

Thermodynamics in the presence of electromagnetic fields

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The physical significance of the internal energy as a state function and of thermodynamic variables in the presence of fields are considered. Intensive variables are formulated in the presence of fields and it is shown that, due to the fact that their form depends on field constraints, they are not unique. Four different pairs of pressure and chemical potential corresponding to four different field constraints are identified for the case of a uniformly magnetized continuum. This multiplicity of form of the pressure and chemical potential is a consequence of the effect of fields on thermodynamic systems and their environment. It is shown that the differential expressing the net effect of fields on the internal energy of a thermodynamic system must be exact. This is shown to apply for the analysis of electrostatic and magnetoquasistatic fields, regarding their thermodynamic properties and conditions of equilibrium. Discrete systems are defined as those involving field lines that cross their boundaries. The magnetic field which is energized by a polarized discrete system, outside its boundaries, is defined as pertaining to the system. It is claimed that internal energy, i.e., in its literal thermodynamic meaning, does not exist in discrete magnetized systems where part or all of their magnetic energy may be stored outside their boundaries. Once this externally stored energy is defined as having a source which is internal to the system, then the concept of internal energy can still be used. Finally, intensive thermodynamic variables are formulated for discrete systems. These variables are shown to have the same multiplicity of form under different field constraints.

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I. INTRODUCTION

Thermodynamics in the absence of fields is a well established science. However, it seems that the representation of the effect of fields in terms of thermodynamic variables is still not well understood. The notion that the effect of fields can be expressed by adding extra terms to previous formulas seemed to be a straightforward solution to the problem but as Guggenheim [1] puts it, "There is, however, a serious incidental difficulty, namely, that of finding the correct general expression for magnetic work." The attempts that were made over the years to formulate a comprehensive and unified theory of thermodynamics in the presence of fields [1–7] seem to be only partially successful. It seems that a central problem is whether it is possible and if so, how to express the effect of fields in terms of the conventional combination of extensive and intensive variables. As is well known, this is the backbone of thermodynamic formulations of energy, potential functions, and the Maxwell relations. Another problem is to guarantee that the energy of systems in fields is indeed a state function that qualifies as internal energy of these systems. This internal energy must also be a first order homogeneous function of its extensive variables so that they can be Euler integrated. The fact that fields involve interactions at a distance is not covered properly by ordinary thermodynamics. For example, in ordinary thermodynamics only direct work that is done on or by the system can change its internal energy. However, when fields are involved, work that is performed on other systems that are not part of the one being considered can change its potential energy. In this

context, it is known that the energy of a system can be changed by a field without the need to change any of its extensive variables. This aspect requires appropriate thermodynamic formulations. The constraints that can be set on field variables are also different from those that are known to apply in ordinary, field free thermodynamic systems. Furthermore, in the presence of fields, the current thermodynamic formulations do not provide a definite answer if the energy stored in the field outside the boundaries of the system can be considered as part of its own energy.

In this work, we attempt to formulate thermodynamic variables in the presence of fields. We focus on magnetoquasistatic fields for demonstration of the theory. This is done for the case in which the field dependent energy is a state function that has an exact differential. The incorporation of this exact differential and the differential of the internal energy (which prevails in the absence of the field) into a new exact differential produces different sets of thermodynamic variables depending on the field constraints. The theory is then developed, in detail, for the case of a linearly magnetizable continuum and its implications for charged and discrete systems are considered.

II. THEORY

A. Thermodynamic field variables

Classical thermodynamics postulates that for each system there exists a state function called the internal energy U that depends on the entropy, volume, and mass of this system. The first law of thermodynamics states that

$$dU = dQ + dW, \quad (1)$$

where dQ and dW are the heat input and work done on the system. Neither Q nor W is a state function, but their integrated combination is. Standard presentation of the change in U is given in terms of a sum of $n + 1$ products, each consisting of an intensive variable and a differential of its extensive conjugate variable

$$dU = \sum_{i=0}^n \xi_i dX_i, \quad (2)$$

where

$$\xi_i = (\partial U / \partial X_i)_{X_j}, \quad X_j \neq X_i, \quad i, j = 0, 1, \dots, n. \quad (3)$$

In Eq. (2), $\xi_i dX_i$ are generally not exact differentials, but their sum, i.e., dU , must be one. An important property of ordinary thermodynamic variables is that they can be Euler integrated. This gives

$$U = \sum_{i=0}^n \xi_i X_i. \quad (4)$$

In Eq. (4) the values of all terms $\xi_i X_i$ are independent of the path used to obtain the final levels of ξ_i and X_i . Hence, in this sense, each term of Eq. (4) is a state function. Obviously, the sum of these state functions yields also a state function that in this case is the internal energy U . Since U must be a state function, any addition of another set of independent terms beyond the original $n + 1$ that correspond to U must comply with the requirement that the new sum also be a state function. Otherwise, this precludes the possibility that the new sum will comply with the postulate that the internal energy is a state function and, hence, it would not be possible to identify this new sum as an internal energy.

For example, if U_j is the internal energy of the j th system and there are j' such systems, then $U = \sum_{j=1}^{j'} U_j$ constitutes the internal energy of the combined system. However, if we now add to this sum an independent variable W' which is not a state function, then $\sum_{j=1}^{j'} U_j + W' = U + W'$ would not qualify as a new internal energy. The same applies to Eq. (2), which can be extended as follows:

$$dU' = \sum_{j=1}^{j'} dU_j = \sum_{j=1}^{j'} \sum_{i=0}^n \xi_{ij} dX_{ij}, \quad (5)$$

where

$$dU_j = \sum_{i=0}^n \xi_{ij} dX_{ij}. \quad (6)$$

Since dU' is the sum of exact differentials dU_j , it must be exact also and, hence, it qualifies as a state function, i.e., the internal energy of the combined j' systems. However, this would be violated had we attempted to add terms, or a set of independent terms, that do not combine to an exact differential. This approach must be applied also in the case of fields. Thus, the net combined effect of the field must appear as an exact differential. This condition must be satisfied if it is to be added as a set of thermodynamic terms that become part of the overall internal

energy. Otherwise, the result would not be consistent with the requirement that the sum remains an exact differential of a state function. It follows that if we denote the differential effect of the k th field $k = 1, 2, \dots, k'$ by dU_{fk} , then for the j th system

$$dU_j = \sum_{i=0}^n \xi_{ij} dX_{ij} + dU_f, \quad (7)$$

where dU_f , which denotes the total change in the internal energy due to the combined effect of all k' fields, must be an exact differential and is given by

$$dU_f = \sum_{k=1}^{k'} dU_{fk}. \quad (8)$$

In this sense, the field is not different from any other system that is combined with the one being considered, irrespective of whether this combined system is real or conceptual (i.e., for the purpose of analysis only).

Equation (7) shows that unless dU_f can be presented as

$$dU_f = \sum_{i=n+1}^{n'} \xi_{ij} dX_{ij} \quad (9)$$

and Euler integrated to give

$$U_f = \sum_{i=n+1}^{n'} \xi_{ij} X_{ij}, \quad (10)$$

then the Gibbs Duhem equation would not hold for the thermodynamic system under the action of the fields considered. It seems that the properties of electromagnetic and acceleration fields do not always make it possible to satisfy the above conditions. Hence, the Gibbs Duhem equation is not expected to hold generally for systems in these fields.

