

Dynamic constitutive relations for polarization and magnetization

James Baker-Jarvis* and Pavel Kabos

National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303-3328

(Received 23 April 2001; published 26 October 2001)

In this paper we develop constitutive relations for materials where the magnetization and polarization may depend on both the electric and magnetic fields. The approach is general, and is based on a previously developed statistical-mechanical theory. We include the quadrupole-moment density as well as the dipole-moment density in the microscopic displacement field. This yields an electric gradient term in the constitutive equations. This leads to origin invariance in the multipole moments from which Maxwell's equations are defined. We present generalizations of Debye and Landau-Lifshitz equations of motion which are valid for nonequilibrium and contain memory. The reversible and relaxation terms in the polarization and magnetization evolution equations include the possibility of magnetoelectric coupling. Using constitutive relationship, we derive evolution equations for the displacement and induction fields from a Hamiltonian approach.

DOI: 10.1103/PhysRevE.64.056127

PACS number(s): 05.90.+m, 41.20.-q

I. INTRODUCTION

Artificial ferrite-ferroelectric composites, photonic band-gap crystals, and metamaterials are being used in emerging electronic technologies. New materials combine ferroelectrics, ferrites, and ferromagnetic materials into thin films or composites to obtain a desired response. Metamaterials, composed of wires and resonators, have a unique permittivity and permeability response. For development of new composites it is crucial to have a fundamental understanding of the coupled response in the constitutive relations for Maxwell's equations. To establish this relationship in such complicated systems, in this paper we study the foundations of the time evolution of the electric polarization and magnetization by a Liouville-based, projection-operator, nonequilibrium statistical-mechanical theory. The goal is to present a theory for constitutive parameters in Maxwell's equations starting from microscopic quantities that are averaged to obtain macroscopic quantities. We apply the developed theory to magnetoelectric and chiral media. For the history of the projection operator approach, see Refs. [1–5]. We do not discuss specific, field-dependent constitutive relationships.

Maxwell's equations in material media require the specification of the magnetization and polarization as functions of the applied fields. Complications arise because the magnetization and polarization depend not only on the applied field, but also on the internal energy. In magnetoelectric media the driving can be both electric and magnetic. In this paper we develop a system of equations that describes electromagnetic driving with magnetoelectric coupling. These equations can be used in Maxwell's equations with appropriate boundary conditions to yield a closed system of equations.

Magnetic response originates in moving charge, intrinsic angular momentum, and spin. If an external magnetic field is applied to a material, the material responds by a precession of the magnetic moments. In the case of magnetic-field driving, the Landau-Lifshitz or Bloch equations phenomenologi-

cally describe the magnetization time evolution as a function of the magnetic field and internal energy interactions. Dielectric behavior, on the other hand, originates from charge and electric multipole moments. Electric moments are formed from charge separation. The description of dielectric relaxation is complicated because the translation and rotation of charge and dipoles induces magnetic fields and moments in the material. Induced and permanent electric dipoles rotate in an applied electric field due to the applied torque. However, since the ratio of electric to thermal energy is usually small, thermal effects tend to randomize the orientation of permanent dipoles. Therefore, for low field strengths and at ambient temperatures, few dipoles in an ensemble of dipoles follow the applied electric field. However, this small percentage of dipoles can produce appreciable polarization.

The simultaneous application of electric and magnetic fields in complex materials can produce very complex behavior. A particular example is magnetoelectric materials [6–12]. Magnetoelectric coupling occurs in crystals having the requisite symmetry and lattice coupling between the electric and magnetic moments. Hornreich and Shtrikman [13] and Rado [14] found that the origin of magnetoelectric behavior was the electric-field-induced g shift, spin-orbit interaction, exchange energies, and the electric-field-induced shift in single-ion anisotropy energy. Magnetoelectric effects also occur in materials moving in relation to the observer. The underlying electrodynamics is complicated by induced fields interacting with electric and magnetic moments. That is, the spin orientation is coupled to the electric multipole through the lattice. In such materials the application of electric or magnetic fields produces magnetization or polarization, respectively. Magnetization orientations may change due to the application of electric fields. Electric-dipole moments can also be modified by application of magnetic fields through lattice deformation.

The outline of the paper is as follows. We present a general approach for the combined magnetic and dielectric response in complex media. In Sec. II, we overview constitutive relationships in electromagnetic theory. In Sec. II B, we define the polarization, magnetization, internal energy, and associated Hamiltonian. In Sec. II C we develop the

*NIST, Radio-Frequency Technology Division, MS 813.01.
Email address: jjarvis@boulder.nist.gov

statistical-mechanical foundations for the analysis. In Secs. IID and IIE we derive evolution equations for the polarization, magnetization, internal-energy density, and entropy. In Sec. IIF we develop a linear approximation for polarization and magnetization. In Sec. IIG we present special cases for the magnetization evolution. In Sec. III we use the constitutive relations and derive evolution equations for the displacement and induction fields. Additionally, general expressions for charge and energy conservation are derived. In Sec. IV we investigate a number of special cases using the equations derived in Sec. IIC.

II. MICROSCOPIC CONSTITUTIVE QUANTITIES

A. Constitutive relations and theoretical constraints

In order to solve electromagnetic relaxation and propagation problems, Maxwell's equations require the specification of relationships between the polarization and magnetization, and electric, magnetic fields, and their space and time derivatives, in the form of constitutive relations. This relationship can be expressed as $\mathbf{P} \Leftrightarrow \{\mathbf{E}, \mathbf{H}\}$, $\mathbf{M} \Leftrightarrow \{\mathbf{H}, \mathbf{E}\}$. The double-headed arrow in this relation indicates that the relationship could be local or nonlocal in time and space, and that the constitutive relation may be linear or nonlinear functions of the driving fields, or contain various derivatives of the driving fields [15,16].

The dielectric polarization is odd under parity and even under time reversal. The magnetization is even under parity transformation and odd under time reversal. These symmetry relationships place constraints on the nature of the constitutive relationships [17–34]. \mathbf{B} and \mathbf{E} are widely accepted as the fundamental fields rather than \mathbf{D} and \mathbf{H} , and we agree with this interpretation (see, for example, the covariant derivation of Maxwell's equations [25]). However, in this paper we use \mathbf{E} and \mathbf{H} as driving fields. We are interested in constitutive relationships, so we may write, for example, $\mathbf{B} = \mu\mathbf{H}$ rather than the reverse.

B. Formulation of the problem

When driven by time-dependent applied magnetic or electric fields, a material may attain induced in addition to permanent magnetic moments [26]. Locally, the total magnetic moment is built from intrinsic and orbital angular momentum and current-induced magnetic moments [27]. The atomic or other charge-motion magnetic moments are included because we consider nonequilibrium systems. We do not use relative coordinates from the nuclei to the electrons as in Ref. [24].

The authors of Refs. [16,25,27,28] showed that for multipole expansion truncation consistency and origin invariance in Maxwell's equation, the displacement vector needs to include a quadrupole term in addition to the dipole moment density. The macroscopic displacement and induction fields are related to the macroscopic magnetization \mathbf{M} and polarization \mathbf{P} and applied fields \mathbf{E} and \mathbf{H} by

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

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

where ϵ_0 and μ_0 are the permittivity and permeability of vacuum, $\tilde{\mathbf{Q}}$ is the macroscopic quadrupole moment, and $\tilde{\mathbf{P}}$ is the dipole-moment density, whereas \mathbf{P} is the effective macroscopic polarization which includes the macroscopic quadrupole-moment density term.

We will now define the macroscopic polarization and magnetization in terms of the microscopic densities. The microscopic dipole density plus the quadrupole-moment contribution for N particles is defined as

$$\mathbf{p} = \sum_{j=1} \mathbf{r}_j e_j \delta(\mathbf{r} - \mathbf{r}_j) - \frac{1}{2} \sum_{j=1} e_j (\mathbf{r}_j \mathbf{r}_j) \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_j) = \sum_j \mathbf{p}_j, \quad (3)$$

The charge e_j can be positive or negative, for example, it is negative for electrons and positive for protons. Here we sum over bound charge that is electrically neutral as a whole. Overall dipole bound charge neutrality is required in order for the net dipole moment to be independent of origin. The free charge need not be neutral as a whole. The free-charge kinetic energy is included in the internal energy.

The microscopic magnetic-moment density can be written in terms of intrinsic magnetic moments \mathbf{m}_{li} and the magnetic dipole density due to charge motion \mathbf{m}_O as

$$\mathbf{m} = \sum_i \left\{ \gamma_{li} \mathbf{j}_i(\mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_i) - \frac{\gamma_{ei}}{e_i} \boldsymbol{\pi}_i \times \mathbf{p}_i \right\} \equiv \sum_i \mathbf{m}_{li} + \mathbf{m}_O, \quad (4)$$

$\gamma_{ei} = \mu_0 e_i / 2M_i$ where M_i is mass and e_i is the charge located at position \mathbf{r}_i . \mathbf{j} is the intrinsic spin, and \mathbf{r}_i is the position of particle i with a canonical momentum, $\boldsymbol{\pi}_i = M_i \dot{\mathbf{r}}_i + e_i \mathbf{A}_i$. Note that γ_{ei} can be positive or negative depending on the sign of the charge. The spin gyromagnetic ratios are defined by $\gamma_{li} = g_i \mu_0 e_i / 2M_i$, and for an electron $g \approx 2$.

The expected value of the macroscopic magnetization is separated into intrinsic and magnetization due to charge motion, $\mathbf{M}(\mathbf{r}, t) \equiv \langle \mathbf{m} \rangle \equiv \text{Tr}[\mathbf{m}\rho(t)] = \sum_i \langle \mathbf{m}_{li} \rangle(\mathbf{r}, t) + \langle \mathbf{m}_O \rangle(\mathbf{r}, t)$, where ρ is the statistical-density operator that satisfies Liouville's equation and is reviewed in Appendix C. The expected macroscopic polarization is $\mathbf{P}(\mathbf{r}, t) \equiv \langle \mathbf{p} \rangle \equiv \text{Tr}[\mathbf{p}\rho(t)]$, and the expected macroscopic internal-energy density is $\langle U \rangle \equiv \text{Tr}[U\rho(t)] \equiv \mathcal{U}(\mathbf{r}, t)$. Both \mathbf{p} and \mathbf{m} implicitly depend on functions of the electric and magnetic fields. Modeling induced electric moments requires a knowledge of the positions of all the charges in the molecules. Modeling of permanent electric dipoles requires only a knowledge of the coordinates of the dipole, in which case the integrations simplify in the expectation calculations.

C. Statistical-mechanical theory

We now use statistical-mechanical theory to develop evolution equations [3]. The analysis is semiclassical in that we use Poisson brackets between position and momentum variables and also include intrinsic angular momentum. In this section we define the Hamiltonian, then introduce the entropy, and then derive expressions for the polarization, magnetization, and internal-energy density in terms of Lagrange

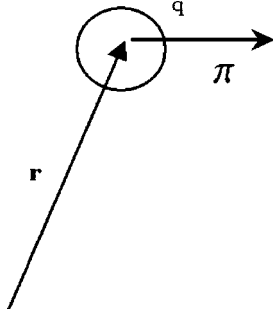


FIG. 1. Coordinate system with position and momentum of charge r_i , $\vec{\pi}_i$.

multipliers. The Lagrange multipliers are determined for the linear response. The expressions for the polarization, magnetization, and internal energy-density will be used in Sec. II D for a derivation of evolution equations.

