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On Onsager relations and linear electromagnetic materials

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Abstract

We investigated the Onsager relations in the context of electromagnetic constitutive relations of linear, homogeneous materials. We determined that application of the Onsager relations to the constitutive equations relating **P** and **M** to both **E** and **B** is in accord with Lorentz reciprocity as well as the Post constraint. Our conclusions are particularly significant for research on linear magnetoelectric materials.
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1. Introduction

In two seminal papers published in 1931 [1,2], with the assumption of microscopic reversibility, Onsager derived a set of reciprocity relations applicable to coupled linear phenomenons at macroscopic length scales. Fourteen years later, Casimir [3] improved the foundations of the Onsager relations. Initially considered applicable to purely instantaneous phenomenons—or, at least, when "time-lag can be neglected" [1, p. 419]—the Onsager relations widened in scope as a result of the fluctuation–dissipation theorem [4] to time-harmonic phenomenons [5]. Sections 123–125 of the famous textbook of Landau and Lifshitz on statistical physics provide a lucid introduction to the Onsager relations [6], but we also recommend a perusal of a classic monograph by de Groot [7]. A modern appraisal has been provided by Berdichevsky [8], whose paper motivated the work leading to this communication.

Our focus is the *correct* application of the Onsager relations for linear electromagnetic materials. This issue can be traced back to a 1973 paper by Rado [9]. This paper contains a major conflict between a consequence of the assumption of material response without any delay whatsoever and the Onsager relations as expounded by Callen et al. [5]. The former is definitely a noncausal assumption in electromagnetism [10,11], leading to false symmetries between the electromagnetic constitutive parameters [12]. Furthermore, Rado considered **E** and **H** as primitive fields, but **E** and **B** are taken to be the primitive fields in *modern electromagnetism* [13–15]. To the best of our knowledge, no other *original* investigation of the Onsager relations in electromagnetism exists.

Due to the currently increasing emphasis on engineered nanomaterials [16,17] and complex electromagnetic materials [18,19], it is imperative that the application of fundamental principles (such as the Onsager relations) be carefully examined with modern terminology. Accordingly, in the following sections, we first review the Onsager relations in general. Then we apply the Onsager relations to the electromagnetic constitutive relations of linear, homogeneous,

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bianisotropic materials. We show that a naïve application to constitutive equations relating **D** and **H** to both **E** and **B** yields unphysical results, but that application to constitutive equations relating **P** and **M** to both **E** and **B** is in accord with Lorentz reciprocity [20] as well as the Post constraint [21,22].

2. Onsager relations

Let us consider the linear macroscopic constitutive

$$L_m = \sum_{n=1}^{N} \Phi_{mn} F_n, \quad m \in [1, N], \tag{1}$$

where $N > 1$, L_m are the *Onsager fluxes* and F_m are the *Onsager forces*. The Onsager relations deal with the constitutive parameters Φ_{mn}.

The derivation of the Onsager relations proceeds with the postulation of N state variables a_n, $n \in [1, N]$. The state variables are divided into two groups. The first $\tilde{N} \leqslant N$ state variables are supposed to be *even* and the remaining $N - \tilde{N}$ state variables are supposed to be *odd* with respect to a reversal of velocities of the microscopic particles constituting the linear medium; in other words,

$$\overline{a_m(t)a_n(t + \tau)} = \overline{a_m(t)a_n(t - \tau)},$$
$$\text{if} \quad \begin{cases} m \in [1, \tilde{N}] \text{ and } n \in [1, \tilde{N}] \\ \text{or} \\ m \in [\tilde{N} + 1, N] \text{ and } n \in [\tilde{N} + 1, N] \end{cases} \tag{2}$$

and

$$\overline{a_m(t)a_n(t + \tau)} = -\overline{a_m(t)a_n(t - \tau)},$$
$$\text{if} \quad \begin{cases} m \in [1, \tilde{N}] \text{ and } n \in [\tilde{N} + 1, N] \\ \text{or} \\ m \in [\tilde{N} + 1, N] \text{ and } n \in [1, \tilde{N}], \end{cases} \tag{3}$$

where the overbar indicates averaging over time t [3].

