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Entropy of electromagnetic polarization

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The entropy of electromagnetic polarization is considered in this paper. It is shown that unless the nonfield entropy, and not the total entropy, is used as the independent variable in the expression for the internal energy, the first law is violated and the meaning of heat flow, as given by the second law, is contradicted. The total entropy and its field and nonfield components are shown to be state functions. The field entropy comprises contributions from the field generated by the contents of the system and stored within as well as outside its boundaries. The contribution of the field stored outside the system boundaries is derived and demonstrated for the case of a uniformly polarized sphere. Finally, expressions are derived for field entropies and entropy densities, in composite systems, using the concept of interaction entropy. The results are shown to be fundamentally different compared to those used in the current literature.

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THEORY

The meaning of entropy in the presence of quasistatic electromagnetic fields requires clarification as it is often misinterpreted in expressions for the internal energy in the presence of fields. Furthermore, no account is made for the effect of the field, generated by the contents of a system outside its physical boundaries, on this entropy (Refs. [1–3]). The meaning of entropy in the presence of electromagnetic fields can be elucidated by realizing the symmetry between the energy and entropy functions, e.g., with respect to their being a state function and the fundamental sets of independent variables used to characterize them. The internal energy $\hat{U}$ in the presence of a magnetic field is given by (Ref. [4])

$$\hat{U}=U+U_M, \quad U=U(S,V,N,\mathbf{B}=\mathbf{0}),$$

$$U_M=U_M(S,V,N,\mathbf{B}), \tag{1}$$

where U and U_M are components of the internal energy $\hat{U}=\hat{U}(S,V,N,\mathbf{B})$ due to nonfield variables and due to the presence of the field, respectively, and $U_M(\mathbf{B}=\mathbf{0})=0$ must hold. Note that by virtue of $U=U(S,V,N,\mathbf{B}=\mathbf{0})$, $U_M=U_M(U,\mathbf{B})$, and hence also $\hat{U}=\hat{U}(U,\mathbf{B})$, are equivalent to $U_M=U_M(S,V,N,\mathbf{B})$, and $\hat{U}=\hat{U}(S,V,N,\mathbf{B})$, respectively. In this presentation, U being independent of $\mathbf{B}$, agrees with its definition as a nonfield independent variable. This variable determines, together with $\mathbf{B}$, the energy U_M that is stored in the field. The symmetry between the energy and entropy representations suggests that the counterpart of $U_M=U_M(U,\mathbf{B})$ in the energy representation, can be $S_M=S_M(S,\mathbf{B})$ in the entropy representation, so that S_M and S stand for field and nonfield entropies, respectively. The set $S,V,N,\mathbf{B}$ consists of four independent variables: entropy, volume, mass, and induction of the field, respectively. As S is (by definition) independent of $\mathbf{B}$, it has the clear meaning of field independent, or alternatively nonfield entropy (in agreement with the above entropy representation). Consequently, the meaning of entropy in

$$d\hat{U}=\hat{T}\,dS-\hat{P}\,dV+\hat{\zeta}\,dN+\int_{V'}\mathbf{H}\cdot d\mathbf{B}\,dV \tag{2}$$

is not total entropy ($\hat{S}$, which is the counterpart of $\hat{U}$) but the field independent or nonfield entropy. Note that here $\hat{T}$, $\hat{P}$, $\hat{\zeta}$, $\mathbf{H}$, and V' denote the temperature, pressure, chemical potential, field strength, and volume (usually all space), in which $\mathbf{B}$ exists due to the contents of V.