Suppose that U_{fk} is a function of field dependent variables denoted by Y_m , $m = 1, 2, \dots, m'$,

$$U_{fk} = U_{fk}(Y_1, Y_2, \dots, Y_{m'}). \quad (11)$$

Suppose further that for $m_0 \leq m \leq m'$, $m_0 = 1, 2, \dots, m'$,

$$Y_m = Y_m(X_1, X_2, \dots, X_n). \quad (12)$$

This implies that part or all of the independent field variables, as defined by Eq. (11), are, or can be, made functions of the extensive variables of the thermodynamic systems. The implications of Eqs. (11) and (12) in electromagnetic fields are discussed below and in Sec. II B. The form of Eq. (11), i.e., the nature of the independent variables Y_m , depends on the constraints imposed on the field variables,

$$dU_{fk} = \sum_{m=1}^{m_0-1} (\partial U_{fk} / \partial Y_m) dY_m + \sum_{m=m_0}^{m'} (\partial U_{fk} / \partial Y_m) \sum_{i=0}^n \frac{\partial Y_m}{\partial X_i} dX_i. \quad (13)$$

Note that in Eq. (13), the partial derivatives are taken with respect to the independent variable holding all other variables, e.g., in the given set, fixed.

Combining Eqs. (7), (8), and (13) followed by collection of terms gives

$$dU_j = \sum_{i=0}^n \left[\xi_{ij} + \sum_{k=1}^{k'} \sum_{m=m_0}^{m'} \frac{\partial U_{fk}}{\partial Y_m} \frac{\partial Y_m}{\partial X_i} \right] dX_i + \sum_{k=1}^{k'} \sum_{m=1}^{m_0-1} \frac{\partial U_{fk}}{\partial Y_m} dY_m, \quad (14)$$

where setting $m_0 \geq 2$ indicates that there is at least one Y_m field variable that is independent of the X_i variables. For example, if $k'=1$, $m'=2$, and $m_0=2$, then

$$dU_j = \sum_{i=0}^n \left[\xi_{ij} + \frac{\partial U_{f1}}{\partial Y_2} \frac{\partial Y_2}{\partial X_i} \right] dX_i + (\partial U_{f1} / \partial Y_1) dY_1. \quad (15)$$

Thus the classical intensive variable ξ_{ij} is modified by the field and a new field dependent intensive variable ξ_{fij} , which is conjugate to X_i , can be defined as

$$\xi_{fij} = \xi_{ij} + \sum_{k=1}^{k'} \sum_{m=m_0}^{m'} \frac{\partial U_{fk}}{\partial Y_m} \frac{\partial Y_m}{\partial X_i}. \quad (16)$$

If different constraints imposed on the field variables change m_0 , then according to Eq. (16), the number of terms changes so that different forms of ξ_{fij} correspond to the different constraints. This effect is shown later in detail for the case of electromagnetic fields. Thus, the intensive variables of classical thermodynamics may not be unique when the thermodynamic system is placed under the action of fields. It follows that the field dependent intensive variables can have multiple functional dependence on field variables. The form of this functional dependence is fixed by the constraints imposed on the field variables. In what follows, we show the implications of the theory for the case of magnetic fields.

B. Thermodynamic variables of a magnetizable continuum in a magnetoquasistatic field

Consider a linearly isotropic and uniform continuum that is uniformly magnetized. In the absence of a field, this continuum is characterized by entropy S , volume V , mass N , and internal energy U . Hence,

$$dU = TdS - PdV + \zeta dN, \quad (17)$$

where T , P , and ζ are temperature, pressure, and chemical potential, respectively.

In the presence of the field, the magnetic energy, which is uniformly stored in this linear continuum, is given by [8,9]

$$U_M = \frac{1}{2} V \mathbf{H} \cdot \mathbf{B}, \quad (18)$$

$$\mathbf{B} = \mu \mathbf{H}, \quad (19)$$

where \mathbf{H} is the magnetizing field, μ is the permeability of the contents of V , and \mathbf{B} is the magnetic induction that depends on the magnetization \mathbf{M} of the matter in V .

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}). \quad (20)$$

In Eq. (20), μ_0 is the permeability of free space. Note that Eq. (18) is a consequence of the assumption that the

matter is linear and hence μ is independent of \mathbf{H} .

In this case, the magnetic energy U_M is a state function and, hence, dU_M is an exact differential. The nature of U as an internal energy dictates that dU is also an exact differential. Hence,

$$dU' = dU + dU_M \quad (21)$$

is an exact differential of the combined energies $U' = U + U_M$, which qualifies as the new internal energy of the continuum considered. For the sake of simplicity, it is assumed henceforth that the whole magnetic field is confined to the volume V . Otherwise, integration over the whole magnetized space that is affected by the contents of V must be done in order to determine the magnetic energy associated with V .

Combining Eqs. (17), (18), and (21) gives

$$dU' = TdS - PdV + \zeta dN + d(\frac{1}{2} \mathbf{H} \cdot \mathbf{B} V). \quad (22)$$

Similarly

$$dF' = -SdT - PdV + \zeta dN + d(\frac{1}{2} \mathbf{H} \cdot \mathbf{B} V), \quad (23)$$

$$dG' = -SdT + VdP + \zeta dN + d(\frac{1}{2} \mathbf{H} \cdot \mathbf{B} V), \quad (24)$$

$$d\Omega' = -SdT - PdV - Nd\zeta + d(\frac{1}{2} \mathbf{H} \cdot \mathbf{B} V), \quad (25)$$

where

$$F' = F + U_M = U - TS + U_M, \quad (26)$$

$$G' = G + U_M = U - TS + PV + U_M, \quad (27)$$

$$\Omega' = \Omega + U_M = U - TS - \zeta N + U_M, \quad (28)$$

and F , G , and Ω are the Helmholtz, Gibbs, and Grand canonical potentials in the absence of the field [5].

Thus, by definition, the first three terms on the right-hand side of Eqs. (22)–(25) have their conventional meaning, i.e., in a field free environment. The fourth term gives the net magnetic effect. Note the use of the same V in the second and fourth terms on the right-hand side of Eqs. (22)–(25). In the case of a continuum which is considered below, this is justified. However, in the general case, the two volumes may not be the same. Equations (18) and (19) show that U_M is a function of three variables, i.e., V , \mathbf{B} , and μ or, alternatively, V , \mathbf{H} , and μ .

In view of the fact that the differential work done by external current sources to magnetize a volume V is $V \mathbf{H} \cdot d\mathbf{B}$, it seems advantageous to use the set V , \mathbf{B} , and μ for further analysis. It can readily be shown that

$$dU_M = d(\frac{1}{2} V \mathbf{H} \cdot \mathbf{B}) = \frac{1}{2} \mathbf{H} \cdot \mathbf{B} dV + V \mathbf{H} \cdot d\mathbf{B} - \frac{1}{2} V H^2 d\mu, \quad (29)$$

where

$$(\partial U_M / \partial V)_{\mathbf{B}, \mu} = \frac{1}{2} \mathbf{H} \cdot \mathbf{B},$$

$$(\partial U_M / \partial \mathbf{B})_{V, \mu} = V \mathbf{H}, \quad (\partial U_M / \partial \mu)_{V, \mathbf{B}} = -\frac{1}{2} V H^2.$$

Equation (29) shows that the magnetic energy can be changed by varying one or more of the variables V , \mathbf{B} , and μ . Furthermore, it shows that the magnetic work

term $V\mathbf{H}\cdot d\mathbf{B}$ can be only a part of the change in the internal energy and its use as the only magnetic effect is valid only at fixed V and μ . For linear materials, the permeability μ (being independent of \mathbf{H}) is a function of temperature and density of the contents of V .

$$d\mu = (\partial\mu/\partial T)_\rho dT + (\partial\mu/\partial\rho)_T d\rho. \quad (30)$$

