

Nonequilibrium electromagnetics: Local and macroscopic fields and constitutive relationships

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We study the electrodynamics of materials using a Liouville-Hamiltonian-based statistical-mechanical theory. Our goal is to develop electrodynamics from an ensemble-average viewpoint that is valid for microscopic and nonequilibrium systems at molecular to submolecular scales. This approach is not based on a Taylor series expansion of the charge density to obtain the multipoles. Instead, expressions of the molecular multipoles are used in an inverse problem to obtain the averaging statistical-density function that is used to obtain the macroscopic fields. The advantages of this method are that the averaging function is constructed in a self-consistent manner and the molecules can either be treated as point multipoles or contain more microstructure. Expressions for the local and macroscopic fields are obtained, and evolution equations for the constitutive parameters are developed. We derive equations for the local field as functions of the applied, polarization, magnetization, strain density, and macroscopic fields.

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I. INTRODUCTION

The goal of this paper is to study electrodynamics in materials using a Liouville-Hamiltonian-based projection-operator statistical-mechanical theory. The motivation for writing this paper evolved from a need to apply electromagnetics at the molecular and submolecular scales, in order to relate single-molecule measurements to theory. The important features of our model include a nonequilibrium statistical-mechanical analysis and definition of the macroscopic and local fields, the self-consistent construction of an averaging function for deriving the macroscopic field from the microscopic field, definitions of the susceptibilities, and a comprehensive development of the constitutive relationships for the current density, polarization, magnetization, and strain density. Nonequilibrium aspects include time-dependent fields and variable temperatures.

Previous pioneering microscopic electromagnetic theories developed by Mazur and Nijboer [1], Robinson [2], and Jackson [3] expand the charge density and the coefficients in the expansion are the multipole moments. The averaged molecular multipoles are treated as point multipoles. This works well down to near the molecular level, but breaks down at the molecular to submolecular level. Using Robertson's theory [4], we use an inverse problem to determine the generalized canonical (relevant) statistical-density averaging function from knowledge of the expected values of the polarization, magnetization, internal-energy density, and strain density. This is then used in the Robertson projection-operator theory [4] to derive constitutive evolution equations. The method uses Lagrange multipliers that turn out to be local fields and inverse temperature. Evolution equations are also found for the material parameters. The closed set of coupled nonlinear equations includes equations for the expected values for the polarization, magnetization, local field and macroscopic fields, and strain density. The correspond-

ing evolution equations for these quantities determines the unknowns, which are the local fields and macroscopic polarization, magnetization, and strain density. The macroscopic electric and magnetic fields are also explicitly defined. The method is self-consistent since the relevant statistical density averaging function is a function of the macroscopic observables and therefore the length scales are intrinsically incorporated.

The projection-operator approach produces expressions for the relevant quantities, subject to constraints, by decomposing the statistical density function into relevant and non-relevant components, so that the macrovariables are decomposed into relevant (reversible) and irrelevant (dissipative or entropy producing) components. In the problem at hand the relevant quantities are the macroscopic electromagnetic fields, the polarization and magnetization, the strain density, and the internal-energy density. This allows concentration on the relevant variables while at the same time not discarding important information in the dissipative parts. The relevant density function used in the projection-operator technique allows a systematic and consistent development of the macroscopic and local electromagnetic fields and constitutive relationships. The projection-operator theory we use in this paper is that developed by Robertson [4]. In a linear approximation the resulting equations satisfy the time-invariance and causality requirements of linear systems theory.

Theoretical analysis of the effective local fields is important in dielectric modeling of single-molecule measurements and thin films. Since electrical measurements can now be performed to very small spatial resolutions, we require good models of the macroscopic and local fields at all spatial levels. This is particularly important since it has been found that the Lorentz theory of the local field is not always adequate for predicting polarizabilities [5,6]. Also, when solving Maxwell's equations at the molecular level, definitions of the macroscopic field and constitutive relationships are important.

Much of the work performed in the past on local fields has been for static fields. Mandel and Mazur developed a static theory for the local field in terms of the polarization

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response of a many-body system using a T -matrix formalism [7]. Gubernatis extended the T -matrix formalism [8]. Keller's [9] review article on the local field used an electromagnetic propagator approach. The work in this paper presents an approach different from Keller's in that we use a projection-operator approach. Kubo's linear-response theory has also been used for electromagnetic correlation studies [10,11]. Grandy has recently presented a theory of nonequilibrium processes based on maximum entropy with new insights into Liouville's equation [12].

When electromagnetic fields are applied to a medium, the fields in the material are composed of the effects of both the applied field and the particle back-reaction fields. For example, when an applied electromagnetic field interacts with a dielectric material, the macroscopic and local fields in the material are modified by surface-charge dipole-depolarization fields that oppose the applied field. When considering time-dependent, high-frequency fields, this interaction is more complex. In addition, there are the effects of the internal energy on the resulting electromagnetic behavior. For example, depolarization, demagnetization, thermal expansion, exchange, and anisotropy interactions can all influence the dipole orientations and therefore the fields. Usually these internal energy effects are modeled by an effective field that modifies the applied field. In constitutive modeling for use in Maxwell's equations, our goal is to express the material properties in terms of the macroscopic field, not the applied or effective fields.

The relationships between the applied, macroscopic, local, and the microscopic fields are all important for constitutive modeling. The applied field originates from external charges, whereas the macroscopic fields are averaged quantities. The macroscopic fields in Maxwell's equations are implicitly defined through the constitutive relationships and boundary conditions. The macroscopic field that satisfies Maxwell's equations with appropriate boundary conditions and constitutive relationships is generally not the same as the applied field. The local field is the averaged electromagnetic field at a particle site due to both the applied field and the fields from all of the other dipoles [11,13]. The microscopic field represents the electromagnetic field at the level of averaging used. For example, if averaged at the molecular level, it is the molecular field, if averaging is carried out at the atomic level, it is the atomic field.

Particles interact with the local electromagnetic field. The spatial and temporal resolution contained in the macroscopic variables is directly related to the spatial and temporal detail incorporated in the constitutive relationships.

The formation of the local field is a very complex process whereby the applied field polarizes charge in a specific molecule. Then the molecule's dipole field modifies the dipole orientations of other molecules in close proximity, which then reacts back to produce a correction to the molecule's field. This process gets more complicated for time-dependent behavior. We define the local electromagnetic field as the effective, averaged field at a specific point in a material, which is a function of both the applied and multipole fields in the media. The local field is related to the average macroscopic and microscopic fields in that it is a sum of the macroscopic field and effects of the near field. In ferroelectricity

the local field can become very large and hence there is a need for comprehensive field models.

In the literature of dielectric materials, a number of specific fields have been introduced to analyze polarization phenomena. The field acting on a nonpolar dielectric is commonly called the internal field, whereas the field acting on a permanent dipole moment is called the directing field. The difference between the internal field and directing fields is the averaged reaction field. The reaction field is the result of a dipole polarizing its environment and does not directly influence the orientation of permanent dipoles.

In electrodynamics there have been many variations of ensemble and volumetric averaging methods used to define the macroscopic fields [1-3,7]. In previous ensemble-averaging approaches an approximation to the full statistical density function is used. In the most commonly used approach to microelectromagnetism, the first level of averaging is the molecular moments to produce effective point multipoles. Then there is the averaging to produce the macroscopic fields. Another type of averaging is for the effective local field. Jackson uses a truncated averaging test function to proceed from the microscale to the macroscale fields [3]. Robinson and Mazur use ensemble averaging [1,2]. In these approaches the averaging function is never really explicitly determined or needed, but the function is assumed to vary in a smooth enough manner to allow a Taylor series expansion of the macroscopic charge density to be performed. In our approach the relevant-density averaging function is determined. It is a function of the macroscopic material properties, produces an averaging in a self-consistent manner, and allows the macroscopic and local fields to be defined in terms of the microscopic fields.

This paper is an extension of our previous work, where we developed constitutive relationships using the same statistical-mechanical theory [14]. Here, we expand and simplify the correlation functions and include stress-strain relationships, develop expressions for the effective local fields, express the polarization either as due to point multipoles or as submolecular multipoles, and develop expressions for the susceptibilities. The inclusion of the stress and strain allows the coupling of the mechanical properties to the electrical properties. We define the macroscopic fields in terms of a relevant-density function, or quantum mechanically, the relevant-density operator. In our approach the relevant-density function (operator) is constructed in a self-consistent fashion from the material properties. The correlation functions are expressions of current-current, current-magnon, phonon-phonon, phonon-magnon, and magnon-magnon interactions. In Sec. III we overview past work on the local field. In Sec. IV we define the microscopic constitutive parameters. In Sec. V we present the time evolution of the constitutive parameters and make various approximations. In Sec. VI we present derivations of the local fields, and then in Sec. VII we discuss a definition of the displacement field.

II. CONSTITUTIVE RELATIONS

In materials, Maxwell's equations are not complete until we specify the constitutive relationships between the macro-

scopic polarization, magnetization, and current density as functions of the macroscopic electric and magnetic fields. The relationship of the polarization, magnetization, and current density to the macroscopic electric, magnetic, and stress fields can be expressed as $\{\mathbf{P}, \mathbf{M}, \mathbf{J}\} \leftrightarrow \{\mathbf{E}, \mathbf{H}, \vec{\Sigma}_E\}$, where the double-headed arrow in this relation indicates that the relationship could be nonlocal in time and space and the constitutive relation may be linear or nonlinear functions of the driving fields [15,16]. The constitutive relations contain the contributions from both the electrical and the mechanical properties such as stress and strain and thermal properties such as temperature. When used in Maxwell's equations, the displacement field \mathbf{D} , the induction field \mathbf{B} , and current density \mathbf{J} must be expressed in terms of the macroscopic electromagnetic fields.

