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Time-dependent entropy evolution in microscopic and macroscopic electromagnetic relaxation

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This paper is a study of entropy and its evolution in the time and frequency domains upon application of electromagnetic fields to materials. An understanding of entropy and its evolution in electromagnetic interactions bridges the boundaries between electromagnetism and thermodynamics. The approach used here is a Liouville-based statistical-mechanical theory. I show that the microscopic entropy is reversible and the macroscopic entropy satisfies an *H* theorem. The spectral entropy development can be very useful for studying the frequency response of materials. Using a projection-operator based nonequilibrium entropy, different equations are derived for the entropy and entropy production and are applied to the polarization, magnetization, and macroscopic fields. I begin by proving an exact *H* theorem for the entropy, progress to application of time-dependent entropy in electromagnetics, and then apply the theory to relevant applications in electromagnetics. The paper concludes with a discussion of the relationship of the frequency-domain form of the entropy to the permittivity, permeability, and impedance.

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I. INTRODUCTION

This paper studies time-dependent and the related spectral entropy in materials that occur with the polarization response to applied electromagnetic fields. The goals of this work are to present a fundamental microscopic analysis of the Robertson projection-operator nonequilibrium entropy (RPOE) [6], characterize the electromagnetic entropy and the spectral entropy of polarization, and relate these results to dielectric and magnetic relaxation. The approach uses a Liouville-Hamiltonian-based statistical-mechanical theory, which is valid for nonequilibrium states. I will show that the microscopic RPOE satisfies all the requirements of a nonequilibrium entropy and the evolution of the entropy satisfies an exact *H* theorem. I also generalize the results to thermally driven systems. In the last section I relate the theoretical results to high-frequency dielectric relaxation and electrical impedance. The spectral entropy as developed here is shown to be important in studying high-frequency material properties.

The use of time-dependent entropy in the analysis of electromagnetic dielectric and magnetic interactions with materials has been isolated to a few applications [1–4]. Much of the work performed to date has been limited to static and quasistatic analyses that describe adiabatic demagnetization and depolarization. Knowledge of entropy and its evolution bridges the boundaries between electromagnetism and nonequilibrium thermodynamics. For static fields, the electromagnetic interaction is modeled as action at a distance and the change in entropy occurs only through flow of heat into or out of the system. For nonequilibrium states the entropy changes due to relaxation.

Robertson's exact statistical-mechanical theory provides a solid basis for this analysis [5,6]. The theory can be formulated either quantum mechanically or classically. It also lends itself well to linear response and thereby, the development of susceptibilities. Robertson's analysis was an extension of the work of Zwanzig and others [7]. Oppenheim and Levine extended Robertson's work, included a more general initial condition, and studied a linear approximation to entropy evolution [8]. Recently, Nettleton has studied approximations to the entropy evolution and the initial condition [9–11].

II. THEORETICAL ANALYSIS OF THE ENTROPY

A. Background

In this section we overview the derivation of the projection-operator based entropy and related evolution equations and then derive general expression for the microscopic and macroscopic entropy and its evolution. I begin by considering a general formulation of entropy evolution for an isolated system, dynamically driven by a set of fields; for example electromagnetic fields. Although the system is thermally isolated, dissipation of heat by the applied fields occurs in lossy materials. In general, changes in the nonequilibrium entropy originate from heat moving through the system boundaries and through internal relaxation. In the case at hand we assume that the system is thermally isolated, but is influenced by external electromagnetic fields, so entropy changes are due to relaxation. Although there is at present no generally accepted expression for the nonequilibrium entropy we know that it must satisfy certain conditions. These conditions include reducing to the equilibrium entropy and yielding the correct thermodynamics in equilibrium, for a closed system the evolution must be positive, the microscopic entropy must be reversible, and finally it should be derivable from an exact statistical-mechanical model. The RPOE satisfies all of these requirements. In the past, the positivity constraint has not been proven; however, in this section we prove a theorem for the positivity of RPOE evolution.

The dynamical variables are a set of quantum-mechanical operators, or classically, a set of functions of phase

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$F_1(\mathbf{r}), F_2(\mathbf{r}), \ldots$. For normalization, $F_0=1$ is included in the set. I will use a quantum-mechanical analysis, but the reader can easily translate this into classical-mechanical language by replacing all operators with functions, traces by integrations over phase variables, and commutators with Poisson brackets. These operators are, for example, the internal energy density $u(\mathbf{r})$, and the electromagnetic polarizations $\mathbf{m}(\mathbf{r})$, $\mathbf{p}(\mathbf{r})$. The operators F_n are functions of $\mathbf{r}$ and phase variables, but are not time dependent. The time dependence enters when the expectation value or trace is taken and through the driving fields. Associated with these operators are a set of thermodynamic fields, that are not operators, such as generalized temperature T and the local electromagnetic fields $\mathbf{E}_p$ and $\mathbf{H}_m$. The associated Hamiltonian $\mathcal{H}(t)$ is time dependent because the applied fields are time dependent.