Consider a dielectric and magnetic material immersed in electric and magnetic fields. The applied Maxwell fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$ are turned on at $t=0$, and drive the non-equilibrium process. We assume that the wavelength of the field is much longer than the particle dimensions. In a finite time after a field is applied, relaxation occurs in the material which modifies the interaction field. In this analysis we limit relaxation time to $\tau \gg \hbar/kT$.

In classical mechanics the dynamical state is specified by the phase coordinates \mathbf{r}_i and momenta $\boldsymbol{\pi}_i$ for each degree of freedom (see Fig. 1). This dependence for all particles is denoted by the variable Γ . The applied electric and magnetic fields are functions of \mathbf{r} and t and not functions of the phase-space coordinates.

The trace (Tr) is defined in classical mechanics as integration over phase variables and quantum mechanically as a trace of the operators. The definition of the classical-mechanical trace is

$$\text{Tr}(\cdot) = \int (\cdot) d\mathbf{r}_1 \cdots d\mathbf{r}_N d\boldsymbol{\pi}_1 \cdots d\boldsymbol{\pi}_N \equiv \int (\cdot) d\Gamma. \quad (5)$$

The Hamiltonian in volume V includes potential and kinetic energy interaction of moments with applied fields, dipole-dipole interactions, magnetic anisotropy, and other interactions. We separate the Hamiltonian into internal energy density, Stark, and Zeeman interactions (see Appendix A)

$$\mathcal{H}(t) = \int d^3\mathbf{r} \{ U(\mathbf{r}, \Gamma) - \mathbf{p}(\mathbf{r}, \Gamma) \cdot \mathbf{E}(\mathbf{r}, t) - \mathbf{m}(\mathbf{r}, \Gamma) \cdot \mathbf{H}(\mathbf{r}, t) \}. \quad (6)$$

U is the internal-energy density which contains the lattice electrostatic and magnetostatic energies, the kinetic energy of the bound and free charge, and other interactions. \mathbf{p} , \mathbf{m} , and U , are functions of \mathbf{r} and positions and momenta of all the particles, but have no explicit time dependence. Time dependence in these quantities is obtained after taking the trace. The effect of the inclusion of the quadrupole term in \mathbf{p} is to include in the Hamiltonian the gradient of the electric field which interacts with the quadrupole moment. This electric-field gradient is also present in the equations of mo-

tion for the polarization and magnetization which we later derive. These gradients of the electric field terms have been shown to be important in constitutive modeling [28]. If even higher-order moments were included in the definitions of \mathbf{p} and \mathbf{m} , then higher-order field derivatives would be included in the Hamiltonian.

Calculation of the equations of motion is based on Poisson-bracket or commutator relations. The kinetic energy and magnetic terms in the internal energy do not commute with the polarization and, therefore, when calculating the time evolution, will contribute to $[\mathbf{p}, F]$. We use the symbols $[\cdot]$ for either classical-mechanical Poisson brackets or quantum-mechanical commutators (see Appendix A). In this paper, intrinsic spin is treated quantum mechanically. Here F is the internal energy (as compared with U which is the internal-energy density). \mathbf{m} and the magnetic dipole-dipole interaction do not commute with \mathbf{m} , and therefore will contribute to $[\mathbf{m}, F]$. We separate the internal energy into lattice potential energy F_0 and lump the balance into G , or $F = F_0 + G$.

In addition to ρ , the projection-operator statistical-mechanical theory uses a relevant canonical-density function σ . σ does not satisfy Liouville's equation, but an exact equation of motion can be constructed in terms of ρ , σ , and a projection operator [1]. The basis of the projection-operator method is the projection out of the relevant variable contribution and the lumping the rest into relaxation or dissipative terms. σ can be constructed by maximizing the information entropy at specific times,

$$S(t) = -k \text{Tr}[\sigma(t) \ln \sigma(t)], \quad (7)$$

subject to constraints on relevant variables \mathbf{M} , \mathbf{P} , and \mathcal{U} [1]. This yields

$$\begin{aligned} \sigma(t) = \frac{1}{Z} \exp \left(- \int d^3\mathbf{r}' \{ \beta(\mathbf{r}', t) U(\mathbf{r}') \right. \\ \left. - \beta(\mathbf{r}', t) \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_M(\mathbf{r}', t) \right. \\ \left. - \beta(\mathbf{r}', t) \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_P(\mathbf{r}', t) \} \right). \quad (8) \end{aligned}$$

The initial condition is $\sigma(t=0) = \rho(t=0)$, (this condition can be generalized, see Oppenheim and Levine [4]). The partition function is

$$\begin{aligned} Z = \text{Tr} \left[\exp \left(- \int d^3\mathbf{r}' \{ \beta(\mathbf{r}', t) U(\mathbf{r}') - \beta(\mathbf{r}', t) \right. \right. \\ \left. \left. \times \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_M(\mathbf{r}', t) - \beta(\mathbf{r}', t) \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_P(\mathbf{r}', t) \} \right) \right], \quad (9) \end{aligned}$$

where Z is the partition function, $\beta(\mathbf{r}, t) = 1/kT(\mathbf{r}, t)$, $\beta(\mathbf{r}, t) \mathbf{E}_P(\mathbf{r}, t)$, and $\beta(\mathbf{r}, t) \mathbf{H}_M(\mathbf{r}, t)$ are Lagrangian multipliers related to the inverse temperature and electromagnetic fields that interact with \mathbf{p} and \mathbf{m} , where k is Boltzmann's constant and \mathbf{E} and \mathbf{H} are applied fields, whereas \mathbf{E}_P and \mathbf{H}_M are effective local fields which do not depend on the phase.

The constraints are

$$\begin{aligned} \mathbf{M}(\mathbf{r}, t) &= \langle \mathbf{m} \rangle \\ &= \frac{1}{Z} \text{Tr} \left[\mathbf{m}(\mathbf{r}) \exp \left(- \int d^3 \mathbf{r}' \{ \beta(\mathbf{r}', t) U(\mathbf{r}') \right. \right. \\ &\quad \left. \left. - \beta(\mathbf{r}', t) \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_M(\mathbf{r}', t) \right. \right. \\ &\quad \left. \left. - \beta(\mathbf{r}', t) \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_P(\mathbf{r}', t) \right) \right], \end{aligned} \quad (10)$$

$$\begin{aligned} \mathbf{P}(\mathbf{r}, t) &= \langle \mathbf{p} \rangle \\ &= \frac{1}{Z} \text{Tr} \left[\mathbf{p}(\mathbf{r}) \exp \left(- \int d^3 \mathbf{r}' \{ \beta(\mathbf{r}', t) U(\mathbf{r}') \right. \right. \\ &\quad \left. \left. - \beta(\mathbf{r}', t) \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_M(\mathbf{r}', t) \right. \right. \\ &\quad \left. \left. - \beta(\mathbf{r}', t) \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_P(\mathbf{r}', t) \right) \right], \end{aligned} \quad (11)$$

$$\begin{aligned} \mathcal{U}(\mathbf{r}, t) &= \langle U \rangle \\ &= \frac{1}{Z} \text{Tr} \left[U(\mathbf{r}) \exp \left(- \int d^3 \mathbf{r}' \{ \beta(\mathbf{r}', t) U(\mathbf{r}') \right. \right. \\ &\quad \left. \left. - \beta(\mathbf{r}', t) \mathbf{m}(\mathbf{r}') \cdot \mathbf{H}_M(\mathbf{r}', t) \right. \right. \\ &\quad \left. \left. - \beta(\mathbf{r}', t) \mathbf{p}(\mathbf{r}') \cdot \mathbf{E}_P(\mathbf{r}', t) \right) \right]. \end{aligned} \quad (12)$$

At this stage of development we have expressed the expected values of the magnetization, polarization, and internal-energy density as functionals of Lagrange multipliers which are interpreted as electric and magnetic fields and inverse temperature. The Lagrangian multipliers can be expressed in terms of \mathbf{M} , \mathbf{P} , and \mathcal{U} . A linear approximation for these quantities is obtained in Sec. II D. Then we develop evolution equations for these quantities.

D. Evolution equations

In this section we use the statistical-mechanical projection-operator theory to derive time-evolution equations for the magnetization, polarization, and internal-energy density [1]. If we apply Eq. (C10) from Appendix C and Eq. (6) to the case of simultaneously applied electric and magnetic fields incident on a material containing intrinsic and induced magnetic moments and permanent and induced electric moments, we find

$$\begin{aligned} \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t} &= \gamma_{\text{eff}} \mathbf{M}(\mathbf{r}, t) \times [\mathbf{H}(\mathbf{r}, t) - \mathbf{H}_{MM}(\mathbf{r}, t)] + \langle \dot{\mathbf{m}} \rangle \\ &+ \int d^3 \mathbf{r}' \int_0^t \text{Tr} \{ [\mathbf{m}(\mathbf{r}), \mathcal{H}(\mathbf{r}, t)] \mathcal{T}(\Gamma, t, \tau) \\ &\times (1 - P(\Gamma, \tau)) \} [\mathbf{m}(\mathbf{r}'), \sigma(\Gamma, \tau)] \cdot \{ \mathbf{H}(\mathbf{r}', \tau) \\ &- \mathbf{H}_M(\mathbf{r}', \tau) \} d\tau + \int d^3 \mathbf{r}' \end{aligned}$$

$$\begin{aligned} &\times \int_0^t \text{Tr} \{ [\mathbf{m}(\mathbf{r}), \mathcal{H}(\mathbf{r}, t)] \mathcal{T}(\Gamma, t, \tau) (1 - P(\Gamma, \tau)) \\ &\times [\mathbf{p}(\mathbf{r}'), \sigma(\Gamma, \tau)] \} \cdot \{ \mathbf{E}(\mathbf{r}', \tau) - \mathbf{E}_P(\mathbf{r}', \tau) \} d\tau, \end{aligned} \quad (13)$$

where we divided the magnetic field from the internal energy into purely magnetic and magneto-electric components as

$$\mathbf{H}_M = \mathbf{H}_{MM} + \mathbf{H}_{ME}, \quad (14)$$

and \mathbf{H}_{ME} appears in the magnetoelectric term, $\dot{\mathbf{m}}$, as we will see shortly, and

$$\begin{aligned} \frac{\partial \mathbf{P}(\mathbf{r}, t)}{\partial t} &= \langle \dot{\mathbf{p}} \rangle + \int d^3 \mathbf{r}' \int_0^t \text{Tr} \{ [\mathbf{p}(\mathbf{r}), \mathcal{H}(\mathbf{r}, t)] \mathcal{T}(\Gamma, t, \tau) [1 \\ &- P(\Gamma, \tau)] [\mathbf{p}(\mathbf{r}'), \sigma(\Gamma, \tau)] \} \cdot \{ \mathbf{E}(\mathbf{r}', \tau) \\ &- \mathbf{E}_P(\mathbf{r}', \tau) \} d\tau + \int d^3 \mathbf{r}' \\ &\times \int_0^t \text{Tr} \{ [\mathbf{p}(\mathbf{r}), \mathcal{H}(\mathbf{r}, t)] \mathcal{T}(\Gamma, t, \tau) [1 - P(\Gamma, \tau)] \\ &\times [\mathbf{m}(\mathbf{r}'), \sigma(\Gamma, \tau)] \} \cdot \{ \mathbf{H}(\mathbf{r}', \tau) - \mathbf{H}_M(\mathbf{r}', \tau) \} d\tau. \end{aligned} \quad (15)$$

\mathcal{T} is an evolution operator and P is a projection operator, defined in Appendix C. The projection operator in the relaxation term subtracts flux and assures the proper behavior of the correlation functions at large time. The reversible terms reduce to 0 when there is no correlation between the magnetization and polarization.

