On Onsager Relations and Linear Electromagnetic Materials

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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.

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, 14, 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, 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 equations

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

where \( N > 1 \), \( L_m \) are the Onsager fluxes and \( F_m \) are the Onsager forces. The Onsager relations deal with the constitutive parameters \( \Phi_{mn} \).

The derivation of the Onsager relations proceeds with the postulation of \( \tilde{N} \) state variables \( a_n, n \in [1, N] \). The state variables are divided into two groups. The first \( \tilde{N} \leq N \) 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,

\[
\frac{a_m(t) a_n(t + \tau)}{a_m(t) a_n(t - \tau)} = \begin{cases} 
1 & m \in [1, \tilde{N}] \text{ and } n \in [1, \tilde{N}] \\
0 & \text{or}
\end{cases}
\]

\[
\text{if } \begin{cases} m \in [\tilde{N} + 1, N] \text{ and } n \in [\tilde{N} + 1, N]
\end{cases}
\]
and

$$a_m(t)a_n(t + \tau) = -a_m(t)a_n(t - \tau),$$

if \( m \in [1, \tilde{N}] \) and \( n \in [\tilde{N} + 1, N] \)

or

\( m \in [\tilde{N} + 1, N] \) and \( n \in [1, \tilde{N}] \),

(3)

where the overbar indicates averaging over time \( t \).

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

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

(4)

the Onsager forces are defined as

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

(5)

and the coefficients \( g_{mn} \) help define the deviation \( \Delta S \) of the entropy from its equilibrium value as the quadratic expression

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

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

(6)

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

$$\Phi_{mn} = \Phi_{nm},$$

if \( m \in [1, \tilde{N}] \) and \( n \in [1, \tilde{N}] \)

or

\( m \in [\tilde{N} + 1, N] \) and \( n \in [\tilde{N} + 1, N] \)

(7)

and

$$\Phi_{mn} = -\Phi_{nm},$$

if \( m \in [1, \tilde{N}] \) and \( n \in [\tilde{N} + 1, N] \)

or

\( m \in [\tilde{N} + 1, N] \) and \( n \in [1, \tilde{N}] \).

(8)
In an external magnetostatic field $B_{dc}$, (7) and (8) are modified to

$$\Phi_{mn}(B_{dc}) = \Phi_{nm}(-B_{dc}),$$

if

$$m \in [1, \tilde{N}] \quad \text{and} \quad n \in [1, \tilde{N}]$$

or

$$m \in [\tilde{N} + 1, N] \quad \text{and} \quad n \in [\tilde{N} + 1, N]$$

and

$$\Phi_{mn}(B_{dc}) = -\Phi_{nm}(-B_{dc}),$$

if

$$m \in [1, \tilde{N}] \quad \text{and} \quad n \in [\tilde{N} + 1, N]$$

or

$$m \in [\tilde{N} + 1, N] \quad \text{and} \quad n \in [1, \tilde{N}],$$

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

$$D_j = \sum_{k=1}^{3} \epsilon_{jk} \circ E_k + \xi_{jk} \circ B_k$$

$$H_j = \sum_{k=1}^{3} \xi_{jk} \circ E_k + \nu_{jk} \circ B_k,$$

$$j \in [1, 3].$$

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 \[13\] \[14\] \[15\]. 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

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

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:

\[ \Lambda_{mn}(B_{dc}) = \Lambda_{nm}(-B_{dc}) , \quad m \in [1, 3] \, , \, n \in [1, 3] \]
\[ \Lambda_{mn}(B_{dc}) = \Lambda_{nm}(-B_{dc}) , \quad m \in [4, 6] \, , \, n \in [4, 6] \]
\[ \Lambda_{mn}(B_{dc}) = -\Lambda_{nm}(-B_{dc}) , \quad m \in [1, 3] \, , \, n \in [4, 6] \}