In Robertson's approach [6] there are two density operators. The first is the statistical-density operator $\rho(t)$ that satisfies the Liouville equation $\partial\rho/\partial t = -i\mathcal{L}\rho$, where $\mathcal{L}(t)$ is the time-dependent Liouville operator, and the other density function is a relevant canonical-density operator $\sigma(t)$, which is developed by maximizing the information entropy subject to constraints on the expected values of operators. Although σ is not a solution to Liouville's equation, ρ can be written as a sum of σ plus a correction term. The RPOE is

$$S(t) = -k_B \mathrm{Tr}(\sigma(t) \ln \sigma(t)), \tag{1}$$

where k_B is Boltzmann's constant, and Tr denotes trace. σ is obtained by maximizing the entropy subject to constraints on the expectations of the quantum-mechanical operators $\langle F_n(\mathbf{r})\rangle = \mathrm{Tr}(F_n(\mathbf{r})\sigma(t))$. Maximization by the common variational procedure leads to the generalized canonical density

$$\sigma(t) = \exp(-\lambda(t) * F(\mathbf{r})) \tag{2}$$

with

$$\mathrm{Tr}(\exp(-\lambda(t) * F)) = 1, \tag{3}$$

where the $\lambda(\mathbf{r},t)$ are Lagrangian multipliers that correspond to local nonquantized fields, such as temperature and electromagnetic fields. I use Robertson's notation $\lambda * F = \int d^3r \Sigma_n \lambda_n(r,t) F_n(r)$. The constraints for n=0,1,2,3... are

$$\mathrm{Tr}(F_n\rho(t)) \equiv \langle F_n\rangle = \mathrm{Tr}(F_n \exp(-\lambda(t) * F)). \tag{4}$$

Robertson developed an exact equation for $\rho(t)$, that contains memory, in terms of $\sigma(t)$,

$$\rho(t) = \sigma(t) - \int_0^t d\tau \mathcal{T}(t,\tau)\{1 - P(\tau)\} i\mathcal{L}(\tau)\sigma(\tau), \tag{5}$$

for the initial condition $\rho(0)=\sigma(0)$. Oppenheim and Levine [8] generalized the analysis of Robertson to include the initial condition $\rho(0)-\sigma(0)=\chi(0)$, where $\chi(0)$ is the initial state. Using Liouville's equation and Eq. (5), the first order in time, exact nonlinear differential equations for the expected values with an initial condition on $\chi(0)$ are [6]

$$\frac{\partial\langle F_n\rangle}{\partial t} = \langle \dot{F}_n\rangle + \mathrm{Tr}(\dot{F}\mathcal{T}(t,0)\chi(0)) + \int d^3r' \int_0^t \mathrm{Tr}(i\mathcal{L}F_n(\mathbf{r})\mathcal{T}(t,\tau) \times [1 - P(\tau)] i\mathcal{L}\sigma(\tau)), \tag{6}$$

where $\mathcal{T}$ is an evolution operator, $\mathcal{T}(t,t)=1$, and satisfies

$$\frac{\partial \mathcal{T}(t,\tau)}{\partial\tau} = \mathcal{T}(t,\tau)[1 - P(\tau)] i\mathcal{L}(\tau), \tag{7}$$

where P is a projection operator (see Robertson [6]). Equations (4) and (6) form a closed system. The procedure for solution is to solve Eqs. (4) for the Lagrange multipliers in terms of $\langle F_i\rangle$ and then use these in Eq. (6). For operators that are odd under time reversal, such as magnetic moment, the first term on the right hand side (RHS) of Eq. (6) is nonzero, whereas for functions even under time reversal, such as dielectric polarization and microscopic entropy, this term is zero. However, the third term in Eq. (6) in any dissipative system is nonzero.

The dynamical evolution is denoted by

$$\dot{F}_n = i\mathcal{L}F_n. \tag{8}$$

It can be shown that [5]

$$i\mathcal{L}\sigma(t) = -\lambda(t) * \dot{F}'\sigma(t), \tag{9}$$

which by taking the trace, yields [see Ref. [8], Eq. (4.7)]

$$\mathrm{Tr}(i\mathcal{L}\sigma) = 0, \tag{10}$$

where the $'$ denotes Kubo transform.

B. Local entropy

We define the microscopic local entropy as

$$s(t) = -k_B \ln(\sigma) = k_B\lambda(\mathbf{r},t) * F(\mathbf{r}). \tag{11}$$

$F_0=1$ has been included in the set of operators for normalization. Therefore the macroscopic maximum entropy is

$$S(t) = \langle s(t)\rangle = k_B\lambda * \langle F\rangle. \tag{12}$$

The microscopic entropy is related to the change in energy in the system due to generalized driving fields divided by the temperature. The dynamical microscopic entropy evolution is

$$\dot{s}(t) = -k_B i\mathcal{L} \ln\sigma = k_B\lambda * \dot{F}'. \tag{13}$$

For classical analysis, $\dot{F}' = \dot{F}$.

