.5) we obtain the following boundary problem for determining the total field $-\nabla \xi^t$:

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^t + \hat{\mathbf{P}}(-\nabla \xi^t) \chi_{\Omega} + \mathbf{P}^e] = \rho^e & \text{on } V, \\ \xi^t - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^t - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \hat{\mathbf{P}}(-\nabla \xi^t) \chi_{\Omega} + \mathbf{P}^e] - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (6.3)$$

²¹This assumption is for the sake of proving the equivalence of different variational formulations. It would be unnecessary if the relations between different formulations are of no interest.

²²A somewhat natural but more restrictive assumption is to require $\mathbf{P} \mapsto \Phi(\mathbf{P})$ is strictly convex on V , which is satisfied by linear dielectric media. This assumption eliminates the possibility of microstructuring between multiple equilibria.

In principle we may solve the above boundary value problem for $-\nabla\zeta^t$, and then by the constitutive law determine polarization as well as other quantities of interest. From this viewpoint, the key in analyzing electrostatics of continuum bodies still hinges on solving (6.3) — the Maxwell's equations with a general constitutive law.

It is always possible to identify an energy functional with its Euler-Lagrange equation equivalent to the boundary value problem (6.3) *without introducing the concept of polarization at all*. To see this, we consider an energy functional

$$H[\zeta] = \int_V [W(\mathbf{x}, -\nabla\zeta) - \rho^e\zeta - \mathbf{P}^e \cdot \nabla\zeta] + \int_{\Gamma_R} \left[\frac{1}{2}k\zeta^2 - \zeta(k\xi_b + \sigma_0) \right]. \quad (6.4)$$

where $W(\mathbf{x}, \cdot) : \mathbb{R}^3 \rightarrow \mathbb{R}$ is an energy density as a function of total electric field, and $\rho^e, \mathbf{P}^e, k, \xi_b, \sigma_0$ are defined as in §2.1. Below the \mathbf{x} -dependence of W is sometimes dropped for brevity. Denote by

$$D_{\mathbf{E}}W(\mathbf{E}) = \frac{\partial W(\mathbf{E})}{\partial \mathbf{E}}.$$

Further, in terms of a scalar potential ζ we consider the variational problem:

$$\min_{\zeta \in \mathbb{W}_{\xi_b}} H[\zeta], \quad \mathbb{W}_{\xi_b} := \{\zeta \in \mathbb{W} : \zeta = \xi_b \text{ on } \Gamma_D\}. \quad (6.5)$$

Standard first variation calculations show that the Euler-Lagrange equation associated with (6.5) is given by

$$\begin{cases} \operatorname{div}[D_{\mathbf{E}}W(-\nabla\zeta) + \mathbf{P}^e] = \rho^e & \text{on } V, \\ \zeta - \xi_b = 0 & \text{on } \Gamma_D, \\ -[D_{\mathbf{E}}W(-\nabla\zeta) + \mathbf{P}^e] \cdot \mathbf{n} + k(\zeta - \xi_b) - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (6.6)$$

Comparing (6.6) with (6.3), we see that the two boundary value problems will be exactly the same if for any $\mathbf{E} \in \mathbb{R}^3$,

$$D_{\mathbf{E}}W(\mathbf{E}) = \epsilon_c \mathbf{E} + \hat{\mathbf{P}}(\mathbf{E})\chi_{\Omega} \quad \text{on } V.$$

Let $\Phi^* : \mathbb{R}^3 \rightarrow \mathbb{R}$ be such that $D_{\mathbf{E}}\Phi^* = \hat{\mathbf{P}}(\mathbf{E})$ for any $\mathbf{E} \in \mathbb{R}^3$ ²³. Then if the energy density function $W(\mathbf{E})$ is chosen as

$$W(\mathbf{E}) = \frac{\epsilon_c}{2}|\mathbf{E}|^2 + \Phi^*(\mathbf{E})\chi_{\Omega} \quad \text{on } V, \quad (6.8)$$

comparing (6.6) with (6.3) we find the variational principle (6.5) imply the same Euler-Lagrange equations as (2.22), and hence the same electric fields, electric displacements, etc if the solution to (6.3) is unique (within a constant).

²³By (6.1) we have $\frac{\partial \hat{E}_i}{\partial P_j} = \frac{\partial^2 \Phi}{\partial P_i \partial P_j}$, and hence by (6.2), $[\frac{\partial \hat{P}_i}{\partial E_j}] = \left[\frac{\partial^2 \Phi}{\partial P_i \partial P_j}(\hat{\mathbf{P}}(\mathbf{E})) \right]^{-1}$. That is, $\frac{\partial \hat{P}_i}{\partial E_j} = \frac{\partial \hat{P}_j}{\partial E_i}$. Therefore, there exists a scalar function $\mathbf{E} \mapsto \Phi^*(\mathbf{E})$ such that $D_{\mathbf{E}}\Phi^*(\mathbf{E}) = \hat{\mathbf{P}}(\mathbf{E})$. Clearly, there is an arbitrary integration constant in $\Phi^*(\mathbf{E})$, which is subsequently determined by requiring that $\Phi(\hat{\mathbf{P}}(0)) + \Phi^*(0) = 0$. Then we have that if (6.1) (or, equivalently, (6.2)) is invertible,

$$\Phi(\mathbf{P}) + \Phi^*(\mathbf{E}) = \mathbf{P} \cdot \mathbf{E} \quad (6.7)$$

since $\frac{\partial}{\partial P_i} [\Phi(\mathbf{P}) + \Phi^*(\hat{\mathbf{E}}(\mathbf{P})) - \mathbf{P} \cdot \hat{\mathbf{E}}(\mathbf{P})] = E_i + P_j \frac{\partial \hat{E}_j}{\partial P_i} - E_i - P_j \frac{\partial \hat{E}_j}{\partial P_i} = 0$.