The fields and material-related quantities in Maxwell's equations must satisfy underlying symmetries. For example, the dielectric polarization and electric fields are odd under parity and even under time-reversal transformations. The magnetization and induction fields are even under parity transformation and odd under time reversal. These symmetry relationships place constraints on the nature of the allowed constitutive relationships and require the constitutive relations to manifest related symmetries [1,17–25]. The evolution equations for the constitutive relationships need to be causal and in linear approximations must satisfy time-invariance properties.

In any complex lossy system, there is conversion of energy from one form to another— for example, electromagnetic to thermal energy. The coupling of electromagnetic fields to phonons— that is, lattice vibrations— is through the polariton quasiparticle. Magnetic coupling is through magnons and spin waves. These effects are manifest in the constitutive relations and the resultant permittivity and permeability.

It has been well established that \mathbf{E} and \mathbf{B} are the fundamental electromagnetic fields and have the origin of static charge, moving charge, and spin. However, when free charge is present, there are both free and bound currents and we feel it is more instructive to deal with \mathbf{E} and \mathbf{H} as fields that drive \mathbf{D} and \mathbf{B} . This approach separates the free-charge current density (\mathbf{J}) from the bound-charge current density ($\partial\mathbf{P}/\partial t$). In a statistical-mechanical approach the microscopic fields are electric \mathbf{e} , magnetic \mathbf{h} , polarization \mathbf{p} , quadrupole density \vec{q} , displacement \mathbf{d} , magnetization \mathbf{m} , induction \mathbf{b} , strain density $\vec{\epsilon}_s$, and current density \mathbf{j} . These all depend on the classical phase-space variables or quantum mechanically are operators. The corresponding macroscopic fields \mathbf{E} , \mathbf{H} , \mathbf{P} , \mathbf{D} , \mathbf{M} , \mathbf{B} , $\vec{\epsilon}$, and \mathbf{J} are averaged fields in the material and do not depend on the phase-space variables, but rather only on the macrovariables \mathbf{r} and t [26]. The macroscopic quantities are related in an average sense to the microscopic quantities through the relevant density function. The macroscopic displacement and induction fields \mathbf{D} and \mathbf{B} are related to the macroscopic electric field \mathbf{E} and magnetic field \mathbf{H} , \mathbf{M} , and \mathbf{P} by

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \vec{\mathbf{P}} - \nabla \cdot \vec{\mathbf{Q}} \equiv \epsilon_0 \mathbf{E} + \mathbf{P}, \quad (1)$$

$$\mathbf{B} = \mu_0 \mathbf{H} + \mu_0 \mathbf{M}, \quad (2)$$

and

$$\mathbf{J} = \mathbf{f}(\mathbf{E}, \mathbf{H}), \quad (3)$$

where \mathbf{f} is a function of the electric and magnetic fields, ϵ_0 and μ_0 are the permittivity and permeability of vacuum, and $\vec{\mathbf{Q}}$ is the macroscopic quadrupole moment density. $\vec{\mathbf{P}}$ is the macroscopic dipole-moment density, whereas \mathbf{P} is the effective macroscopic polarization that includes the macroscopic quadrupole-moment density contribution that is needed for origin invariance in Maxwell's equations [1–3,16,27].

III. LOCAL, MICROSCOPIC, AND MACROSCOPIC FIELDS IN MATERIALS

In the literature, the effective local field is commonly modeled by the Lorentz field, which is defined as the field in a cavity that is carved out of a material around a specific site, but excludes the field of the observation dipole. A well-known example of the relationship between the applied, macroscopic, and local fields is given by an analysis of the Lorentz spherical cavity in a static electric field. In this example, the applied field, depolarization field, and macroscopic field are related by

$$\mathbf{E} = \mathbf{E}_a - \frac{1}{3\epsilon_0} \mathbf{P}. \quad (4)$$

For a Lorentz sphere the local field is well known to be a sum of applied, depolarization, Lorentz, and atomic fields [9,28]:

$$\mathbf{E}_p = \mathbf{E}_a + \mathbf{E}_{depol} + \mathbf{E}_{Lorentz} + \mathbf{E}_{atom}. \quad (5)$$

For cubic lattices in a sphere, the applied field is related to the macroscopic field and polarization by

$$\mathbf{E}_p = \mathbf{E} + \frac{1}{3\epsilon_0} \mathbf{P}. \quad (6)$$

In the case of a sphere, the macroscopic field equals the applied field. Onsager generalized the Lorentz theory by distinguishing between the internal field that acts on induced dipoles and the directing field that acts on permanent dipoles [11]. Some of the essential problems encountered in microscopic constitutive theory center around the local field. Note that there has been recent research that indicates that the Lorentz local field does not always lead to the correct polarizabilities in some materials [5].

The field that polarizes a molecule is the local field $\mathbf{p} \approx \alpha \mathbf{E}_p$. In order to use this expression in Maxwell's equations, the local field needs to be expressed in terms of the macroscopic field $\mathbf{E}_p = \beta \mathbf{E}$, where β is some function. Calculation of this relationship is not always simple. Since the local field is related to the macroscopic field, the polarizabilities, permittivity, and permeability absorb parts of the local field— for example, $\mathbf{p} \approx \alpha \beta \mathbf{E}$. The local field is composed of the macroscopic field and a material-related field as in Eq. (6). Part of the local field is contributed by effects of external parameters such as thermal expansion and quantum effects.

These additional degrees of freedom are contained in the internal energy. In Sec. VI we will generalize the local field to include time-dependent behavior.

IV. POLARIZATION, MAGNETIZATION, AND STRAIN DENSITY

In this section we will define the microscopic polarization, magnetization, and strain density. Later we will use constraints on the theoretical expected values of the polarization, magnetization, strain density, and internal energy to build a relevant-density function [4]. This density function is only part of the full statistical density function that describes the N -body system completely. Using this formalism, exact evolution equations are derived for \mathbf{P} , \mathbf{M} , and $\vec{\mathcal{E}}$. This accomplishes an averaging that we feel is more self-consistent than that used in most statistical-mechanical approaches because the relevant-density function, being the relevant contribution, incorporates the exact values of the macroscopic polarization, magnetization, strain density, and internal energy [1,2]. The relevant-density function provides the required smoothing, and the expected values are determined through Lagrange multipliers. However, the resultant equations are highly nonlinear. The Lagrange multipliers are functions of the macroscopic polarization, magnetization, and internal-energy density, but not the phase-space variables.

In the approach of Mazur and Nijboer, Robinson, and Jackson [1–3] the charge density is expanded in a Taylor's series and the multipole moments are identified. These moments are calculated about each molecular center of mass and are treated as point multipoles. This type of averaging produces a homogenization to the molecular level. Of course the homogenization can take place on smaller scales such as atomic moments. Our approach differs from previous work in that we use the moments defined at a specific scale to determine the averaging function and then use this function to calculate expected values.

Here we construct the relevant statistical-density function from microscopic multipoles, which are incorporated in the Robertson projection-operator model. It has been shown that for origin invariance in Maxwell's equations it is necessary to include a quadrupole contribution in addition to the electric dipole moment in the constitutive relationship for the displacement field, whereas only the magnetic dipole moment needs to be included in the constitutive relationship for the induction field. Since molecular and atomic moments are measurable quantities, we utilize the commonly used definition for the effective microscopic dipole moment [3]. With this averaging the phase-space variables become the molecular centers of mass. The dipole and quadrupole moments are

$$\mathbf{p}_{dn} = \sum_{j(n)} \mathbf{r}_{jn} e_j, \quad (7)$$

$$\vec{q}_n = \frac{1}{2} \sum_{k(n)} e_k \mathbf{r}_{kn} \mathbf{r}_{kn}. \quad (8)$$

However, the theory developed in this paper is not limited to homogenization at the molecular level and a more micro-

scopic approach could be used by decomposing the molecule moments [14]. The vectors $\mathbf{r}_{jn} = \mathbf{r}_j - \mathbf{r}_n$ are from the center of mass of the molecule \mathbf{r}_n to the j th charge. Higher-order moments are defined in a similar fashion as in Jackson [3]. The n indicates the n th molecule and $j(n)$ indicates the j th charge in the n th molecule at the center of mass \mathbf{r}_n of the n th molecule. The sum in Eq. (7) is over the bound charge. The free charge need not be neutral as a whole and contributes to the kinetic energy contained in the internal energy. The total dipole moment is calculated by integrating Eq. (7) over space. The sign of the charge e_j is, for example, negative for electrons and positive for protons. The effective (with quadrupole contribution) microscopic polarization is [3]

$$\mathbf{p} = \sum_n \mathbf{p}_{dn} \delta(\mathbf{r} - \mathbf{r}_n) - \nabla \cdot \vec{q}, \quad (9)$$

where

$$\vec{q} = \sum_n \vec{q}_n \delta(\mathbf{r} - \mathbf{r}_n). \quad (10)$$

Note that the polarization is not represented as an explicit function of the electric field. This dependence enters through the expectations with the relevant statistical function and Liouville's equation. If higher-order moments need to be included, then these moments can be inserted as additional constraints. In the approach used in this paper we do not expand the charge density using a distribution function, but rather use the moments to determine the distribution function (or relevant density function). The existence of the multipole moments automatically assumes a degree of averaging. The expected value of the polarization is $\mathbf{P} \equiv \langle \mathbf{p} \rangle = \text{Tr}(\mathbf{p}\rho)$, where ρ is the full statistical-density function (operator) that satisfies Liouville's equation. In a classical analysis the trace is defined as an integration over phase-space variables. In classical mechanics the dynamical state is specified by the phase coordinates \mathbf{r}_i and momenta $\vec{\pi}_i$ for each degree of freedom. This dependence for all particles is denoted by the variable Γ .

The macroscopic applied electric and magnetic fields \mathbf{E}_a , \mathbf{H}_a are functions of only \mathbf{r} and t and not functions of the phase-space coordinates.