If the change in μ is solely due to a change in density, then dropping the subscript T , it can be expressed in terms of the change of mass and volume as

$$d\mu = (\partial\mu/\partial\rho)d\rho = \frac{1}{V} \frac{\partial\mu}{\partial\rho} dN - \frac{1}{V\rho} \frac{\partial\mu}{\partial\rho} dV, \quad (31)$$

where in deriving Eq. (31) use was made of

$$d\rho = \left[\frac{\partial\rho}{\partial N} \right]_V dN + \left[\frac{\partial\rho}{\partial V} \right]_N dV$$

and $\rho = N/V$. Combining Eqs. (22), (29), and (31) and rearranging terms gives

$$dU' = TdS - \left[P - \frac{1}{2}\mathbf{H}\cdot\mathbf{B} - \frac{1}{2}H^2\rho \frac{\partial\mu}{\partial\rho} \right] dV + \left[\zeta - \frac{1}{2}H^2 \frac{\partial\mu}{\partial\rho} \right] dN + V\mathbf{H}\cdot d\mathbf{B}. \quad (32)$$

Equation (32) has the form of Eqs. (14) and (15) for $n=2$, $j=j'=1$, $k'=1$, $m_0=2$. Here, $Y_1=\mathbf{B}$ and $Y_2=\mu$, $X_0=S$, $X_1=V$, $X_2=N$. For example,

$$\frac{\partial U_{f1}}{\partial Y_2} \frac{\partial Y_2}{\partial X_1} = \frac{\partial U_{f1}}{\partial\mu} \frac{\partial\mu}{\partial V}$$

$$U_{f1} = \frac{1}{2}VB^2/\mu, \quad \partial U_{f1}/\partial\mu = -\frac{1}{2}VH^2.$$

From Eq. (31),

$$\partial\mu/\partial V = -\frac{1}{V\rho} \frac{\partial\mu}{\partial\rho}.$$

Hence,

$$\frac{\partial U_{f1}}{\partial Y_2} \frac{\partial Y_2}{\partial X_1} = \frac{1}{2}H^2\rho \frac{\partial\mu}{\partial\rho}. \quad (33)$$

This gives the third term of the coefficient of dV in Eq. (32). Similarly, it is straightforward to show that

$$\frac{\partial U_{f1}}{\partial Y_2} \frac{\partial Y_2}{\partial X_2} = -\frac{1}{2}H^2 \frac{\partial\mu}{\partial\rho}. \quad (34)$$

This gives the second term of the coefficient of dN in Eq. (32).

Note that the second term in the coefficient of dV in Eq. (32) arises from the first term on the right-hand side of Eq. (29). Since the independent variable of this term is V , it can be considered to be an ordinary thermodynamic variable. However, if we choose otherwise, then setting $Y_3=V$ gives $(\partial U_{f1}/\partial Y_3)(\partial Y_3/\partial V) = \frac{1}{2}\mathbf{H}\cdot\mathbf{B}$, which is the second term of the coefficient of dV in Eq. (32). Equation (32) shows that at fixed \mathbf{B} , one can define the pressure and chemical potential of the continuum in V as

$$P_{\mathbf{B},N} = P - \frac{1}{2}\mathbf{H}\cdot\mathbf{B} - \frac{1}{2}H^2\rho \frac{\partial\mu}{\partial\rho}, \quad (35)$$

$$\zeta_{\mathbf{B},V} = \zeta - \frac{1}{2}H^2 \frac{\partial\mu}{\partial\rho}. \quad (36)$$

The subscripts \mathbf{B},N and \mathbf{B},V denote the variables in addition to S that are kept fixed when P and ζ are evaluated as partial derivatives of U , respectively.

Note that $P_{\mathbf{B},N}$ and $\zeta_{\mathbf{B},V}$ correspond to the coefficients of dX_1 and dX_2 at $Y_1=\text{const.}$ in Eq. (15). This is the first, but not the only, pair of intensive variables of the magnetizable continuum. As shown below, the imposition of different constraints on the field variables produces additional and different such pairs. At fixed \mathbf{H} the last term on the right-hand side of Eq. (32) is a sole function of μ .

$$V\mathbf{H}\cdot d\mathbf{B} = VH^2 d\mu. \quad (37)$$

Combining Eqs. (31), (32), and (37) and rearranging terms gives

$$dU'(\mathbf{H}=\text{const.}) = TdS - \left[P - \frac{1}{2}\mathbf{H}\cdot\mathbf{B} + \frac{1}{2}H^2\rho \frac{\partial\mu}{\partial\rho} \right] dV + \left[\zeta + \frac{1}{2}H^2 \frac{\partial\mu}{\partial\rho} \right] dN. \quad (38)$$

Equation (38) facilitates a definition of the second pair of pressure and chemical potential as

$$P_{\mathbf{H},N} = P - \frac{1}{2}\mathbf{H}\cdot\mathbf{B} + \frac{1}{2}H^2\rho \frac{\partial\mu}{\partial\rho}, \quad (39)$$

$$\zeta_{\mathbf{H},V} = \zeta + \frac{1}{2}H^2 \frac{\partial\mu}{\partial\rho}. \quad (40)$$

At fixed \mathbf{B} and μ , the second and third terms of Eq. (29) vanish and, hence,

$$d\left(\frac{1}{2}V\mathbf{H}\cdot\mathbf{B}\right) = \frac{1}{2}\mathbf{H}\cdot\mathbf{B}dV = \frac{1}{2\rho}\mathbf{H}\cdot\mathbf{B}dN, \quad \mathbf{B}=\text{const.}, \quad \mu=\text{const.} \quad (41)$$

In Eq. (41), use was made of $\rho V = N$, $dV = (1/\rho)dN$, with ρ being fixed due the constraint that μ is fixed. Equation (41) facilitates the definition of two equivalent pairs of pressure and chemical potentials depending on the selection of either V or N as the independent variable. If V is selected, then combining Eqs. (22) and (29) gives

$$dU'(\mathbf{B}=\text{const.}, \mu=\text{const.}) = TdS - (P - \frac{1}{2}\mathbf{H}\cdot\mathbf{B})dV + \zeta dN. \quad (42)$$

Hence

$$P_{\mathbf{B},\mu} = P - \frac{1}{2}\mathbf{H}\cdot\mathbf{B}, \quad (43)$$

$$\zeta_{\mathbf{B},\mu} = \zeta. \quad (44)$$

If N is selected as the independent variable in Eq. (41), then

$$dU'(\mathbf{B}=\text{const.}, \mu=\text{const.}) \\ = TdS - PdV + \left[\zeta + \frac{1}{2\rho} \mathbf{H} \cdot \mathbf{B} \right] dN, \quad (45)$$

$$P_{\mathbf{B},\mu} = P, \quad (46)$$

$$\zeta_{\mathbf{B},\mu} = \zeta + \frac{1}{2\rho} \mathbf{H} \cdot \mathbf{B}. \quad (47)$$

It follows that the set of three different constraints, i.e., fixed \mathbf{B} , fixed \mathbf{H} , and fixed \mathbf{B} and μ (which is equivalent to fixed \mathbf{B} and \mathbf{H}) yields three different pairs of field dependent pressure and chemical potential, i.e., $P_{\mathbf{B},N}, \zeta_{\mathbf{B},V}$; $P_{\mathbf{H},N}, \zeta_{\mathbf{H},V}$; and $P_{\mathbf{B},\mu}, \zeta_{\mathbf{B},\mu}$, respectively. The first constraint imposes a condition of fixed flux linkage with the source of the field and hence no electrical work is done by this source on the system (i.e., on the contents of V). This results in a process of conversion of the field energy to other forms such as mechanical energy and vice versa. The second constraint involves energy exchange with the source of the field, which may add or absorb energy from the system, through changes in the flux linkage at the source.