Therefore from Eqs. (8)–(10), and (13), the local-entropy evolution satisfies

$$\langle \dot{s}(t)\rangle = \mathrm{Tr}(\dot{s}(t)\sigma) = k_B \mathrm{Tr}(\lambda * \dot{F}'\sigma) = -k_B \mathrm{Tr}(i\mathcal{L}\sigma) = 0. \tag{14}$$

This results from the thermally closed system being dynamically driven. This is a consequence of the fact that all of the underlying microscopic equations, that is the Liouville, Schrödinger, and Maxwell equations, are time symmetric.

The dynamical evolution is only the first term in Eq. (6). In addition, in many-body systems, there are contributions due to fluctuations, the third term in Eq. (6). As the system is dynamically driven by applied fields, the material relaxes and local fields are formed in the material that differ from the applied fields. As a consequence, a new energy distribution is formed. The origin of relaxation is the process of transforming from applied fields acting on the material to local fields acting on materials. If we use Eq. (6) with F_n replaced by $s(t)=k_B\lambda(t,\mathbf{r})*F(\mathbf{r})$, use the definitions of $\dot{s}$ and the trace, and the vanishing of the initial state term, we obtain an expression of a microscopic H theorem,

$$\begin{aligned}\frac{\partial S(t)}{\partial t} &= \mathrm{Tr}(\dot{s}\mathcal{T}(t,0)\chi(0)) \\ &\quad + \frac{1}{k_B}\int_0^t \mathrm{Tr}(i\mathcal{L}s(t)\mathcal{T}(t,\tau)i\mathcal{L}s(\tau)\sigma(\tau))d\tau \\ &= \frac{1}{k_B}\int_0^t \mathrm{Tr}(i\mathcal{L}s(t)\mathcal{T}(t,\tau)i\mathcal{L}s(\tau)\sigma(\tau))d\tau \geqslant 0. \qquad (15)\end{aligned}$$

The semidefiniteness is proven as follows: if we use Eq. (7) and operate with σ on the right sides and use the fact that $i\mathcal{L}\sigma=-\lambda*\dot{F}'\sigma$, we can solve by iteration to obtain $\mathcal{T}(t,\tau)=1-\int_\tau^t\mathcal{T}(t,\theta)\dot{s}(\theta)d\theta/k_B+\cdots\rightarrow\exp(-(1/k_B)\int_\tau^t\dot{s}(\theta)d\theta)$. Time ordering is assumed. Then we use a Taylor series expansion of this form of $\mathcal{T}$ in Eq. (15). The projection operator term in Eq. (7) does not contribute. Finally, we use the condition that the trace of the odd powers of $\dot{s}$ times σ vanish, whereas the trace of the even powers survive and are all positive. Although the trace of the microscopic entropy vanishes, irreversibility is generated by the time and spatial correlations between the microscopic entropy densities throughout the material. To summarize, for a dynamically driven system, the expected value of the microscopic entropy is zero; however, the fluctuations are nonzero and produce irreversibility and positive macroscopic entropy evolution. The positive entropy evolution is a direct result of symmetry and the vanishing of the trace of operators that change sign under time reversal.

For an open, thermally driven system, Robertson has shown that the only change to Eq. (6) is the addition of a source or sink. The source or sink is denoted by $\Delta\dot{S}$ [12]. Therefore for thermally driven entropy evolution, the only change from Eq. (15) is the addition of a thermal entropy source or sink on the RHS of Eq. (15). The input of thermal energy into an open system can be used to obtain an organized state or a more disorganized state. Therefore the entropy is not necessarily semipositive definite for an open system. Due to the additional source, the Lagrangian multipliers for a thermally driven system will be different than for a dynamically driven system. The second law states that an isolated system will evolve towards equilibrium and therefore entropy will increase to a state with maximum entropy. However, an open system can use the flow of energy through the system to maintain a state of negative entropy production [13].

III. ENTROPY AND ENTROPY EVOLUTION IN ELECTRODYNAMICS

A. Entropy in electromagnetism

The goal of this section is to develop the relationship between time-dependent electromagnetic polarization and the entropy. The analysis is for the entropy of material particles that have average polarizations **P** and **M**, which are subjected to electromagnetic driving. The analysis will develop equations in both the time and frequency domains [14,15].

In order to study relaxation, we consider a thermally insulated material. The system is driven by high-frequency fields, so it is not in equilibrium. The net entropy will increase due to the tendency to relax from a nonequilibrium state to an equilibrium state.

We consider a system subjected to applied electromagnetic fields $\mathbf{E}_a$ and $\mathbf{H}_a$ at temperature T. The microscopic internal-energy density, polarization, and magnetization are u, $\mathbf{p}$, and $\mathbf{m}$. The constraints are on the internal-energy density, polarization, and magnetization: $\mathcal{U}=\mathrm{Tr}(u\sigma)$, $\mathbf{P}=\mathrm{Tr}(\mathbf{p}\sigma)$, and $\mathbf{M}=\mathrm{Tr}(\mathbf{m}\sigma)$. $\mathbf{p}$, $\mathbf{m}$, and u, are functions of $\mathbf{r}$ and phase variables for the positions and momenta of all the particles, but have no explicit time dependence. The Hamiltonian in volume V is

$$\mathcal{H}(t)=\int d^3r\{u(\mathbf{r})-\mathbf{p}(\mathbf{r})\cdot\mathbf{E}_a(\mathbf{r},t)-\mathbf{m}(\mathbf{r})\cdot\mathbf{H}_a(\mathbf{r},t)\}. \qquad (16)$$

u contains the lattice potential energies, the kinetic energy of the bound and free charge, dipole-dipole, and other interactions before application of the fields.