Interpretation of S [in Eq. (2)] as the total entropy contradicts the definition of $\hat{T}\,dS$ as heat $d\hat{Q}$ that flows across the system boundaries, as well as the first law. Suppose S is defined as $S=S(\mathbf{B}=\mathbf{0})+S_M$, where $S(\mathbf{B}=\mathbf{0})$ and S_M denote the nonfield entropy and field entropy, respectively. When the field is absent $S_M=0$ so that $S=S(\mathbf{B}=\mathbf{0})$. As S_M is generated by action at a distance, dS_M and hence also $\hat{T}\,dS$ does not vanish in adiabatic magnetization [e.g., when no heat is allowed to flow across the system boundaries and $dS(\mathbf{B}=\mathbf{0})=0$]. Consequently, $d\hat{Q}$ (being in this case equal to $\hat{T}\,dS_M$) does not vanish contrary to the process being defined as adiabatic. It follows that, in this case, the process can be defined as being adiabatic only with respect to $S(\mathbf{B}=\mathbf{0})$, but not with respect to S_M. Furthermore, in adiabatic magnetization [fixed $S(\mathbf{B}=\mathbf{0})$] at fixed V and N, the only contribution to the $d\hat{U}$ is from the magnetic work term. Hence, by virtue of the first law $d\hat{U}=\int_{V'}\mathbf{H}\cdot d\mathbf{B}\,dV$, at fixed S, V, N. The extra term due to the field entropy $\hat{T}\,dS_M$, being unaccounted for, violates the first law. Consequently, the entropy S in Eq. (2) must stand for the nonfield component of the total entropy, and the magnetic entropy must arise from the magnetic work term. This agrees with the requirement of independence of S from the field $\mathbf{B}$. In contrast, the entropy S_M due to the magnetic field must be a function of $\mathbf{B}$.

The fundamental role of the nonfield entropy can be demonstrated by the effect of the heat delivered by a nonmagnetic heat source to a magnetized system at fixed V, N, and $\mathbf{B}$. Note that in this work, "fixed V" implies that V is fixed with respect to size, shape, position, and orientation, and "fixed $\mathbf{B}$" also implies that no work is delivered by the current sources of **B** to the system. The heat $d\hat{Q}$ is delivered (across the system boundaries) by the heat source at the equilibrium temperature $\hat{T}$. By virtue of the second law

$$d\hat{Q}=\hat{T}\,dS, \tag{3}$$

where dS denotes the entropy of the system.

Next we seek to establish the meaning of S. First we assume that it stands for the total entropy of the system. The heat induces a simultaneous change in nonfield and field energies. At fixed V, N, and **B**, the change in field energy arises due to a change in permeability. Hence

$$d\hat{Q}=dQ+dQ_M \quad \text{fixed } V,N,\mathbf{B}, \tag{4}$$

where dQ and dQ_M denote the components of the heat that induces (at the equilibrium temperature $\hat{T}$) the change in the nonfield and field energies, respectively. By virtue of the second law, dS must also have similar components. Hence,

$$dS=dS(B=0)+dS_M, \tag{5}$$

$$dQ=\hat{T}dS, \quad dQ_M=\hat{T}dS_M. \tag{6}$$

Equation (6) states that the change in the field energy (e.g., due to dQ_M) is a function of S_M and not of $S(\mathbf{B}=\mathbf{0})$. This contradicts the fact that at fixed $V,N,\mathbf{B}$, the field energy is a function of the system's permeability. At fixed V, N, and **B**, the permeability is a function of temperature and hence also of $S(\mathbf{B}=\mathbf{0})$. Consequently, S cannot stand for the total entropy $\hat{S}$ and must represent the nonfield entropy $S(\mathbf{B}=\mathbf{0})$, as the fundamental entropy variable. Furthermore, following the choice of S as the independent variable, the transformation of heat into field energy must be expressible in terms of the field-dependent temperature $\hat{T}$. Recall that at $\mathbf{B}=\mathbf{0}$, the heat flow $dQ=T\,dS$ is expressed in terms of $T=T(S,V,N,\mathbf{B}=\mathbf{0})$ and the independent variable S. This gives

$$d\hat{Q}=\hat{T}\,dS, \quad \hat{T}=T+T_M, \tag{7}$$

$$dQ=T\,dS, \quad dQ_M+T_M dS, \tag{8}$$

where by virtue of Eq. (1), $T=(\partial U/\partial S)_{V,N}$ and $T_M=(\partial U_M/\partial S)_{V,N,\mathbf{B}}$ are defined as the nonfield and field components (Ref. [4]) of the temperature $\hat{T}=(\partial\hat{U}/\partial S)_{V,N,\mathbf{B}}$.