Two remarks are in order regarding the non-uniqueness of variational principles corresponding to an equivalent set of *field* equations and boundary conditions. First, the free energy and the principle of minimum free energy, being thermodynamic concepts, clearly cannot be inferred from the field equations and constitutive laws (1.1). This is of critical importance in analyzing quasi-static evolutions, e.g., phase transitions, of the system since, as one will see shortly (cf., (6.9)), \tilde{F} being the free energy implies opposite force on an internal variable of the system to the force implied by H being the free energy²⁴. Further, one may be motivated to ponder on the microscopic foundation of the physical concept of “polarization” and whether it is needed at all for electrostatics at a fundamental level. There appears to be no simple uncontentious answer to this question. At the practical level, the concept of polarization is obviously convenient for many physical and mathematical reasonings, though it gives rise to quite a bit confusions as well from its ambient-medium-dependent nonlocal characteristics.

Further, when the system or the extended system are in equilibrium (i.e., (6.6) is satisfied), the two energies are related by

$$\tilde{F}[\mathbf{P}] + H[\xi^t] = 0, \quad (6.9)$$

which may be regarded as a generalization of the underlying identity enabling us to estimate the effective properties of composites by well-known Hashin-Shtrikman variational principle. To see this, we notice that the bulk integrals in the sum of (6.4) and (2.14) are given by

$$\begin{aligned} & \int_V \left[W(-\nabla \xi^t) - \rho^e \xi^t - \mathbf{P}^e \cdot \nabla \xi^t + \chi_\Omega \Phi(\mathbf{P}) + \frac{\epsilon_c}{2} |\nabla \xi^t|^2 \right] \\ &= \int_V \left[-\rho^e \xi^t - \mathbf{P}^e \cdot \nabla \xi^t - \mathbf{P} \cdot \nabla \xi^t + \epsilon_c |\nabla \xi^t|^2 \right] \quad (\text{cf., (6.7), (6.8)}) \\ &= - \int_{\partial V} \xi^t \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}) \quad (\text{cf., the first of (2.15) with } \zeta = \xi^t) \\ &= \int_{\Gamma_R} \xi^t (-k \xi^t + k \xi_b + \sigma_0) - \int_{\Gamma_D} \xi^t \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}^e + \mathbf{P}), \end{aligned}$$

which precisely cancels the the surface integrals in the sum of (6.4) and (2.14).

For clarity we summarize below.

Theorem 1 *Let $V, \Gamma_D, \Gamma_R, \xi^t, \rho^e, \mathbf{P}^e, k, \sigma_0, \xi_b$ be defined as in §2.1. Consider two functionals \tilde{F}, H given by*

$$\begin{aligned} \tilde{F}[\mathbf{P}] &= \int_V \left[\Phi(\mathbf{P}) \chi_\Omega + \frac{\epsilon_c}{2} |\nabla \xi^t|^2 \right] + \int_{\Gamma_R} \frac{1}{2} k (\xi^t)^2 + \int_{\Gamma_D} \xi_b \mathbf{n} \cdot [-\epsilon_c \nabla \xi^t + \mathbf{P} + \mathbf{P}^e], \\ H[\zeta] &= \int_V [W(-\nabla \zeta) - \rho^e \zeta - \mathbf{P}^e \cdot \nabla \zeta] + \int_{\Gamma_R} \left[\frac{1}{2} k \zeta^2 - \zeta (k \xi_b + \sigma_0) \right], \end{aligned}$$

respectively. If for any $\mathbf{x} \in \Omega$ the mapping defined by (6.1) is invertible, the function W is given by (6.8), and the pair (\mathbf{P}, ξ^t) satisfy $\mathbf{P} = \chi_\Omega \hat{\mathbf{P}}(-\nabla \xi^t)$ and (6.3) (i.e., are stationary points of \tilde{F} and H , respectively), then the identity (6.9) holds. If, in addition, $\mathbf{P} \mapsto \Phi(\mathbf{P})$ is strictly convex on V , then both stationary points (\mathbf{P}, ξ^t) are minimizers and henceforth,

$$\min_{\mathbf{P} \in \mathcal{P}} \tilde{F}[\mathbf{P}] + \min_{\zeta \in \mathbb{W}_{\xi_b}} H[\zeta] = 0. \quad (6.10)$$

²⁴In the analogous formulations of elasticity, $H[\zeta]$, instead of $\tilde{F}[\mathbf{P}]$, is the free energy, where ζ is interpreted as displacement and \mathbf{P} as eigenstress.