In terms of the state variables, the Onsager fluxes are defined as

$$L_m = \frac{\partial}{\partial t} a_m, \quad m \in [1, N]; \tag{4}$$

the *Onsager forces* are defined as

$$F_m = -\sum_{n=1}^{N} g_{mn} a_n, \quad m \in [1, N]; \tag{5}$$

and the coefficients g_{mn} help define the deviation ΔS of the entropy from its equilibrium value as the quadratic expression [7]

$$\Delta S = -\frac{1}{2} \sum_{m=1}^{\tilde{N}} \sum_{n=1}^{\tilde{N}} g_{mn} a_m a_n$$
$$- \frac{1}{2} \sum_{m=\tilde{N}+1}^{N} \sum_{n=\tilde{N}+1}^{N} g_{mn} a_m a_n. \tag{6}$$

In consequence of the microscopic reversibility indicated by (2) and (3), the constitutive parameters satisfy the Onsager relations

$$\Phi_{mn} = \Phi_{nm},$$
$$\text{if} \quad \begin{cases} m \in [1, \tilde{N}] \text{ and } n \in [1, \tilde{N}] \\ \text{or} \\ m \in [\tilde{N} + 1, N] \text{ and } n \in [\tilde{N} + 1, N] \end{cases} \tag{7}$$

and

$$\Phi_{mn} = -\Phi_{nm},$$
$$\text{if} \quad \begin{cases} m \in [1, \tilde{N}] \text{ and } n \in [\tilde{N} + 1, N] \\ \text{or} \\ m \in [\tilde{N} + 1, N] \text{ and } n \in [1, \tilde{N}]. \end{cases} \tag{8}$$

In an external magnetostatic field $\mathbf{B}_{dc}$, (7) and (8) are modified to

$$\Phi_{mn}(\mathbf{B}_{dc}) = \Phi_{nm}(-\mathbf{B}_{dc}),$$
$$\text{if} \quad \begin{cases} m \in [1, \tilde{N}] \text{ and } n \in [1, \tilde{N}] \\ \text{or} \\ m \in [\tilde{N} + 1, N] \text{ and } n \in [\tilde{N} + 1, N] \end{cases} \tag{9}$$

and

$$\Phi_{mn}(\mathbf{B}_{dc}) = -\Phi_{nm}(-\mathbf{B}_{dc}),$$
$$\text{if} \quad \begin{cases} m \in [1, \tilde{N}] \text{ and } n \in [\tilde{N} + 1, N] \\ \text{or} \\ m \in [\tilde{N} + 1, N] \text{ and } n \in [1, \tilde{N}], \end{cases} \tag{10}$$

respectively.

3. Application to linear electromagnetism

3.1. Constitutive equations for D and H

Let us now consider a linear, homogeneous, bianisotropic medium. Its constitutive equations can be written in a Cartesian coordinate system as

$$\left. \begin{array}{l} D_j = \sum_{k=1}^{3} \varepsilon_{jk} \circ E_k + \xi_{jk} \circ B_k \\ H_j = \sum_{k=1}^{3} \zeta_{jk} \circ E_k + v_{jk} \circ B_k \end{array} \right\}, \quad j \in [1, 3]. \tag{11}$$

We have adopted here the modern view of electromagnetism, wherein **E** and **B** are the primitive fields while **D** and **H** are the induction fields [13–15]. The operation $\circ$ indicates a temporal convolution operation in the time domain, and simple multiplication in the frequency domain [23].

Now, **D** and **E** are even, but **H** and **B** are odd, with respect to time-reversal. With that in mind, we can rewrite (11) compactly as

$$Q_m = \sum_{n=1}^{N} \Lambda_{mn} \circ F_n, \quad m \in [1, N], \tag{12}$$

where $F_m = E_m$, $F_{m+3} = B_m$, $Q_m = D_m$ and $Q_{m+3} = H_m$ for $m \in [1, 3]$; furthermore, $\tilde{N} = 3$ and $N = 6$.

With the assumption of microscopic reversibility, application of the Onsager relations (9) and (10) yields the following symmetries:

$$\Lambda_{mn}(\mathbf{B}_{dc}) = \Lambda_{nm}(-\mathbf{B}_{dc}), \qquad m \in [1, 3], \quad n \in [1, 3],$$
$$\Lambda_{mn}(\mathbf{B}_{dc}) = \Lambda_{nm}(-\mathbf{B}_{dc}), \qquad m \in [4, 6], \quad n \in [4, 6],$$
$$\Lambda_{mn}(\mathbf{B}_{dc}) = -\Lambda_{nm}(-\mathbf{B}_{dc}), \quad m \in [1, 3], \quad n \in [4, 6].$$
$$(13)$$

Eqs. (13) imply that

$$\varepsilon_{jk}(\mathbf{B}_{dc}) = \varepsilon_{kj}(-\mathbf{B}_{dc}),$$
$$v_{jk}(\mathbf{B}_{dc}) = v_{kj}(-\mathbf{B}_{dc}),$$
$$\xi_{jk}(\mathbf{B}_{dc}) = -\zeta_{kj}(-\mathbf{B}_{dc}). \qquad (14)$$