This formulation agrees with the fact that S and S_M are related as cause and effect variables. A change in S produces (at fixed **B**) a change in permeability μ, and consequently, also in the field strength $\mathbf{H}=\mathbf{B}/\mu$. These changes effect the change in $S_M=S_M(S,\mathbf{B})$. The change in S_M does not follow from the flow of magnetic entropy, but rather as a result of local changes induced by the change in S. Furthermore, at fixed V, N, **B**, $dQ=dU$, $dQ_M=dU_M$, and $d\hat{Q}=d\hat{U}$. Hence, Eq. (4) agrees with Eq. (1), as expected.

The symmetry between U and S means that when the former is expressed as $U=U(S,V,N)$, the latter is expressible as $S=S(U,V,N)$. Similarly, in the presence of the field $\hat{U}=\hat{U}(U,\mathbf{B})=(S,V,N,\mathbf{B})$ calls for $\hat{S}=\hat{S}(S,\mathbf{B})=\hat{S}(U,V,N,\mathbf{B})$. Note that, in the energy representation, using the set $U,\mathbf{B}$, in conjunction with $U=U(S,V,N)$, gives the fundamental set $S,V,N,\mathbf{B}$. In the entropy representation, using the set $S,\mathbf{B}$ in conjunction with $S=S(U,V,N)$ gives the fundamental set $U,V,N,\mathbf{B}$. As indicated previously, the symmetry between $\hat{U}$ and $\hat{S}$ requires that the counterpart of Eq. (1) be as follows:

$$\hat{S}=S+S_M, \quad S=S(U,V,N,\mathbf{B}=0), \quad S_M=S_M(U,V,N,\mathbf{B}). \tag{9}$$

In Eq. (9), $\hat{S}$, S, and S_M must each be a state function, and $S_M(\mathbf{B}=\mathbf{0})=0$ must hold. This conforms with the fact that by definition both $\hat{S}$ and S are state functions so that S_M must also possess this property. Thus, as expected, the set $\hat{S}$, S, and S_M (of entropy variables) is symmetrical to the set $\hat{U}$, U, and U_M (of energy variables) regarding the fact that each comprises three state functions. There is a fundamental difference between the way S and S_M change. The nonfield entropy is transferable through contact from one system to another and as such, must flow across physical boundaries. In contrast, S_M (which arises due to flow of electromagnetic power across the system boundary that constitutes action at a distance) relates to local properties, e.g., as dictated by the field **B** at the level of S, V, and N that characterize the system, or else $s=S/V$ and $\rho=N/V$ that apply at each point. Note that the same observation applies to the difference between U and U_M, i.e., a change in U involves contact and flow of energy across boundaries, whereas a change in U_M can occur solely due to action at a distance.

Evaluation of U_M can be done as follows: The magnetic internal energy U_M of a system is defined as

$$U_M=\int_{V'}\int_0^{\mathbf{B}}\mathbf{H}\cdot d\mathbf{B}\,\delta V-U_{Ma}, \quad \text{fixed } S,V,N,\mathbf{H}=\mathbf{B}/\mu, \tag{10}$$

$$U_{Ma}=\int_{V'}\int_0^{\mathbf{B}_a}(\mathbf{H}\cdot d\mathbf{B})_a\,\delta V, \tag{11}$$

where U_M and U_{Ma} denote the magnetic energy stored in V' due to the same intensity (e.g., current levels) of the field sources in the presence and the absence of the system, and subscript a denotes absence of the system. Imposition of fixed S, V, N means that the process is adiabatic, e.g., with respect to the nonfield entropy, and the system is isolated with respect to mechanical interactions and flow (e.g., through contact) of heat and mass across its fixed boundaries. However, as already mentioned, this does not preclude a change in S_M that results from long-range field interactions. At fixed **B**, V, and N, U_M is a function of μ, which in turn is a sole function of S. Under these conditions $T=T(S)$ so that $S=S(T)$, and hence $\mu=\mu[S(T)]=\mu(T)$ can be safely used. This gives

$$(\partial U_M/\partial T)_{V,N,\mathbf{B}} = \int_{V'} \int_0^{\mathbf{B}} \left(\frac{\partial \mathbf{H}}{\partial T} \right)_{V,N,\mathbf{B}} \cdot d\mathbf{B}\,\delta V - (\partial U_{Ma}/\partial T)_{V,N,\mathbf{B}}, \quad \mathbf{H}=\mathbf{B}/\mu. \tag{12}$$