When specialized to affine Dirichlet boundary conditions, the above theorem establishes the relation between the well-known Hashin-Shtrikman variational principle and the effective properties of composites.

Theorem 2 *Suppose that V is open bounded, $\rho^e = \mathbf{P}^e = 0$, $\Gamma_D = \partial V$, $\xi_b = -\mathbf{E}_0 \cdot \mathbf{x}$ on ∂V for some $\mathbf{E}_0 \in \mathbb{R}^3$, for any $\mathbf{x} \in \Omega$ the mapping defined by (6.1) is invertible, and that \mathbf{P} , ξ^t satisfy $\mathbf{P} = \hat{\mathbf{P}}(-\nabla \xi^t)$ on V and (6.3). Let $\bar{\mathbf{P}} = \mathop{\text{f}}_V \mathbf{P}$, $\xi = \xi^t + \mathbf{E}_0 \cdot \mathbf{x}$,*

$$W^e(\mathbf{E}_0) := \mathop{\text{f}}_V W(-\nabla \xi^t), \quad \Phi^e(\bar{\mathbf{P}}) := \mathop{\text{f}}_V \left[\Phi(\mathbf{P}) + \frac{\epsilon_c}{2} |\nabla \xi|^2 \right], \quad (6.11)$$

where $\mathop{\text{f}}_V$ denotes the average value of the integrand on V . Then $D_{\mathbf{E}} W^e(\mathbf{E}_0) = \epsilon_c \mathbf{E}_0 + \bar{\mathbf{P}}$, and

$$\Phi^e(\bar{\mathbf{P}}) - \frac{\epsilon_c}{2} |\mathbf{E}_0|^2 + W^e(\mathbf{E}_0) = \bar{\mathbf{P}} \cdot \mathbf{E}_0. \quad (6.12)$$

If, in addition, $\mathbf{P} \mapsto \Phi(\mathbf{P})$ is convex, then

$$\Phi^e(\bar{\mathbf{P}}) = \min_{\mathop{\text{f}}_V \mathbf{P} = \bar{\mathbf{P}}} \mathop{\text{f}}_V \left[\Phi(\mathbf{P}) + \frac{\epsilon_c}{2} |\nabla \xi|^2 \right]$$

and

$$W^e(\mathbf{E}_0) = \frac{\epsilon_c}{2} |\mathbf{E}_0|^2 + \sup_{\bar{\mathbf{P}} \in \mathbb{R}^3} \{ \bar{\mathbf{P}} \cdot \mathbf{E}_0 - \Phi^e(\bar{\mathbf{P}}) \}.$$

We remark that by (6.3), $\xi = \xi^t + \mathbf{E}_0 \cdot \mathbf{x}$ satisfies

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi + \mathbf{P}] = 0 & \text{on } V, \\ \xi = 0 & \text{on } \partial V, \end{cases}$$

and may be interpreted as the ‘‘microscopic’’ electrostatic potential induced by polarization \mathbf{P} .

Proof: Without loss of generality, assume that the volume of domain V is one. Consider a perturbation of the boundary condition $\xi_b \rightarrow \xi'_b = -(\mathbf{E}_0 + \delta \mathbf{a}) \cdot \mathbf{x}$ ($\delta \ll 1$), and denote by $(\mathbf{P}_\delta, \xi_\delta^t)$ the pair satisfying $\mathbf{P}_\delta = \hat{\mathbf{P}}(-\nabla \xi_\delta^t)$ on V and (6.6). Then by definition,

$$W^e(\mathbf{E}_0 + \delta \mathbf{a}) - W^e(\mathbf{E}_0) = - \int_V D_{\mathbf{E}} W(-\nabla \xi^t) \cdot \nabla (\xi_\delta^t - \xi^t) + o(\delta).$$

Since $D_{\mathbf{E}} W(-\nabla \xi^t) = -\epsilon_c \nabla \xi^t + \mathbf{P}$ is divergence free, by the divergence theorem we have

$$\begin{aligned} - \int_V D_{\mathbf{E}} W(-\nabla \xi^t) \cdot \nabla (\xi_\delta^t - \xi^t) &= - \int_{\partial V} (\xi_\delta^t - \xi^t) \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}) \\ &= \delta \mathbf{a} \cdot \int_{\partial V} \mathbf{x} \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}) = \delta \mathbf{a} \cdot \int_V (-\epsilon_c \nabla \xi^t + \mathbf{P}). \end{aligned}$$

Therefore,

$$D_{\mathbf{E}} W^e(\mathbf{E}_0) = \int_V (-\epsilon_c \nabla \xi^t + \mathbf{P}), \quad \text{i.e.,} \quad \bar{\mathbf{P}} = \int_V \mathbf{P} = D_{\mathbf{E}} W^e(\mathbf{E}_0) - \epsilon_c \mathbf{E}_0. \quad (6.13)$$

In addition, the boundary integral in $\tilde{F}[\mathbf{P}]$ is given by

$$\int_{\partial V} -(\mathbf{E}_0 \cdot \mathbf{x}) \mathbf{n} \cdot (-\epsilon_c \nabla \xi^t + \mathbf{P}) = -\mathbf{E}_0 \cdot D_{\mathbf{E}} W^e(\mathbf{E}_0) = -\epsilon_c |\mathbf{E}_0|^2 - \mathbf{E}_0 \cdot \bar{\mathbf{P}}. \quad (6.14)$$

Equation (6.12) follows by inserting (6.11), (6.13) and (6.14) into (6.9). ■

The above theorem shows that the Hashin-Shtrikman type estimates on energies can be similarly derived for inhomogeneous media of any microstructure; an underlying homogenization theory is *not* needed for such estimates.