Most of the analysis in this paper is performed classically; however, it could easily be performed, with minor modifications, as a quantum-mechanical analysis where the Poisson brackets are replaced with commutators and the expectations become traces of operators. The definition of the classical trace is

$$\text{Tr}(\rho) = \int () d\mathbf{r}_1 \dots d\mathbf{r}_N d\vec{\pi}_1 \dots d\vec{\pi}_N \equiv \int () d\Gamma, \quad (11)$$

and the expected value is written as

$$\langle F \rangle = \text{Tr}(F\rho). \quad (12)$$

The molecular dipole magnetic moment of the n th molecule, \mathbf{m}_{dn} , can be written in terms of intrinsic magnetic-spin moments \mathbf{m}_{dn} and any other contribution due to charge motion of the form $(e_j/2M_j)\mathbf{r}_{jn} \times \vec{\pi}_{jn}$. The spin gyromagnetic ratios are defined by $\gamma_{ij} = g_j e_j / 2M_j$, with $g \approx 2$ for an electron. The

canonical momentum of the j th charge in molecule n relative to the center of mass is $\vec{\pi}_{jn} = M_j \dot{\mathbf{r}}_{jn} + e_j \mathbf{a}(\mathbf{r}_j)$, where $\mathbf{a}(\mathbf{r}_j)$ is the microscopic vector potential. In addition to molecular moments there may also be moments due to domains and eddy currents. The total microscopic magnetization is then the sum over magnetic moments of the molecules times a δ function:

$$\mathbf{m}(\mathbf{r}) = \sum_n \mathbf{m}_{dn} \delta(\mathbf{r} - \mathbf{r}_n). \quad (13)$$

$\mathbf{M}(\mathbf{r}, t) \equiv \langle \mathbf{m} \rangle \equiv \text{Tr}[\mathbf{m}\rho(t)]$. Higher magnetic moments could also be included.

In addition to the polarization and magnetization, we will assume that the specimen is acted on by a strain-density tensor $\vec{\epsilon}_{ij(s)}(\mathbf{r})$.

Modeling of induced electric moments requires a knowledge of the positions of all the charge in the molecules and therefore a finer level of homogenization. Modeling of permanent electric dipoles requires only knowledge of the coordinates of the dipole and therefore the expectation calculations simplify.

V. EVOLUTION EQUATIONS FOR POLARIZATION, MAGNETIZATION, AND STRAIN DENSITY

A. Relevant density function

The goal of this section is to develop the relevant-density function and expressions for the time evolution of the polarization, magnetization, and strain density [14,29]. The analysis is semiclassical and in the equations of motion we use Poisson brackets between position and momentum variables, and also include intrinsic angular momentum.

We consider the system to be dynamically driven by applied electromagnetic fields and thermally isolated from the surroundings. We assume that the currents and charge creating the applied fields are external to the system. In this section we define the Hamiltonian, introduce the information entropy, and then derive expressions for the macroscopic polarization, magnetization, strain density, and internal-energy density. These expressions will be used in the next section for derivation of evolution equations.

The Hamiltonian contains the interaction of the applied electric field with the electric polarization, the interaction of the applied magnetic field with the magnetization, the interaction of the applied stress interaction with the strain density, and the internal-energy density. The internal-energy density U includes the potential-energy density $[\sum_i \rho_{(i)} \phi(\mathbf{r}_i)]$ and kinetic-energy density of the lattice in the unperturbed Hamiltonian \mathcal{H}_0 , plus dipole-dipole interactions, exchange interactions, magnetic anisotropy, and other interactions]:

$$\mathcal{H}(t) = \int d^3\mathbf{r} \left\{ U(\mathbf{r}, \Gamma) - \mathbf{p}(\mathbf{r}, \Gamma) \cdot \mathbf{E}_a(\mathbf{r}, t) - \mu_0 \mathbf{m}(\mathbf{r}, \Gamma) \cdot \mathbf{H}_a(\mathbf{r}, t) - \frac{1}{2} \vec{\epsilon}_s(\mathbf{r}, \Gamma) : \vec{\Sigma}_a(\mathbf{r}, t) \right\}. \quad (14)$$

Note that $:\cdot:$ denotes tensor contraction. The microscopic quantities \mathbf{p} , \mathbf{m} , $\vec{\epsilon}_s$, and U are functions of \mathbf{r} and positions

and momenta of all the particles, but have no explicit time dependence. The time dependence enters through the dynamics, after taking the expectation. The Hamiltonian is time dependent through the applied fields. If the closed system is in contact with a heat reservoir, this term must also be included in the internal-energy density.

The kinetic energy and angular momentum-related terms in the internal energy do not commute with the polarization and therefore, when calculating the time evolution, will contribute when calculating the Poisson bracket (commutator) $[\mathbf{p}, U]$. We use the symbols $[\cdot, \cdot]$ for either classical-mechanical Poisson brackets or quantum-mechanical commutators. The magnetization \mathbf{m} and the magnetic dipole-dipole interaction do not commute with \mathbf{m} and therefore will contribute to $[\mathbf{m}, U]$. The polarization \mathbf{p} and $\vec{\epsilon}$ do commute with themselves, whereas \mathbf{m} does not. In addition to ρ , the Robertson projection operator, statistical-mechanical theory uses a relevant-density function σ that does not satisfy Liouville's equation, but an exact relationship can be constructed in terms of ρ , σ , and a projectionlike operator [4]. σ characterizes the local state at any time in terms of Lagrange multipliers that are functions of the macroscopic electromagnetic and thermodynamic quantities. The basis of the Robertson projection-operator method involves the separation of the relevant-variable contributions from the relaxation and dissipative terms. The reader is referred to Robertson's papers for further details of the method [4,30] and other papers [14,31]. In this formalism the statistical-density function (operator) ρ is related to the relevant-density function σ by

$$\rho(t) = \sigma(t) - \int_0^t d\tau \mathcal{T}(t, \tau) \{1 - P(\tau)\} i\mathcal{L}(\tau) \sigma(\tau), \quad (15)$$

where \mathcal{L} is Liouville's operator, which in a classical analysis satisfies $i\mathcal{L}A = -[\mathcal{H}, A]$ and quantum-mechanical analysis satisfies $i\mathcal{L}A = i[\mathcal{H}, A]/\hbar$. Note, for a quantum mechanical analysis i/\hbar must be included in all $[\mathcal{H}, A]$ brackets in this paper. Also, P is a non-Hermitian projectionlike operator [4] defined by the functional derivative

$$P(t)A \equiv \sum_{n=1}^m \int d^3r \frac{\delta \sigma(t)}{\delta \langle F_n \rangle} \text{Tr}(F_n A), \quad (16)$$

for any quantum-mechanical operator A and, as a consequence, $\partial \sigma / \partial t = P \partial \rho / \partial t$. The integrating factor operator $\mathcal{T}(t, \tau)$ satisfies the initial-value problem

$$\frac{\partial \mathcal{T}(t, \tau)}{\partial \tau} = \mathcal{T}(t, \tau) \{1 - P(\tau)\} i\mathcal{L}, \quad (17)$$

with initial condition $\mathcal{T}(t, t) = 1$. In the limit of linear response, \mathcal{T} reduces to $[\exp(i(t-\tau)\mathcal{L}_0)]$, where \mathcal{L}_0 is the approximate Liouville's operator, as in the Kubo theory, corresponding to an equilibrium Hamiltonian. All of the operators \mathcal{T} , P , and \mathcal{L} are linear. The statistical-density function in Eq. (15) is given by a reversible-density term plus an irreversible term.

The relevant-density function σ is constructed through theoretical constraints on the polarization, magnetization, strain density, and internal-energy density by maximizing the

information entropy for each time t . The entropy is defined as

$$S(t) = -k\text{Tr}[\sigma(t)\ln \sigma(t)], \quad (18)$$

where k is Boltzmann's constant. Maximizing this entropy subject to constraints on the multipole moments and internal energy yields the most probable relevant density function that describes the statistical particle interactions forming the macroscopic electromagnetic behavior. The entropy is maximized subject to constraints on the expected values of the relevant variables \mathbf{F}_j , which are the macroscopic variables \mathbf{M} , \mathbf{P} , \mathcal{U} , and $\vec{\epsilon}_s$:

$$\langle \mathbf{F}_i(\mathbf{r}, t) \rangle = \frac{1}{Z} \text{Tr} \left[\mathbf{F}_i(\mathbf{r}) \exp \left(- \int d^3\mathbf{r}' \sum_j \lambda_j(\mathbf{r}', t) \lambda_j \cdot \mathbf{F}_j(\mathbf{r}') \right) \right]. \quad (19)$$

Higher-order multipoles could also be included. This equation is a relationship between the relevant macroscopic variables and the Lagrange multiplier fields. The partition function is

$$Z = \text{Tr} \left(\exp \left[- \int d^3\mathbf{r}' \left\{ \beta(\mathbf{r}', t) \left(U(\mathbf{r}') - \mu_0 \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_m(\mathbf{r}', t) - \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_p(\mathbf{r}', t) - \frac{1}{2} \vec{\epsilon}_s(\mathbf{r}') : \vec{\Sigma}_\epsilon(\mathbf{r}', t) \right) \right\} \right] \right), \quad (20)$$

where the Lagrangian multipliers are related to the inverse temperature $\beta(\mathbf{r}, t) = 1/kT(\mathbf{r}, t)$ (where k is Boltzmann's constant), normalized electromagnetic fields $-\beta(\mathbf{r}, t)\mathbf{E}_p(\mathbf{r}, t)$, $-\beta(\mathbf{r}, t)\mu_0\mathbf{H}_m(\mathbf{r}, t)$, and stress fields $-\beta\vec{\Sigma}_\epsilon/2$. These Lagrangian multiplier fields interact with the microscopic polarization \mathbf{p} , magnetization \mathbf{m} , and strain density $\vec{\epsilon}_s$. \mathbf{E}_a and \mathbf{H}_a are applied fields, whereas \mathbf{E}_p and \mathbf{H}_m are effective local fields that interact with \mathbf{p} and \mathbf{m} . These constraints are incorporated into the entropy expression by use of Lagrange multipliers, and the resulting variational expression is maximized to obtain the relevant-density function

$$\sigma(t) = \frac{1}{Z} \exp \left[- \int d^3\mathbf{r}' \left\{ \beta(\mathbf{r}', t) \left(U(\mathbf{r}') - \mu_0 \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_m(\mathbf{r}', t) - \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_p(\mathbf{r}', t) - \frac{1}{2} \vec{\epsilon}_s(\mathbf{r}') : \vec{\Sigma}_\epsilon(\mathbf{r}', t) \right) \right\} \right]. \quad (21)$$

The initial condition is $\sigma(t=0) = \rho(t=0)$ [4,32]. Since σ is a relevant, local-equilibrium density function, all expectations taken with respect to relevant variables are called reversible.