Using Eqs. (6), (13), (15), and (C1), we find that the internal-energy density evolves as

$$\frac{\partial \mathcal{U}(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{J}_q = \mathbf{E}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{P}(\mathbf{r}, t)}{\partial t} + \mathbf{H}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t}, \quad (16)$$

where we included an additional divergence term for thermal driving by heat exchange with the surroundings, $\nabla \cdot \mathbf{J}_q$ (see Robertson's thermal-driving formalism [33]). Equations (13), (15), and (16) are exact within the approximations in the multipole moments, and valid for nonequilibrium states. As a consequence of the generality of the formulation, the nonlinear correlation functions must be approximated and interpreted. The relaxation kernels can be approximated in many ways (see Refs. [2], [29]). These equations can then be linearized and solved using Fourier analysis.

We now calculate the so-called reversible terms in the equations of motion (13), (15), and (16) (see Appendix B):

$$\begin{aligned} \text{Tr}(i\mathcal{L}\mathbf{m}\sigma) &= \text{Tr}([\mathcal{H}, \mathbf{m}]\sigma) \\ &= \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{m} \cdot \mathbf{H} d^3 \mathbf{r} \right] \sigma \right) + \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{p} \cdot \mathbf{E} d^3 \mathbf{r} \right] \sigma \right) \\ &\quad - \text{Tr}([\mathbf{m}, F]\sigma) \end{aligned}$$

$$\begin{aligned}
 &= \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{m} \cdot (\mathbf{H} - \mathbf{H}_M) d^3 \mathbf{r} \right] \sigma \right) \\
 &+ \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{p} \cdot (\mathbf{E} - \mathbf{E}_p) d^3 \mathbf{r} \right] \sigma \right). \quad (17)
 \end{aligned}$$

The integrals can be performed because of the delta functions in Eqs. (3) and (4). $\text{Tr}([\mathbf{m}, F]\sigma)$ contains magnetic internal interactions including any magnetoelectric coupling. This term is re-expressed in terms of effective fields \mathbf{H}_M and \mathbf{E}_p as shown in Appendix B. Magnetoelectric effects can also originate from charge translation; however, in this analysis we do not treat media that is moving as a whole. Using commutation relations between the intrinsic angular momenta and Poisson brackets for magnetic dipole moments, we find

$$\begin{aligned}
 &\text{Tr} \left(\left[\mathbf{m}, \int \mathbf{m} \cdot (\mathbf{H} - \mathbf{H}_M) d^3 \mathbf{r} \right] \sigma \right) \\
 &= \left(\sum_i \gamma_{Ii} \langle \mathbf{m}_{Ii} \rangle(\mathbf{r}, t) + \gamma_O \langle \mathbf{m}_O \rangle(\mathbf{r}, t) \right) \\
 &\quad \times [\mathbf{H}(\mathbf{r}, t) - \mathbf{H}_M(\mathbf{r}, t)], \quad (18)
 \end{aligned}$$

where γ_{Ii} are for spin species (i). We neglected the second spatial derivative of the δ function and any field gradients. The magnetic dipole-moment density $\langle \mathbf{m}_O \rangle = \text{Tr}[\sum_i \gamma_{ei} \mathbf{r}_i \times \vec{\pi}_i \delta(\mathbf{r} - \mathbf{r}_i) \sigma]$ can be small in comparison to $\langle \mathbf{m}_{Ii} \rangle$. For a single spin species, the right hand side of Eq. (18) can be approximated as $\gamma_{\text{eff}} \mathbf{M} \times (\mathbf{H} - \mathbf{H}_M)$. Noting that \mathbf{m}_I commutes with \mathbf{p} , and using Eq. (14), we see that the magnetoelectric term in Eq. (13) can be expressed as

$$\begin{aligned}
 \langle \dot{\mathbf{m}} \rangle &= - \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{m} \cdot \mathbf{H}_{ME} d^3 \mathbf{r} \right] \sigma \right) \\
 &- \text{Tr} \left(\left[\mathbf{m}_O, \int \mathbf{p} \cdot (\mathbf{E} - \mathbf{E}_p) d^3 \mathbf{r} \right] \sigma \right). \quad (19)
 \end{aligned}$$

Calculating the Poisson brackets between the magnetic-dipole angular momentum and polarization, we find that Eq. (19) is

$$\begin{aligned}
 \langle \dot{\mathbf{m}} \rangle(\mathbf{r}, t) &= - \sum_i |\gamma_{ei}| \text{Tr}[\delta(\mathbf{r} - \mathbf{r}_i) \sigma \mathbf{r}_i \times |e_i| \mathbf{E}(\mathbf{r}_i, t)] \\
 &+ \sum_i |\gamma_{ei}| \text{Tr}[\delta(\mathbf{r} - \mathbf{r}_i) \sigma \mathbf{r}_i \times |e_i| \mathbf{E}_p(\mathbf{r}_i, t)] - \gamma_{\text{eff}} \mathbf{M} \\
 &\quad \times \mathbf{H}_{ME}. \quad (20)
 \end{aligned}$$

In Eq. (20) the first term on the right-hand side (rhs) denotes the interaction with \mathbf{E} -field and the second term the interaction with \mathbf{E}_p field, the quadrupole term cancels with the derivative of the delta function in the dipole-moment density.

For the polarization we have

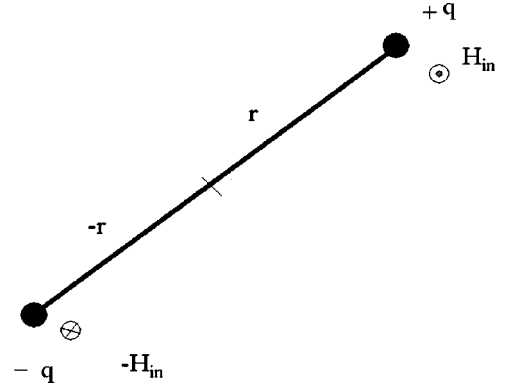


FIG. 2. Model of a rotating dipole and induced magnetic fields.

$$\begin{aligned}
 \langle \dot{\mathbf{p}} \rangle(\mathbf{r}, t) &= \text{Tr}(i\mathcal{L}\mathbf{p}\sigma) = \text{Tr}([\mathcal{H}, \mathbf{p}]\sigma) \\
 &= \text{Tr} \left(\left[\mathbf{p}, \int \mathbf{m} \cdot \mathbf{H} d^3 \mathbf{r} \right] \sigma \right) + \text{Tr} \left(\left[\mathbf{p}, \int \mathbf{p} \cdot \mathbf{E} d^3 \mathbf{r} \right] \sigma \right) \\
 &\quad - \text{Tr}([\mathbf{p}, F]\sigma) \\
 &= \text{Tr} \left(\left[\mathbf{p}, \int \mathbf{m} \cdot (\mathbf{H} - \mathbf{H}_M) d^3 \mathbf{r} \right] \sigma \right) \\
 &\quad + \text{Tr} \left(\left[\mathbf{p}, \int \mathbf{p} \cdot (\mathbf{E} - \mathbf{E}_p) d^3 \mathbf{r} \right] \sigma \right). \quad (21)
 \end{aligned}$$

The term containing only polarization in Eq. (21) is 0, because \mathbf{p} commutes with itself. $\text{Tr}([\mathbf{p}, F]\sigma)$ contains all reversible polarization internal energy interactions including effects of magnetoelectric coupling.

$$\begin{aligned}
 \langle \dot{\mathbf{p}} \rangle(\mathbf{r}, t) &= \sum_i |e_i| \text{Tr}[\delta(\mathbf{r} - \mathbf{r}_i) \sigma \mathbf{r}_i \times |\gamma_{ei}| \mathbf{H}(\mathbf{r}_i, t)] \\
 &\quad - \sum_i |e_i| \text{Tr}[\delta(\mathbf{r} - \mathbf{r}_i) \sigma \mathbf{r}_i \times |\gamma_{ei}| \mathbf{H}_M(\mathbf{r}_i, t)]. \quad (22)
 \end{aligned}$$

The first term on the right hand side denotes the interaction with \mathbf{H} field and the second term the interaction with the \mathbf{H}_M field.

\mathbf{H}_M in Eqs. (20) and (22), contains effects from demagnetization, induced fields, magnetoelectric interaction, and other interactions with the internal energy. As we will see in the applications, this field can be the origin of Thomas precession or spin-orbit interaction. Similarly, the \mathbf{E}_p field in Eqs. (20) and (22) contains depolarization, induced electric fields formed by changing magnetic flux, magnetoelectric, and other interactions with the internal energy (see Fig. 2).

We see from Eq. (4) that the reversible bound current defined by Eq. (22) is related to the vector-potential momentum and the time integral of the magnetic part of the Lorentz force. The first term is related to changes in the magnetic moment due to an applied electric field acting on dipolar moments. We expect this term to be small. The term containing \mathbf{E}_p is related to changes in magnetic moments from the torque due to the Coulomb forces from induced electric

fields; that is, $\sum_i \gamma_{ei} \mathbf{r}_i \times e_i \mathbf{E}_P$. The term containing \mathbf{H}_M in Eq. (22) is related to the magnetic field induced in the dipole rotation and other internal-energy interactions. Equation (22) includes the charge current of, for example, a polar molecule rotating in an electric field. $\langle \dot{\mathbf{m}} \rangle$ can be seen from Eq. (4) to be proportional to \mathbf{r} crossed into the Coulomb electric force. In the case of no polarization-magnetization interaction, $\langle \dot{\mathbf{m}} \rangle$ goes to zero. In this case the constitutive equations decouple; Eq. (13) reduces to a generalized magnetization-evolution equation, and Eq. (15) reduces to a generalized polarization-evolution equation. In Sec. II F examples are presented for $\dot{\mathbf{p}}$ and $\dot{\mathbf{m}}$ when permanent dipole and magnetic moments rotate due to applied fields.