In V, $\partial \mathbf{H}/\partial T = -(\mathbf{B}/\mu^2)\partial\mu/\partial T$. Outside V, in the region $V'-V$, $\mathbf{H}$ and hence $\partial\mathbf{H}/\partial T$ can be a function of two permeabilities (e.g., of V and $V'-V$). This arises from the solution of the field equations. These solutions give, in general, $\mathbf{H}$ as a function of the permeabilities prevailing both in V and $V'-V$ (Ref. [5]) (see example of a sphere in a uniform field below). Hence, a change in μ due to a change in T in V, can change $\mathbf{H}$ in $V'-V$, with significant contribution to the integral of Eq. (12) from both regions.

Subtraction of TS from both sides of Eq. (1) followed by differentiation gives

$$d(\hat{U}-TS) = -S\,dT - p\,dV + \zeta\,dN + dU_M. \tag{13}$$

At fixed $V,N,\mathbf{B}$, $U_M = U_M(S)$, $T=T(S)$, $dT=(\partial T/\partial S)dS$. Hence,

$$dU_M = \left(\frac{\partial U_M}{\partial S}\right) dS = \left(\frac{\partial U_M}{\partial T}\right)\left(\frac{\partial T}{\partial S}\right) dS = \left(\frac{\partial U_M}{\partial T}\right) dT,$$

so that, $T_M = (\partial U_M/\partial S)_{V,N,\mathbf{B}}$ and $S_M = -(\partial U_M/\partial T)_{V,N,\mathbf{B}}$ [see Eq. (14)]. Here S_M and T_M are the magnetic components of $\hat{S}$ and $\hat{T}$, respectively. Using Eqs. (12) and (13), and rearranging gives

$$d(\hat{U}-TS) = -(S+S_M)dT,$$

$$S_M = -(\partial U_M/\partial T)_{V,N,\mathbf{B}}, \quad \text{fixed } V,N,\mathbf{B}, \tag{14}$$

$$S_M = -\int_{V'} \int_0^{\mathbf{B}} \left(\frac{\partial \mathbf{H}}{\partial T} \right)_{V,N,\mathbf{B}} \cdot d\mathbf{B}\,\delta V + S_{Ma}, \quad \text{fixed } V,N,\mathbf{B}, \tag{15}$$

where S_{Ma} denotes the value of S_M in the absence of the system.

It follows that, unless the $\mathbf{H}$ field is confined to V and vanishes elsewhere, the contribution of the magnetic field, which is generated by a system, to its magnetic entropy, comes from all space. This fundamental property of S_M has not been addressed as yet. If the $\mathbf{H}$ field vanishes outside V, i.e., in $V'-V$, then Eq. (15) can be expressed as

$$S_M = \int_V \int_0^{\mathbf{B}} \frac{\mathbf{B}\cdot d\mathbf{B}}{\mu^2} \left(\frac{\partial \mu}{\partial T} \right)_{V,N,\mathbf{B}} dV + S_{Ma}, \quad \text{fixed } V,N,\mathbf{B}, \quad \mathbf{H}=0 \quad \text{outside } V. \tag{16}$$

Note that here, use was made of $\mathbf{B}$ independent of T, so that

$$\partial\mathbf{H}/\partial T = \partial(\mathbf{B}/\mu)/\partial T = -(\mathbf{B}/\mu^2)(\partial\mu/\partial T).$$