Under the condition of the first constraint, adding permeable matter to a system at fixed volume decreases its magnetic energy and hence $\zeta_{\mathbf{B},V}$ contains a negative term due to the field. Under the condition of the second constraint, the reverse is true. This gives rise to the positive, field dependent term in $\zeta_{\mathbf{H},V}$. Under the condition of the third constraint, addition of a magnetized continuum at fixed \mathbf{B} and μ increases the volume, mass, and, hence, also the magnetic energy of the system. This gives rise to the positive term in $\zeta_{\mathbf{B},\mu}$.

Equations (35), (36), (39), and (40) show that the field dependent pressure and chemical potential are functions of $\rho(\partial\mu/\partial\rho)$ and $(\partial\mu/\partial\rho)$, respectively. It follows that at fixed temperature, the form of these pressure and chemical potential variables depends on the form of $\mu=\mu(\rho)$. Let this form be expressed as

$$\mu = C\rho + \mu_0, \quad (48)$$

where, in the general case, C can be a function of temperature, pressure, and of ρ . If C is a sole function of temperature, then at constant temperature it is fixed and hence

$$\partial\mu/\partial\rho = C = (\mu - \mu_0)/\rho. \quad (49)$$

Note that the partial derivative in Eq. (49) is evaluated at fixed temperature [see Eq. (30) for notation]. For the sake of brevity, this notation is also followed in the rest of this work. In this case, substitution of Eq. (49) in Eqs. (35) and (36) and in Eqs. (39) and (40) gives

$$P_{\mathbf{B},N} = P + \frac{1}{2}\mu_0 H^2 - \mathbf{H} \cdot \mathbf{B} = P - \frac{1}{2}\mu_0 H^2 - \mu_0 \mathbf{M} \cdot \mathbf{H}, \quad (50)$$

$$\zeta_{\mathbf{B},V} = \zeta + \frac{1}{2\rho} \mu_0 H^2 - \frac{1}{2\rho} \mathbf{H} \cdot \mathbf{B} = \zeta - \frac{\mu_0}{2\rho} \mathbf{M} \cdot \mathbf{H}, \quad (51)$$

$$P_{\mathbf{H},N} = P - \frac{1}{2}\mu_0 H^2, \quad (52)$$

$$\zeta_{\mathbf{H},V} = \zeta - \frac{1}{2\rho} \mu_0 H^2 + \frac{1}{2\rho} \mathbf{H} \cdot \mathbf{B} = \zeta + \frac{1}{2\rho} \mu_0 \mathbf{M} \cdot \mathbf{H}. \quad (53)$$

Hence,

$$P_{\mathbf{B},N} = P_{\mathbf{H},N} - \mu_0 \mathbf{M} \cdot \mathbf{H}, \quad (54)$$

$$\zeta_{\mathbf{B},V} = \zeta_{\mathbf{H},V} - \frac{1}{\rho} \mu_0 \mathbf{M} \cdot \mathbf{H}. \quad (55)$$

For further details on the physical significance of the above chemical potentials, using the point of view of the electric work done at the terminals, see the Appendix.

Equations (22), (32), and (42) show that under one constraint, i.e., fixed \mathbf{B} , fixed \mathbf{H} , or fixed \mathbf{B} and fixed μ , dU' can be expressed as

$$dU' = TdS - \hat{P}dV + \hat{\zeta}dN, \quad (56)$$

where, at fixed \mathbf{B} ,

$$\hat{P} = P_{\mathbf{B},N}, \quad (57)$$

$$\hat{\zeta} = \zeta_{\mathbf{B},V}, \quad (58)$$

at fixed \mathbf{H} ,

$$\hat{P} = P_{\mathbf{H},N} \quad (59)$$

$$\hat{\zeta} = \zeta_{\mathbf{H},V}, \quad (60)$$

at fixed \mathbf{B} and μ ,

$$\hat{P} = P_{\mathbf{B},\mu}, \quad (61)$$

$$\hat{\zeta} = \zeta_{\mathbf{B},\mu}. \quad (62)$$

Since \hat{P} and $\hat{\zeta}$ are proper pressure and chemical potential, they can be used directly, i.e., as ordinary pressure and chemical potential, to set the conditions of equilibrium of magnetizable systems in magnetic fields. These conditions are

$$\hat{P} = \text{const.}, \quad (63)$$

$$\hat{\zeta} = \text{const.} \quad (64)$$

The significance of $\hat{\zeta}$ can be shown with respect to processes that involve mass transfer under the action of fields. This field dependent chemical potential (which, according to different field constraints, has multiple functional dependence on field variables) can be used to determine driving forces for mass transfer. For example, at fixed \mathbf{B} , the environment set by the magnetic field is such that it enhances mass transfer in the direction of increasing \mathbf{H} . If this mass transfer produces a buildup of ζ [see Eq. (51)] as a result of increased density (or concentration), then the driving force per unit mass is $-\nabla\hat{\zeta}$ and equilibrium prevails when $\nabla\hat{\zeta} = \nabla\zeta - \nabla[(\mu_0/2\rho)\mathbf{M} \cdot \mathbf{H}] = 0$ is satisfied. The physical picture changes when the environment set by the field, e.g., for mass transfer, is dictated by holding \mathbf{H} fixed. In this case, the field enhances mass transfer in the direction of decreasing \mathbf{B} , which coincides with the one of decreasing local density (or concentration) of the permeable matter. It follows that except for the cases where ζ can be changed by means other than density or concentration (i.e., by temperature or other fields), it reinforces the action of the magnetic field in driving mass transfer away from regions of higher density or higher concentration.

Note that at fixed \mathbf{B} (which implies fixed flux linkage with the current sources), the energy for the mass transfer process of permeable matter is supplied by the field into which the mass is transferred. At fixed \mathbf{H} , this energy, supplied by the external current sources as the magnetic energy, which is stored in the region that absorbs the permeable mass, must increase.

If in Eq. (48) C is a sole function of ρ , i.e., $C = C(\rho)$, then

$$\frac{\partial \mu}{\partial \rho} = \frac{\mu - \mu_0}{\rho} + \rho \frac{\partial C}{\partial \rho}. \quad (65)$$

In this case,

$$\begin{aligned} P_{\mathbf{B},N} &= P + \frac{1}{2}\mu_0 H^2 - \mathbf{H} \cdot \mathbf{B} - \frac{1}{2}H^2 \rho^2 \frac{\partial C}{\partial \rho} \\ &= P - \frac{1}{2} \left[2\mu - \mu_0 + \rho^2 \frac{\partial C}{\partial \rho} \right] H^2, \end{aligned} \quad (66)$$

$$\begin{aligned} \zeta_{\mathbf{B},V} &= \zeta + \frac{1}{2\rho}\mu_0 H^2 - \frac{1}{2\rho}\mathbf{H} \cdot \mathbf{B} - \frac{1}{2}H^2 \rho \frac{\partial C}{\partial \rho} \\ &= \zeta - \frac{1}{2\rho} \left[\mu - \mu_0 + \rho^2 \frac{\partial C}{\partial \rho} \right] H^2, \end{aligned} \quad (67)$$

$$\begin{aligned} P_{\mathbf{H},N} &= P - \frac{1}{2}\mu_0 H^2 + \frac{1}{2}H^2 \rho^2 \frac{\partial C}{\partial \rho} \\ &= P - \frac{1}{2} \left[\mu_0 - \rho^2 \frac{\partial C}{\partial \rho} \right] H^2, \end{aligned} \quad (68)$$

$$\begin{aligned} \zeta_{\mathbf{H},V} &= \zeta - \frac{1}{2\rho}\mu_0 H^2 - \frac{1}{2\rho}\mathbf{H} \cdot \mathbf{B} + \frac{1}{2}H^2 \rho \frac{\partial C}{\partial \rho} \\ &= \zeta + \frac{1}{2\rho} \left[\mu - \mu_0 + \rho^2 \frac{\partial C}{\partial \rho} \right] H^2. \end{aligned} \quad (69)$$

Note that in Eqs. (67) and (69), $\mu - \mu_0 + \rho^2 \partial C / \partial \rho$ can be considered as an effective susceptibility of the matter. At fixed C this effective susceptibility is simply \mathbf{M}/\mathbf{H} . Thus, if $\partial C / \partial \rho > 0$, then the effective susceptibility exceeds \mathbf{M}/\mathbf{H} , and vice versa.