3.2. Constitutive equations for P and M

When considering a material medium, as distinct from matter-free space (i.e. vacuum), the presence of matter is indicated by the polarization $\mathbf{P} = \mathbf{D} - \varepsilon_o \mathbf{E}$ and the magnetization $\mathbf{M} = \mu_o^{-1}\mathbf{B} - \mathbf{H}$, where ε_o and μ_o are the permittivity and the permeability of matter-free space. Linear constitutive equations for $\mathbf{P}$ and $\mathbf{M}$ can be stated as

$$\left.\begin{array}{l} P_j = \sum_{k=1}^3 \chi_{jk}^{(1)} \circ E_k + \chi_{jk}^{(2)} \circ B_k \\ M_j = \sum_{k=1}^3 \chi_{jk}^{(3)} \circ E_k + \chi_{jk}^{(4)} \circ B_k, \end{array}\right\}, \quad j \in [1, 3], \quad (15)$$

where

$$\varepsilon_{jk} = \varepsilon_o \delta_{jk} + \chi_{jk}^{(1)},$$
$$v_{jk} = \mu_o^{-1} \delta_{jk} - \chi_{jk}^{(4)},$$
$$\xi_{jk} = \chi_{jk}^{(2)},$$
$$\zeta_{jk} = -\chi_{jk}^{(3)}, \qquad (16)$$

and δ_{jk} is the Kronecker delta function.

As $\mathbf{P}$ is even but $\mathbf{M}$ is odd with respect to time-reversal, we can rewrite (15) as

$$R_m = \sum_{n=1}^N \Psi_{mn} \circ F_n, \quad m \in [1, N], \qquad (17)$$

where $R_m = P_m$ and $R_{m+3} = M_m$ for $m \in [1, 3]$. As the microscopic processes underlying the constitutive parameters in (17) are reversible, Ψ_{mn} must satisfy (9) and (10); thus,

$$\Psi_{mn}(\mathbf{B}_{dc}) = \Psi_{nm}(-\mathbf{B}_{dc}), \qquad m \in [1, 3], \quad n \in [1, 3],$$
$$\Psi_{mn}(\mathbf{B}_{dc}) = \Psi_{nm}(-\mathbf{B}_{dc}), \qquad m \in [4, 6], \quad n \in [4, 6],$$
$$\Psi_{mn}(\mathbf{B}_{dc}) = -\Psi_{nm}(-\mathbf{B}_{dc}), \quad m \in [1, 3], \quad n \in [4, 6],$$
$$(18)$$

whence the symmetries

$$\chi_{jk}^{(1)}(\mathbf{B}_{dc}) = \chi_{kj}^{(1)}(-\mathbf{B}_{dc}),$$
$$\chi_{jk}^{(4)}(\mathbf{B}_{dc}) = \chi_{kj}^{(4)}(-\mathbf{B}_{dc}),$$
$$\chi_{jk}^{(2)}(\mathbf{B}_{dc}) = -\chi_{kj}^{(3)}(-\mathbf{B}_{dc}), \qquad (19)$$

are predicted by the Onsager relations as the macroscopic consequences of microscopic reversibility.

3.3. The conflict

Eqs. (19) imply that

$$\varepsilon_{jk}(\mathbf{B}_{dc}) = \varepsilon_{kj}(-\mathbf{B}_{dc}),$$
$$v_{jk}(\mathbf{B}_{dc}) = v_{kj}(-\mathbf{B}_{dc}),$$
$$\xi_{jk}(\mathbf{B}_{dc}) = \zeta_{kj}(-\mathbf{B}_{dc}), \qquad (20)$$

by virtue of (16).

But $(20)_3$ disagrees completely with $(14)_3$. Let us reiterate that both (14) and (20) come about from the application of the Onsager relations, contingent upon the assumption of microscopic reversibility. Yet, at most, only one of the two must be correct.

3.4. Resolution of the conflict

Onsager's own papers help resolve the conflict. His papers were concerned with motion of microscopic particles, and he considered his work to hold true for heat conduction, gaseous diffusion and related transport problems. The Onsager forces must be causative agents, while the Onsager fluxes must be directly concerned with particulate motion. This understanding is reinforced by subsequent commentaries [6,7].

Therefore, in order to *correctly* exploit the Onsager relations in electromagnetics, we must isolate those parts of $\mathbf{D}$ and $\mathbf{H}$ which indicate the presence of a *material*, because microscopic processes cannot occur in matter-free space (i.e. vacuum). The matter-indicating parts of $\mathbf{D}$ and $\mathbf{H}$ are $\mathbf{P}$ and $\mathbf{M}$. *Hence*, (20) *must be accepted and* (14) *must be discarded*.

With $\mathbf{B}_{dc} = \mathbf{0}$, the symmetries (20) coincide—unlike (14)—with those mandated by Lorentz reciprocity [20, Eqs. 23]. Also unlike (14), the symmetries (20) are compatible with the Post constraint [21,22]

$$\sum_{j=1}^3 \xi_{jj} = \sum_{j=1}^3 \zeta_{jj} \qquad (21)$$

which must be satisfied by all (i.e. Lorentz-reciprocal as well as Lorentz-nonreciprocal) linear materials. These two well-known facts also support our decision to discard (14) in favor of (20).

