Projection-operator based statistical mechanical theory of local and macroscopic electromagnetic fields

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Abstract: I study the origins of the applied, macroscopic, and local electromagnetic fields by a statistical-mechanical method. In order to obtain the macroscopic fields from the microscopic fields I use a relevant statistical-density function for ensemble averaging. I present novel equations for the time-dependent local fields as functions of the applied field, polarization, and macroscopic field.

Introduction

As measurements of the electrical properties of materials are made at nanometer scales, there is a need to understand the details of microscopic electromagnetic theory. The goal of this paper is to overview the various fields used in electromagnetism and to present an equation for the time-dependent local field calculated from a statistical-mechanical theory. The details of the statistical-mechanical model are contained in a previous publication [1, 2].

When electromagnetic fields are applied to a material, the fields in the material are comprised of the effects of both the applied field and particle interactions. For example, when an applied electromagnetic field interacts with a dielectric material, the field in the material is modified by a surface-charge dipole-depolarization field that opposes the applied field. In addition there are the effects of the internal energy on the electromagnetic behavior. For example, depolarization, demagnetization, thermal expansion, and quantum interactions all influence the dipole orientations and therefore the fields. In constitutive modeling our goal is to express the material properties in terms of the macroscopic (Maxwell) field and not the applied or effective fields.

The applied field originates from charges external to the specimen under test. The macroscopic field satisfies Maxwell's equations with appropriate boundary conditions and in materials is usually not the same as the applied field, but rather represents an average of the far and near fields. The microscopic field is the electromagnetic field on the atomic scale. The local electromagnetic field is the aver-

age microscopic field at a specific point in a material and can be represented as a sum of the macroscopic field and near-fields. The local field is defined by Ascroft and Mermin as an average of the near fields within a radius r_0 from an observation point $\mathbf{r}$: $\mathbf{E}_L = \mathbf{E} + \mathbf{E}_{near}^{local} - \mathbf{E}_{near}^{macro}$ [3]. It is well-known that in ferroelectricity the local field can become very large so there is a real need for comprehensive models of the local field. Whereas, there has been copious research on static local fields, much less research has been developed for the time-dependent local fields.

The macroscopic field is defined by Ascroft and Mermin as an average of all macroscopic fields in a region r_0 around an observation point $\mathbf{r}$ due to charges in both the near and far regions: $\mathbf{E} = \mathbf{E}_{far}^{macro} + \mathbf{E}_{near}^{macro}$ [3].

Two methods are commonly used to construct the macroscopic field from the microscopic field: ensemble and volume averaging. In this paper we use the former approach. The volume averaging approach to the macroscopic field assumes a spatial distribution function $f(\mathbf{r})$ that satisfies

$$\mathbf{E} = \int d\mathbf{r}' \mathbf{E}_{micro}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}'). \quad (1)$$

The form of the distribution function is seldom explicitly determined and must depend on the material properties. However, in most volume averaging algorithms the averaging distribution is not expressed in terms of the polarization and magnetization. In the ensemble averaging approach a phase-space probability density function that satisfies Liouville's equation is constructed. In our approach [1], the relevant distribution function σ is explicitly constructed to reproduce the macroscopic polarization, magnetization, and internal energy at specific times. The relevant density function σ is only part of the full statistical-density function ρ and the relationship between the two is [2]

$$\rho(t) = \sigma(t) - \int_0^t d\tau T(t, \tau) \{1 - P(\tau)\} iL(\tau) \sigma(\tau). \quad (2)$$

We see that the full statistical-density function, that fully describes the microstructure, is separated into

relevant and irreversible components. The irreversible part originates from loss. The integrating factor is $T(t, \tau)$ satisfies the initial value problem

$$\frac{\partial T(t, \tau)}{\partial \tau} = T(t, \tau)\{1 - P(\tau)\}i\mathcal{L}, \quad (3)$$