E. Nonequilibrium entropy evolution

We can also calculate the nonequilibrium entropy from Eq (7):

$$\begin{aligned} S(t) &= -k \text{Tr}[\sigma(t) \ln \sigma(t)] \\ &= \int d^3 \mathbf{r} \frac{1}{T} [\mathcal{U}(\mathbf{r}, t) \\ &\quad - \mathbf{P}(\mathbf{r}, t) \cdot \mathbf{E}_P(\mathbf{r}, t) - \mathbf{M}(\mathbf{r}, t) \cdot \mathbf{H}_M(\mathbf{r}, t)] + k \ln Z, \end{aligned} \quad (23)$$

and the entropy rate is, using Eq. (16),

$$\begin{aligned} \frac{dS(t)}{dt} &= -k \text{Tr} \left(\frac{d\sigma(t)}{dt} \ln \sigma(t) \right) \\ &= \int d^3 \mathbf{r} \frac{1}{T} \left\{ \frac{\partial \mathcal{U}}{\partial t} - \frac{\partial \mathbf{P}_{\text{relax}}}{\partial t} \cdot \mathbf{E}_P - \frac{\partial \mathbf{M}_{\text{relax}}}{\partial t} \cdot \mathbf{H}_M \right\} \\ &= \int d^3 \mathbf{r} \left\{ -\nabla \cdot \mathbf{J}_s - \frac{\mathbf{J}_s \cdot \nabla T}{T} \right\} + \frac{1}{k} \int_0^t \int d\tau d^3 \mathbf{r}' d^3 \mathbf{r}'' \\ &\quad \times \text{Tr}[\dot{s}(\mathbf{r}, t) \mathcal{T}(1-P) \dot{s}^k(\mathbf{r}', \tau)], \end{aligned} \quad (24)$$

where the thermal driving entropy flux from the surroundings [35,36] is $\mathbf{J}_s = \mathbf{J}_q/T$. In the case of thermal isolation, this term is 0. The last integrals on the rhs of Eq. (24) are the entropy production. The subscript (relax) indicates only the relaxation part of Eqs. (13) and (15) is used. Also the microscopic entropy density rate is $\dot{s} = (\dot{U} - \dot{\mathbf{p}} \cdot \mathbf{E}_P - \dot{\mathbf{m}} \cdot \mathbf{H}_M)/T$, where the dot is defined in Eq. (C10). Here \dot{U} is the dynamical evolution and does not contain the thermal driving energy density. The superscript k indicates Kubo transform [3]; classically, $a^k = a$. We have not been able to show that the entropy-rate correlation function on the rhs of (24) is strictly ≥ 0 . The reversible terms do not contribute directly the entropy rate, since $\text{Tr}(\dot{\mathbf{i}}\mathcal{L}\sigma) = 0$.

F. Linear approximation

In order to use Eqs. (13) and (15), we need to obtain approximations for the Lagrangian multipliers representing the effective electric and magnetic fields $\mathbf{E}_P(\mathbf{r}, t)$ and $\mathbf{H}_M(\mathbf{r}, t)$.

In a linear approximation for σ , we use a zero-order equilibrium canonical-density function in terms of lattice internal energy F_0 :

$$\sigma_0 = \exp(-\beta F_0) / \text{Tr}[\exp(-\beta F_0)].$$

F_0 depends on the positions of all of charges in the lattice. It is independent of the kinetic energy, electric-moment density, and magnetic-moment density. We assume that part of the internal energy, G , contains the electric and magnetic dipole-dipole interactions, kinetic energy, and other interactions. If we expand Eq. (11) for a small argument, in a high-temperature approximation, assume $\mathbf{p} \cdot \mathbf{E}_P$, $\mathbf{m} \cdot \mathbf{H}_M$, and G are small relative to kT , and keep only terms linear in \mathbf{E}_P , \mathbf{H}_M , and G , in volume V we find

$$\begin{aligned} \frac{\mathbf{P}(\mathbf{r}, t)}{V} &\approx \frac{\langle \mathbf{p}(1 - \beta G) \rangle_0}{V} + [\beta \langle \mathbf{pp} \rangle_0 - \beta^2 \langle \mathbf{p}\{\mathbf{p}, G\} \rangle_0] \cdot \mathbf{E}_P(\mathbf{r}, t) \\ &\quad + [\beta \langle \mathbf{pm} \rangle_0 - \beta^2 \langle \mathbf{p}\{\mathbf{m}, G\} \rangle_0] \cdot \mathbf{H}_M(\mathbf{r}, t) \end{aligned} \quad (25)$$

or

$$\begin{aligned} \mathbf{P}(\mathbf{r}, t) &= \langle \mathbf{p}(1 - \beta G) \rangle_0 + \tilde{\chi}_{0pp} \cdot [\vec{\mathbf{I}} - \vec{\mathbf{N}}_{pp}] \cdot \mathbf{E}_P(\mathbf{r}, t) + \tilde{\chi}_{0pm} [\vec{\mathbf{I}} \\ &\quad - \vec{\mathbf{N}}_{pm}] \cdot \mathbf{H}_M(\mathbf{r}, t) \\ &\equiv \langle \mathbf{p} \rangle_0 + \vec{R}_1 \cdot \mathbf{E}_P + \vec{R}_2 \cdot \mathbf{H}_M, \end{aligned} \quad (26)$$

where the zero-order static susceptibility per unit volume is $\tilde{\chi}_{0pp} = \beta V \langle \mathbf{pp} \rangle_0$, $\tilde{\chi}_{0pm} = \beta V \langle \mathbf{pm} \rangle_0$, $\{\}$ denotes an anticommutator, and the subscript on the brackets indicate that σ_0 is used in the expectations. In nonpyroelectric materials, $\langle \mathbf{p}(1 - \beta G) \rangle_0 = \mathbf{0}$. The tensors $\vec{\mathbf{N}}_{ij}$ contain depolarization, demagnetization, and other interactions contained in G , where

$$\vec{\mathbf{N}}_{pp} = \beta \{ \langle \mathbf{pp} \rangle_0 \}^{-1} \langle \mathbf{p}\{\mathbf{p}, G\} \rangle_0 = \beta^2 \tilde{\chi}_{0pp}^{-1} \langle \mathbf{p}\{\mathbf{p}, G\} \rangle_0, \quad (27)$$

$$\vec{\mathbf{N}}_{pm} = \beta \{ \langle \mathbf{pm} \rangle_0 \}^{-1} \langle \mathbf{p}\{\mathbf{m}, G\} \rangle_0 = \beta^2 \tilde{\chi}_{0pm}^{-1} \langle \mathbf{p}\{\mathbf{m}, G\} \rangle_0. \quad (28)$$

Assuming $\vec{\mathbf{N}}_{pp}$ and $\vec{\mathbf{N}}_{pm}$ are small, since $G/kT \ll 1$, we may expand Eq. (26) to obtain the effective local field

$$\begin{aligned} \mathbf{E}_P(\mathbf{r}, t) &\approx (\vec{\mathbf{I}} + \vec{\mathbf{N}}_{pp}) \tilde{\chi}_{0pp}^{-1} \{ \mathbf{P}(\mathbf{r}, t) - \tilde{\chi}_{0pm} [\vec{\mathbf{I}} - \vec{\mathbf{N}}_{pm}] \cdot \mathbf{H}_M(\mathbf{r}, t) \} \\ &\approx \tilde{\chi}_{0pp}^{-1} \mathbf{P}(\mathbf{r}, t) + \vec{\mathbf{L}}_p \cdot \mathbf{P}(\mathbf{r}, t), \end{aligned} \quad (29)$$

where the electric depolarization tensor is defined as

$$\vec{\mathbf{L}}_p \equiv \beta^2 \tilde{\chi}_{0pp}^{-1} \langle \mathbf{p}\{\mathbf{p}, G\} \rangle_0 \tilde{\chi}_{0pp}^{-1} = \vec{\mathbf{N}}_{pp} \cdot \tilde{\chi}_{0pp}^{-1}. \quad (30)$$

Equation (30) represents the depolarization tensor in terms of the dipole-dipole interaction potential energy. The magnetization can be approximated as

$$\begin{aligned} \frac{\mathbf{M}(\mathbf{r}, t)}{V} &\approx \frac{\langle \mathbf{m}(1 - \beta G) \rangle_0}{V} + [\beta \langle \mathbf{m}\mathbf{m} \rangle_0 \\ &\quad - \beta^2 \langle \mathbf{m}\{\mathbf{m}, G\} \rangle_0] \cdot \mathbf{H}_M(\mathbf{r}, t) + [\beta \langle \mathbf{m}\mathbf{p} \rangle_0 \\ &\quad - \beta^2 \langle \mathbf{m}\{\mathbf{p}, G\} \rangle_0] \cdot \mathbf{E}_P(\mathbf{r}, t) \end{aligned} \quad (31)$$

or

$$\begin{aligned} \mathbf{M}(\mathbf{r}, t) &= \langle \mathbf{m}(1 - \beta G) \rangle_0 + \tilde{\chi}_{0mm}^{-1} \cdot [\tilde{\mathbf{I}} - \tilde{\mathbf{N}}_{mm}] \cdot \mathbf{H}_M(\mathbf{r}, t) \\ &\quad + \tilde{\chi}_{0mp}^{-1} \cdot [\tilde{\mathbf{I}} - \tilde{\mathbf{N}}_{mp}] \cdot \mathbf{E}_P(\mathbf{r}, t) \\ &\equiv \langle \mathbf{m} \rangle_0 + \tilde{\mathbf{R}}_3 \cdot \mathbf{E}_P + \tilde{\mathbf{R}}_4 \cdot \mathbf{H}_M. \end{aligned} \quad (32)$$

In antiferromagnetic, paramagnetic, and diamagnetic materials there is no net magnetization in the absence of an applied field. The coefficient $\tilde{\mathbf{R}}_3$ is related to the α in Rado's theory [9,14].

The demagnetization tensors are

$$\tilde{\mathbf{N}}_{mm} = \beta \{ \langle \mathbf{m}\mathbf{m} \rangle_0 \}^{-1} \langle \mathbf{m}\{\mathbf{m}, G\} \rangle_0 = \beta^2 \tilde{\chi}_{0mm}^{-1} \langle \mathbf{m}\{\mathbf{m}, G\} \rangle_0 \quad (33)$$

and

$$\tilde{\mathbf{N}}_{mp} = 2\beta \{ \langle \mathbf{m}\mathbf{p} \rangle_0 \}^{-1} \langle \mathbf{m}\{\mathbf{p}, G\} \rangle_0 = \beta^2 \tilde{\chi}_{0mp}^{-1} \langle \mathbf{m}\{\mathbf{p}, G\} \rangle_0, \quad (34)$$

where the susceptibilities per unit volume are $\tilde{\chi}_{0mm} = \beta V \langle \mathbf{m}\mathbf{m} \rangle_0$ and $\tilde{\chi}_{0mp} = \beta V \langle \mathbf{m}\mathbf{p} \rangle_0$. Since $G/kT \ll 1$, we can assume $\tilde{\mathbf{N}}_{mm}$ is small, and we may expand Eq. (32) to obtain the effective field

$$\begin{aligned} \mathbf{H}_M(\mathbf{r}, t) &\approx (\tilde{\mathbf{I}} + \tilde{\mathbf{N}}_{mm}) \cdot \tilde{\chi}_{0mm}^{-1} [\mathbf{M}(\mathbf{r}, t) \\ &\quad - \tilde{\chi}_{0mp}^{-1} \cdot [\tilde{\mathbf{I}} - \tilde{\mathbf{N}}_{mp}] \cdot \mathbf{E}_P(\mathbf{r}, t)] \\ &\approx \tilde{\chi}_{0mm}^{-1} \cdot \mathbf{M}(\mathbf{r}, t) + \tilde{\mathbf{L}}_m \cdot \mathbf{M}(\mathbf{r}, t), \end{aligned} \quad (35)$$

$$\tilde{\mathbf{L}}_m \equiv \beta^2 \tilde{\chi}_{0mm}^{-1} \cdot \langle \mathbf{m}\{\mathbf{m}, G\} \rangle_0 \cdot \tilde{\chi}_{0mm}^{-1} = \tilde{\mathbf{N}}_{mm} \cdot \tilde{\chi}_{0mm}^{-1}. \quad (36)$$

For magnetic materials Eq (35) yields well-known results. Depolarization has its origin in the potential field created by the polarized bound charge which creates an opposing electric field. Demagnetization is related to the analogous spin effects.