The literature on linear magnetoelectric materials is replete with the use of (14), derived most prominently by O'Dell [24, Eq. 2.64]; and Rado [9] appears to have distorted his initial results in order to confirm to that derivation. Thus, the impact of the correct application of the Onsager relations should be felt mostly in research on magnetoelectric materials [12]. A secondary impact shall be on the inadequately measured properties of the so-called Tellegen medium and Tellegen particles, a review of which is available elsewhere [22, Section 5].

4. Concluding remarks

In this communication, we first reviewed the Onsager relations which delineate the macroscopic consequences of microscopic reversibility in linear materials. Then we applied the relations to the electromagnetic constitutive relations of homogeneous bianisotropic materials. We determined that a naïve application to constitutive equations relating **D** and **H** to both **E** and **B** yields unphysical results, but that application to constitutive equations relating **P** and **M** to both **E** and **B** is in accord with Lorentz reciprocity as well as the Post constraint.

References

[1] Onsager L. Reciprocal relations in irreversible processes. I. Phys Rev 1931;37:405–26.

[2] Onsager L. Reciprocal relations in irreversible processes. II. Phys Rev 1931;38:2265–79.

[3] Casimir HBG. On Onsager's principle of microscopic reversibility. Rev Mod Phys 1945;17:343–50.

[4] Callen HB, Greene RF. On a theorem of irreversible thermodynamics. Phys Rev 1952;86:702–10.

[5] Callen HB, Barasch ML, Jackson JL. Statistical mechanics of irreversibility. Phys Rev 1952;88:1382–6.

[6] Landau LD, Lifshitz EM. Statistical physics, part 1. Oxford, UK: Pergamon Press; 1980.

[7] de Groot SR. Thermodynamics of irreversible processes. Amsterdam, The Netherlands: North-Holland; 1963 (Chapters 1, 2 and 11).

[8] Berdichevsky VL. Structure of equations of macrophysics. Phys Rev E 2003;68:066126.

[9] Rado GT. Reciprocity relations for susceptibilities and fields in magnetoelectric antiferromagnets. Phys Rev B 1973;8:5239-42. See (i) the conflict between Eq. (13) of this paper derived using the Onsager relations and Eq. (9) which emerges from the (falsely) noncausal assumption that actual materials can respond without any delay, and (ii) the artifice of Eq. (14) to resolve the conflict.

[10] Weiglhofer WS, Lakhtakia A. On causality requirements for material media. AEÜ Int J Electron Commun 1996;50:389–91.

[11] Tip A. Linear dispersive dielectrics as limits of Drude–Lorentz systems. Phys Rev E 2004;69:016610.

[12] Lakhtakia A. An investigative report on the constructive (*sic*) relations of linear magnetoelectric media. Int J Infrared Millimeter Waves 1994;15:1363–72.

[13] López Dávalos A, Zanette D. Fundamentals of electromagnetism. Berlin: Springer; 1999.

[14] Jackson JD. Classical electrodynamics. 3rd ed., New York, NY, USA: Wiley; 1999 (Section 6.6).

[15] Post EJ. Separating field and constitutive equations in electromagnetic theory. In: Weiglhofer WS, Lakhtakia A, editors. Introduction to complex mediums for optics and electromagnetics. Bellingham, WA, USA: SPIE Press; 2003.

[16] US National Research Council: Condensed-matter and materials physics—basic research for tomorrow's technology. Washington, DC, USA: National Academy Press; 1999.

[17] Nalwa HS, editor. Encyclopedia of nanoscience and nanotechnology. Stevenson Ranch CA, USA: American Scientific Publishers; 2004.

[18] Singh ON, Lakhtakia A, editors. Electromagnetic fields in unconventional materials and structures. New York, NY, USA: Wiley; 2000.

[19] Weiglhofer WS, Lakhtakia A, editors. Introduction to complex mediums for optics and electromagnetics. Bellingham, WA, USA: SPIE Press; 2003.

[20] Kong JA. Theorems of bianisotropic media. Proc IEEE 1972;60:1036–46.

[21] Weiglhofer WS, Lakhtakia A. The Post constraint revisited. AEÜ Int J Electron Commun 1998;52:276–9.

[22] Lakhtakia A. On the genesis of the Post constraint in modern electromagnetism. Optik 2004;115:151–8.

[23] Weiglhofer WS. Constitutive characterization of simple and complex mediums. In: Weiglhofer WS, Lakhtakia A, editors. Introduction to complex mediums for optics and electromagnetics. Bellingham, WA, USA: SPIE Press; 2003.

[24] O'Dell TH. The electrodynamics of magneto-electric media. Amsterdam, The Netherlands: North-Holland; 1970.

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