The form of Eq. (16) holds in certain cases, where the contribution of matter outside V, e.g., in $V'-V$, can be incorporated into a thermodynamic permeability. For example, in the case of a linear sphere in a uniform magnetic field (Ref. [4]), the thermodynamic permeability is defined by

$$\mu_s = \tfrac{1}{9}\mu_1(\mu_1/\mu_2 - 2\mu_2/\mu_1 + 1). \tag{17}$$

Equations (10) (with V' replaced by V) and (16) can be used for this case once μ is replaced by μ_s. The result is that S_M depends on both μ_1 and μ_2, which denote the magnetic permeabilities of the contents of the sphere and of the space surrounding it, respectively. If the reference entropy S_{Ma} is assumed to vanish, the material is linear and the $\mathbf{H}$ field is uniform in V, but vanishes elsewhere, then using the fact that in this case μ is independent of the field, Eqs. (15) and (16) reduce to the well-known form of S_M (Refs. [1,4])

$$S_M = \frac{1}{2} V H^2 \left(\frac{\partial \mu}{\partial T} \right). \tag{18}$$

In contrast, the field of a uniformly magnetized sphere of volume V does not vanish outside its boundaries, so that in this case

$$U_M = \tfrac{1}{2} V \mu_s H_1^2 = \tfrac{1}{18} V B^2 (1/\mu_2 - 2\mu_2/\mu_1^2 + 1/\mu_1), \quad \mathbf{H}_1 = \mathbf{B}/\mu_1, \tag{19}$$

$$S_M = -\left(\frac{\partial U_M}{\partial T}\right)_{V,N,\mathbf{B}} = \frac{1}{18} V H_1^2 \left[\left(\frac{\mu_1^2}{\mu_2^2} + 2 \right) \frac{\partial \mu_2}{\partial T} - \left(\frac{4\mu_2}{\mu_1} - 1 \right) \frac{\partial \mu_1}{\partial T} \right], \tag{20}$$

where $\mathbf{H}_1$ is the field inside V,

$$\mathbf{H}_1 = \frac{3\mu_2}{\mu_1 + 2\mu_2} \mathbf{H}_0, \tag{21}$$

and $\mathbf{H}_0$ is the uniform field that gives rise to $\mathbf{H}_1$. Note that for a sphere in free space, $\mu_2 = \mu_0$ and the first term in brackets on the right-hand side of Eq. (20) vanishes. However, this does not change the fact that there is a contribution to the field entropy of the sphere by the surrounding free space (which is energized by the content of the sphere). Furthermore, if $\mu_2/\mu_1 \to 0$, then $\mathbf{H}_1 \to \mathbf{0}$, but neither the energy ($\frac{1}{2} V \mu_s H_1^2$) nor the field entropy of the sphere vanish. In this case Eqs. (19) and (20) give

$$U_M = \tfrac{1}{2} V \mu_2 H_0^2, \quad \mu_2/\mu_1 \to 0, \tag{22}$$

$$S_M = \tfrac{1}{2} V H_0^2 (\partial\mu_2/\partial T), \quad \mu_2/\mu_1 \to 0. \tag{23}$$

Comparing Eqs. (18) and (23) shows that in the two extreme cases, the magnetic entropy of the sphere has the same form apart from using the field and permeability that characterize the space in which it is stored. Furthermore, as the field $\mathbf{H}_1$ inside V is a function of both μ_1 and μ_2, it is impossible to express the field energy U_M and entropy S_M by variables that pertain exclusively to the contents of V. This is in agreement with the fact that both U_M and S_M have contributions from the field, generated by the contents of V over all space.

Note that accounting for the field entropy of a finite system, that is stored over all space, is important regarding expressions of probability density of fluctuations in the proximity of equilibrium. For further details, see the recent work on fluctuations in the presence of the field by Dumitru and Boer [6].

The analysis presented hitherto applies also to electric polarization, once the magnetic variables **B**, **H**, and μ are replaced by **D**, **E**, and ε, which denote electric displacement, electric field intensity, and permittivity, respectively. In what follows the entropy of a composite system is considered. Hitherto, the analysis was restricted to single systems. Next, the case of composite systems, comprising interacting subsystems, is considered.