Consider the case where the material satisfies the Clausius-Mosotti model of magnetostriction [9]. In this case,

$$\mu = \frac{3\mu_0 K_1 \rho}{1 - K_1 \rho} + \mu_0 = K(\rho)\rho + \mu_0, \quad (70)$$

$$K(\rho) = \frac{3\mu_0 K_1}{1 - K_1 \rho}, \quad (71)$$

$$\partial K(\rho) / \partial \rho = \frac{3\mu_0 K_1^2}{(1 - K_1 \rho)^2}, \quad (72)$$

$$\partial \mu / \partial \rho = \frac{3\mu_0 K_1}{(1 - K_1 \rho)^2} = \frac{K(\rho)}{1 - K_1 \rho} = \frac{\mu - \mu_0}{\rho(1 - K_1 \rho)}, \quad (73)$$

$$P_{\mathbf{B},N} = P - \frac{1}{2}\mathbf{H} \cdot \mathbf{B} - \frac{\mu_0}{2}\mathbf{M} \cdot \mathbf{H} / (1 - K_1 \rho), \quad (74)$$

$$\zeta_{\mathbf{B},V} = \zeta - \frac{\mu_0}{2\rho}\mathbf{M} \cdot \mathbf{H} / (1 - K_1 \rho), \quad (75)$$

$$P_{\mathbf{H},N} = P - \frac{1}{2}\mathbf{H} \cdot \mathbf{B} + \frac{\mu_0}{2}\mathbf{M} \cdot \mathbf{H} / (1 - K_1 \rho), \quad (76)$$

$$\zeta_{\mathbf{H},V} = \zeta + \frac{\mu_0}{2\rho}\mathbf{M} \cdot \mathbf{H} / (1 - K_1 \rho). \quad (77)$$

Note that if $K_1 \rho \ll 1$, then $K(\rho) = K$ becomes practically a constant. In this case, Eqs. (74) and (75) reduce to Eqs. (50) and (51) and Eqs. (76) and (77) to Eqs. (52) and (53), respectively.

The different sets of constraints discussed up to this point resulted in field dependent pressure and chemical potential variables. It is possible, however, to impose another set of constraints that results in pressure and chemical potentials that are independent of the field. This set of constraints is fixed V and μ , and assuming that at fixed temperature, μ is a sole function of ρ , as per Eqs. (48) and (49), this implies that N is also fixed. Combining Eqs. (22) and (29) at fixed V and μ , and, hence, also fixed N gives

$$dU' = TdS + V\mathbf{H} \cdot d\mathbf{B}. \quad (78)$$

Integration of Eq. (78) at fixed T , V , and μ , and using $\mathbf{B} = \mu\mathbf{H}$, gives

$$U' = TS + \frac{1}{2}V\mathbf{H} \cdot \mathbf{B} + \text{const.} \quad (79)$$

Integration of Eq. (22) at fixed T , P , and ζ gives

$$U' = TS - PV + \zeta N + \frac{1}{2}V\mathbf{H} \cdot \mathbf{B}. \quad (80)$$

Hence, the constant in Eq. (79) is equal to $-PV + \zeta N$, where P and ζ are the same pressure and chemical potentials that prevail in the absence of the field, i.e., they are also independent of the field. In this case, the only source for the change in the magnetic energy of the contents of V can be \mathbf{H} provided that it varies exclusively with the sources, (e.g., currents) that generate the field. This is the well known work of magnetization of a fixed volume that contains a mass of fixed permeability. It follows that P, ζ is the fourth, field independent, pair of pressure and chemical potential that prevail under the constraint of fixed V and μ .

C. Thermodynamic variables of an electrically polarizable continuum in an electric field

The thermodynamic variables of a linear electrically polarizable continuum can be obtained by substitution of \mathbf{E} , \mathbf{D} , and ϵ for \mathbf{H} , \mathbf{B} , and μ in Eqs. (22)–(80), where \mathbf{E} , \mathbf{D} , and ϵ are the electric field strength, electric displacement, and permittivity, respectively. In Eqs. (50), (51), (53)–(55), and (74)–(77), the electric counterpart of $\mu_0\mathbf{M}$ is the electric polarization vector \mathbf{P}_E .

D. Formulations of thermodynamic relations for magnetizable systems

The conventional thermodynamic treatment includes formulations of thermodynamic potentials and Maxwell relations. These formulations depend on the possibility of expressing the magnetic term in the same form as other terms that appear in Eq. (2), i.e., as $\xi_i dX_i$, $i = 0, 1, \dots, n$.

Equations (22) and (29) show that this can be achieved subject to the condition of fixed $V=V_M$ and μ . In this case,

$$\begin{aligned} dU'(V_M=\text{const.}, \mu=\text{const.}) \\ &= TdS - PdV + \xi dN + V\mathbf{H} \cdot d\mathbf{B} \\ &= TdS - PdV + \xi dN + \mathbf{H} \cdot d(\mathbf{B}V) \end{aligned} \quad (81)$$

The condition of fixed V applies here to the uniformly magnetizable volume, i.e., to V_M and not necessarily to the volume of the whole system. Thus, unless the system consists exclusively of magnetizable volume, then holding V (which pertains to the term $V\mathbf{H} \cdot d\mathbf{B}$) fixed at $V=V_M$ does not necessarily impose $dV=0$ in the term $-PdV$. We shall continue to use the same symbol (i.e., V) for volume in the differentials of pressure and magnetic work, but bearing in mind that it can have different meanings. Thus for isotropic materials the definition of \mathbf{H} as the intensive conjugate of $\mathbf{B}V$ gives in this case

$$H = [\partial U'(V_M=\text{const.}, \mu=\text{const.}) / \partial (BV)]_{S, V, N}, \quad (82)$$

where V in BV pertains to the magnetized volume, whereas constant V concerns the volume of the whole system.

The internal energy $U'(V_M=\text{const.}, \mu=\text{const.})$ can now be used to formulate Legendre transformations and Maxwell relations in the ordinary way. These formulations are available in standard literature and hence will not be repeated here. Note that if the magnetizable volume V_M is indeed identical with V , i.e., the whole system is magnetizable, and μ is a sole function of N , then from Eq. (32)

$$VH = (\partial U' / \partial B)_{S, V, N} \quad (83)$$

and, since V is fixed,

$$H = [\partial U' / \partial (BV)]_{S, V, N}. \quad (84)$$

In this case, $U'(V=\text{const.}, N=\text{const.})$ can be used to formulate Legendre transformations of field variables.