To summarize, we have expressed the expected values of the magnetization, polarization, strain-density, and internal-energy density as functions of Lagrange multipliers. The relevant-density function σ is a function of the Lagrange multipliers and characterizes the local-equilibrium state. In order to determine these quantities, evolution equations are required. The evolution equations will be developed in the next section. The statistical density function is expressed in terms of the relevant statistical-density function (operator). In this respect the resulting evolution equations are exact.

Example: the density function and calculation of the po-

larization. As a simple example, we consider a collection of charges in a z -directed electric field. We neglect the internal energy. The microscopic polarization is defined as $\mathbf{p} = \sum_n \mathbf{p}_{dn} \delta(\mathbf{r} - \mathbf{r}_n)$, the Lagrange multiplier is $\lambda_1 = -E_p \mathbf{e}_z / kT$. We consider only expectation of a single dipole moment. The relevant density function is

$$\sigma = \frac{1}{Z} \exp \left(\sum_n \mathbf{p}_n \cdot \mathbf{E}_p / kT \right). \quad (22)$$

The macroscopic dipole moment of $\mathbf{p}_{d(z)}$ is

$$\begin{aligned} \mathbf{P}_{d(z)} &= \int d\Gamma \mathbf{p}_{d(z)} \sigma(\Gamma) = \frac{2\pi}{Z} \int_0^\pi d\theta p_{d(z)} \sin \theta \cos \theta \\ &\times \exp \left(\frac{\sum_i p_{d(z)} E_p(r_i) \cos \theta}{kT} \right) \mathbf{e}_z \\ &\approx \frac{p_{d(z)}^2 E_p(r_1)}{3kT} \mathbf{e}_z, \end{aligned} \quad (23)$$

where the the last term in Eq. (24) is a high-temperature approximation. $\int d\Gamma$ denotes integration over phase variables. The partition function is

$$\begin{aligned} Z &= \int d\Gamma \exp \left(\frac{\sum_i \mathbf{p}_{d(z)} \cdot \mathbf{E}_p(r_i)}{kT} \right) \\ &= 2\pi \int \sin \theta \exp \left(\frac{\sum_i p_{d(z)} E_p(r_i) \cos \theta}{kT} \right) d\theta. \end{aligned} \quad (25)$$

The result given in Eq. (24) is the same as obtained by rotational-diffusion approaches. Equation (24) could be used to determine the effective local field \mathbf{E}_p .

B. Equations of motion for \mathbf{P} , \mathbf{M} , and $\vec{\epsilon}$

Using the Robertson formalism, equations of motion for the relevant variables can be developed (see Appendix A). In this paper, we give only the results of the equations of motion and refer the reader to previous work for details [14]. For each of the constraint variables we have

$$\begin{aligned} \frac{\partial \langle \mathbf{F}_m(\mathbf{r}, t) \rangle}{\partial t} &= - \text{Tr}([\mathcal{H}, \mathbf{F}_m] \sigma) \\ &- \sum_i \int d^3\mathbf{r}' \int_0^t \text{Tr}([\mathcal{H}(t), \mathbf{F}_m(\mathbf{r}')] \\ &\times \mathcal{T}(t, \tau) (1 - P(\Gamma, \tau)) [\Delta \mathcal{H}_i(\mathbf{r}', \tau), \sigma(\tau)] d\tau. \end{aligned} \quad (26)$$

In Eq. (26), $\mathbf{F}_1 = \mathbf{m}$, $\mathbf{F}_2 = \mathbf{p}$, $\mathbf{F}_3 = \vec{\epsilon}$, $\Delta \mathcal{H}_1 = -\mu_0 \mathbf{m} \cdot (\mathbf{H}_a - \mathbf{H}_m)$, $\Delta \mathcal{H}_2 = -\mathbf{p} \cdot (\mathbf{E}_a - \mathbf{E}_m)$, and $\Delta \mathcal{H}_3 = -\frac{1}{2} \vec{\epsilon} : (\vec{\Sigma}_a - \vec{\Sigma}_\epsilon)$ (see Appendix B). The magnetic reversible term is $\text{Tr}([\mathcal{H}, \mathbf{m}] \sigma) = -\mu_0 \gamma_{eff} \mathbf{M}(\mathbf{r}, t) \times [\mathbf{H}_a(\mathbf{r}, t) - \mathbf{H}_m(\mathbf{r}, t)] - \text{Tr}([\mu_0 \mathbf{m}, \mathbf{p} \cdot (\mathbf{E}_a - \mathbf{E}_p)] \sigma) - \text{Tr}[\mu_0 \mathbf{m}, \frac{1}{2} \vec{\epsilon} : (\vec{\Sigma}_a - \vec{\Sigma}_\epsilon)] \sigma$, where γ_{eff} is an effective gyromagnetic ratio. The other reversible terms can be

calculated by evaluating the Poisson brackets or commutators of the relevant variables with the Hamiltonian. Note that the term $[U, \sigma]$ in the above has been eliminated in terms of the effective local fields \mathbf{H}_m , \mathbf{E}_p , $\vec{\Sigma}_\varepsilon$ (see Appendix B). The projection operator in the relaxation term subtracts flux and assures proper behavior of the correlation functions at large times. The cross-coupled terms in Eq. (26) reduce to 0 when there is no correlation between the magnetization, polarization, and strain density. We note that the macroscopic fields do not occur explicitly in Eq. (26). A relationship will later be derived between the applied fields \mathbf{E}_a , \mathbf{H}_a , $\vec{\Sigma}_a$, effective local fields \mathbf{E}_p , \mathbf{H}_m , $\vec{\Sigma}_\varepsilon$, and the macroscopic fields \mathbf{E} , \mathbf{H} , $\vec{\Sigma}_E$.

C. Approximations to the Poisson brackets

The evolution equations are relatively complicated, and for further analysis simplifications are needed. Fortunately, the forms of these equations do lend themselves to simplification. We note that the commutators in the evolution equation are material-related quantities. These commutators can be approximated. For example, the polarization-current density, neglecting strain behavior, is

$$\begin{aligned} \mathbf{j}_{p(1)} &\equiv -[\mathcal{H}, \mathbf{p}(\mathbf{r})] \\ &\approx -[u, \mathbf{p}] - \left[\mathbf{p}, \mu_0 \int \mathbf{m} \cdot \mathbf{H}_a d^3r \right] \\ &\approx \sum_i \frac{\rho_{p(i)}}{M_i} \vec{\pi}_i - \left[\mathbf{p}, \mu_0 \int \mathbf{m} \cdot \mathbf{H}_a d^3r \right], \end{aligned} \quad (27)$$

where u is the internal energy and $\vec{\pi}$ is the particle momentum. Also, using the knowledge that \mathbf{p} does not depend on momenta and the definition of the Poisson brackets $[\mathbf{p}, \sigma] = \sum_{ik} (\partial \mathbf{p} / \partial r_{ik}) (\partial \sigma / \partial \pi_{ik})$ we have

$$\begin{aligned} [\mathbf{p}(\mathbf{r}), \sigma] &\approx \beta [u, \mathbf{p}] \sigma + \beta \left[\mathbf{p}, \mu_0 \int \mathbf{m} \cdot \mathbf{H}_m d^3r \right] \sigma \\ &\approx -\beta \sum_i \frac{\rho_{p(i)}}{M_i} \vec{\pi}_i \sigma + \beta \sum_i \vec{\omega}_{im} \times \mathbf{p}_i \sigma, \end{aligned} \quad (28)$$

where we used $\nabla \cdot \mathbf{p} = -\rho_p$, the kinetic energy in the internal energy, assumed β is constant, and $\vec{\omega}_{im}$ is an effective angular velocity. The first term on the right-hand side (RHS) of Eq. (28) is a current due to linear bound-charge (dipole) transport and the second term is due to charge rotation.