7 Applications

7.1 Maxwell stress

In continuum mechanics, it is often convenient to express balance laws as pointwise differential equations. Also, non-smooth distributions of charge density and polarization are frequently encountered in a continuum medium, e.g., a conductor and a heterogeneous dielectric medium with sharp interfaces. We are therefore motivated to seek a local differential form of the force formula (2.26), i.e., a tensor field $\mathbf{T} : V \rightarrow \mathbb{R}^{3 \times 3}$, such that ²⁵

$$\operatorname{div} \mathbf{T} = \mathbf{b} := -\rho^t \nabla \xi^t - (\nabla \nabla \xi^t) \mathbf{P}^t \quad \text{on } V, \quad (7.1)$$

where the vector field $\mathbf{b} : V \rightarrow \mathbb{R}^3$ can be interpreted as a body force due to electrostatic interactions, and div operates on the row vectors of \mathbf{T} . By the divergence theory, the force on a subdomain $\mathcal{P} \subset V$ can then be rewritten as

$$\mathbf{f} = \int_{\mathcal{P}} \operatorname{div} \mathbf{T} = \int_{\partial \mathcal{P}} \mathbf{T} \mathbf{n}, \quad (7.2)$$

where the last equality requires the tensor field \mathbf{T} be continuous up to $\partial \mathcal{P}$.

We now solve (7.1) for \mathbf{T} . First, we notice that solutions are not unique, even if a boundary condition is supplemented. If \mathbf{T} is a solution to (7.1), then $\mathbf{T} + \mathbf{T}_0$ is also a solution for any tensor field $\mathbf{T}_0 : V \rightarrow \mathbb{R}^{3 \times 3}$ satisfying

$$\begin{cases} \operatorname{div} \mathbf{T}_0 = 0 & \text{on } V, \\ \mathbf{T}_0 \mathbf{n} = 0 & \text{on } \partial V. \end{cases}$$

To find a special solution to (7.1), for simplicity we assume (ρ^t, \mathbf{P}^t) are smooth on V . Then by (2.5) we find that for any $\mathbf{x} \in V$,

$$\begin{cases} \operatorname{div} [(-\nabla \xi^t) \otimes (-\epsilon_c \nabla \xi^t + \mathbf{P}^t)] = (\nabla \nabla \xi^t) (\epsilon_c \nabla \xi^t - \mathbf{P}^t) - \rho^t \nabla \xi^t, \\ \nabla \left(\frac{\epsilon_c}{2} |\nabla \xi^t|^2 \right) = \epsilon_c \nabla \nabla \xi^t (\nabla \xi^t). \end{cases} \quad (7.3)$$

Recall that $\mathbf{E}^t = -\nabla \xi^t$ is the total electric field, $\mathbf{D}^t = \epsilon_c \mathbf{E}^t + \mathbf{P}^t$ is the total electric displacement and \mathbf{I} is the identity matrix. We define the *Maxwell stress* as

$$\mathbf{T}_M = \mathbf{E}^t \otimes \mathbf{D}^t - \frac{\epsilon_c}{2} |\mathbf{E}^t|^2 \mathbf{I}. \quad (7.4)$$

By (7.3), we have

$$\operatorname{div} \mathbf{T}_M = -\rho^t \nabla \xi^t - (\nabla \nabla \xi^t) \mathbf{P}^t = \mathbf{b} \quad \text{on } V.$$

We remark that for non-smooth (ρ^t, \mathbf{P}^t) such that $\nabla \nabla \xi^t$ is unbounded, the physical meaning of Maxwell stress and the right hand side of (7.1) shall be interpreted according to the right hand

²⁵It is more natural to study Maxwell stress on the entire domain V instead of being restricted to Ω . Clearly, the force equation (2.26) applies to external distribution of charges and polarizations as well.

side of (7.2) which has less stringent requirement on the differentiability of ξ^t . In particular, we can conclude that the Maxwell stress and hence the body force on any subdomain $\mathcal{P} \subset V$ is well-defined for (ρ^t, \mathbf{P}^t) such that ξ^t is Lipschitz continuous (i.e., $W^{1,\infty}$), e.g., (ρ^t, \mathbf{P}^t) is piecewise smooth and bounded on V .