The entropy of a magnetizable continuum

The entropy of a magnetizable continuum can be evaluated as follows. At fixed V and ρ and hence also fixed N , the change in the magnetic energy due to a change in temperature is

$$d(\frac{1}{2}V\mu H^2) = \frac{1}{2}VH^2 d\mu + V\mu H dH, \quad (85)$$

$$d\mu = (\partial\mu / \partial T)_{\rho} dT, \quad (86)$$

$$dH = d(B/\mu) = -(B/\mu^2) d\mu, \quad (87)$$

therefore,

$$d(\frac{1}{2}V\mu H^2) = -\frac{1}{2}VH^2 (\partial\mu / \partial T)_{\rho} dT. \quad (88)$$

Note that μ (which is independent of \mathbf{H}) is assumed to be the only parameter that is affected directly by the change in temperature. Alternatively, the change in \mathbf{B} or \mathbf{H} due to the change in temperature is assumed to be solely due to the change in μ which is dependent on temperature

but not on \mathbf{H} . This is the reason for the implied condition of fixed B in the expression of dH as a function of $d\mu$. Furthermore, at fixed \mathbf{B} no exchange of magnetic energy between the contents of V and the current sources exists. In this case, all the energy input used to decrease μ appears in the form of magnetic energy.

Combining Eqs. (23) and (88) at fixed V and ρ gives

$$dF' = -[S + \frac{1}{2}VH^2 (\partial\mu / \partial T)_{\rho}] dT. \quad (89)$$

It follows that the entropy at the field \mathbf{H} is given by

$$S_H = S + \frac{1}{2}VH^2 (\partial\mu / \partial T)_{\rho}, \quad (90)$$

where S is the entropy in the absence of the field.

In the process where \mathbf{H} is held fixed as the rise in temperature decreases the permeability μ , the whole heat input is used to perform work on the current sources, i.e., via the decreasing \mathbf{B} field. Thus, in this process there is no net change in the internal energy of the system and, recalling that V and ρ (and hence also N) are also fixed, the entropy remains fixed at the level of S_H . Note that, in the general case, i.e., the case of nonlinear matter, $\mu = \mu(\mathbf{H}, T, \rho)$ and, hence, its partial derivative with respect to temperature must be evaluated at fixed \mathbf{H} and ρ . It is only for the case of linear matter that $(\partial\mu / \partial T)_{\mathbf{H}, \rho} = (\partial\mu / \partial T)_{\rho}$. Equation (90) agrees with the entropy derived by Guggenheim [1] and by Landau and Lifshitz [13] for dielectrics in an electric field. However, the point made here is that this result is the consequence of using directly the exact differential of the magnetic energy without the need to resort to transformations.

E. Thermodynamic variables of discrete systems

The thermodynamic formulation of discrete systems in electromagnetic fields must account for the following effects.

- (1) The capability to interact at a distance.
- (2) The position of the system can effect its energy. This property does not appear in ordinary thermodynamics, i.e., in the absence of fields.
- (3) The energy of a system of fixed extensive variables and position is dependent on the strength of the field, in this fixed position, or, alternatively, on the potential that characterizes the field in this position. This property does not appear in ordinary thermodynamics, i.e., in the absence of fields.

(4) The energy of a polarized discrete system involves the whole space affected by this system. Consequently, polarized discrete systems can overlap due to interpenetration of fields that each of them generates.

In order to illustrate the above effects, their significance in a system of charges and a discrete magnetized body is considered.

1. Electric work on charges

We shall show that the work done to bring a new charge from infinity into a field that exists due to a stationary assembly of other charges, is divided between the work necessary to raise the potential of the stationary

charges and the work actually done on the new charge.

The work W of assembling n charges q_1, q_2, \dots, q_n from infinity is given by [10,11]

$$W = \frac{1}{2} \sum_{i=1}^n q_i \psi_i, \quad (91)$$

where ψ_i is the electric potential at the final position of q_i after the assembly process has been completed. In a process where the charges are brought one after the other from infinity to their final position, the work W_n done on the last charge q_n is

$$\begin{aligned} W_n &= q_n \psi_n = \frac{1}{2} \sum_{i=1}^n q_i \psi_i - \frac{1}{2} \sum_{i=1}^{n-1} q_i \psi_i' \\ &= \frac{1}{2} q_n \psi_n + \frac{1}{2} \sum_{i=1}^{n-1} q_i (\psi_i - \psi_i'). \end{aligned} \quad (92)$$

Hence,

$$q_n \psi_n = \sum_{i=1}^{n-1} q_i (\psi_i - \psi_i'). \quad (93)$$

This result also applies to an infinitesimal charge dq_n which induces an infinitesimal change in the potential of the rest of the charges.

$$\psi_n dq_n = \sum_{i=1}^{n-1} q_i d\psi_i. \quad (94)$$

Equations (93) and (94) are in agreement with Green's reciprocity theorem [11], which can be used as an alternative way to derive them.

Equation (94) shows that the work done in bringing dq_n from infinity is equal to the work necessary to raise the potential of the charges which are the source of ψ_n . Equation (92), in conjunction with Eq. (93), shows that the work $W_n = q_n \psi_n$ is divided equally between the part that is necessary to raise the potential of the charges that are the source of ψ_n and the actual work done on q_n .

This shows that the two alternative ways of changing the energy of a charge, or an assembly of charges, i.e., by moving them to a position of different potential or by changing the potential at their fixed position, are completely equivalent. This expected result agrees with the fact that $q_i \psi_i$, $i=1, 2, \dots, n$, are state functions. Thus, the incorporation of this state function as part of the internal energy is acceptable provided that it is used as an exact differential. Thus, the differential effect of n point charges which are part of a thermodynamic system can be expressed as

$$dU_q = d \left[\frac{1}{2} \sum_{i=1}^n q_i \psi_i \right]. \quad (95)$$

Hence,

$$dU'' = dU + dU_q = TdS - PdV + \zeta dN + d \left[\frac{1}{2} \sum_{i=1}^n q_i \psi_i \right], \quad (96)$$

where U'' is the combined internal energy of the thermo-

dynamic system inclusive of the charges. If the system can be expressed in terms of a uniform charge density q_v in dV , where ψ can be considered as being fixed, then $dU_q = d \left(\frac{1}{2} \int_V \psi q_v dV \right)$.

If ψ is fixed across V , then

$$dU'' = TdS - PdV + \zeta dN + d \left(\frac{1}{2} V q_v \psi \right). \quad (97)$$

The same procedure used to define thermodynamic variables under different constraints for the case of magnetic fields can also be used here. Note that for the case where dq_n is brought from infinity into the system, we have

$$d \left[\frac{1}{2} \sum_{i=1}^n q_i \psi_i \right] = \frac{1}{2} \sum_{i=1}^{n-1} q_i d\psi_i + \frac{1}{2} \psi_n dq_n = \psi_n dq_n$$

as required. However, Eqs. (95), (96), and (97) also account for the case where only ψ_i are variable at fixed q_i .

For example, suppose the thermodynamic system contains the $n-1$ charges q_1, q_2, \dots, q_{n-1} and the charge q_n is brought from infinity to a position which is outside the system, where the potential is ψ_n . The work done in this process, which is $\psi_n q_n$, is evenly divided so that half of it is used to raise the energy of the system, i.e., by $\frac{1}{2} \psi_n q_n$; see Eq. (92). Thus, interaction at a distance and the subsequent rise in the potentials of the charges of the system constitute the mechanism by which the energy of the system is raised, while keeping all its extensive variables fixed. Had we used, instead of Eq. (95),

$$dU_q = \sum_{i=1}^n \psi_i dq_i, \quad (98)$$

Eq. (96) would have been replaced by

$$dU'' = TdS - PdV + \zeta dN + \sum_{i=1}^n \psi_i dq_i, \quad (99)$$

where dq_i is the change of the i th charge exclusively within the system. Since, in the example above, there is no change in either the position or the amount of the $n-1$ charges and q_n does not exist in the system, one would obtain $dU'' = 0$ instead of the correct result, which is $dU'' = \frac{1}{2} \psi_n dq_n$. It is only when the charges are brought into the system that Eq. (99) is acceptable. In all cases where the field changes due to processes that start and end outside the system, Eq. (96) holds while Eq. (99) fails to provide the correct answer.