The relevant generalized canonical density is obtained by maximizing the entropy in Eq. (1) subject to the constraints (see Robertson [6] and Baker-Jarvis and Kabos [16]),

$$\begin{aligned}\sigma(t)=\frac{1}{Z}\exp\biggl(-\int d^3r'(\beta(r',t)u(r')-\beta(r',t)\mathbf{p}(r')\cdot\mathbf{E}_p(r',t) \\ -\beta(r',t)\mu_0\mathbf{m}(r')\cdot\mathbf{H}_m(r',t))\biggr), \qquad (17)\end{aligned}$$

where Z is the partition function, the Lagrange multipliers that do not depend on phase variables are the inverse generalized temperature $\beta=1/k_BT$ and generalized local fields $\mathbf{E}_p$, $\mathbf{H}_m$. The microscopic entropy density for a system subjected to applied electric and magnetic fields is

$$s(t)=\int(1/T)[u-\mathbf{p}\cdot\mathbf{E}_p-\mu_0\mathbf{m}\cdot\mathbf{H}_m]d^3r+k_B\ln Z, \quad (18)$$

where $\mathcal{F}=-k_BT\ln Z$ is the free-energy density. The microscopic entropy rate is

$$\dot{s}(t)=\int\frac{1}{T}[\dot{u}-\dot{\mathbf{p}}\cdot\mathbf{E}_p-\mu_0\dot{\mathbf{m}}\cdot\mathbf{H}_m]d^3r, \qquad (19)$$

and by Eq. (10), $\langle\dot{s}\rangle=0$. The fundamental equation for the macroscopic entropy is obtained from Eqs. (1) and (17),

$$S(t) = -k_B \mathrm{Tr}(\sigma(t)\ln \sigma(t)) = \int d^3r \frac{1}{T}[\mathcal{U}(\mathbf{r},t) - \mathbf{P}(\mathbf{r},t)\cdot \mathbf{E}_p(\mathbf{r},t) - \mu_0 \mathbf{M}(\mathbf{r},t)\cdot \mathbf{H}_m(\mathbf{r},t)] + k_B \ln Z. \tag{20}$$

We see that for a given internal energy, a highly polarized state where the dipoles and field are aligned has lower entropy. In equilibrium any changes in entropy relate to heat exchange with a reservoir. For nonequilibrium systems, the entropy can change even if it is thermally isolated, due to internal relaxation.

B. Electromagnetic entropy evolution

In this section we will obtain balance equations for the entropy utilizing Maxwell's equations. In order to proceed we need general equations of motion for the polarizations. We have previously obtained general equations of motion for magnetic and dielectric polarization from Eq. (6), neglecting the initial-state contribution, that are expressed in terms of the differences between the applied and local fields [16–18]. I reproduce them here for the present analysis. Using Eq. (6) the equation of motion for the magnetization, neglecting electric interactions, is

$$\frac{\partial \mathbf{M}(\mathbf{r},t)}{\partial t} \approx -\mu_0|\gamma_{eff}|\mathbf{M}(\mathbf{r},t)\times \mathbf{H}(\mathbf{r},t) + \int d^3r' \int_0^t \overleftrightarrow{\chi}_{m0}\cdot \overleftrightarrow{\mathbf{K}}_m(\mathbf{r},t,\mathbf{r}',\tau)\cdot (\mathbf{H}_a(\mathbf{r}',\tau) - \mathbf{H}_m(\mathbf{r}',\tau))d\tau, \tag{21}$$

where

$$\overleftrightarrow{\mathbf{K}}_m(\mathbf{r},t,\mathbf{r}',\tau) = \frac{\mu_0}{k_B T}\mathrm{Tr}\big(i\mathcal{L}(t)\mathbf{m}(\mathbf{r})\mathcal{T}(t,\tau)(1-P(\tau)) \times i\mathcal{L}(\tau)\mathbf{m}(\mathbf{r}')\sigma(\tau)\big)\cdot \overleftrightarrow{\chi}_{m0}^{-1}, \tag{22}$$

and where $\overleftrightarrow{\chi}_{m0} = \mu_0 \int d^3r \beta\langle \mathbf{mm}\rangle_0$ is the static magnetic susceptibility. The detailed form of the correlation functions do not concern us here.