The reader may have noticed that the permittivity used in (7.4) is that of the ambient medium ϵ_c instead of the local permittivity in some derivations, e.g., Stratton (1941, p. 137). A heuristic explanation is as follows: the perturbation (2.27) is disruptive for displacement; the gap between the perturbed subbody \mathcal{P}_δ and the rest of body $\Omega \setminus \mathcal{P}$ has zero polarization, i.e., filled with the “unpolarizable” ambient medium with zero internal energy whereas in the derivation of Stratton (1941, p. 137) the perturbation is required to be continuous in terms of displacement. Moreover, in regard of the freedom in choosing the comparison or background medium (cf. § 5), the body force (7.1) arising from “electrostatic interactions” depends on the background medium or the definition of total field energy. Therefore, the formulation of mechanical balance laws and boundary conditions requires particular cautions but will not be addressed here; the interested reader is referred to Pao (1978) and reference therein for elaborated discussions.

7.2 Forces on a point charge and dipole and boundary effects

In applications of field-controlled self-assembly, separation and concentration, electric or magnetic suspensions, electric or magnetic tweezers, etc, it is of interest to calculate the force on a point charge and dipole in the presence of a boundary device. In addition to a point charge q or point dipole \mathbf{p} at $\mathbf{x}_0 \in \Omega$ (without loss of generality, assume \mathbf{x}_0 is the origin), we assume there are smooth charge density ρ^{rg} and polarization \mathbf{P}^{rg} on V . That is, the total charge and polarization is given by

$$(\rho^t, \mathbf{P}^t) = (\rho^{rg}, \mathbf{P}^{rg}) + (q, 0)\delta_0 \quad \text{or} \quad (\rho^t, \mathbf{P}^t) = (\rho^{rg}, \mathbf{P}^{rg}) + (0, \mathbf{p})\delta_0,$$

where δ_0 is the Dirac function at the origin. We first consider a point charge. Clearly, the total field is given by

$$\mathbf{E}^t = \mathbf{E}^{rg} + \mathbf{E}^{pt}, \quad \mathbf{E}^{pt} = -\nabla \xi^{pt} = \frac{1}{4\pi\epsilon_c} \frac{q\mathbf{e}_r}{r^2},$$

where $\mathbf{e}_r = \mathbf{x}/|\mathbf{x}|$ is the radian unit vector,

$$\xi^{pt} = \frac{1}{4\pi\epsilon_c} \frac{q}{r}$$

is the electrostatic potential of the point charge q in \mathbb{R}^3 , and the regular field $\mathbf{E}^{rg} = -\nabla \xi^{rg}$ is smooth and bounded on a neighborhood of the origin, satisfying

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^{rg} + \mathbf{P}^{rg}] = \rho^{rg} & \text{on } V, \\ \xi^{rg} + \xi^{pt} - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^{rg} + \xi^{pt} - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla (\xi^{rg} + \xi^{pt}) + \mathbf{P}^{rg}] - \sigma_0 = 0 & \text{on } \Gamma_R. \end{cases} \quad (7.5)$$

As usual we denote by

$$\mathbf{D}^{rg} = \epsilon_c \mathbf{E}^{rg} + \mathbf{P}^{rg}, \quad \nabla \cdot \mathbf{D}^{rg} = \rho^{rg}. \quad (7.6)$$

The force on the point charge may be calculated as follows. First, let ρ_ϵ be a smooth sequence of smeared point charges. Let B_η be a fixed ball centered at the origin of radius η . As $\epsilon \rightarrow 0$, the

total field on ∂B_η converges to the limit \mathbf{E}^t uniformly. By (7.2) the force on the ball B_η is given by

$$\mathbf{f}_\eta = \int_{\partial B_\eta} \left[(\mathbf{E}^{rg} + \mathbf{E}^{pt}) \otimes (\mathbf{D}^{rg} + \epsilon_c \mathbf{E}^{pt}) - \frac{\epsilon_c |\mathbf{E}^{rg} + \mathbf{E}^{pt}|^2}{2} \mathbf{I} \right] \mathbf{e}_r.$$

Expanding the integrand on the right hand side of the above equation we obtain

$$\begin{aligned} \mathbf{f}_\eta = \int_{\partial B_\eta} \left[\mathbf{E}^{rg}(\mathbf{D}^{rg} \cdot \mathbf{e}_r) + \mathbf{E}^{pt}(\mathbf{D}^{rg} \cdot \mathbf{e}_r) + \epsilon_c \mathbf{E}^{rg}(\mathbf{E}^{pt} \cdot \mathbf{e}_r) + \epsilon_c \mathbf{E}^{pt}(\mathbf{E}^{pt} \cdot \mathbf{e}_r) \right. \\ \left. - \epsilon_c (\mathbf{E}^{rg} \cdot \mathbf{E}^{pt}) \mathbf{e}_r - \frac{\epsilon_c}{2} (|\mathbf{E}^{rg}|^2 + |\mathbf{E}^{pt}|^2) \mathbf{e}_r \right]. \end{aligned}$$