Similarly, had we used, as suggested by Hatsopoulos and Keenan [12], instead of Eq. (95)

$$dU_q = \sum_{i=1}^n q_i d\psi_i, \quad (100)$$

Eq. (96) would have been replaced by

$$dU'' = TdS - PdV + \zeta dN + \sum_{i=1}^n q_i d\psi_i. \quad (101)$$

Clearly, Eq. (101) does not account for the case of bringing the charges q_i at fixed levels of ψ_i .

2. Discrete magnetizable systems

Energy of a discrete magnetizable body. A discrete magnetized body is defined here as a body having clear physical boundaries that do not enclose the field lines completely. Alternatively, the field lines of a discrete magnetized body cross the physical boundaries that separate this body from other materials, phases, or space. Subject to this definition, an ideal continuous toroid which is magnetized with no fringing field is a continuum and does not qualify as a discrete body. If, in the same toroid, a gap is opened, then the whole toroidal section excluding the gap becomes a discrete body. This is due to the fact that field lines cross its boundaries into and from the gap. The same applies to magnetic circuits such as yokes that are used in transformers. When the yoke is continuous and no fringing of field lines exists, it acts as a continuum. However, when a gap is opened, field lines cross the yoke-gap interfaces and the whole yoke, excluding the gap, becomes a discrete body. A uniformly magnetized sphere, or ellipsoid, is a classic example of a discrete body from which field lines extend all over space. This is in contrast to the examples of the toroid and yoke, where the field is usually confined to a relatively small space. Note that in the above examples, internal parts of the discrete bodies can still qualify as continua. The theory of electromagnetism provides formulations of the energy associated with discrete magnetized bodies. However, a serious question arises concerning which part of this energy should be associated with the body when the latter is defined as a thermodynamic system.

Consider a magnetizable discrete body of volume V_M . This body is defined as the thermodynamic system. The work required by an external current source to magnetize this body is given by

$$W_M = \int_{V_S} \int_0^B \mathbf{H} \cdot d\mathbf{B} dV, \quad (102)$$

where V_S denotes that the integration must be performed over the entire space affected by the body. If the discrete body is infinitely permeable, then the field inside it vanishes and so does the energy that can be stored within its boundaries, i.e., in V_M . In this case [8] the energy is stored outside the body, i.e., in $V_S - V_M$. Thus, the magnetized body which is infinitely permeable stores all its energy outside its boundaries. If the permeability of the body is finite, then energy is stored inside as well as outside its boundaries.

Since ordinary thermodynamics assumes that the internal energy of a system is a function only of the contents, e.g., entropy, volume and mass, of the system, it does not provide an appropriate formulation for cases where energy is stored outside the system boundaries. Alternatively, ordinary thermodynamics does not provide an appropriate formulation for the case where the system is a source of energy that may be stored outside its own boundaries. If one attempts to apply Eq. (22) to a hypothetical linear discrete body of infinite permeability by defining the body as the thermodynamic system, then the magnetic term vanishes and, consequently, the system acts as if it were nonmagnetic thermodynamically. However, when this system is demagnetized, it performs work on the electric

current sources that magnetized it in the first place. This suggests that the energy stored outside the system should be included as part of its own energy, as is indeed stated by Landau and Lifshitz regarding polarized conductors [13]. In this sense there is no such thing as pure internal energy in the case of systems comprising magnetized discrete bodies. However, if one still chooses to use the term internal energy (which implies that all the energy is confined to the boundaries of the system), then it must be stressed that all the energy stored outside the system is assigned (by definition) to this system as being its sole source.

It follows that for a discrete one-component and uniformly magnetized system, the energy, or internal energy, in its generalized sense as defined above, can be presented in the form

$$dU'' = TdS - PdV + \zeta dN + d \left[\int_{V_S} \int_0^B \mathbf{H} \cdot d\mathbf{B} dV \right]. \quad (103)$$

Equation (103) shows the clear distinction between the volume V of the system and the volume V_S that is affected by its field. Note that in the general case V_S is simply the whole space, whereas only for cases where the field is completely confined within the boundaries of the system is the use of $V_S = V$ justified.

Equation (103) relates the different components of the energy to sources that either exist within the system boundaries or are stored outside them. According to this model, the energy stored in a gap of an excited and infinitely permeable yoke pertains to the current sources as well as to the yoke, and the latter can be defined as a thermodynamic system. The yoke is a source of field and hence this field pertains to the yoke system.

Suppose that we do not accept the notion that the field which is excited by the yoke pertains to the yoke system. This makes the gap an independent system having an energy of its own. Consider such a gap of volume V that consists of free space. The magnetic energy stored in this gap is $\frac{1}{2}V\mu_0 H^2$. Consider a second system having a volume V_1 (consisting of free space) which is enclosed by nonmagnetic walls. This system can fit into the gap. Initially, the second system is placed on a nonmagnetic frictionless horizontal plane that extends far away from the gap and then it is moved quasistatically into the gap. In this process, effectively no work is done on the second system, but as it enters the gap the magnetic energy that becomes enclosed by its boundaries rises from zero (when it is outside and far away from the gap) up to $\frac{1}{2}V_1\mu_0 H^2$ when it is completely inside the gap. Thus, at the end of the process the internal energy of the second system increased by $\frac{1}{2}V_1\mu_0 H^2$, no work was performed and no heat crossed its boundaries. This seems to contradict the first law of thermodynamics. However, this discrepancy is eliminated once the magnetic energy stored in the gap is assigned to its sources, i.e., to the yoke and current sources. In the latter case, the insertion of the second system into the gap does not change the status of the magnetic energy. This is in spite of the fact that now magnetic field energy resides within the boundaries of the second system in addition to its being part of the gap.

Once we have accepted the notion that the energy gen-

erated by a discrete system pertains to this system, irrespective of its being stored within or outside its boundaries, then the same must be true regarding the entropy that depends on and arises due to the existence of this energy. If it were not so, then the fundamental principles of thermodynamics would not hold in such systems. For example, suppose that in the previous example the gap as well as the space around the yoke consist of a permeable gas at fixed mass, temperature, and pressure. When the field is on, the field dependent energy and entropy of the gas in the gap are positive and negative, respectively, while far away from the gap they vanish. Repeating our thought experiment of pushing the system of volume V_1 into the gap (holding all properties of the yoke, gap, and gas fixed) results in a simultaneous net rise in the energy and decrease in the entropy. This violates the basic thermodynamic postulate that the entropy is an increasing function of energy and vice versa. If we had assumed that the energy pertains to the yoke system while the entropy does not, then the result of our experiment would indicate (e.g., for the system of volume V_1) a spontaneous decrease of entropy at fixed energy, which is also unacceptable. Thus, both the field dependent energy and entropy must pertain to their sources and not necessarily to the region in space where they exist. It follows that a fundamental aspect of thermodynamics in the presence of quasistatic electric and magnetic fields is that the energy and entropy that exist in a given region of space cannot be separated from their sources.

3. Formulations of thermodynamic variables

The formulation of thermodynamic variables of discrete systems must embody the fact that part of the energy and entropy exist outside their physical boundaries. Further complications arise due to the fact that, in the general case, the field is not uniform and hence the implications of thermodynamic variables derived using the conventional formalism may not be clear. Therefore, we restrict the formulations to uniformly magnetized systems, but without restricting the field that may be nonuniform outside their boundaries.

Consider a uniformly magnetized discrete system of volume V and homogeneous and isotropic permeability μ .