with initial condition $T(t, t) = 1$, P is a non-hermitian projection-like operator, and $\mathcal{L}$ is Liouville's operator. All of the operators T , P , and $\mathcal{L}$ are linear. For a system in equilibrium, $\rho \propto \exp(-\mathcal{H}/kT)$ where $\mathcal{H}$ is the Hamiltonian, T is temperature, and k is Boltzmann's constant. We define the macroscopic electric and magnetic fields as the ensemble-averaged microscopic fields with respect to σ : $\mathbf{E} = Tr(\mathbf{e}\sigma)$, $\mathbf{H} = Tr(\mathbf{h}\sigma)$. The field that polarizes a molecule is the local field $\mathbf{E}_L$ and the polarization is $\mathbf{p} = \alpha\mathbf{E}_L$, where α is the polarizability. In order to use this expression in Maxwell's equations the local field needs to be expressed in terms of the macroscopic field $\mathbf{E}_L = \beta\mathbf{E}$, where β is some function. Calculation of this relationship is not always simple.

Lorentz and Onsager local fields

In this section we overview the static theory of the local field. Dielectric and magnetic materials may contain both permanent and induced dipole moments. Commonly, the local field for materials without permanent dipole moments is modeled by the Lorentz field, which is defined as the field in a cavity that is carved out of the material around a specific molecule. It is important to note that recent research indicates that in some materials, the Lorentz local field does not lead to the correct polarizabilities[4]. A well-known example of the relationship between the applied, macroscopic, and local fields is given by a Lorentz spherical cavity in a static electric field. In this example, the applied field, depolarization field, and macroscopic field in a sphere are related by

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

where the macroscopic polarization is $\mathbf{P} = \epsilon_0(\epsilon_r - 1)\mathbf{E} = (N\alpha/V)\mathbf{E}_L$, where N is the number of molecules in the volume V and ϵ_0 is the permittivity of vacuum. In the Lorentz model, the local field is a sum of applied, depolarization, Lorentz, and atomic fields [5]

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

For cubic lattices in a sphere, the average atomic field vanishes and the local field satisfies

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

In general, the local field is larger than the macroscopic field and in this example it is equal to the applied field. Therefore the field acting on a dipole is larger than the macroscopic field and must be accounted for in the constitutive equations. The Lorentz field is related to the macroscopic field as

$$\mathbf{E}_L = \frac{1}{3}(\epsilon_r + 2)\mathbf{E}. \quad (7)$$

Onsager modified the Lorentz theory by separating the local field into a cavity field $\mathbf{E}_C$ and reaction field $\mathbf{E}_R$. The Onsager cavity field is

$$\mathbf{E}_C = \frac{3\epsilon_r}{2\epsilon_r + 1}\mathbf{E}. \quad (8)$$

The cavity field is the field that acts on the permanent dipole moment. We note that as $\epsilon_r \rightarrow \infty$, $\mathbf{E}_C \rightarrow 1.5\mathbf{E}$, but $\mathbf{E}_L \rightarrow \infty$. The Onsager reaction field is proportional to the dipole moment $\mathbf{m}$

$$\mathbf{E}_R = g\mathbf{m}, \quad (9)$$

where g depends on the permittivity[6]. Therefore the reaction field does not influence the permanent moment orientation, but does influence the induced moment.

The formation of the local field is a very complex process. The applied field polarizes charge in a specific molecule, then the molecule's dipole field modifies the dipole orientations of other molecules in close proximity. This then produces another field correction to the molecule's field. This all gets more complicated for time-dependent behavior. We call the local electromagnetic field the locally-averaged field at a specific point in a material and is a function of both the applied and multipole fields in the media.

Statistical-mechanical projection-operator approach

In our approach developed in [7], the distribution function σ is explicitly constructed from the macroscopic polarization, magnetization, and internal energy in a self-consistent fashion. We use constraints

on the theoretical expected values of the polarization and internal energy to build a relevant generalized canonical-density function σ by maximizing the information entropy (see references [1, 2]) The relevant density function is the ensemble averaging analog of the volume-averaging density function f . In (2) we see that σ is only part of the full statistical-density function that describes the N-body system completely. Using this formalism, exact evolution equations can be derived for the polarization $\mathbf{P}$, the magnetization $\mathbf{M}$, and current density $\mathbf{J}$ [1].