Using Eqs. (26) and (32) we can solve for \mathbf{E}_P and \mathbf{H}_M when there is no magnetization or polarization in the absence of applied fields:

$$\begin{aligned} \mathbf{E}_P &= [\tilde{\mathbf{R}}_3 - \tilde{\mathbf{R}}_4 \cdot \tilde{\mathbf{R}}_2^{-1} \cdot \tilde{\mathbf{R}}_1]^{-1} \cdot [\mathbf{M} - \tilde{\mathbf{R}}_4 \cdot \tilde{\mathbf{R}}_2^{-1} \cdot \mathbf{P}] \\ &\equiv \tilde{\mathbf{S}}_1 \cdot \mathbf{P} + \tilde{\mathbf{S}}_2 \cdot \mathbf{M}. \end{aligned} \quad (37)$$

and

$$\mathbf{H}_M = \tilde{\mathbf{R}}_2^{-1} \cdot [\mathbf{P} - \tilde{\mathbf{R}}_1 \cdot \mathbf{E}_P] \equiv \tilde{\mathbf{S}}_3 \cdot \mathbf{P} + \tilde{\mathbf{S}}_4 \cdot \mathbf{M}. \quad (38)$$

G. Relaxation approximations

The relaxation kernel can be approximated in the absence of an electric field and no reversible terms to obtain Landau-Lifshitz, Gilbert, or Bloch-Bloembergen equations (see Robertson [2]). In the simplest case of no memory, the kernel is proportional to a delta function. Equations (13) and (15) can be solved by using Eqs. (10)–(12) or their linear approximates. In Sec. II F, applications are presented to illustrate the coupling of induced fields to the electric and magnetic moments. With no electric field driving, for Eq. (13) we have

$$\begin{aligned} \frac{\partial \mathbf{M}(\mathbf{r}, t)}{\partial t} &= \gamma_{\text{eff}} \mathbf{M}(\mathbf{r}, t) \times [\mathbf{H}(\mathbf{r}, t) - \mathbf{H}_M(\mathbf{r}, t)] \\ &\quad + \int d^3 \mathbf{r}' \int_0^t \text{Tr} \{ [\mathbf{m}(\mathbf{r}), \mathcal{H}(\mathbf{r}, t)] \mathcal{T}(\Gamma, t, \tau) \\ &\quad \times [1 - P(\Gamma, \tau)] [\mathbf{m}(\mathbf{r}'), \sigma(\Gamma, \tau)] \} \cdot \{ \mathbf{H}(\mathbf{r}', \tau) \\ &\quad - \mathbf{H}_M(\mathbf{r}', \tau) \} d\tau, \end{aligned} \quad (39)$$

where

$$\begin{aligned} \text{Tr} \{ [\mathbf{m}(\mathbf{r}), \mathcal{H}(\mathbf{r}, t)] \mathcal{T}(\Gamma, t, \tau) [1 - P(\Gamma, \tau)] [\mathbf{m}(\mathbf{r}'), \sigma(\Gamma, \tau)] \} \\ = \tilde{\mathbf{K}}. \end{aligned}$$

The relaxation term reduces to the Landau-Lifshitz relaxation expression when we assume the magnetization relaxes toward the effective magnetic field. This was shown by Robertson [2] for NMR relaxation.

The Gilbert dissipation expression is of the form

$$\propto \mathbf{M} \times \frac{d\mathbf{M}}{dt}. \quad (40)$$

So the loss term in this case assumes that the right hand side of Eq. (13) is orthogonal to \mathbf{M} .

The original Landau-Lifshitz equation is obtained from Eq. (13) if $\mathbf{M} = \tilde{\chi}_{0m} \mathbf{H}_M$ and the kernel is assumed to be a delta function $\propto \tilde{\mathbf{I}} \delta(t - \tau)$ and

$$\frac{d\mathbf{M}}{dt} = \gamma_g \mathbf{M} \times (\mathbf{H} - \tilde{\mathbf{L}}_m \cdot \mathbf{M}) - C (\tilde{\chi}_{0m}^{-1} \cdot \mathbf{M} - \mathbf{H}), \quad (41)$$

where C is a positive constant.

The Bloch-Bloembergen equation can be obtained

$$\frac{d\mathbf{M}}{dt} = \gamma_g \mathbf{M} \times (\mathbf{H} - \tilde{\mathbf{L}}_m \cdot \mathbf{M}) - \tilde{\mathbf{T}} \cdot (\mathbf{M} - \mathbf{M}_0), \quad (42)$$

where $\mathbf{M}_0 = M_0 \mathbf{e}_z$ is the static magnetization, and the applied field contains a static bias magnetic field in the z direction. In Eq. (42) we define

$$\tilde{\mathbf{T}} = \begin{pmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{pmatrix}, \quad (43)$$

and let $\vec{K} = \chi_m \delta(t - \tau) \vec{T}$. We set $\mathbf{H} - \mathbf{H}_M \approx \mathbf{H} - \vec{L}_m \cdot \mathbf{M} - \chi_m^{-1} \mathbf{M}$, where we used $\mathbf{H}_M = \chi_m^{-1} \mathbf{M} + \vec{L}_m \cdot \mathbf{M}$. Then the x and y components of $\mathbf{H} - \vec{L}_m \cdot \mathbf{M}$, in the relaxation term, are neglected, keeping only the z component which is written as $H_z = \chi_m^{-1} M_0$.

III. DISPLACEMENT AND INDUCTION FIELDS

Evolution equations for the displacement and induction fields, charge density, and energy conservation can be obtained from the Poisson-bracket formalism using the constitutive relationships (13) and (15), and Eqs. (1) (2), and identifying \mathbf{E} and \mathbf{H} as Maxwell fields. The magnetic field is expressed in terms of the vector potential, with each particle having a canonical momentum associated with it. The vector potential for particle i is $\mathbf{A}_i(\mathbf{r}) = \mathbf{a}_i \delta(\mathbf{r} - \mathbf{r}_i)$. The Poisson bracket of the vector potential, and displacement fields with themselves yield $[\mathbf{A}_i, \mathbf{A}_j] = 0$, $[\mathbf{d}_i(\mathbf{r}), \mathbf{d}_j(\mathbf{r})] = 0$ and the expected values are $\mathbf{B} = \text{Tr}[\mathbf{b}(\mathbf{r})\rho] = \text{Tr}\{\sum_i \nabla \times [\mathbf{a}_i \delta(\mathbf{r} - \mathbf{r}_i)]\rho\} + \nabla \times \mathbf{A}$, $\nabla \cdot \mathbf{b} = 0$, $\mathbf{D} = \text{Tr}\{[\epsilon_0 \mathbf{E} + \mathbf{p}(\mathbf{r})]\rho\} = \text{Tr}[\mathbf{d}(\mathbf{r})\rho]$.

If we add and subtract $(\epsilon_0 |\mathbf{E}|^2 + \mu_0 |\mathbf{H}|^2)$ from the internal energy density in Eq. (6), then the Hamiltonian can be written as

$$\mathcal{H}(\mathbf{r}) = \int (U_M - \mathbf{d} \cdot \mathbf{E} - \mathbf{b} \cdot \mathbf{H}) d^3 \mathbf{r}, \quad (44)$$

where the Maxwell internal-energy density U_M is a sum of the energy density due to the material U and the energy density in the fields in vacuum. The integration volume in the Hamiltonian is large enough to include all stored field energy.

In the Maxwell approximation because of, $\nabla \cdot \mathbf{E} = \rho_t$, and Ampere's law U_M does not depend on the position coordinates \mathbf{r}_i of the particles but does depend on \mathbf{r} . This is because the electrostatic and magnetostatic lattice energies can be expressed in terms of $\epsilon_0 |\mathbf{E}(\mathbf{r}, t)|^2 + \mu_0 |\mathbf{H}(\mathbf{r}, t)|^2$. U_M does depend on the canonical momentum through the kinetic energy. We define the current density as $\mathbf{J} = \text{Tr}([\mathbf{d}, u_M]\rho)$, where u_M is the Maxwell internal energy. Therefore, using Liouville's equation [Eq. (C1)] Eq. (1), and the definition of the Poisson brackets [Eq. (A3)], and using the results from Appendix E, we find, from a classical analysis,

$$\begin{aligned} \frac{\partial \mathbf{B}}{\partial t} &= \mu_0 \frac{\partial \mathbf{H}}{\partial t} + \frac{\partial \mathbf{M}}{\partial t} = \text{Tr}([\mathcal{H}, \mathbf{b}]\rho) \\ &= -\text{Tr}\left(\left[\int \epsilon_0 |\mathbf{E}|^2 d^3 \mathbf{r} + \sum_j e_j \mathbf{r}_j \cdot \mathbf{E}(\mathbf{r}_j, t) \right. \right. \\ &\quad \left. \left. - \frac{1}{2} \sum_{j=1} e_j(\mathbf{r}_j \mathbf{r}_j) : \nabla \mathbf{E}(\mathbf{r}_j, t), \right. \right. \\ &\quad \left. \left. \sum_i \nabla \times \{[\mathbf{a}(\mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_i)] + \mathbf{A}(\mathbf{r})\} \rho\right) = -\nabla \times \mathbf{E}, \end{aligned} \quad (45)$$

where, to obtain the last expression, we took the trace and integrated by parts. We have $\text{Tr}([u_M, \mathbf{b}]\rho) = 0$ since u_M does not depend on \mathbf{r}_i .

The displacement field satisfies

$$\begin{aligned} \frac{\partial \mathbf{D}}{\partial t} &= \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} = \text{Tr}([\mathcal{H}, \mathbf{d}]\rho) \\ &= \text{Tr}\left(\left[\epsilon_0 \mathbf{E} + \sum_j e_j \mathbf{r}_j \delta(\mathbf{r} - \mathbf{r}_j) - \frac{1}{2} \sum_{j=1} e_j(\mathbf{r}_j \mathbf{r}_j) \cdot \nabla \right. \right. \\ &\quad \left. \left. \times \delta(\mathbf{r} - \mathbf{r}_j), \right. \right. \\ &\quad \left. \left. \sum_i \nabla_i \times \mathbf{a}_i \cdot \mathbf{H}(\mathbf{r}_i, t) + \int_{\text{vac}} \nabla \times \mathbf{A} \cdot \mathbf{H}(\mathbf{r}, t) d^3 \mathbf{r} \right] \rho\right) \\ &\quad - \text{Tr}([\mathbf{d}, u_M]\rho) = \nabla \times \mathbf{H} - \mathbf{J}. \end{aligned} \quad (46)$$

$\epsilon_0 |\mathbf{E}|^2$ does not contribute to the Poisson brackets in Eq. (45). When taking the spatial derivative in the trace, the quadrupole term cancels with the derivative of the delta function in the dipole-moment density (see Appendix E).