Since \mathbf{E}^{rg} and \mathbf{D}^{rg} are smooth and bounded on ∂B_η , we estimate the right hand side of the above equation term by term as follows:

$$\begin{aligned} \int_{\partial B_\eta} \mathbf{E}^{rg}(\mathbf{D}^{rg} \cdot \mathbf{e}_r) &= O(\eta^2), \\ \int_{\partial B_\eta} \mathbf{E}^{pt}(\mathbf{D}^{rg} \cdot \mathbf{e}_r) &= \int_{\partial B_\eta} \mathbf{E}^{pt}[\mathbf{e}_r \cdot \mathbf{D}^{rg} + r \mathbf{e}_r \cdot (\nabla \mathbf{D}^{rg}) \mathbf{e}_r + \dots] = \frac{1}{3\epsilon_c} q \mathbf{D}^{rg} + O(\eta^2), \\ \epsilon_c \int_{\partial B_\eta} \mathbf{E}^{rg}(\mathbf{E}^{pt} \cdot \mathbf{e}_r) &= \frac{1}{4\pi} \int_{\partial B_\eta} \mathbf{E}^{rg} \frac{q}{r^2} = q \mathbf{E}^{rg} + O(\eta^2), \\ \epsilon_c \int_{\partial B_\eta} \mathbf{E}^{pt}(\mathbf{E}^{pt} \cdot \mathbf{e}_r) &= \frac{1}{4\pi} \int_{\partial B_\eta} \mathbf{E}^{pt} \frac{q}{r^2} = 0, \\ \epsilon_c \int_{\partial B_\eta} \mathbf{e}_r(\mathbf{E}^{pt} \cdot \mathbf{E}^{rg}) &= \frac{1}{3} q \mathbf{E}^{rg} + O(\eta^2), \\ \int_{\partial B_\eta} \frac{\epsilon_c}{2} (|\mathbf{E}^{rg}|^2 + |\mathbf{E}^{pt}|^2) \mathbf{e}_r &= O(\eta^2), \end{aligned}$$

where all fields and their derivatives on the right hand sides of the above equations are evaluated at the origin. In addition, we have made use of the following identities:

$$\int_{\partial B_\eta} \mathbf{e}_r \otimes \mathbf{e}_r = \frac{4\pi\eta^2}{3} \mathbf{I}, \quad \int_{\partial B_\eta} \mathbf{e}_r = 0, \quad \int_{\partial B_\eta} \mathbf{e}_r \otimes \mathbf{e}_r \otimes \mathbf{e}_r = 0.$$

Therefore, upon sending $\eta \rightarrow 0$, by (7.6) we conclude that the force on the point charge and point dipole at the origin is given by

$$\mathbf{f} = q \mathbf{E}^{rg} + \frac{1}{3\epsilon_c} q \mathbf{P}^{rg} \Big|_{\mathbf{x}=0}. \quad (7.7)$$

By regarding a point dipole as the limit of two opposite equal charge q separated by \mathbf{p}/q and sending $q \rightarrow +\infty$, by (7.7) we find the force on a point dipole \mathbf{p} is given by

$$\mathbf{f} = \mathbf{p} \cdot \nabla \mathbf{E}^{rg} + \frac{1}{3\epsilon_c} \mathbf{p} \cdot \nabla \mathbf{P}^{rg} \Big|_{\mathbf{x}=0}. \quad (7.8)$$

We remark that the dependence of the force on the local polarization may appear to be somewhat strange. However, it is consistent with an intuitive expectation. That is, by symmetry the force experienced by a point charge should not change if an infinitesimal ball around the point charge

of uniform polarization is removed. Indeed, in this process, the change of polarization and electric field is given by

$$\mathbf{E}^{rg}(0) \rightarrow \mathbf{E}^{rg}(0) + \frac{1}{3\epsilon_c} \mathbf{P}(0), \quad \mathbf{P}(0) \rightarrow 0.$$

and henceforth, the force remains unchanged according to (7.7).

Further, from the definition of regular field (7.9), it is conceptually appealing to decompose it into two parts:

$$-\nabla \xi^{rg} = -\nabla \xi^e - \nabla \xi^{im},$$

where the “external field” is determined by

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi^e + \mathbf{P}^{rg}] = \rho^{rg} & \text{on } V, \\ \xi^e - \xi_b = 0 & \text{on } \Gamma_D, \\ k(\xi^e - \xi_b) - \mathbf{n} \cdot [-\epsilon_c \nabla \xi^e + \mathbf{P}^{rg}] - \sigma_0 = 0 & \text{on } \Gamma_R, \end{cases} \quad (7.9)$$

and the “image field” is determined by²⁶

$$\begin{cases} -\epsilon_c \Delta \xi^{im} = 0 & \text{on } V, \\ \xi^{im} + \xi^{pt} = 0 & \text{on } \Gamma_D, \\ k(\xi^{im} + \xi^{pt}) + \epsilon_c \mathbf{n} \cdot \nabla(\xi^{im} + \xi^{pt}) = 0 & \text{on } \Gamma_R. \end{cases} \quad (7.10)$$

In the absence of regular external sources (i.e., $\mathbf{P}^{rg} = \rho^{rg} = \xi_b = \sigma_0 = 0$), the regular field consists only of image field and the force formula (7.7) characterizes the “self-interaction” of the point charge or dipole mediated by the boundary.