The polarization rate without magnetic effects is

$$\frac{\partial \mathbf{P}(\mathbf{r},t)}{\partial t} = \int d^3r' \int_0^t \overleftrightarrow{\chi}_{e0}\cdot \overleftrightarrow{\mathbf{K}}_e(\mathbf{r},t,\mathbf{r}',\tau)\cdot (\mathbf{E}_a(\mathbf{r}',\tau) - \mathbf{E}_p(\mathbf{r}',\tau))d\tau, \tag{23}$$

where

$$\overleftrightarrow{\mathbf{K}}_e(\mathbf{r},t,\mathbf{r}',\tau) = \frac{1}{k_B T}\mathrm{Tr}\big(i\mathcal{L}(t)\mathbf{p}(\mathbf{r})\mathcal{T}(t,\tau)i\mathcal{L}(\tau)\mathbf{p}(\mathbf{r}')\sigma(\tau)\big)\cdot \overleftrightarrow{\chi}_{e0}^{-1}, \tag{24}$$

where we used the fact $\mathbf{p}$ commutes with itself and $\overleftrightarrow{\chi}_{e0} = \int d^3r \beta\langle \mathbf{pp}\rangle_0$ is the static electric susceptibility. Equations (21) and (23) are exact and with an appropriate kernels, Debye, Landau-Lifshitz, and other approximate equations follow. We will need linear approximations to the local fields $\mathbf{E}_p$ and $\mathbf{H}_m$ (see Ref. [16]) that can be obtained by expanding $\mathbf{P}$, $\mathbf{M}$, and $\mathcal{U}$ to first order, so that $\mathbf{E}_p \approx \mathbf{P}/\chi_{e0} + \overleftrightarrow{L}_e\cdot \mathbf{P}/\chi_{e0}$, where $\overleftrightarrow{L}_e$ is the depolarization tensor, and the macroscopic field is $\mathbf{E}\approx \mathbf{E}_a - \overleftrightarrow{L}_e\cdot \mathbf{P}/\chi_{e0}$. There are similar expressions for the local magnetic field. A linear approximation to the generalized temperature can also be found by expansion of the internal-energy constraint $\beta = (\mathcal{U}_0 - \mathcal{U})(1 + V\langle u\mathbf{p}\rangle_0\cdot \mathbf{E}_p/\langle u^2\rangle_0 + V\langle u\mathbf{m}\rangle_0\cdot \mathbf{H}_m/\langle u^2\rangle_0)/\langle u^2\rangle_0$.

The time rate of change of entropy in a material confined, for example, in a waveguide, is given by

$$\begin{aligned}\frac{dS(t)}{dt} &= -k_B \frac{d}{dt}\mathrm{Tr}(\sigma(t)\ln \sigma(t)) \\ &= \int d^3r \frac{1}{T}\left\{\frac{\partial \mathcal{U}}{\partial t} - \frac{\partial \mathbf{P}}{\partial t}\cdot \mathbf{E}_p - \mu_0 \frac{\partial \mathbf{M}}{\partial t}\cdot \mathbf{H}_m\right\} \\ &= \int d^3r \frac{1}{T}\left\{\frac{\partial \mathbf{P}(\mathbf{r},t)}{\partial t}\cdot (\mathbf{E}_a(\mathbf{r},t) - \mathbf{E}_p(\mathbf{r},t)) + \mu_0 \frac{\partial \mathbf{M}(\mathbf{r},t)}{\partial t}\cdot (\mathbf{H}_a(\mathbf{r},t) - \mathbf{H}_p(\mathbf{r},t))\right\},\end{aligned} \tag{25}$$

where only the relaxation components survive in $\partial \mathbf{P}/\partial t$ and $\partial \mathbf{M}/\partial t$. Also we used $\langle \dot{s}\rangle = 0$ and by use of the Hamiltonian in Eq. (16) we have used

$$\frac{\partial \mathcal{U}}{\partial t} = \frac{\partial \mathbf{P}}{\partial t}\cdot \mathbf{E}_a + \mu_0 \frac{\partial \mathbf{M}}{\partial t}\cdot \mathbf{H}_a. \tag{26}$$

Note that $\mathcal{U}$ does not contain the vacuum field energy densities $\epsilon_0|\mathbf{E}|^2 + \mu_0|\mathbf{H}|^2$, but only the particle internal energy densities. The positivity of the last line in Eq. (25) can be understood as follows: if $\mathbf{E}_a > \mathbf{E}_p$, then the polarization will increase, whereas if $\mathbf{E}_a < \mathbf{E}_p$ then the polarization will decrease. In both cases the net result is an increasing time evolution of the entropy. Equation (25) is an expression of the first law of thermodynamics for nonequilibrium systems: $d\mathcal{U} = TdS + dW$. Here, $d\mathcal{U}$ is the change in internal energy and dW is the work performed. Changes in entropy of an electromagnetically driven material are closely tied to changes in stored energy.