Using only the kinetic energy of the free charge T_f and neglecting the bound-charge dependence, the current density is

$$\begin{aligned} \mathbf{J}(\mathbf{r}_i) &= \text{Tr}([\mathbf{d}, u_M]\rho) \\ &= \sum_i \text{Tr}\left(\frac{e_i}{M_i} (\vec{\pi}_{i(t)} - e \mathbf{A}_{i(f)}) \delta(\mathbf{r} - \mathbf{r}_i) \rho\right) \\ &= \sum_i \text{Tr}\left(\frac{e_i}{M_i} (\vec{\pi}_{i(f)} - e \mathbf{A}_{i(f)}) \delta(\mathbf{r} - \mathbf{r}_i) \sigma\right) \\ &\quad + \int d^3 \mathbf{r}' \int_0^t \sum_i \text{Tr}\left(\frac{e_i}{M_i} (\vec{\pi}_{i(f)} - e \mathbf{A}_{i(f)}) \delta(\mathbf{r} - \mathbf{r}_i) \right. \\ &\quad \left. \times \mathcal{T}(t, \tau) \{1 - P(\tau)\} [\mathbf{p}(\mathbf{r}'), \sigma]\right) [\mathbf{E}(\mathbf{r}', \tau) \\ &\quad - \mathbf{E}_p(\mathbf{r}', \tau)] d\tau + \int d^3 \mathbf{r}' \int_0^t \sum_i \text{Tr}\left(\frac{e_i}{M_i} (\vec{\pi}_{i(f)} \right. \\ &\quad \left. - e \mathbf{A}_{i(f)}) \delta(\mathbf{r} - \mathbf{r}_i) \mathcal{T}(t, \tau) \{1 - P(\tau)\} [\mathbf{m}(\mathbf{r}'), \sigma]\right) \\ &\quad \times [\mathbf{H}(\mathbf{r}', \tau) - \mathbf{H}_M(\mathbf{r}', \tau)] d\tau. \end{aligned} \quad (47)$$

When Eqs. (13) and (15) are used in Eqs. (45) and (46), we obtain general evolution equations for the displacement and induction fields. In addition we have

$$\nabla \cdot \mathbf{B} = 0. \quad (48)$$

The bound charge density from Eq. (1) is

$$\begin{aligned} \nabla \cdot \mathbf{P} &= \text{Tr}\left(\sum_i e_i \mathbf{r}_i \cdot \nabla \delta(\mathbf{r} - \mathbf{r}') \rho - \frac{1}{2} \sum_{j=1} e_j(\mathbf{r}_j \mathbf{r}_j) : \nabla \nabla \right. \\ &\quad \left. \times \delta(\mathbf{r} - \mathbf{r}_j) \rho\right) = -\rho_b, \end{aligned} \quad (49)$$

where the sum is over the bound charge. Therefore, since $\nabla \cdot \mathbf{E} = \rho_t$,

$$\nabla \cdot \mathbf{D} = \text{Tr} \left(\sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i) \rho \right) = \rho_f. \quad (50)$$

Maxwell's equations (45)–(50) and (10)–(12), together with boundary conditions, determine \mathbf{E} , \mathbf{H} , \mathbf{E}_p , \mathbf{H}_M , β , \mathbf{M} , and \mathbf{P} .

The equation of continuity for charge conservation can be obtained from Eqs. (46) and (50):

$$\begin{aligned} \frac{\partial \text{Tr}(\sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i) \rho)}{\partial t} + \text{Tr} \left(\sum_i \frac{e_i (\dot{\tilde{\mathbf{p}}}_{i(f)} - e \mathbf{A}_{i(f)})}{M_i} \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_i) \rho \right) &= \frac{\partial \text{Tr}(\sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i) \rho)}{\partial t} \\ + \nabla \cdot \text{Tr} \left(\sum_i \frac{e_i (\dot{\tilde{\mathbf{p}}}_{i(f)} - e \mathbf{A}_{i(f)})}{M_i} \delta(\mathbf{r} - \mathbf{r}_i) \rho \right) &= 0, \end{aligned} \quad (51)$$

where the first term on the right-hand side is $\partial \rho_f / \partial t$, and the last Tr term is equal to \mathbf{J} .

The sums here are over all free charge. From Eq. (16) we see that the time derivative of the Maxwell internal-energy density, $\mathcal{U}_M = \text{Tr}(U_M \rho)$, is

$$\frac{\partial \mathcal{U}_M(\mathbf{r}, t)}{\partial t} = \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} \cdot \mathbf{E}(\mathbf{r}, t) + \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} \cdot \mathbf{H}(\mathbf{r}, t). \quad (52)$$

This is the same expression as derived by Landau and Lifschitz using another approach [6]. For linear systems the integral of Eq. (52) can be performed to obtain

$$\mathcal{U}_M = \frac{1}{2} [\mathbf{D} \cdot \mathbf{E}(\mathbf{r}, t) + \mathbf{B} \cdot \mathbf{H}(\mathbf{r}, t)]. \quad (53)$$

Using Eqs. (45), (46), (47), and (52), we obtain the general equation of energy conservation

$$\frac{\partial \mathcal{U}_M}{\partial t} + \nabla \cdot \mathbf{S} = -\mathbf{J} \cdot \mathbf{E}, \quad (54)$$

where the Poynting vector is $\mathbf{S} = \mathbf{E} \times \mathbf{H}$. Equations (52) and (54) are general, and are not limited to linear dielectrics. The entropy for an electromagnetic field, including a heat flux from the surroundings $\mathbf{J}_q = T \mathbf{J}_s$

$$\begin{aligned} \frac{dS(t)}{dt} = \int d^3 \mathbf{r} \left(-\nabla \cdot \mathbf{J}_s + \frac{1}{T} \left\{ -\mathbf{J}_s \cdot \nabla T + \mathbf{J} \cdot (\mathbf{E}_p - \mathbf{E}) \right. \right. \\ \left. \left. - \left(\mu_0 \frac{\partial \mathbf{H}}{\partial t} + \nabla \times \mathbf{E} \right) \cdot (\mathbf{H} - \mathbf{H}_M) \right. \right. \\ \left. \left. - \left(\epsilon_0 \frac{\partial \mathbf{E}}{\partial t} - \nabla \times \mathbf{H} \right) \cdot (\mathbf{E} - \mathbf{E}_p) \right\} \right). \end{aligned} \quad (55)$$

IV. APPLICATIONS TO MAGNETOELECTRIC AND ARTIFICIAL MEDIA

A. Magnetoelectric media

Usually magnetoelectric media are analyzed in terms of linear constitutive relations between the electric field and the

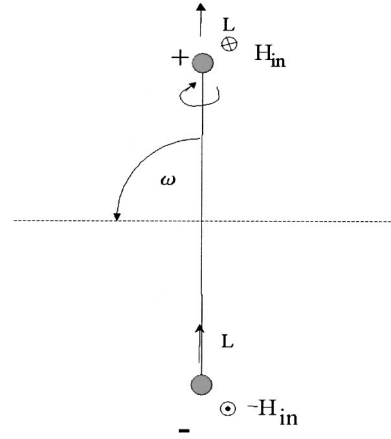


FIG. 3. Model of a rotating dipole with oriented magnetic moments with induced magnetic fields $\pm H_{in}$. Also indicated is the angular momentum of the magnetic moments with angular momentum L .

magnetization. If we use Eq. (32) we obtain a relation analogous to that obtained by Rado [9]:

$$\begin{aligned} \frac{\mathbf{M}(\mathbf{r}, t)}{V} &= [\beta \langle \mathbf{m} \mathbf{m} \rangle_0 - \beta^2 \langle \mathbf{m} \{ \mathbf{m}, G \} \rangle_0] \cdot \mathbf{H}_M(\mathbf{r}, t) + [\beta \langle \mathbf{m} \mathbf{p} \rangle_0 \\ &\quad - \beta^2 \langle \mathbf{m} \{ \mathbf{p}, G \} \rangle_0] \cdot \mathbf{E}_p(\mathbf{r}, t) \\ &\approx \tilde{\beta} \cdot \mathbf{H}_M(\mathbf{r}, t) + \tilde{\alpha} \cdot \mathbf{E}_p(\mathbf{r}, t). \end{aligned}$$

B. Artificial media

In this section we illustrate the dynamics of electric and magnetic field coupling in the reversible terms [Eqs. (20) and (22)] for various special cases. We assume a dynamical model with no relaxation. Relaxation could be included, but makes the analysis less transparent.

We assume a perfectly rigid electric dipole that is free to rotate. Intrinsic magnetic moments are rigidly coupled to the charges. To obtain these specialized cases, the density function in Eqs. (20) and (22) is assumed to constrain the charges to a rigid dipole with aligned magnetic moments.

If an electric field is applied to a dipole without magnetic moments, the dipole rotates because of the applied electric torque. The rotation produces induced magnetic fields from each charge, but in opposite directions. This produces induced magnetic moments in opposite directions. This is because γ_e changes sign for $\pm e$. We now study special cases of coupled magnetic moments and charge movement.

1. Case 1: electric driving

In the first application, we consider a rigid, rotating electric dipole in an applied electric field where each particle has an intrinsic magnetic moment, as shown in Fig. (3). The magnetic moment is constrained to align with the electric dipole. This is a magnetoelectric, Tellegen model in an applied electric field [11]. We use the phrase ‘‘Tellegen model’’ since the media do not seem to exist in nature. If only an electric field is applied, the dipole will rotate and

produce induced magnetic fields. At the same time the magnetic moment is forced to rotate.

In this case the Hamiltonian contains the Zeeman and Stark interactions and kinetic energy of the moving charges. We neglect all contributions to the internal energy except the kinetic energy.