The relevant canonical density, σ , is constructed by maximizing the information entropy for each time t

$$S(t) = -kTr(\sigma(t) \ln \sigma(t)), \quad (10)$$

subject to constraints on the expected values of the relevant variables $\mathbf{F}_j$. These relevant variables $\mathbf{F}_j$ are for example, the polarization $\mathbf{P}$, magnetization $\mathbf{M}$, and internal-energy density $\mathcal{U}$. The constraints are the expected values of the relevant microscopic variables with respect to σ

$$\begin{aligned} \langle \mathbf{F}_i(\mathbf{r}, t) \rangle \\ = \frac{1}{Z} Tr \left(\mathbf{F}_i(\mathbf{r}) \exp \left(- \int d^3 \mathbf{r}' \sum_j \lambda_j(\mathbf{r}', t) \mathbf{F}_j(\mathbf{r}') \right) \right). \end{aligned} \quad (11)$$

These constraints are incorporated into the information-entropy expression by use of Lagrange multipliers λ_j and the resulting variational expression is maximized to obtain the relevant canonical-density function

$$\sigma(t) = \frac{1}{Z} \exp \left(- \int d^3 \mathbf{r}' \sum_j \lambda_j(\mathbf{r}', t) \cdot \mathbf{F}_j(\mathbf{r}') \right), \quad (12)$$

where Z is the partition function. The relevant density function σ accomplishes an averaging that we feel is more self-consistent than that used in most statistical-mechanical approaches because the canonical-density function, being the relevant contribution of the full statistical density function ρ , incorporates the exact values of the polarization, magnetization, and internal energy at all times and positions[8, 9]. For comparison purposes, Jackson uses a volume averaging test function[10]. Robinson uses a truncated ensemble approach[9, 10] and Mazur[8] uses the ensemble distribution function ρ directly for averaging. We can extract the relationship between the macroscopic, local, and applied fields by requiring the expected value of the effective-microscopic

fields $\mathbf{e}$ and $\mathbf{h}$ to be a local fields $\mathbf{E}_L$ and $\mathbf{H}_L$. These local fields are exact generalizations of (1). These definitions of the macroscopic fields make sense because σ is the generalized canonical-density function for the relevant variables, constructed from the macroscopic $\mathbf{P}$ and other relevant variables. If we multiply Eq. (2) by the microscopic fields and integrate over the phase variables, the time-dependent local fields can be written as

$$\begin{aligned} \mathbf{E}_L(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, t) + \\ \int d^3 \mathbf{r}' \int_0^t d\tau Tr \{ \mathbf{e}(\mathbf{r}) T(t, \tau) \{ 1 - P \} [\mathbf{p}(\mathbf{r}'), \sigma] \} \cdot \mathbf{E}(\mathbf{r}', \tau), \end{aligned} \quad (13)$$

$$\begin{aligned} \mathbf{H}_L(\mathbf{r}, t) = \mathbf{H}(\mathbf{r}, t) + \\ \int d^3 \mathbf{r}' \int_0^t d\tau Tr \{ \mathbf{h}(\mathbf{r}) T(t, \tau) \{ 1 - P \} [\mathbf{m}(\mathbf{r}'), \sigma] \} \cdot \mathbf{H}(\mathbf{r}', \tau), \end{aligned} \quad (14)$$

where $[\cdot]$ denotes Poisson bracket. For comparison purposes we can expand (11) to obtain the following approximations to the local fields given by (13) and (14)

$$\mathbf{E}_L(\mathbf{r}, t) \approx \overset{\leftarrow}{\chi}_{0pp}^{-1} \mathbf{P}(\mathbf{r}, t) + \overset{\rightarrow}{\mathbf{L}}_p \cdot \mathbf{P}(\mathbf{r}, t), \quad (15)$$

$$\mathbf{H}_L(\mathbf{r}, t) \approx \overset{\leftarrow}{\chi}_{0mm}^{-1} \mathbf{M}(\mathbf{r}, t) + \overset{\rightarrow}{\mathbf{L}}_m \cdot \mathbf{M}(\mathbf{r}, t). \quad (16)$$