C. Macroscopic electromagnetic entropy evolution

If we use Maxwell's equations, we have an alternative expression for the entropy evolution. This evolution equation contains Poynting flux where electromagnetic energy can enter or exit the system through the system ports such as waveguides,

$$\begin{aligned}\frac{dS(t)}{dt} - \int dA \frac{1}{T}\{\mathbf{E}_p(\mathbf{r},t)\times \mathbf{H}_m(\mathbf{r},t)\}\cdot \mathbf{n} &= \int d^3r \left[\frac{1}{T}\frac{\partial \mathcal{U}}{\partial t} - \frac{\nabla T}{T^2}\cdot \{\mathbf{E}_p(\mathbf{r},t)\times \mathbf{H}_m(\mathbf{r},t)\}\right] \\ &\quad + \int d^3r \frac{1}{T}\left[\mathbf{J}\cdot \mathbf{E}_p(\mathbf{r},t) + \frac{\epsilon_0}{2}\frac{\partial |\mathbf{E}_p(\mathbf{r},t)|^2}{\partial t} + \frac{\mu_0}{2}\frac{\partial |\mathbf{H}_m(\mathbf{r},t)|^2}{\partial t}\right].\end{aligned} \tag{27}$$

In Eq. (27), $-\mathbf{E}_p\times \mathbf{H}_m/T$ forms an entropy flux, where $\mathbf{n}$ is the outward normal to the surface. $\mathbf{J}\cdot\mathbf{E}_p$ is the dissipated power density from the local fields. The last terms in Eq. (27) represent the stored-field energies since we are studying the entropy in relation to polarization and not the fields. The term proportional to the temperature gradient is a phonon-electromagnetic flux that under the appropriate conditions could lead to minimum-entropy production [13]. In equilibrium the only contribution to the increasing entropy would be from the dissipative term. We see that the entropy change $\delta Q/T$ is due to a virtual heat δQ in the relaxation process, which is manifested as heating of the lattice, polarization, and as an entropy flux traveling through the material.

D. Spectral entropy

Since the entropy evolution is related to the energy dissipated by the driving fields and internal relaxation, this change in entropy must be related to the stored energy, electrical impedance, permittivity, and permeability. In electrical measurements we generally work in the frequency domain. The spectral entropy for a system at constant temperature can be calculated, assuming a $e^{i\omega t}$ time dependence for $\Delta S(t)$, so that $\Delta S(\omega)=\Delta S'(\omega)-i\Delta S''(\omega)$. We can relate the power required to polarize or depolarize a material, at constant temperature to a polarization impedance, $Z_p=R_p+iX_p$. This impedance is only part of the total impedance. From energy conservation $\Delta S''\geqslant 0$. From Eq. (25) the change in entropy relative to application of an applied field is defined as

$$\begin{aligned}\Delta S'(\omega) &= \mathrm{Re}\int d^3r\frac{1}{2T}[\mathbf{P}^*\cdot(\mathbf{E}_a-\mathbf{E}_p)-\mu_0\mathbf{M}\cdot(\mathbf{H}_a^*-\mathbf{H}_m^*)]\\ &\approx \mathrm{Re}\int d^3r\frac{1}{2T}[\mathbf{P}^*\cdot(\mathbf{E}-\mathbf{P}/\chi_{e0})\\ &\quad -\mu_0\mathbf{M}\cdot(\mathbf{H}^*-\mathbf{M}^*/\chi_{m0})]\\ &= \int d^3r\frac{1}{2T}[\chi_e'|\mathbf{E}|^2-\mu_0\chi_m'|\mathbf{H}|^2\\ &\quad +\mu_0|\mathbf{M}|^2/\chi_{m0}-|\mathbf{P}|^2/\chi_{e0}]\\ &= \frac{|I|^2X_p}{\omega T},\end{aligned} \tag{28}$$

$$\begin{aligned}\Delta S''(\omega) &= \mathrm{Im}\int d^3r\frac{1}{2T}[\mathbf{P}^*\cdot(\mathbf{E}_a-\mathbf{E}_p)-\mu_0\mathbf{M}\cdot(\mathbf{H}_a^*-\mathbf{H}_m^*)]\\ &\approx \int d^3r\frac{1}{2T}[\chi_e''|\mathbf{E}|^2+\mu_0\chi_m''|\mathbf{H}|^2]=\frac{|I|^2R_p}{\omega T},\end{aligned} \tag{29}$$

where I is an effective current passing through the material. For conductive materials, a dc loss term σ/ω can be added to the imaginary part of the susceptibility χ_e''. The imaginary part of the spectral entropy relates to increases in entropy due to heating, whereas the real part relates to entropy changes due to stored energy and organization. For example, a system of charged particles, initially randomized, can form an ordered state as it goes into resonance or systemic rotation. A resonant state stores energy. The real part of the spectral entropy relates to changes in stored energy as the material attempts to relax and can be positive or negative. If a static field is applied to a material therefore in a short time equilibrium is attained so that there is no further internal relaxation, and $\Delta S\rightarrow 0$. Even in a dissipative system at frequencies below molecular resonances, there is generally some stored energy in the polarization process and therefore a nonzero S'.