The kinetic energy is

$$T = \frac{1}{2} I |\boldsymbol{\omega}_e|^2 = \frac{|\chi_e|}{2} |\mathbf{H}_{\text{in}(e)}|^2, \quad (56)$$

where $\mathbf{H}_{\text{in}(e)}$ is the induced screening magnetic field due to the charge motion, and χ_e is the induced diamagnetic susceptibility which is related to the moment of inertia by $|\chi_e| = \langle I \rangle \gamma_e^2$. $\mathbf{H}_{\text{in}(e)}$ is the part of \mathbf{H}_M induced from charge motion, and $\boldsymbol{\omega}_e = |\gamma_e| \mathbf{H}_{\text{in}(e)}$. The mechanical torque can be extracted by considering the time rate of change of the electric internal energy in Eqs. (56) and (16). This yields

$$\langle I \rangle \frac{d\boldsymbol{\omega}_e}{dt} = \frac{|\chi_e|}{|\gamma_e|} \frac{d\mathbf{H}_{\text{in}(e)}}{dt} = \mathbf{P}_e \times \mathbf{E}. \quad (57)$$

We use the convention that positive $\mathbf{H}_{\text{in}(e)}$ is in the same direction as positive $\boldsymbol{\omega}_e$, and $\boldsymbol{\omega}_e$ is positive for the counter-clockwise rotation of the dipole. The polarization satisfies

$$\frac{d\mathbf{P}_e}{dt} = \boldsymbol{\omega}_e \times \mathbf{P}_e = -\mathbf{P}_e \times |\gamma_e| \mathbf{H}_{\text{in}(e)}. \quad (58)$$

In this case the magnetization from Eq. (22) satisfies

$$\begin{aligned} \frac{d\mathbf{M}_e}{dt} &= \sum_{i=1}^2 \gamma_{ei} e_i \mathbf{r}_i \times \mathbf{E}_{\text{in}(i)} = |\gamma_e| \mathbf{P}_e \times \mathbf{E}_{\text{in}} = \frac{|\gamma_e| |\mathbf{P}_e|}{|\mathbf{M}_e|} \mathbf{M}_e \times \mathbf{E}_{\text{in}} \\ &= -|\gamma_g| \mathbf{M}_e \times \mathbf{H}_{\text{in}(E)}, \end{aligned} \quad (59)$$

where, by Lenz' Law, an electric field \mathbf{E}_{in} is induced by the interaction of the permanent magnetic moments, with the induced magnetic fields $\mathbf{H}_{\text{in}(e)}$ caused by the rotation of the charge. This simple result describes a process for obtaining magnetization changes from an applied electric field. In the Tellegen model the electric field drives the magnetization through \mathbf{E}_{in} interacting with the permanent electric moment. This is a type of spin-orbit coupling. The induced electric field is related to an effective magnetic field by

$$\mathbf{E}_{\text{in}} = -\frac{|\gamma_g| |\mathbf{M}_e|}{|\gamma_e| |\mathbf{P}_e|} \mathbf{H}_{\text{in}(E)}. \quad (60)$$

The torque from the induced electric field is equivalent to a magnetic field $\mathbf{H}_{\text{in}(E)}$ acting on the permanent magnetic moments, where $\mathbf{H}_{\text{in}(E)} = \mathbf{H}_{\text{in}(e)} |\gamma_e| / |\gamma_g|$.

2. Case 2: magnetic driving

As another simple example we consider the same rotating dipole as in the previous case, but instead of an applied electric field we have an applied magnetic field. The magnetic moment will precess about the applied magnetic field and the electric dipole is forced to follow, thus exhibiting gyroelec-

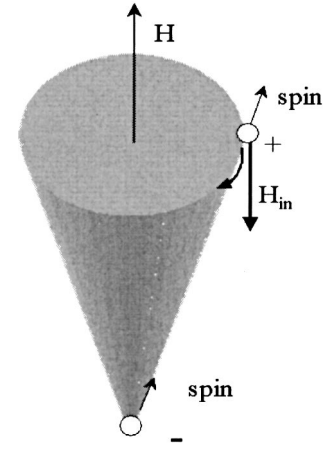


FIG. 4. Model of precessing magnetic moments with an attached electric dipole.

tric behavior as shown in Fig. 4 [14]. The orbiting charge produces an induced diamagnetic magnetic field $\mathbf{H}_{\text{in}(m)}$ in opposition to the applied field.

$\mathbf{H}_{\text{in}(m)}$ is obtained from the mechanical torque

$$\frac{|\chi_e|}{|\gamma_e|} \frac{d\mathbf{H}_{\text{in}(m)}}{dt} = \mathbf{M}_m \times \mathbf{H}. \quad (61)$$

The polarization satisfies Eq. (13):

$$\frac{d\mathbf{P}_m}{dt} = |\gamma_e| \mathbf{P}_m \times (\mathbf{H} - \mathbf{H}_{\text{in}(m)}). \quad (62)$$

In this example the applied magnetic field in Eq. (22) does not cancel out, since only the positive charge is orbiting (precessing). The charge at the vertex is assumed to be pointlike so that the induced magnetic field is negligible.

The magnetization satisfies

$$\frac{d\mathbf{M}_m}{dt} = |\gamma_g| \mathbf{M}_m \times (\mathbf{H} - \mathbf{H}_{\text{in}(M)}). \quad (63)$$

The induced magnetic field subtracts from the applied field, since it is diamagnetic. We can relate $\mathbf{H}_{\text{in}(M)} = (1 - |\gamma_e|/|\gamma_g|) \mathbf{H} + |\gamma_e| \mathbf{H}_{\text{in}(m)} / |\gamma_g|$.

3. Application to chiral media

In the final application, we consider a system with unbalanced charge and no permanent magnetic moments. In this case we have only current-induced magnetic moments and charge-induced electric moments.

Consider a charged bead, free to slide on a spiral, as shown in Fig. 5. If a frequency-dependent magnetic field is applied in the plane of the spiral, a magnetic moment will be induced in the opposite direction of the applied field and, by Lenz' Law, an electric field will be induced in the wire which will slide the bead on the spiral, causing electric polarization. This is chiral behavior, as opposed to a magneto-electric effect. Conversely, if an electric field is applied, the sliding bead produces an induced magnetic moment. In this type of analysis there are no microscopic magnetoelectric

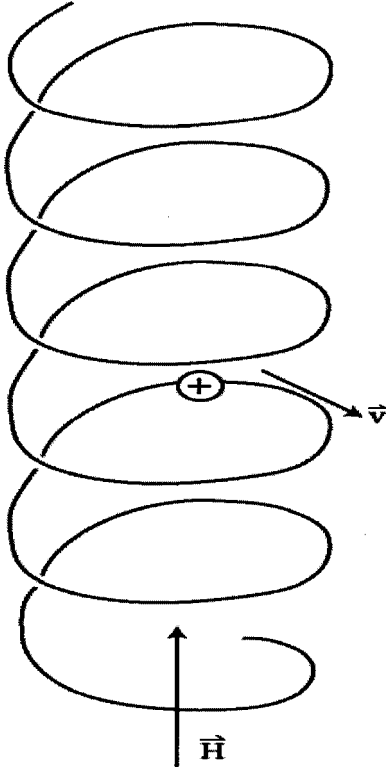


FIG. 5. Model of chiral material.

effects in Eqs. (20) and (22) since there is no coupling of the microscopic magnetic moments to the electric moments to the lattice. Rather the movement of the free unbalanced charge is due to the current density \mathbf{J} in Maxwell's equations [30].

The constitutive relations for this application are given by Eqs. (26) and (32), or they can be more generally obtained, following Ref. [29], by taking linear approximations to Eqs. (13) and (15), neglecting the reversible terms, Fourier transforming, and solving for the frequency-dependent polarization and magnetization.

V. CONCLUSIONS

In this paper we have derived a statistical-mechanical theory for polarization and magnetization evolution for a system of particles using a projection-operator approach. We started from microscopic expressions for the polarization, magnetization, and internal-energy density. These quantities were then averaged to obtain macroscopic expressions. Then generalized, nonlocal equations of motion were derived for the polarization, magnetization, displacement, induction, and internal energy, which included effects of memory and non-equilibrium. We studied the coupling of the polarization and magnetization in complex media, and found that a nonequilibrium coupling can exist between the magnetization and polarization.

The internal energy was studied and decomposed into lattice potential energy, kinetic energy, energy due to permanent and induced dipole moments and angular momentum, and other interactions. In limiting cases the evolution equa-

tions decouple and reduce to well-known equations. A quadrupole term was included in the displacement field that yields origin invariance. Evolution equations for the displacement and induction fields, with generalized constitutive relations, were derived using a Hamiltonian approach. General expressions for the dielectric and induction field evolution and charge and energy conservation were derived. In this theory symmetries in the constitutive relations are based on Hamiltonian mechanics, and therefore the constraint on constitutive relations developed by Post is satisfied [31]. In order to develop specific models for materials the approach in this paper requires an estimation of correlation functions. A number of simple cases were presented, in order to illustrate the results of the theoretical work. Simple examples of magnetoelectric coupling were studied in detail. In these cases we were able to describe the coupling between polarization and magnetization. In the last application we contrasted the chiral behavior of free charge traveling on a spiral with magnetoelectric media. We found that chiral behavior can be described by Maxwell's equations with constitutive relationships of the forms of Eqs. (26) and (32). On the other hand, magnetoelectric media can require more fundamental additions to the magnetization and polarization evolution equations.

ACKNOWLEDGMENTS

We wish to thank B. Stamps, A. Shivola, and R. E. Raab for helpful comments. J.B.J. would like to thank Baldwin Robertson for introducing him to various aspects of his projection-operator theory.

APPENDIX A: HAMILTONIAN AND POISSON BRACKETS

A material with charged particles with an electric dipole moment and an intrinsic spin moment in applied magnetic and electric fields, with electrostatic energy $e\phi$, has an approximate Hamiltonian

$$\mathcal{H} = \frac{1}{2M} (\boldsymbol{\pi} - e\mathbf{A})^2 - \boldsymbol{\mu} \cdot \mathbf{H} - e\mathbf{r} \cdot \mathbf{E} + \frac{1}{2} \int (\epsilon_0 |\mathbf{E}|^2 + \mu_0 |\mathbf{H}|^2) d^3\mathbf{r} + V. \quad (\text{A1})$$

We can separate free from lattice charges, and expand the lattice contribution, using $\mathbf{A} = \frac{1}{2}(\mathbf{H} \times \mathbf{r})$ and angular momentum $\mathbf{L} = \mathbf{r} \times \vec{\boldsymbol{\pi}}$, to obtain

$$\begin{aligned} & \frac{1}{2M} (\boldsymbol{\pi} - e\mathbf{A})^2 + \frac{1}{2M} (\boldsymbol{\pi}_f - e\mathbf{A}_f)^2 - \boldsymbol{\mu} \cdot \mathbf{H} \\ &= \frac{1}{2M} (\boldsymbol{\pi}_f - e\mathbf{A}_f)^2 - (\gamma_e \mathbf{L} + \boldsymbol{\mu}) \cdot \mathbf{H} + \frac{1}{2M} (|\boldsymbol{\pi}|^2 + e^2 |\mathbf{A}|^2). \end{aligned} \quad (\text{A2})$$

The last terms are due to the motion of the lattice as a whole in a magnetic field. This and the kinetic energy of the free charge is included in the internal energy.