The magnetic-current density also contains a linear current due to spin transport, plus a precession contribution

$$\begin{aligned} \mathbf{j}_{m(1)} &\equiv -[H, \mathbf{m}(\mathbf{r})] \\ &\approx -[u, \mathbf{m}] - \left[\mathbf{m}, \mu_0 \int \mathbf{m} \cdot \mathbf{H}_a d^3r \right] \\ &= \sum_i \frac{\rho_{d(i)}}{M_i} \vec{\pi}_i - \mu_0 \gamma_e \int \mathbf{m} \times \mathbf{H}_a d^3r \end{aligned} \quad (29)$$

and

$$\begin{aligned} [\mu_0 \mathbf{m}(\mathbf{r}), \sigma] &\approx \beta [u, \mu_0 \mathbf{m}] \sigma + \beta \left[\mu_0 \mathbf{m}, \mu_0 \int \mathbf{m} \cdot \mathbf{H}_m d^3r \right] \sigma \\ &\approx -\sum_i \beta \mu_0 \frac{\rho_{d(i)}}{M_i} \vec{\pi}_i \sigma + \beta \mu_0^2 \gamma_e \int \mathbf{m} \times \mathbf{H}_m d^3r \sigma, \end{aligned} \quad (30)$$

where ρ_d is the effective magnetization-charge density satisfying $\nabla \cdot \mathbf{m} \approx -\rho_d$. Note that the first current term in each of these expressions contains linear velocities and the second contains rotational motion. The correlation between the rotational parts in the magnetic-current density yields spin waves, and the nonrotational is related to spin transport and magnon-electron interactions [33–35]. Finally, the strain-current densities are defined by the relations

$$\vec{j}_{\varepsilon(1)}(\mathbf{r}) = -[\mathcal{H}, \vec{\mathcal{E}}(\mathbf{r})]. \quad (31)$$

D. Approximations to the local and macroscopic fields

In order to obtain approximations to the local fields \mathbf{E}_p , \mathbf{H}_m in terms of the macroscopic fields we can expand Eq. (19) to first order:

$$\mathbf{E}_p(\mathbf{r}, t) \approx \vec{\chi}_{0pp}^{-1} \mathbf{P}(\mathbf{r}, t) + \vec{\mathbf{L}}_p \cdot \mathbf{P}(\mathbf{r}, t), \quad (32)$$

$$\mathbf{H}_m(\mathbf{r}, t) \approx \vec{\chi}_{0mm}^{-1} \mathbf{M}(\mathbf{r}, t) + \vec{\mathbf{L}}_m \cdot \mathbf{M}(\mathbf{r}, t), \quad (33)$$

and

$$\vec{\Sigma}_\varepsilon(\mathbf{r}, t) \approx \vec{\chi}_{0\varepsilon\varepsilon}^{-1} \vec{\mathcal{E}}(\mathbf{r}, t) + \vec{\mathbf{L}}_\varepsilon \cdot \vec{\mathcal{E}}(\mathbf{r}, t), \quad (34)$$

where $\vec{\mathbf{L}}_p$, $\vec{\mathbf{L}}_m$, and $\vec{\mathbf{L}}_\varepsilon$ are dielectric, magnetic, and strain depolarization tensors [14] and $\vec{\chi}_{0ee}$, $\vec{\chi}_{0mm}$, and $\vec{\chi}_{0\varepsilon\varepsilon}$ are the static susceptibilities.

In materials the macroscopic fields differ from the applied fields in that they contain the effects of surface-depolarization charge that modify the applied field. For example, the macroscopic electric field is approximated as $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_a(\mathbf{r}, t) - \vec{\mathbf{L}}_p \cdot \mathbf{P}(\mathbf{r}, t)$. This same form holds for the magnetic and stress fields.

In a first-order linear approximation, the constitutive relations can be obtained from Eq. (19):

$$\mathbf{P} \approx \chi_{ee} \mathbf{E}_p + \chi_{em} \mathbf{H}_m + \vec{\chi}_{es} \cdot \vec{\Sigma}_\varepsilon + \vec{\chi}_{eu} (T - T_0) \quad (35)$$

where the terms correspond, respectively, to dielectric relaxation, magnetoelectricity, piezoelectricity, and pyroelectricity,

$$\mathbf{M} \approx \chi_{me} \mathbf{E}_p + \chi_{mm} \mathbf{H}_m + \vec{\chi}_{ms} \cdot \vec{\Sigma}_\varepsilon + \vec{\chi}_{mu} (T - T_0), \quad (36)$$

where the terms correspond respectively to magnetoelectricity, magnetic relaxation, piezomagnetic, and pyromagneticity, and

$$\vec{\mathcal{E}} \approx \vec{\chi}_{se} \cdot \mathbf{E}_p + \vec{\chi}_{sm} \cdot \mathbf{H}_m + \vec{\chi}_{ss} \cdot \vec{\Sigma}_\varepsilon + \vec{\chi}_{su} (T - T_0), \quad (37)$$

where the terms correspond respectively to piezoelectricity, piezomagnetic, strain relaxation, and thermal expansion.

Example: the Lorentz local field. As a check on the interpretation of \mathbf{E}_p as a local field, we consider Eq. (32) for the case of a cavity in a dielectric. For an ellipsoid, the depolarization factor is $L_p = (\epsilon_{r(2)} - \epsilon_{r(1)}) / \epsilon_{r(1)}(\epsilon_{r(2)} - 1)$. Therefore, for a sphere the local field reduces to the Lorentz local field

$$\mathbf{E}_p(\mathbf{r}, t) \approx \tilde{\chi}_{0pp}^{-1} \mathbf{P}(\mathbf{r}, t) + \tilde{L}_p \cdot \mathbf{P}(\mathbf{r}, t) = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0}. \quad (38)$$

$$\begin{aligned} \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t} &\approx \mu_0 \gamma_{eff} \mathbf{M}(\mathbf{r}, t) \times \mathbf{H}(\mathbf{r}, t) \\ &- \int d^3 \mathbf{r}' \int_0^t \underbrace{\text{Tr} \left\{ \beta \mathbf{j}_{m(1)}(\mathbf{r}, t) \mathcal{T}(t, \tau) (1 - P(\tau)) [\mu_0 \mathbf{m}(\mathbf{r}', \sigma(\tau))] \right\}}_{\tilde{K}_m} \cdot \tilde{\chi}_{0mm}^{-1} \cdot \left(\mathbf{M}(\mathbf{r}', \tau) - \tilde{\chi}_{0mm} \cdot \mathbf{H}(\mathbf{r}', \tau) \right) d\tau. \end{aligned} \quad (39)$$

Note that for electrons γ_{eff} is negative. In a linear approximation, when the time dependence is in the form of a convolution, the magnetic susceptibility tensor can be identified as

$$\tilde{\chi}_m(\mathbf{k}, \omega) = [1 + i\omega \tilde{K}_m^{-1}(\mathbf{k}, \omega)]^{-1} \tilde{\chi}_{0mm}, \quad (40)$$

where the frequency dependence denotes the Fourier transform and $\tilde{K}_m^{-1}(\mathbf{k}, \omega)$ is the relaxation-time tensor. Equation (40) yields an interpretation of the relaxation-time kernel as a distribution of relaxation times.

E. Simplified expressions for the evolution equations

Since the equations are exact, the constitutive evolution equations can be very complicated and in actual applications simplifications need to be applied. In this section we apply our approximations and drop the cross-coupling terms in the equations of motion in Eq. (26). In this section the absolute value of e is used in γ . Using the approximations developed in the previous sections for the magnetization, with no cross coupling, we have

F. Bloch-Bloembergen

In the special case of a δ -function response in Eq. (39), with $\tilde{K}_m = \tilde{K}_{0mm} \delta(t - \tau) \delta(\mathbf{r} - \mathbf{r}') / \tau_m$, we have a variant of the Bloch-Bloembergen equation:

$$\begin{aligned} \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t} &\approx \mu_0 \gamma_{eff} \mathbf{M}(\mathbf{r}, t) \times \mathbf{H}(\mathbf{r}, t) - [\mathbf{M}(\mathbf{r}, t) \\ &- \tilde{\chi}_{0mm} \cdot \mathbf{H}(\mathbf{r}, t)] / \tau_m. \end{aligned} \quad (41)$$

Landau-Lifshitz equation

In the special case where the kernel in Eq. (39) is

$$\tilde{K}_m(\mathbf{r}, t, \mathbf{r}', \tau) = \frac{\mu_0 \alpha \gamma \{ \mathbf{M}(\mathbf{r}, t) \times [\mathbf{M}(\mathbf{r}, t) \times \mathbf{H}(\mathbf{r}, t)] \} \{ \mathbf{M}(\mathbf{r}', \tau) \times [\mathbf{M}(\mathbf{r}', \tau) \times \mathbf{H}(\mathbf{r}', \tau)] \}}{|\mathbf{M}| [\mathbf{M}(\mathbf{r}, t) \times \mathbf{H}(\mathbf{r}, t)] \cdot [\mathbf{M}(\mathbf{r}', \tau) \times \mathbf{H}(\mathbf{r}', \tau)]} \delta(t - \tau) \delta(\mathbf{r} - \mathbf{r}'), \quad (42)$$

we recover the Landau-Lifshitz equation

$$\begin{aligned} \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t} &\approx \mu_0 \gamma \mathbf{M}(\mathbf{r}, t) \times \mathbf{H}(\mathbf{r}, t) - \frac{\mu_0 \alpha \gamma}{|\mathbf{M}|} \mathbf{M}(\mathbf{r}, t) \times [\mathbf{M}(\mathbf{r}, t) \\ &\times \mathbf{H}(\mathbf{r}, t)]. \end{aligned} \quad (43)$$

The approximation for the polarization rate is

$$\begin{aligned} \frac{\partial \mathbf{P}(\mathbf{r}, t)}{\partial t} &= -\text{Tr}([H, \mathbf{p}]\sigma) - \int d^3 \mathbf{r}' \int_0^t \text{Tr} \{ \beta \mathbf{j}_{p(1)}(\mathbf{r}, t) \mathcal{T}(t, \tau) [1 \\ &- P(\Gamma, \tau)] [\mathbf{p}(\mathbf{r}', \sigma(\tau))] \cdot \tilde{\chi}_{0ee}^{-1} \cdot [\mathbf{P}(\mathbf{r}', \tau) \\ &- \tilde{\chi}_{0ee} \cdot \mathbf{E}(\mathbf{r}', \tau)] d\tau. \end{aligned} \quad (44)$$

This equation is a generalization of the Debye equation of motion, and for linear response the Fourier transform can be used to obtain the polarization in terms of the macroscopic field. In a linear approximation, the electric susceptibility tensor is

$$\vec{\chi}_e(\mathbf{k}, \omega) = [1 + i\omega \vec{K}_e^{-1}(\mathbf{k}, \omega)]^{-1} \vec{\chi}_{0ee}. \quad (45)$$

Debye response occurs when the relaxation-time tensor $\vec{\chi}_e^{-1}(\mathbf{k}, \omega)$ is a constant τ_0 . The strain-density rate without cross-coupling satisfies

$$\begin{aligned} \frac{\partial \vec{\mathcal{E}}(\mathbf{r}, t)}{\partial t} = & -\text{Tr}([\mathcal{H}, \vec{\mathcal{E}}]\sigma) - \int d^3r' \int_0^t \text{Tr}\{\beta \vec{j}_{\varepsilon(1)} \mathcal{T}(t, \tau) [1 - P(\tau)] \\ & \times [\vec{\mathcal{E}}_s(\mathbf{r}'), \sigma(\tau)]\} \cdot \vec{\chi}_{0ee}^{-1} \cdot [\vec{\mathcal{E}}(\mathbf{r}', \tau) \\ & - \vec{\chi}_{0ee} \cdot \vec{\Sigma}_E(\mathbf{r}', \tau)] d\tau. \end{aligned} \quad (46)$$

In a linear approximation, the strain-stress tensor susceptibility is

$$\vec{\chi}_\varepsilon(k, \omega) = [1 + i\omega \vec{K}_\varepsilon^{-1}(k, \omega)]^{-1} \cdot \vec{\chi}_{0\varepsilon\varepsilon}. \quad (47)$$

In the projection-operator method that forms the basis of our work, the calculation and simplification of the projection and evolution operators are complicated; however, Nettleton [31] has studied methods for simplifications of the correlation functions that occur in the Robertson theory.