E. Application to dielectric and magnetic response

The entropy evolution for dielectric relaxation is the semipositive definite quantity

$$\begin{aligned}\frac{dS(t)}{dt} &= \int d^3r\int d^3r'\int d\tau\frac{1}{T}(\mathbf{E}_a(\mathbf{r},t)\\ &\quad -\mathbf{E}_p(\mathbf{r},t))\cdot\overset{\leftrightarrow}{\chi}_{e0}\cdot\overset{\leftrightarrow}{\mathbf{K}}_e(\mathbf{r},t,\mathbf{r}',\tau)\cdot(\mathbf{E}_a(\mathbf{r}',\tau)\\ &\quad -\mathbf{E}_p(\mathbf{r}',\tau)).\end{aligned} \tag{30}$$

There are many models for magnetic relaxation. For magnetic response an approximation to the entropy evolution related to the Landau-Lifshitz relaxation [19] can be found from Eq. (25) to be the semipositive definite quantity

$$\frac{dS(t)}{dt}=\frac{\mu_0|\gamma|\alpha}{|\mathbf{M}|}\int\frac{1}{T}[(\mathbf{M}(t)\times\mathbf{H}(t))\cdot(\mathbf{M}(t)\times\mathbf{H}(t))]dV, \tag{31}$$

where α is the Landau-Lifshitz damping factor and γ is the gyromagnetic ratio.

Application 1:

As an application to dielectric relaxation we consider a simple model and study the polarization relaxation and entropy change. We assume that the polarization satisfies a damped harmonic oscillator equation $d\mathbf{P}/dt=-\gamma_e(\mathbf{P}-\chi_{e0}\mathbf{E}_0)$, where γ_e is a damping coefficient. For this example, we use Eq. (25) for spatial invariant polarization. We assume we have $P(t=0)=\chi_{e0}E_0$. When the constant electric field E_0 is turned off at $t=0$, we have $P(t)=e^{-\gamma_e t}\chi_{e0}E_0$. Since the field is described by a step function we assume in the material $E_p=E_0$ and $E_a=0$. The polarization entropy density evolution is described by $dS/dt=k_Be^{-\gamma_e t(\gamma_e\chi_{e0}E_0^2/k_BT)}$. If instead we have an initially unpolarized state and turn the field on at $t=0$, $E_p=0$, and $E_a=E_0$, we have $P(t)=\chi_{e0}E_0(1-e^{-\gamma_e t})$. In this case dS/dt is the same as the previous example.

Application 2:

Consider the same example as studied for dielectric polarization in the previous subsection, but now the material has both dielectric and magnetic properties and we include a constant applied magnetic field in addition to the constant electric field. For simplicity, for heavily damped magnetic relaxation, we assume that the magnetization satisfies the same equation as the polarization in the previous section, but with τ_e replaced with τ_m and χ_{e0} replaced with χ_{m0}. Then the entropy-density evolution for dielectric and magnetic, highly damped relaxation with no free charge present is from Eq. (27)

$$\frac{dS}{dt} = k_B\left[\frac{\mu_0 A}{V}(\mathbf{E}\times\mathbf{H})\cdot\mathbf{n}e^{-(\gamma_e+\gamma_m)t} - \gamma_e\epsilon_0|\mathbf{E}|^2e^{-\gamma_e t} - \gamma_m\mu_0|\mathbf{H}^2|e^{-\gamma_m t}\right]\frac{1}{k_BT}. \tag{32}$$

F. Relationship of spectral entropy to the electric permittivity

Let us now consider the linear spectral polarization entropy that is due to the application of a field. We wish to develop a measurable quantity for harmonic-frequency excitation. By Eqs. (28) and (29), the spectral-entropy density is related to the linear permittivity as

$$\Delta S_d'(\omega) = k_B\left[\frac{[\epsilon_r'(\omega)-\epsilon_\infty][\epsilon_{rs}-\epsilon_r'(\omega)]-\epsilon_r''^2(\omega)}{\epsilon_{rs}-\epsilon_\infty}\frac{\epsilon_0|\mathbf{E}(\omega)|^2}{2k_BT}\right], \tag{33}$$

and

$$\Delta S_d''(\omega) = k_B\left[\frac{\epsilon_0\epsilon_r''(\omega)|\mathbf{E}(\omega)|^2}{2k_BT}\right], \tag{34}$$

where ϵ_{rs} is the relative static permittivity, ϵ_r', ϵ_r'' are the real and imaginary parts of the relative permittivity, and ϵ_0 is the permittivity of free space. The linear, initial permeability may satisfy analogous equations.

In order to analyze the interpretation of the real part of the spectral entropy we can use Eq. (23) to obtain a very general expression for the electric susceptibility,

$$\chi_e(\omega) = \frac{\chi_{e0}}{1+i\omega(\Theta_r+i\Theta_i)} = \chi_{e0}\frac{1-\omega\Theta_i(\omega)}{[1-\omega\Theta_i(\omega)]^2+\omega^2\Theta_r^2(\omega)} - i\chi_{e0}\frac{\omega\Theta_r(\omega)}{[1-\omega\Theta_i(\omega)]^2+\omega^2\Theta_r^2(\omega)}. \tag{35}$$

The complex relaxation times are related to the complex poles. The complex relaxation times are $\Theta_{relax} = 1/\tilde{K}_e(\omega) = \Theta_r(\omega)+i\Theta_i(\omega)$, where $\tilde{K}_e(\omega)$ is the Fourier transform of the kernel in Eq. (24). $\omega\Theta_i$ is an even function of ω and $\omega\Theta_r$ is an odd function. In general, the poles for χ_e appear either on or off the positive imaginary axis [the complex roots of $1+i\omega(\Theta_r+i\Theta_i)=0$]. For Debye relaxation the pole is on the positive imaginary axis and $\Theta_i=0$. For resonant systems in the upper half plane, there are symmetric off-axis poles relative to the imaginary axis.