Equations (13) imply that

\[ \begin{align*}
\epsilon_{jk}(B_{dc}) &= \epsilon_{kj}(-B_{dc}) \\
\nu_{jk}(B_{dc}) &= \nu_{kj}(-B_{dc}) \\
\xi_{jk}(B_{dc}) &= -\zeta_{kj}(-B_{dc})
\end{align*} \]

\[ \text{(14)} \]

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 the polarization \( P = D - \epsilon_o E \) and the magnetization \( M = \mu_o^{-1}B - H \), where \( \epsilon_o \) and \( \mu_o \) are the permittivity and the permeability of matter–free space. Linear constitutive equations for \( P \) and \( M \) can be stated as

\[ \begin{align*}
P_j &= \sum_{k=1}^{3} \chi_{jk}^{(1)} \circ E_k + \chi_{jk}^{(2)} \circ B_k \\
M_j &= \sum_{k=1}^{3} \chi_{jk}^{(3)} \circ E_k + \chi_{jk}^{(4)} \circ B_k
\end{align*} \]

\[ \text{, } j \in [1, 3] \]

\[ \text{(15)} \]

where

\[ \begin{align*}
\epsilon_{jk} &= \epsilon_o \delta_{jk} + \chi_{jk}^{(1)} \\
\nu_{jk} &= \mu_o^{-1} \delta_{jk} - \chi_{jk}^{(4)} \\
\xi_{jk} &= \chi_{jk}^{(2)} \\
\zeta_{jk} &= -\chi_{jk}^{(3)}
\end{align*} \]

\[ \text{, } j \in [1, 3] \]

\[ \text{(16)} \]

and \( \delta_{jk} \) is the Kronecker delta function.

As \( P \) is even but \( M \) is odd with respect to time–reversal, we can rewrite (15) as

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

\[ \text{, } m \in [1, N] \]

\[ \text{(17)} \]
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, $\Psi_{mn}$ must satisfy (9) and (10); thus,

$$
\begin{align*}
\Psi_{mn}(B_{dc}) &= \Psi_{nm}(-B_{dc}) , & m \in [1, 3] , n \in [1, 3] \\
\Psi_{mn}(B_{dc}) &= \Psi_{nm}(-B_{dc}) , & m \in [4, 6] , n \in [4, 6] \\
\Psi_{mn}(B_{dc}) &= -\Psi_{nm}(-B_{dc}) , & m \in [1, 3] , n \in [4, 6] 
\end{align*}
$$

whence the symmetries

$$
\begin{align*}
\chi^{(1)}_{jk}(B_{dc}) &= \chi^{(1)}_{kj}(-B_{dc}) \\
\chi^{(4)}_{jk}(B_{dc}) &= \chi^{(4)}_{kj}(-B_{dc}) \\
\chi^{(2)}_{jk}(B_{dc}) &= -\chi^{(3)}_{kj}(-B_{dc}) 
\end{align*}
$$

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

### 3.3 The Conflict

Equations (19) imply that

$$
\begin{align*}
\epsilon_{jk}(B_{dc}) &= \epsilon_{kj}(-B_{dc}) \\
\nu_{jk}(B_{dc}) &= \nu_{kj}(-B_{dc}) \\
\xi_{jk}(B_{dc}) &= \zeta_{kj}(-B_{dc}) 
\end{align*}
$$

by virtue of (16).

But (20) disagrees completely with (14). 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 \( D \) and \( H \) which indicate the presence of a material, because microscopic processes cannot occur in matter–free space (i.e., vacuum). The matter–indicating parts of \( D \) and \( H \) are \( P \) and \( M \). Hence, (20) must be accepted and (14) must be discarded.

With \( B_{dc} = 0 \), 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]

\[
\sum_{j=1}^{3} \xi_{jj} = \sum_{j=1}^{3} \zeta_{jj} \quad (21)
\]

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).

### 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.

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[9] G.T. Rado, Reciprocity relations for susceptibilities and fields in magneto-electric antiferromagnets. Phys. Rev. B 8 (1973), 5239–5242. 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.

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