VI. LOCAL FIELDS

We still need to express the local fields in terms of the macroscopic fields. We can extract the relationship between the macroscopic, local, and applied fields multiplying Eq. (15) by the microscopic field and taking the trace and by requiring the expected value of the respective microscopic electric and magnetic fields \mathbf{e} and \mathbf{h} to be the effective local fields \mathbf{E}_p and \mathbf{H}_m . With this assumption we have

$$\begin{aligned} \text{Tr}(\mathbf{e}\rho) & \equiv \mathbf{E}_p(\mathbf{r}, t) \\ & = \text{Tr}(\mathbf{e}\sigma) + \int d^3r' \int_0^t d\tau \text{Tr}\{\mathbf{e}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\mathcal{H}, \sigma(\tau)]\} \\ & = \mathbf{E} - \int d^3r' \int_0^t d\tau \text{Tr}(\beta \mathbf{e}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\mathbf{p}(\mathbf{r}'), \sigma] \cdot [\mathbf{E}_a(\mathbf{r}', \tau) - \mathbf{E}_p(\mathbf{r}', \tau)] \\ & \quad - \int d^3r' \int_0^t d\tau \text{Tr}(\beta \mathbf{e}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\mu_0 \mathbf{m}(\mathbf{r}'), \sigma] \cdot [\mathbf{H}_a(\mathbf{r}', \tau) - \mathbf{H}_m(\mathbf{r}', \tau)] \\ & \quad - \int d^3r' \int_0^t d\tau \text{Tr}(\beta \mathbf{e}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\vec{\mathcal{E}}_s(\mathbf{r}'), \sigma] : [\vec{\Sigma}_a(\mathbf{r}', \tau) - \vec{\Sigma}_\varepsilon(\mathbf{r}', \tau)], \end{aligned} \quad (48)$$

and

$$\begin{aligned} \text{Tr}(\mathbf{h}\rho) & \equiv \mathbf{H}_m(\mathbf{r}, t) \\ & = \text{Tr}(\mathbf{h}\sigma) + \int d^3r' \int_0^t d\tau \text{Tr}\{\mathbf{h}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\mathcal{H}, \sigma]\} \\ & = \mathbf{H} - \int d^3r' \int_0^t d\tau \text{Tr}(\beta \mathbf{h}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\mu_0 \mathbf{m}(\mathbf{r}'), \sigma] \cdot [\mathbf{H}_a(\mathbf{r}', \tau) - \mathbf{H}_m(\mathbf{r}', \tau)] \\ & \quad - \int d^3r' \int_0^t d\tau \text{Tr}(\beta \mathbf{h}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\mathbf{p}(\mathbf{r}'), \sigma] \cdot [\mathbf{E}_a(\mathbf{r}', \tau) - \mathbf{E}_p(\mathbf{r}', \tau)] \\ & \quad - \int d^3r' \int_0^t d\tau \text{Tr}(\beta \mathbf{h}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \quad \times [\vec{\mathcal{E}}_s(\mathbf{r}'), \sigma] : [\vec{\Sigma}_a(\mathbf{r}', \tau) - \vec{\Sigma}_\varepsilon(\mathbf{r}', \tau)]. \end{aligned} \quad (49)$$

A similar equation holds for the strain fields. Equations (48) and (49) define the relationship between the microscopic, local, applied, and macroscopic fields.

We have defined the macroscopic fields as the expectation of the microscopic field with respect to the relevant statistical density function σ :

$$\mathbf{E}(\mathbf{r}, t) = \text{Tr}[\mathbf{e}(\mathbf{r})\sigma], \quad (50)$$

$$\mathbf{H}(\mathbf{r}, t) = \text{Tr}[\mathbf{h}(\mathbf{r})\sigma], \quad (51)$$

$$\vec{\Sigma}_E(\mathbf{r}, t) = \text{Tr}[\vec{\Sigma}(\mathbf{r})\sigma]. \quad (52)$$

In addition, the macroscopic charge density is defined in terms of the microscopic charge density as $\langle \rho_t \rangle = \text{Tr}(\rho_t \sigma)$.

These definitions of the macroscopic fields in Eqs. (50)–(52) make sense because σ is the density function for the relevant variables such that the expectation taken with the microscopic relevant variables is required to match the macroscopic variables \mathbf{P} , \mathbf{M} , $\vec{\mathcal{E}}$, and U . Therefore \mathbf{E} , \mathbf{H} , and $\vec{\Sigma}_E$ are the relevant macroscopic fields. Equations (48), (49), and (19) are coupled equations for \mathbf{E} , \mathbf{H} , $\vec{\Sigma}_E$, \mathbf{E}_p , \mathbf{H}_m , and $\vec{\Sigma}_\varepsilon$. Equations (48) and (49) serve as the definitions of \mathbf{E} and \mathbf{H} and also show how the Lagrange multipliers \mathbf{E}_p and \mathbf{H}_m are related to the microscopic fields. The relaxation terms in Eqs. (48) and (49) are correlation functions between the field at \mathbf{r} and the time-rate of change of the relevant-density function.

Equation (50) can be compared to the most commonly used way to construct the macroscopic field from the microscopic field. In this commonly used approach, a distribution function $f_d(\mathbf{r})$ is postulated according to the length scale and wavelength of interest, where

$$\mathbf{E} = \int d\mathbf{r}' e(\mathbf{r} - \mathbf{r}') f_d(\mathbf{r}'). \quad (53)$$

However, the distribution function f_d is seldom explicitly needed or determined in the analysis. In general, this distri-

bution function must depend on the material properties since it is the constitutive relations that determine f . In our approach the averaging function is explicitly constructed in terms of the polarization, magnetization, strain density, and internal-energy density in a self-consistent fashion.

These definitions of the local fields in Eqs. (48) and (49) are exact generalizations of the Lorentz expression, Eq. (6), and that given by Robinson [2]. We can approximate these expressions for the local field:

$$\begin{aligned} \mathbf{E}_p(\mathbf{r}, t) \approx & \mathbf{E}(\mathbf{r}, t) + \int d^3r' \int_0^t \text{Tr}(\beta \mathbf{e}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \times [\mathbf{p}(\mathbf{r}'), \sigma(\tau)]) \cdot \vec{\chi}_{0pp}^{-1} \cdot [\mathbf{P}(\mathbf{r}', \tau) \\ & - \vec{\chi}_{0pp} \cdot \mathbf{E}(\mathbf{r}', \tau)] d\tau, \end{aligned} \quad (54)$$

$$\begin{aligned} \mathbf{H}_m(\mathbf{r}, t) \approx & \mathbf{H}(\mathbf{r}, t) + \int d^3r' \int_0^t \text{Tr}(\beta \mathbf{h}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \times [\mu_0 \mathbf{m}(\mathbf{r}'), \sigma(\tau)]) \cdot \vec{\chi}_{0mm}^{-1} \cdot [\mathbf{M}(\mathbf{r}', \tau) \\ & - \vec{\chi}_{0mm} \cdot \mathbf{H}(\mathbf{r}', \tau)] d\tau, \end{aligned} \quad (55)$$

and

$$\begin{aligned} \vec{\Sigma}_e(\mathbf{r}, t) \approx & \vec{\Sigma}_E(\mathbf{r}, t) + \int d^3r' \int_0^t \text{Tr}(\beta \vec{\Sigma}(\mathbf{r}) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ & \times [\sigma(\tau), \vec{\varepsilon}_s(\mathbf{r}')] : \vec{\chi}_{0ee}^{-1} : [\vec{\mathcal{E}}(\mathbf{r}', \tau) \\ & - \vec{\chi}_{0ee} : \vec{\Sigma}_E(\mathbf{r}', \tau)] d\tau. \end{aligned} \quad (56)$$

VII. DISPLACEMENT AND INDUCTION FIELDS

We now want to define the displacement vector on a nearly microscopic level. For time-dependent fields in materials, only the part of the microscopic electric field in Eq. (50) contributes to \mathbf{d} as in Eq. (50). As noted by Jackson [3], at a truly microscopic level it makes little sense to define the displacement field since it is a byproduct of the averaging used. We define the displacement field (operator) as $\mathbf{d}(\mathbf{r}) = \epsilon_0 \text{Tr}(\mathbf{e}\sigma) + \epsilon_0 [\mathbf{e}(\mathbf{r}) - \text{Tr}(\mathbf{e}\rho)] + \mathbf{p}(\mathbf{r})$. The macroscopic displacement vector is defined as

$$\begin{aligned} \mathbf{D}(\mathbf{r}, t) = \langle \mathbf{d}\rho \rangle = & \epsilon_0 \text{Tr}(\mathbf{e}\sigma) + \text{Tr}(\mathbf{p}\rho) = \epsilon_0 \mathbf{E} + \text{Tr}(\mathbf{p}\sigma) = \epsilon_0 \mathbf{E}(\mathbf{r}, t) \\ & + \mathbf{P}(\mathbf{r}, t). \end{aligned} \quad (57)$$

Since the polarization \mathbf{P} may depend on the magnetic field, it is possible that \mathbf{D} can depend on the magnetic field. The definition of the macroscopic free-charge density is

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \nabla \cdot \text{Tr}[\mathbf{d}(\mathbf{r})\rho] = \text{Tr}\left(\sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i)\sigma\right) = \text{Tr}(\rho_t \sigma), \quad (58)$$

where ρ_t is the microscopic total-charge density.