As an example, we assume V is the half-space $\{z > 0\}$ and consider a point charge q at $(0, 0, h)$. Assume $\Gamma_R = \{(x, y, z) : z = 0\}$ and $\mathbf{P}^{rg} = \rho^{rg} = \xi_b = \sigma_0 = 0$. Clearly, the external field $-\nabla \xi^e = 0$. By (7.7) we have

$$\mathbf{f} = -\frac{q^2}{4\pi\epsilon_c(2h)^2} \mathbf{e}_z \quad \text{if } k \rightarrow +\infty \text{ (Dirichlet);} \quad \frac{q^2}{4\pi\epsilon_c(2h)^2} \mathbf{e}_z \quad \text{if } k = 0 \text{ (Neumann).}$$

Note that the above force is independent of the sign of the charge, attractive for Dirichlet boundary condition, repulsive for Neumann boundary condition, and scales as $1/h^2$ ²⁷. Moreover, if the point charge is replaced by a point dipole \mathbf{p} at h , the force on the dipole is clearly given by

$$\mathbf{f} = -\frac{|\mathbf{p}|^2}{4\pi\epsilon_c(2h)^2} \mathbf{e}_z \quad \text{if } k \rightarrow +\infty \text{ (Dirichlet);} \quad \frac{|\mathbf{p}|^2}{4\pi\epsilon_c(2h)^2} \mathbf{e}_z \quad \text{if } k = 0 \text{ (Neumann),}$$

which is independent of the direction of the dipole \mathbf{p} .

7.3 Effective properties of nonlinear dielectric composites

In the study of heterogeneous media, it is frequently necessary to coarse-grain the original problem and derive the “effective” properties of the medium since fine-scale oscillations are of little interest

²⁶In the context of linear elasticity this concept was introduced by Eshelby (1957, 1961).

²⁷Repulsion between a charge and a Neumann boundary is really not a surprise if one thinks of the analogous interaction between a superconductor and a magnet.

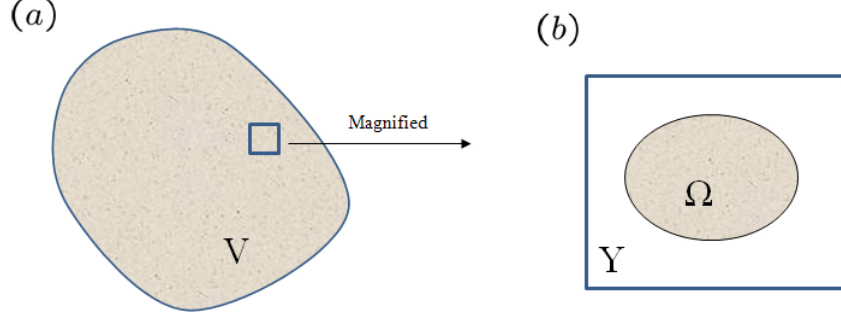


Figure 3: A two-phase composite: (a) the overall composite body; (b) a representative volume element of a rectangular unit cell with an inclusion.

from a macroscopic viewpoint. In this section we consider, as illustrated in Fig. 3, a model of two-phase dielectric composites with a periodic array of identical particles embedded in a linear isotropic matrix of permittivity ϵ_c . Let Y be a unit cell or a representative volume element associated with the periodicity, $\Omega \subset Y$ be the domain occupied by the particle, and $\theta = |\Omega|/|Y|$ be the volume fraction of the particles. The dielectric behavior of the particle is prescribed by a smooth, nonnegative, (not necessarily convex) internal energy density function $\Phi : \mathbb{R}^3 \rightarrow \mathbb{R}$. We assume that the overall composite body V is much larger than the particle (i.e., scale-separation). Then the macroscopic coarse-grained behavior of the composite may be well described by an effective internal energy density:

$$\Phi^e(\bar{\mathbf{P}}) := \min_{\mathbf{P} \in \mathcal{P}(\bar{\mathbf{P}})} \left\{ \theta \int_{\Omega} \Phi(\mathbf{P}) + \frac{\epsilon_c}{2} \int_Y |\nabla \xi|^2 \right\}, \quad (7.11)$$

where $\bar{\mathbf{P}} \in \mathbb{R}^3$ is the average polarization on a unit cell Y ,

$$\mathcal{P}(\bar{\mathbf{P}}) := \left\{ \mathbf{P} : \int_Y \mathbf{P} = \bar{\mathbf{P}}, \mathbf{P} = 0 \text{ on } Y \setminus \Omega \right\}, \quad (7.12)$$

and the microscopic electric field $-\nabla \xi$ is determined by

$$\begin{cases} \operatorname{div}[-\epsilon_c \nabla \xi + \mathbf{P} \chi_{\Omega}] = 0 & \text{on } Y, \\ \text{periodic boundary conditions} & \text{on } \partial Y. \end{cases} \quad (7.13)$$