The spectral-entropy density related to Eq. (35) is

$$\Delta S_d'(\omega) = -k_B\frac{\omega\Theta_i(\omega)}{[1-\omega\Theta_i(\omega)]^2+\omega^2\Theta_r^2(\omega)}\frac{\chi_{e0}E_0^2}{2k_BT}, \tag{36}$$

and

$$\Delta S_d''(\omega) = k_B\frac{\omega\Theta_r(\omega)}{[1-\omega\Theta_i(\omega)]^2+\omega^2\Theta_r^2(\omega)}\frac{\chi_{e0}E_0^2}{2k_BT}. \tag{37}$$

Therefore we see that $\Delta S_d'(\omega)$ relates primarily to Θ_i and $\Delta S_d''(\omega)$ relates primarily to Θ_r. In Fig. 1 we plot the normalized forms of Eqs. (36) and (37). For simple resonant response, since $\Theta_i \propto \omega$ is positive, $\Delta S_d'(\omega) < 0$ and achieves a minimum at resonance. The relaxation entropy goes to zero as $\omega \to 0$ and is maximum near the loss peaks and again goes to zero at high frequencies. The Cole-Cole, Cole-Davidson [20], and related models of dielectric relaxation all modify the Debye model in a way that can be related to adding a complex component to the relaxation time [20]. For example, in the Cole-Davidson model $\chi=\chi_0/(1+i\tau\omega)^\alpha$ for small α is $\approx\chi_{e0}/[1+\alpha\ln(1+i\omega\tau_r)]=\chi_{e0}/\{1+i\omega[\alpha\theta/\omega - i\alpha\ln(\sqrt{1+\omega^2\tau_r^2})/\omega]\}$, where $\theta=\arctan\omega\tau_r$. In this example, $\Theta_r=\alpha\theta/\omega$ and $\Theta_i=-\alpha\ln(\sqrt{1+\omega^2\tau_r^2})/\omega$ and therefore the response is relaxation. The spectral entropy is then calculated from Eqs. (36) and (37). In Fig. 1 we show the frequency dependence and spectral entropy for the Cole-Davidson model. For the Debye relaxation discussed in Sec. III E, Θ_i and Θ_r are independent of frequency, so that

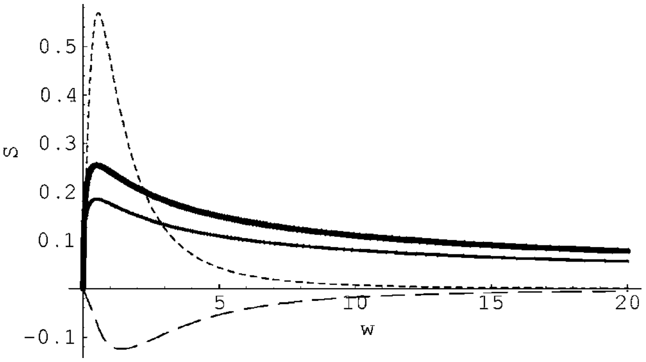

FIG. 1. Normalized plot of the spectral entropy as a function of angular frequency. The negative and positive dashed curves are Eqs. (36) and (37), respectively, for $\Theta_i \propto \omega$. The real part and imaginary parts of the Cole-Cole equation, $\chi_{e0}/[1+(i\omega\Theta_r)^\alpha]$, with $\alpha=0.6$, $\Theta_r=2$, $\Theta_i\omega=0.5$, are given in the thin and thick solid curves, respectively. All curves are scaled with $\chi_{e0}E_0^2/2T=1$.

$$\Delta S_d'(\omega) = 0, \tag{38}$$

and

$$\Delta S_d''(\omega) = k_B\frac{\omega\tau_e}{1+\omega^2\tau_e^2}\frac{\chi_{e0}E_0^2}{2k_BT}. \tag{39}$$

In the Debye model the imaginary part of the spectral entropy is zero. This illustrates the point that in the Debye model there is no imaginary part of the relaxation time or stored polarization energy, but rather pure dissipation and therefore only dissipative entropy. The Drude model is the special case where $\Theta_i \propto \omega$. The Drude model incorporates resonance to first order, and therefore the real part of the spectral entropy is nonzero.

IV. CONCLUSIONS

This paper developed the theory underlying time-dependent electromagnetic entropy and derived spectral entropy for electromagnetic driving from first principles, proved a general *H* theorem, applied the results to microscopic electromagnetism, and related it to relaxation. The approach uses a previously developed Liouville-Hamiltonian-based statistical-mechanical theory. I developed the relationship of the spectral entropy to the permittivity, permeability, and impedance. In highly dissipative relaxations, the spectral entropy is dominated by the imaginary part. Measurements of the permittivity indicate that there are important effects of the real part of the entropy, which corresponds to reactive energy.

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