Similarly the microscopic magnetic induction field is defined, in terms of the microscopic field and the magnetic moments \mathbf{m} , to be $\mathbf{b}(\mathbf{r}) = \mu_0 \text{Tr}(\mathbf{h}\sigma) + \mu_0 [\mathbf{h}(\mathbf{r}) - \text{Tr}(\mathbf{h}\rho)] + \mu_0 \mathbf{m}(\mathbf{r})$. Therefore the macroscopic induction field is

$$\mathbf{B}(\mathbf{r}, t) = \mu_0 \mathbf{H} + \mu_0 \text{Tr}(\mathbf{m}\sigma) = \mu_0 \mathbf{H}(\mathbf{r}, t) + \mu_0 \mathbf{M}(\mathbf{r}, t). \quad (59)$$

The induction field satisfies

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = \nabla \cdot \text{Tr}[\mathbf{b}(\mathbf{r})\rho] = 0. \quad (60)$$

We use these results when we derive Maxwell's equations from first principles (see Appendix D) from Liouville's equation.

VIII. CONCLUSION

In this paper we studied the local and macroscopic fields and the constitutive relationships as functions of the microscopic and applied fields. We developed expressions for the local electric, magnetic, and strain-density fields in terms of the macroscopic and applied fields using a projection-operator, statistical-mechanical theory that is valid to the submolecular level. The macroscopic fields are defined as the expectation of the microscopic fields with respect to the relevant-density function and the local fields are defined as the expectation of the microscopic fields with respect to the full statistical-density function. This theory incorporates a self-consistent averaging procedure for obtaining the macroscopic polarization, magnetization, and strain density from the microscopic quantities, which is valid at all length scales. The constitutive relationships are expressed in terms of the macroscopic fields, derived from first principles, and include effects of the temperature, strain, and internal-energy density interactions. Our method deviates from the methods developed by Mazur and Nijboer, Robinson, and Jackson in that we construct the averaging function by using constraints on the polarization, magnetization, internal-energy density, and strain density [see Eq. (19)]. In the inverse problem the relevant distribution function is used for averaging of the microscopic fields. These equations plus evolution constitutive equations in Eq. (26) determine the Lagrange multipliers and macroscopic polarization, magnetization, internal-energy density, and strain density.

The local field is composed of the macroscopic field and a material-related field. Part of the local field may be due to effects of external parameters such as temperature and quantum effects. The internal and free energies affect the electromagnetic behavior. For example, the temperature, exchange, and anisotropy interactions all influence the dipole orientations and therefore the fields. Usually these internal-energy effects are modeled by an effective field.

The correlation functions are expressed in terms of current-current correlations, phonon-phonon interactions, phonon-magnon interactions, and magnon-magnon interactions. Application of the derived theory yields extensions of the Debye and Landau-Lifshitz equations. In the Appendixes we also show how Maxwell's equations evolve naturally out of the projection-operator formalism and define a nonequilibrium entropy for time-dependent electromagnetic response.

APPENDIX A: EQUATION OF MOTION

Using this formalism an equation of motion has been developed [4]

$$\frac{\partial \langle F_m \rangle}{\partial t} = \langle i\mathcal{L}F_m \rangle_t - \int_0^t \text{Tr}\{[\mathcal{H}, F_m]\mathcal{T}(1-P)[\mathcal{H}, \sigma(\tau)]\}d\tau, \quad (\text{A1})$$

where classically $\langle i\mathcal{L}F_m \rangle = -\text{Tr}\{[\mathcal{H}, F_m]\sigma\}$ or quantum mechanically $\langle i\mathcal{L}F \rangle = (i/\hbar)\text{Tr}\{[\mathcal{H}, F]\sigma\}$. The first term on the right side of Eq. (A1) is the reversible or convection term; the second is the relaxation term. Equation (A1) is exact and has been used for other applications [30].

APPENDIX B: SIMPLIFICATION

We can eliminate the effects of the internal energy u in the current term in Eq. (26) using the following argument:

$$\left[\beta u - \sum_{i=1}^N \lambda_i \cdot \mathbf{F}_i, \sigma \right] = 0 = \beta[u, \sigma] - \sum_{i=1}^N [\lambda_i \cdot \mathbf{F}_i, \sigma]. \quad (\text{B1})$$

Therefore,

$$\beta[u, \sigma] = \left[\sum_{i=1}^N \lambda_i \cdot \mathbf{F}_i, \sigma \right]. \quad (\text{B2})$$

APPENDIX C: ENTROPY IN TIME-DEPENDENT ELECTROMAGNETISM

The Hamiltonian is time dependent because the applied fields are time dependent. Since we are considering a closed system, it is thermally insulated from its surroundings. However, heat may be generated by dissipative interactions of the fields with the dipole moments, producing thermal energy from the electromagnetic field $\Delta Q/\text{sec} = \int \mathbf{J} \cdot \mathbf{E} dV$. The net work related to the field change from \mathbf{H} to \mathbf{H}_a is contained in the dipole-dipole internal energy and changes in kinetic energy. If the applied field is turned off, no more work is performed on the system, and the temperature and fields will adjust to a state of maximum entropy as it approaches a thermodynamic equilibrium, with a time-independent Hamiltonian. The entropy change $dS = dQ/T$ is due to the system going from a nonequilibrium state to the equilibrium state, and in the process $\Delta S \geq 0$.

We can calculate the nonequilibrium entropy for the whole system from Eq. (18):

$$S(t) = -k\text{Tr}[\sigma(t)\ln \sigma(t)] = \int d^3\mathbf{r} \frac{1}{T} \left[\mathcal{U}(\mathbf{r}, t) - \mathbf{P}(\mathbf{r}, t) \cdot \mathbf{E}_p(\mathbf{r}, t) - \mu_0 \mathbf{M}(\mathbf{r}, t) \cdot \mathbf{H}_m(\mathbf{r}, t) - \frac{1}{2} \vec{\mathcal{E}}(\mathbf{r}, t) : \vec{\Sigma}_\varepsilon(\mathbf{r}, t) \right] + k \ln Z. \quad (\text{C1})$$

The last term is related to the free energy $F = -kT \ln Z$.

The time rate of change of entropy of the system that is driven electromagnetically is

$$\begin{aligned} \frac{dS(t)}{dt} &= -k\text{Tr} \left(\frac{d\sigma(t)}{dt} \ln \sigma(t) \right) \\ &= \int d^3\mathbf{r} \frac{1}{T} \left\{ \frac{\partial U}{\partial t} - \frac{\partial \mathbf{P}_{relax}}{\partial t} \cdot \mathbf{E}_a - \mu_0 \frac{\partial \mathbf{M}_{relax}}{\partial t} \cdot \mathbf{H}_a - \frac{1}{2} \frac{\partial \vec{\mathcal{E}}}{\partial t} : \vec{\Sigma}_a \right\} \\ &= \int d^3\mathbf{r} \frac{1}{T} \left\{ \frac{\partial \mathbf{P}(\mathbf{r}, t)_{relax}}{\partial t} \cdot [\mathbf{E}_p(\mathbf{r}, t) - \mathbf{E}_a(\mathbf{r}, t)] + \mu_0 \frac{\partial \mathbf{M}(\mathbf{r}, t)_{relax}}{\partial t} \cdot [\mathbf{H}_p(\mathbf{r}, t) - \mathbf{H}_a(\mathbf{r}, t)] + \frac{1}{2} \frac{\partial \vec{\mathcal{E}}}{\partial t} : (\vec{\Sigma}_\varepsilon - \vec{\Sigma}_a) \right\} \\ &\approx \int d^3\mathbf{r} \frac{1}{T} \left\{ \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} \cdot \mathbf{E}(\mathbf{r}, t) + \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} \cdot \mathbf{H}(\mathbf{r}, t) - \frac{1}{2} \frac{\partial}{\partial t} (\epsilon_0 |\mathbf{E}|^2 + \mu_0 |\mathbf{H}|^2) + \frac{1}{2} \frac{\partial \vec{\mathcal{E}}}{\partial t} : \vec{\Sigma}_a \right\}. \quad (\text{C2}) \end{aligned}$$

The subscript (*relax*) indicates that only the relaxation part of Eq. (26) is used. The RHS of Eq. (C2) is the entropy production [36,37]. The reversible terms do not contribute directly to the entropy rate because $\text{Tr}(i\mathcal{L}\sigma) = 0$. Zimmels [38] has noted that when calculating the entropy in an electromagnetic system, the entropy without the system in place must be subtracted when using \mathbf{D} and \mathbf{B} as field variables. Equation (C2) manifests this in the subtracted terms. The last equality in Eq. (C2) shows that the entropy production is the difference between the entropy rates with and without the system in place. We have used the fact that in vacuum there is no stress or strain.

In the equilibrium limit, in terms of the macroscopic fields [38],

$$TdS = \int (d\mathcal{U}_M - \mathbf{E} \cdot d\mathbf{D} - \mathbf{H} \cdot d\mathbf{B})dV, \quad (\text{C3})$$

where dS denotes only changes in the nonelectromagnetic entropy and \mathcal{U}_M is the total Maxwell internal-energy density.