The difficulty in calculating the effective internal energy density arises from the last term on the right hand side of (7.11) for its nonlocal dependence on the state variable \mathbf{P} . However, it is well known that equation (7.13) admits a closed-form solution in the dilute limit (i.e., $Y = \mathbb{R}^3$) for a uniformly polarized ellipsoidal Ω . Based on this solution effective properties of dielectric composites has been estimated for composites in the dilute limit (Maxwell, 1873; Milton, 2002, ch. 10), and for finite volume fraction by self-consistent scheme or Mori-Tanaka theory (Benveniste, 1987; Dunn, 1995; Milton, 2002, § 10.5). A second closed-form solution was recently found for uniformly polarized periodic E-inclusions, i.e., Ω is such that the overdetermined problem

$$\begin{cases} \Delta u = \theta - \chi_{\Omega} & \text{on } Y, \\ \nabla \nabla u = -(1 - \theta) \mathbf{Q} & \text{on } \Omega, \\ \text{periodic boundary conditions} & \text{on } \partial Y, \end{cases} \quad (7.14)$$

admits a solution, where the 3×3 shape matrix \mathbf{Q} is symmetric, nonnegative and $\text{Tr}(\mathbf{Q}) = 1$. In the dilute limit and in the context of ferromagnetics, the shape matrix \mathbf{Q} can be identified as the demagnetization matrix of an ellipsoid. Typical periodic E-inclusions for various shape matrix, volume fraction and unit cell have been shown in Liu *et al.* (2007; 2008).

By (7.14) one immediately sees that if $\mathbf{P} = \bar{\mathbf{P}}/\theta$ is uniform on Ω , a solution to (7.13) is given by

$$-\nabla\xi = \frac{1}{\theta\epsilon_c} \nabla(\bar{\mathbf{P}} \cdot \nabla u),$$

and henceforth,

$$\frac{\epsilon_c}{2} \int_Y |\nabla\xi|^2 = \frac{\theta}{2} \int_\Omega \mathbf{P} \cdot \nabla\xi = \frac{1-\theta}{2\theta\epsilon_c} \bar{\mathbf{P}} \cdot \mathbf{Q}\bar{\mathbf{P}}.$$

Let $\Phi^{**} : \mathbb{R}^3 \rightarrow \mathbb{R}$ is the convex envelope of Φ :

$$\Phi^{**}(\mathbf{P}) = \sup\{\varphi(\mathbf{P}) : \varphi \leq \Phi \text{ and } \varphi \text{ is convex}\},$$

and

$$\Phi_L^e(\bar{\mathbf{P}}) := \theta\Phi^{**}(\bar{\mathbf{P}}/\theta) + \frac{1-\theta}{2\theta\epsilon_c} \bar{\mathbf{P}} \cdot \mathbf{Q}\bar{\mathbf{P}}, \quad (7.15)$$

It can be shown that for periodic E-inclusions with shape matrix \mathbf{Q} and volume fraction θ , the effective internal energy density $\Phi^e(\bar{\mathbf{P}})$ is precisely given by $\Phi_L^e(\bar{\mathbf{P}})$. A proof of this statement may be constructed following DeSimone and James (2002, Theorem 4.1; Lemma A.1) and Theorem 2.35 in Dacorogna (2008, p. 52).

Moreover, it is worthwhile noticing a microstructure-independent property of (7.13). Consider three uniform polarizations on an arbitrary domain $\Omega \subset Y$ of volume fraction θ : $\mathbf{P}_i^* = p_0/\theta \mathbf{e}_i \chi_\Omega$ ($i = 1, 2, 3$) for some $p_0 \in \mathbb{R}$, where $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ form an orthonormal basis of \mathbb{R}^3 . Let ξ_i^* be the corresponding solutions to (7.13). Then by Fourier analysis or divergence theorem, we find that

$$\sum_{i=1}^3 \frac{\epsilon_c}{2} \int_Y |\nabla\xi_i^*|^2 = \frac{(1-\theta)p_0^2}{2\theta\epsilon_c}.$$

Then, by (7.11) the above equation implies an upper bound on a summation of effective internal density:

$$\sum_{i=1}^3 \Phi^e(p_0 \mathbf{e}_i) \leq \sum_{i=1}^3 \theta\Phi(p_0/\theta \mathbf{e}_i) + \frac{(1-\theta)p_0^2}{2\theta\epsilon_c}. \quad (7.16)$$

We remark that the above microstructure-independent bound implies the familiar Hashin-Shtrikman bound if Φ is quadratic and convex. If $\Phi(\mathbf{P}) = \alpha|\mathbf{P}|^\beta$ for some $\beta \geq 1$ and $\alpha > 0$ and the effective internal energy is assumed to be ‘‘isotropic’’: $\Phi^e(\mathbf{P}) = \varphi^e(|\mathbf{P}|)$, then by (7.16) we have

$$\varphi^e(p_0) \leq \alpha\theta^{1-\beta}|p_0|^\beta + \frac{(1-\theta)p_0^2}{6\theta\epsilon_c} \quad \forall p_0 \in \mathbb{R}, \quad (7.17)$$

which is an optimal bound since the equality holds for periodic E-inclusions with $\mathbf{Q} = \mathbf{I}/3$, see (7.15). We remark that a lower bound for φ^e can be derived by considering inhomogeneous background comparison medium or the dual variational formulation.

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