Example 1: The Lorentz local field

As a check on the interpretation of $\mathbf{E}_L$ in (15) as a local field, we consider Eq. (15) for the case of a cavity in a dielectric. For an ellipsoid the depolarization factor is: $L_p = (\epsilon_r(2) - \epsilon_r(1)) / \epsilon_r(1)(\epsilon_r(2) - 1)$. Therefore for a sphere the local field reduces to the Lorentz local field (6)

$$\mathbf{E}_L(\mathbf{r}, t) \approx \overset{\leftarrow}{\chi}_{0pp}^{-1} \mathbf{P}(\mathbf{r}, t) + \overset{\rightarrow}{\mathbf{L}}_p \cdot \mathbf{P}(\mathbf{r}, t) = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0}. \quad (17)$$

Example 2: The relevant density function and calculation of the polarization

As a simple example, we consider a collection of N dipole moments in a z-directed electric field. The microscopic polarization is defined as $\mathbf{p} = \sum_i e_i \mathbf{r}_i \delta(\mathbf{r} - \mathbf{r}_i)$, $\lambda_1 = -\mathbf{E}_L/kT$. The relevant density function is

$$\sigma = \frac{1}{Z} \exp \left(\sum_j e_j \mathbf{r}_j \cdot \mathbf{E}_L/kT \right). \quad (18)$$

The macroscopic polarization is

$$\begin{aligned} \mathbf{P}(\mathbf{r}) &= \frac{N|e|r}{Z} \int_0^\pi d\theta \cos\theta \sin\theta \exp\left(\frac{|e|rE_L \cos\theta}{kT}\right) \hat{\mathbf{z}} \\ &\approx \frac{N\mu^2 E_L}{3kT} \hat{\mathbf{z}}, \end{aligned} \quad (19)$$

where the molecular permanent moment is $\mu = |e|r$ and the last term in (19) is a high-temperature approximation. $d\Gamma$ denotes integration over phase variables. This is the same result as obtained by rotational-diffusion approaches. The partition function is

$$\begin{aligned} Z &= \int d\Gamma \exp\left(\frac{e_j \mathbf{r}_j \cdot \mathbf{E}_L}{kT}\right) = \\ &\int \sin\theta \exp\left(\frac{\mu E_L \cos\theta}{kT}\right) d\theta. \end{aligned} \quad (20)$$

Conclusion

Projection-operator statistical mechanics can be used to obtain very general relationships for the time and spatial dependent local fields. The local field is composed of the macroscopic field and a material-related field. The first terms in (13) and (14) are the macroscopic fields and the last terms are due to local dipoles. The macroscopic field is the field used in Maxwell's equation and constitutive relationships and is a global average of the applied and depolarization fields. The macroscopic field is generated from the relevant part of the full statistical-density function.

References

- [1] J. Baker-Jarvis and P. Kabos, "Dynamic constitutive relations for polarization and magnetization," *Phys. Rev. E*, vol. 64, pp. 056127-1:14, 2001.
- [2] B. Robertson, "Equations of motion in non-equilibrium statistical mechanics," *Phys. Rev.*, vol. 144, pp. 151-161, April 1966.
- [3] N. W. Ashcroft and N. Mermin, *Solid State Physics*. New York: Holt, Rinehart and Winston, 1976.
- [4] M. E. Crenshaw and C. M. Bowden, "Lorentz local-field effects on spontaneous emission in

dielectric media," *Phys. Rev. A*, vol. 63, pp. 13801-1:13801-5, 2000.

- [5] C. Kittel, *Introduction to Solid State Physics*. New York: John Wiley, sixth edition ed., 1986.
- [6] C. J. F. Bottcher and P. Bordewijk, *Theory of Electric Polarization: Volume 2*, vol. I and II. New York: Elsevier, 1978.
- [7] J. Baker-Jarvis, "The local and macroscopic fields using statistical mechanics," *Phys. Rev E*, 1998. in review.
- [8] P. Mazur and B. R. A. Nijboer, "On the statistical mechanics of matter in an electromagnetic field: I," *Physica*, vol. 14, pp. 971-986, 1953.
- [9] F. N. H. Robinson, *Macroscopic Electromagnetism*. Oxford: Pergamon Press, 1973.
- [10] J. D. Jackson, *Classical Electrodynamics (3rd Ed.)*. New York: John Wiley and Sons, 1999.

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