The Poisson bracket for functions $F(r_1 \dots r_n; \pi_1 \dots \pi_n, t)$ and $G(r_1 \dots r_n; \pi_1 \dots \pi_n, t)$ is defined as

$$[F, G] = \sum_i \left(\frac{\partial F}{\partial r_i} \frac{\partial G}{\partial \pi_i} - \frac{\partial F}{\partial \pi_i} \frac{\partial G}{\partial r_i} \right), \quad (\text{A3})$$

$$[r_i, r_j] = [\pi_i, \pi_j] = 0, \quad (\text{A4})$$

$$[r_j, \pi_j] = \delta_{ij} = -[\pi_j, r_j]. \quad (\text{A5})$$

APPENDIX B: REVERSIBLE TERM

From Eq. (8),

$$\left[\beta \left(F - \int (\mathbf{p} \cdot \mathbf{E}_p + \mathbf{m} \cdot \mathbf{H}_M) d^3 \mathbf{r} \right), \sigma \right] = 0; \quad (\text{B1})$$

therefore

$$[F, \sigma] = \left[\int (\mathbf{p} \cdot \mathbf{E}_p + \mathbf{m} \cdot \mathbf{H}_M) d^3 \mathbf{r}, \sigma \right], \quad (\text{B2})$$

and the polarization current is

$$\begin{aligned} -\text{Tr}(\mathbf{p}[\mathcal{H}, \sigma]) &= -\text{Tr}(\mathbf{p}[F, \sigma]) + \text{Tr} \left(\mathbf{p} \left[\int \mathbf{p} \cdot \mathbf{E} d^3 \mathbf{r}, \sigma \right] \right) \\ &\quad + \text{Tr} \left(\mathbf{p} \left[\int \mathbf{m} \cdot \mathbf{H} d^3 \mathbf{r}, \sigma \right] \right) \\ &= \text{Tr} \left\{ \left[\mathbf{p}, \int \mathbf{p} \cdot (\mathbf{E} - \mathbf{E}_p) d^3 \mathbf{r} \right] \sigma \right\} \\ &\quad + \text{Tr} \left\{ \left[\mathbf{p}, \int \mathbf{m} \cdot (\mathbf{H} - \mathbf{H}_M) d^3 \mathbf{r} \right] \sigma \right\} \\ &= \text{Tr} \left\{ \left[\mathbf{p}, \int \mathbf{m} \cdot (\mathbf{H} - \mathbf{H}_M) d^3 \mathbf{r} \right] \sigma \right\} = \langle \dot{\mathbf{p}} \rangle. \end{aligned} \quad (\text{B3})$$

Using Eq. (14) yields

$$\begin{aligned} -\text{Tr}(\mathbf{m}[\mathcal{H}, \sigma]) &= -\text{Tr}(\mathbf{m}[F, \sigma]) + \text{Tr} \left(\mathbf{m} \left[\int \mathbf{m} \cdot \mathbf{H} d^3 \mathbf{r}, \sigma \right] \right) \\ &\quad + \text{Tr} \left(\mathbf{m} \left[\int \mathbf{p} \cdot \mathbf{E} d^3 \mathbf{r}, \sigma \right] \right) \\ &= \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{m} \cdot (\mathbf{H} - \mathbf{H}_M) d^3 \mathbf{r} \right] \sigma \right) \\ &\quad + \text{Tr} \left(\left[\mathbf{m}, \int \mathbf{p} \cdot (\mathbf{E} - \mathbf{E}_p) d^3 \mathbf{r} \right] \sigma \right) \\ &= \gamma_g \mathbf{M} \times (\mathbf{H} - \mathbf{H}_{MM}) + \langle \dot{\mathbf{m}} \rangle, \end{aligned} \quad (\text{B4})$$

where we used the identity for operators A and B ;

$$\text{Tr}(Ai\mathcal{L}B) = -\text{Tr}(iLA)B. \quad (\text{B5})$$

APPENDIX C: NONEQUILIBRIUM PROBABILITY-DENSITY FUNCTION

In this appendix the projection-operator tools needed for studying relaxation processes treated in this paper are overviewed (see Ref. [3]). We suppress any spatial dependence and use a semiclassical analysis.

The evolution of the statistical density function produced by the dynamics is given both classically and quantum mechanically by

$$\frac{\partial \rho(t)}{\partial t} = [\mathcal{H}(t), \rho] = i\mathcal{L}(t)\rho(t). \quad (\text{C1})$$

Here \mathcal{L} is either the classical or quantum-mechanical Liouville operator.

We assume the set $\{F_i(\mathbf{r})\}$ of functions in phase space that have expectations that are observables. The expectations are defined by $\langle F \rangle = \text{Tr}[F\rho(t)]$. We define a generalized canonical density $\sigma(t)$ that describes the nonequilibrium thermodynamic variables of the system. Following Refs. [1] and [3] the generalized canonical probability density function $\sigma(t)$ at time t satisfies

$$\text{Tr}[F_j(\Gamma)\sigma(t)] = \langle F_j(\Gamma) \rangle. \quad (\text{C2})$$

In this approach $\sigma(t)$ is that part of the nonequilibrium statistical density $\rho(t)$ which is obtained from information at a single instant of time.

The canonical-density function is developed by use of constraint condition (C2) and by maximizing the information entropy to obtain

$$\sigma(t) = \exp(-\lambda * F) \quad (\text{C3})$$

The $*$ operator is defined as

$$\lambda * F = \sum_{n=0}^N \lambda_n(t) F_n. \quad (\text{C4})$$

The Lagrangian multipliers $\lambda_j(t)$ are found by substitution of the calculated expectation values into the constraint condition (C2). Normalization is obtained by setting $F_0 = 1$.

It is necessary to introduce a projection-like operator $P(t)$ [32]. The operator P is linear, non-Hermitian, and is used for separating relevant or observable details from irrelevant details. It satisfies both

$$\partial \sigma / \partial t = P(t) \partial \rho / \partial t \quad (\text{C5})$$

and

$$\sigma(t) = P(t)\rho(t), \quad (\text{C6})$$

and it is defined for operations on a function A by

$$P(t)A = \frac{\delta \sigma(t)}{\delta \langle F \rangle} * \text{Tr}(FA) = F\sigma * \langle FF \rangle^{-1} * \langle FA \rangle, \quad (\text{C7})$$

where δ denotes a functional differentiation. The operator P , a generalization of Zwanzig's time independent projection

operator [32], separates the relevant part from the irrelevant part. The projection operator also contributes to the time dependence of $T(t, \tau)$. $P(t)$ may be expected to correct for the divergence of transport coefficients.

It is possible to show that with the condition, $\rho(0) = \sigma(0)$ [33] (Oppenheim [4] generalized this condition):

$$\rho(t) = \sigma(t) - \int_0^t d\tau \mathcal{T}(t, \tau) \{1 - P(\tau)\} i\mathcal{L}(\tau) \sigma(\tau). \quad (\text{C8})$$

The integrating factor $\mathcal{T}(t, \tau)$ satisfies the initial value problem

$$\frac{\partial \mathcal{T}(t, \tau)}{\partial \tau} = \mathcal{T}(t, \tau) \{1 - P(\tau)\} i\mathcal{L}, \quad (\text{C9})$$

with initial condition $\mathcal{T}(t, t) = 1$. All of operators \mathcal{T} , P , and \mathcal{L} are linear.

Using this formalism an equation of motion can be written

$$\begin{aligned} \frac{\partial \langle F_m \rangle}{\partial t} = & \langle \dot{F}_m \rangle_t - \int_0^t \text{Tr} \{ [\mathcal{H}, F_m] \\ & \times \mathcal{T}(1 - P)[\mathcal{H}, \sigma(\tau)] \} d\tau. \end{aligned} \quad (\text{C10})$$

Here the dot is defined by $\dot{F} = i\mathcal{L}F$. The first term on the right side of Eq. (C10) is the reversible or convection term; the second is the relaxation term. Equation (C10) is exact. This technique has been used for other applications [2].

APPENDIX D: DIELECTRIC RELAXATION

On application of an electric field to a material, relaxation and dissipation occurs and also dipoles may rotate. At ambient temperatures and low field strengths, the ratio satisfies $\mathbf{p} \cdot \mathbf{E}/kT \ll 1$, and thermal effects dominate over dipole energies. This is described by the Langevin equation. As the temperature is decreased and the field strength increased, the thermal energy decreases relative to electrical energy and the probability of rotation of dipoles increases.

We can write the polarization rate as a sum of rotational plus a nonrotational components

$$\frac{d\mathbf{P}}{dt} = \frac{d\mathbf{P}_{\text{rot}}}{dt} + \frac{d\mathbf{P}_{\text{nonrot}}}{dt}. \quad (\text{D1})$$

For rigid body rotation

$$\frac{d\mathbf{P}_{\text{rot}}}{dt} = \langle \boldsymbol{\omega} \rangle \times \mathbf{P}_{\text{rot}} \quad (\text{D2})$$

$\langle \boldsymbol{\omega} \rangle$ is the average radial velocity of the particles. Classically, this equation is to be solved simultaneously with the torque equation (57) for $\langle \boldsymbol{\omega} \rangle$ and \mathbf{P}_{rot} . The effective angular velocity is

$$\langle \boldsymbol{\omega} \rangle = \frac{1}{|\mathbf{P}_{\text{rot}}|^2} \mathbf{P}_{\text{rot}} \times \frac{d\mathbf{P}_{\text{rot}}}{dt}. \quad (\text{D3})$$

If the magnitude $|\mathbf{P}_{\text{rot}}|$ is constant, then $\mathbf{P}_{\text{rot}} \cdot \langle \boldsymbol{\omega} \rangle = 0$.

APPENDIX E: TRACE CALCULATION

In this appendix, an example calculation in Eqs. (45) and (46) is evaluated

$$\begin{aligned} \text{Tr} \left[\sum_j \frac{\partial}{\partial r_{jx}} \left(\epsilon_0 \mathbf{E}(\mathbf{r}, t) + \sum_j e_j \mathbf{r}_j \delta(\mathbf{r} - \mathbf{r}_j) \right. \right. \\ \left. \left. - \frac{1}{2} \sum_{j=1} e_j (\mathbf{r}_j \mathbf{r}_j) \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_j) \right) \frac{\partial}{\partial \pi_{jx}} \sum_j \nabla_j \right. \\ \left. \times \mathbf{a}_j \cdot \mathbf{H}(\mathbf{r}_j, t) \rho \right] \\ = \text{Tr} \left(\sum_j \frac{\partial}{\partial \pi_{jx}} e_j \delta(\mathbf{r} - \mathbf{r}_j) \nabla_j \times \mathbf{H}(\mathbf{r}_j, t) \cdot \mathbf{a}(\mathbf{r}_j) \rho \right) \hat{\mathbf{u}}_1 \\ = \sum_j \frac{\text{Tr}[\nabla_j \times \mathbf{H}(\mathbf{r}_j) \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_j) \rho] \cdot \hat{\mathbf{u}}_1}{\text{Tr}[\delta(\mathbf{r} - \mathbf{r}_j) \rho]} \hat{\mathbf{u}}_1 = \left(\frac{\partial H_y}{\partial z} - \frac{\partial H_z}{\partial y} \right) \hat{\mathbf{u}}_1, \end{aligned} \quad (\text{D4})$$

where $\hat{\mathbf{u}}_i$ are unit vectors. The mean value of a variable \mathbf{a}_i is defined as

$$\frac{\text{Tr}[\mathbf{a}_j \delta(\mathbf{r} - \mathbf{r}_j) \rho]}{\text{Tr}[\delta(\mathbf{r} - \mathbf{r}_j) \rho]} \quad (\text{D5})$$

of the i th particle at position \mathbf{r} at time t (see Ref. [34]). The second derivative of the δ function was neglected. Similarly, the other components can be calculated to obtain the curl of the magnetic field.

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