In equilibrium, the static electromagnetic entropy is

$$\begin{aligned} S_{em} &= - \left(\frac{\partial \mathcal{U}_{em}}{\partial T} \right)_{V, \mathbf{E}, \mathbf{B}} + S_{em(a)} \\ &= - \int \left(\int \frac{\partial \mathbf{E}}{\partial T} \cdot d\mathbf{D} + \int \frac{\partial \mathbf{H}}{\partial T} \cdot d\mathbf{B} \right) dV' + S_{em(a)} \\ &= - \int \left(\int \frac{\partial \mathbf{E}}{\partial T} \cdot d\mathbf{P} + \mu_0 \int \frac{\partial \mathbf{H}}{\partial T} \cdot d\mathbf{M} \right) dV', \quad (\text{C4}) \end{aligned}$$

where we used the approximations to the macroscopic fields. $S_{em(a)}$ is the electromagnetic entropy in the absence of the system, and V' is the total volume where the fields are influenced by the presence of the system, as determined from solution of Maxwell's equations. For linear response with no

temperature dependence in the fields, $\partial \mathbf{E} / \partial T = -(\partial \chi_e / \partial T) \mathbf{D} / \epsilon^2$, $\partial \mathbf{H} / \partial T = -(\partial \chi_m / \partial T) \mathbf{B} / \mu^2$.

APPENDIX D: MAXWELL'S EQUATIONS DERIVED FROM THE FORMALISM

Consider a dielectric-magnetic material immersed in electric and magnetic fields. The applied macroscopic fields are turned on at $t=0$ and drive the nonequilibrium process. In a finite time after a field is applied, relaxation occurs in the material and modifies the molecular-interaction fields in the material. The goal is to derive Maxwell's equations by consideration of the microscopic electromagnetic quantities and the system Hamiltonian. We assume there are both free as well as bound charges in the material.

The microscopic displacement field is defined in terms of the microscopic polarization by Eq. (57). The macroscopic induction field is $\mathbf{B} = \text{Tr}[\mathbf{b}(\mathbf{r})\rho] = \mu_0 \mathbf{H}(\mathbf{r}, t) + \mu_0 \mathbf{M}$. The macroscopic displacement field is $\mathbf{D} = \text{Tr}[\mathbf{d}(\mathbf{r})\rho] = \epsilon_0 \mathbf{E}(\mathbf{r}, t) + \mathbf{P}$. Of course \mathbf{P} and \mathbf{M} can each be functions of both \mathbf{E} and \mathbf{H} .

The Hamiltonian for the system will now be expressed in terms of the macroscopic fields instead of the applied fields. This is accomplished by substituting for the applied field in Eq. (14) in terms of the macroscopic field plus the corrections due to surface depolarization and demagnetization. This is equivalent to subtracting the depolarization and demagnetization potential energy from the internal energy in Eq. (14). The Hamiltonian is

$$\mathcal{H}(\mathbf{r}) = \int (U_M - \mathbf{d} \cdot \mathbf{E} - \mathbf{b} \cdot \mathbf{H}) d^3 \mathbf{r}, \quad (\text{D1})$$

where the Maxwell internal-energy density U_M is a sum of the energy densities due to the material and the fields. U_M depends on the canonical momentum through the kinetic energy. Now we wish to obtain Maxwell's equations from Liouville's equation

$$\frac{\partial \rho(t)}{\partial t} = [\mathcal{H}(t), \rho]. \quad (\text{D2})$$

Using Eq. (D2), and taking the expectation of \mathbf{d} and \mathbf{b} we find

$$\text{Tr} \left(\mathbf{d} \frac{\partial \rho}{\partial t} \right) = \frac{\partial \mathbf{D}}{\partial t} = \text{Tr}(\mathbf{d}[\mathcal{H}, \rho]), \quad (\text{D3})$$

$$\text{Tr} \left(\mathbf{b} \frac{\partial \rho}{\partial t} \right) = \frac{\partial \mathbf{B}}{\partial t} = \text{Tr}(\mathbf{b}[\mathcal{H}, \rho]). \quad (\text{D4})$$

There are two ways to obtain the curl terms in Maxwell's equations. The quantum-mechanical approach is to assume the microscopic field components obey the commutation relations for quantized fields. The classical Poisson-bracket approach in materials for obtaining the curl equation is to write the microscopic induction field as $\mathbf{b} = \nabla \times \mathbf{a}$ (where $e\mathbf{a}$ is the field momentum of a charged particle), $\mathbf{B} = \nabla \times \text{Tr}[\mathbf{a}(\mathbf{r})\rho]$ and use of vector identities, the definition of the divergence of the microscopic displacement vector, and Poisson brackets to obtain the curl expressions in Maxwell's equations. With either approach,

$$\text{Tr}([\mathbf{b} \cdot \mathbf{H}, \mathbf{d}]\rho) = \nabla \times \mathbf{H} \quad (\text{D5})$$

and

$$\text{Tr}([\mathbf{d} \cdot \mathbf{E}, \mathbf{b}]\rho) = -\nabla \times \mathbf{E}. \quad (\text{D6})$$

The current density is related to the kinetic energy of the free charge [39]. We define the current density as $\mathbf{J}(\mathbf{r}, t) = \text{Tr}([\mathbf{d}, u_M]\rho) \approx \text{Tr}([\mathbf{d}, T]\rho)$, where T , the kinetic energy of the free charge expressed in terms of the canonical momentum, is

$$T = \sum_i \frac{\mathbf{\Pi}_i \cdot \mathbf{\Pi}_i}{2m_i}, \quad (\text{D7})$$

where the canonical momentum is $\mathbf{\Pi}_i = \vec{\pi}_{i(f)} - e_i \mathbf{a}_i$. Through evaluation of Poisson brackets and from the definition of the microscopic free charge, the Maxwellian current density is

$$\begin{aligned} \mathbf{J}(\mathbf{r}) &= \text{Tr}([\mathbf{d}, u_M]\rho) \\ &\approx \sum_i \text{Tr}[\mathbf{\Pi}_i \delta(\mathbf{r} - \mathbf{r}_i)\rho] \\ &= \sum_i \text{Tr}[\mathbf{\Pi}_i \delta(\mathbf{r} - \mathbf{r}_i)\sigma] - \int d^3 \mathbf{r}' \int_0^t \sum_i \text{Tr}(\mathbf{\Pi}_i \delta(\mathbf{r} - \mathbf{r}_i) \\ &\quad \times \mathcal{T}(t, \tau) \{1 - P(\tau)\} [\mathbf{p}(\mathbf{r}'), \sigma]) \cdot \mathbf{E} d\tau \\ &\quad - \int d^3 \mathbf{r}' \int_0^t \sum_i \text{Tr}(\mathbf{\Pi}_i \delta(\mathbf{r} - \mathbf{r}_i) \mathcal{T}(t, \tau) \{1 - P(\tau)\} \\ &\quad \times [\mathbf{m}(\mathbf{r}'), \sigma]) \cdot \mathbf{H} d\tau, \end{aligned} \quad (\text{D8})$$

where we have used the following vector relationship to simplify the current density

$$\begin{aligned} (\mathbf{\Pi} \cdot \nabla) \mathbf{d} &= (\nabla \cdot \mathbf{d}) \mathbf{\Pi} - \mathbf{d} \nabla \cdot \mathbf{\Pi} + (\mathbf{d} \cdot \nabla) \mathbf{\Pi} - \nabla \times (\mathbf{d} \times \mathbf{\Pi}) \\ &\approx (\nabla \cdot \mathbf{d}) \mathbf{\Pi} \rightarrow \sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{\Pi}_i. \end{aligned} \quad (\text{D9})$$

Similarly, we use $\nabla \cdot \mathbf{b} = 0$ to show that magnetic free current vanishes: $\text{Tr}([\mathbf{b}, u_M]\rho) = 0$. Therefore combining the results we see we have the macroscopic Maxwell's equations

$$\frac{\partial \mathbf{D}}{\partial t} = \nabla \times \mathbf{H} - \mathbf{J}, \quad (\text{D10})$$

$$\frac{\partial \mathbf{B}}{\partial t} = -\nabla \times \mathbf{E}. \quad (\text{D11})$$

The time derivative of the Maxwell internal-energy density $\mathcal{U}_M = \text{Tr}(U_M \rho)$ can be calculated from Eqs. (38) and (D2):

$$\frac{\partial \mathcal{U}_M(\mathbf{r}, t)}{\partial t} = \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} \cdot \mathbf{E}(\mathbf{r}, t) + \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} \cdot \mathbf{H}(\mathbf{r}, t). \quad (\text{D12})$$

This is the same expression that was derived by Landau using another approach [40]. The relationship of the Maxwell

internal-energy density to the material internal-energy density \mathcal{U} is

$$\frac{\partial \mathcal{U}_M}{\partial t} = \frac{\partial \mathcal{U}}{\partial t} + \frac{1}{2} \left(\epsilon_0 \frac{\partial |\mathbf{E}|^2}{\partial t} + \mu_0 \frac{\partial |\mathbf{H}|^2}{\partial t} \right). \quad (\text{D13})$$

For linear systems, the integral can be performed to obtain

$$\mathcal{U}_M = \frac{1}{2} (\mathbf{D} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{H}). \quad (\text{D14})$$

Using Maxwell's equations we obtain the general equation of energy conservation

$$\frac{\partial \mathcal{U}_M}{\partial t} + \nabla \cdot \mathbf{S}_M = -\mathbf{J} \cdot \mathbf{E}, \quad (\text{D15})$$

where the macroscopic Poynting vector is $\mathbf{S}_M = \mathbf{E} \times \mathbf{H}$. Equations (D12) and (D15) are very general and not limited to linear dielectrics.

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