A composite system comprises subsystems that are characterized by their dimensions and position in space. Two states are defined with respect to the extent of interaction between the subsystems. In the first state, the subsystems are placed far apart so as to warrant the assumption that their mutual interactions vanish. In this state the energy of each system is defined as its own, or self-energy. The second state is characterized by the existence of significant interactions between part or all of the subsystems. In this category, subsystems that are in physical contact, and share common boundaries, are included. Let the field entropy of a composite system, comprising two subsystems, in the first and second state, be denoted by S'_M and S_M, respectively,

$$S'_M = S'_{M1} + S'_{M2}, \tag{24}$$

$$S_M = S_{M1} + S_{M2}, \tag{25}$$

where subscripts 1 and 2 indicate that the variable pertains to the respective subsystems, and the prime refers to the first state.

The interaction entropy S_{M12} prevailing in the second state is defined by

$$S_{M12} = S_M - S'_M, \tag{26}$$

where use was made of the fact that in the first "primed" state, the interaction between subsystems 1 and 2 vanishes.

In the second state, the interaction energy is shared between subsystems 1 and 2. Hence,

$$S_{M1} = S'_{M1} + \tfrac{1}{2} S_{M12} = S'_{M1} + \tfrac{1}{2}(S_M - S'_M), \tag{27}$$

$$S_{M2} = S'_{M2} + \tfrac{1}{2} S_{M21} = S'_{M2} + \tfrac{1}{2}(S_M - S'_M), \tag{28}$$

where $S_{M12} = S_{M21}$.

The variables S'_{M1}, S'_{M2}, S_M, and S'_M can be evaluated, in conjunction with Eq. (15), once the field equations in the two states are solved. Equation (15) cannot be used to evaluate S_{M1} and S_{M2} directly, as they are dependent on the interaction energy that is shared between the two subsystems. This agrees with the fact that Eq. (15) accounts for energy that pertains to a system, or subsystem, which is identified as its exclusive source.

Equation (27) can be used to define (for subsystem 1) intensive, e.g., per unit volume, entropy variables as follows:

$$s_{M1} = s'_{M1} + \tfrac{1}{2} s_{M12} = s'_{M1i} + s'_{M1o} + \tfrac{1}{2} s_{M12}, \tag{29}$$

where $s_{M1} = S_{M1}/V$, $s'_{M1} = S'_{M1}/V$, $s_{M12} = S_{M12}/V$, and subscripts i and o denote the part of S'_{M1} stored within, and outside, the boundaries of the system, respectively.

Equation (29) shows that unless the contributions from interactions and field entropy stored outside the system boundaries vanish, the intensive entropy density differs from the conventional form of classical thermodynamics. It is only when $s'_{M1o} = s_{M12} = 0$ that $s_{M1} = s'_{M1} = s'_{M1i}$ conforms with classical nonfield thermodynamics. As Eq. (29) is general in nature, it applies to the entropy of systems, or subsystems, in states of interaction or noninteraction. If $s_{M12} = 0$, then $s_{M1} = s'_{M1} = s'_{M1i} + s'_{M1o}$ and the entropy density, e.g., per unit volume V of the system, includes a contribution from the field outside its physical boundaries. This is a unique property of the field entropy that does not exist in its nonfield counterpart.

SUMMARY AND CONCLUSIONS

The entropy in the term $\hat{T}\,dS$ that stands for the heat delivered to the system across its boundaries is the nonfield component of the total entropy. The definition of S as the total entropy, in $\hat{T}\,dS$, contradicts the meaning of $d\hat{Q}$ as given by the second law, and violates the first law. As adiabatic magnetization relates to a process whereby a system is magnetized while being thermally insulated, it must be defined as a process at fixed S and not at fixed total entropy $\hat{S}$. Contrary to the case where polarization is absent, quasistatic adiabatic polarization is not isentropic with respect to the total entropy $\hat{S}$. The self-entropy of a polarized system can be stored inside as well as outside its physical boundaries. This entropy is a consequence of the field generated by the contents of the system, irrespective of its storage being within or outside the system.

The entropy of a system consists of self-entropy and half the interaction entropy with other systems. Consequently, the entropy density, e.g., per unit volume of the systems, comprises self and interaction parts, which account for the effect of the field energy stored beyond the system boundaries. This is a unique property, which is imparted to polarizable systems by the presence of polarization fields.

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