The magnetic energy of this system, which equals the magnetic work W_M [see Eq. (102)], is given by

$$U_M = \int_{V_S} \int_0^B \mathbf{H} \cdot d\mathbf{B} dV, \quad (104)$$

where, as before, V_S indicates the entire space that is energized by the field of the system. In the general case, the boundaries of V_S extend to infinity. Similarly to the case of a continuum, the magnetic energy of the discrete system can be presented as a function of its volume V , field \mathbf{B} , and permeability μ .

$$U_M = U_M(V, \mathbf{B}, \mu). \quad (105)$$

This is justified in view of the fact that in magneto-quasistatic systems, the field outside the system is fully determined if the field within and on its boundaries is set. The above is a consequence of Maxwell's equations.

We proceed with the formulation of thermodynamic variables using a similar approach that was applied to continua.

$$dU_M = (\partial U_M / \partial V)_{B, \mu} dV + (\partial U_M / \partial B)_{V, \mu} dB + (\partial U_M / \partial \mu)_{V, B} d\mu, \quad (106)$$

where, in the general case, the term involving the derivative with respect to B stands for the sum of three terms, e.g., with respect to its components. Equation (106) expresses the change of U_M as a function of variables that are defined within the system, but the partial derivatives involve the entire space affected by the changes in these variables. The permeability is a function of the density ρ , temperature T , and the field \mathbf{H} .

$$\mu = \mu(\rho, T, \mathbf{H}), \quad (107)$$

$$d\mu = (\partial \mu / \partial \rho)_{T, \mathbf{H}} d\rho + (\partial \mu / \partial T)_{\rho, \mathbf{H}} dT + (\partial \mu / \partial \mathbf{H})_{\rho, T} d\mathbf{H}, \quad (108)$$

$$d\rho = -\rho V^{-1} dV + V^{-1} dN. \quad (109)$$

Combining Eqs. (106), (108), and (109) and collecting terms gives

$$dU_M = [(\partial U_M / \partial V)_{B, \mu} - (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \rho)_{T, \mathbf{H}} \rho V^{-1}] dV + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \rho)_{T, \mathbf{H}} V^{-1} dN + (\partial U_M / \partial B)_{V, \mu} dB + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial T)_{\rho, \mathbf{H}} dT + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \mathbf{H})_{\rho, T} d\mathbf{H}. \quad (110)$$

If μ is independent of \mathbf{H} , then, at fixed T , combining Eqs. (17), (21), and (110) gives

$$dU' = TdS - [P - (\partial U_M / \partial V)_{B, \mu} + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \rho)_{T, \mathbf{H}} \rho V^{-1}] dV + [\xi + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \rho)_{T, \mathbf{H}} V^{-1}] dN + (\partial U_M / \partial B)_{V, \mu} dB. \quad (111)$$

If T is not fixed, then the use of F' is called for and differentiation of Eq. (26) in conjunction with Eq. (110) gives

$$dF' = -[S - (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial T)_{\rho, \mathbf{H}}] dT - [P - (\partial U_M / \partial V)_{B, \mu} + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \rho)_{T, \mathbf{H}} \rho V^{-1}] dV + [\xi + (\partial U_M / \partial \mu)_{V, B} (\partial \mu / \partial \rho)_{T, \mathbf{H}} V^{-1}] dN + (\partial U_M / \partial B)_{V, \mu} dB. \quad (112)$$

Equations (111) and (112) facilitate the definition of the first pair of pressure and chemical potential and of the entropy of the discrete system, respectively. Using Eq. (111) at fixed S , N , and \mathbf{B} gives $P_{\mathbf{B},N}$ as

$$P_{\mathbf{B},N} = P - (\partial U_M / \partial V)_{\mathbf{B},\mu} + (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial \rho)_{T,\mathbf{H}} V^{-1}, \quad (113)$$

while at fixed S , V , and \mathbf{B} , one obtains $\zeta_{\mathbf{B},V}$ as

$$\zeta_{\mathbf{B},V} = \zeta + (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial \rho)_{T,\mathbf{H}} V^{-1}. \quad (114)$$

The entropy S_H is obtained from Eq. (112) as $(\partial F' / \partial T)_{V,N,\mathbf{B}}$.

$$S_H = S - (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial T)_{\rho,\mathbf{H}}. \quad (115)$$

The second pair of pressure and chemical potential is obtained by setting \mathbf{H} instead of \mathbf{B} fixed.

$$P_{\mathbf{H},N} = P - (\partial U_M / \partial V)_{\mathbf{B},\mu} + [(\partial U_M / \partial \mu)_{V,\mathbf{B}} + H (\partial U_M / \partial \mathbf{B})_{V,\mu}] \times (\partial \mu / \partial \rho)_{T,\mathbf{H}} V^{-1}, \quad (116)$$

$$\zeta_{\mathbf{H},V} = \zeta + [(\partial U_M / \partial \mu)_{V,\mathbf{B}} + H (\partial U_M / \partial \mathbf{B})_{V,\mu}] (\partial \mu / \partial \rho)_{T,\mathbf{H}} V^{-1}. \quad (117)$$

Note that for the case in which U_M satisfies Eq. (18), Eqs. (113) and (114) reduce to Eqs. (35) and (36) and Eqs. (116) and (117) reduce to Eqs. (39) and (40), respectively. The meaning of $P_{\mathbf{B},N}$ and $P_{\mathbf{H},N}$ in discrete systems needs further investigation, since it can readily be shown that $(\partial U_M / \partial V)_{\mathbf{B},\mu}$ depends on the geometry of the system and on how the volume is changed. It seems that $(\partial U_M / \partial V)_{\mathbf{B},\mu}$ represents a collective effect of the stresses existing in the system rather than the conventional pressure. In this sense, $P_{\mathbf{B},N}$ and $P_{\mathbf{H},N}$ of discrete systems should be construed as a consequence of applying direct mathematical formalism to systems in the presence of magnetic fields. The case of electric fields is obtained, as before, by replacing, in the relevant equations, H , B , and μ by E , D , and ϵ , respectively.

III. SUMMARY AND CONCLUSIONS

We summarize our work and draw conclusions as follows.

(1) The internal energy of a system in the presence, as well as in the absence of the field, must be a state function that has an exact differential. This condition can be satisfied if the energy due to the field is also a state function that has an exact differential. It is this exact differential that must be added to the differential of the internal energy, i.e., of the field free system, so that the sum also becomes an exact differential, e.g., of the new field dependent internal energy.

(2) In the presence of fields, the classical intensive variables that become field dependent are modified and their form is determined by the field constraints. This shows that the effect of fields can generate different sets of intensive variables under different field constraints.

(3) For linear magnetizable systems, four different pairs of pressure and chemical potentials are defined for four different sets of field constraints. In this sense, the meanings of pressure and chemical potential that depend on the field are not unique. This reflects the effect of the different environments imposed by the different field constraints on the system and its surroundings.

(4) Positive and negative magnetic chemical potentials are obtained at fixed \mathbf{H} and fixed \mathbf{B} , respectively. At fixed \mathbf{H} the environment of the system, which is set by this constraint, produces an increase in the energy when matter is added to the system, while the reverse is true when \mathbf{B} is held fixed.

(5) The formulation of field dependent thermodynamic potentials and Maxwell relations can be effected in the conventional way using the internal energy at fixed volume and permeability of the magnetizable system.

(6) The theory developed in this work facilitates the evaluation of entropy without the need to resort to transformations of the field variables.

(7) The work done in bringing a charge from infinity to a position where the potential is fixed by other charges is divided evenly between the work required to raise the potential of these charges and the work actually done on the charge considered. This shows that the internal energy of a charged thermodynamic system can be raised by changing its potential while keeping its charges fixed.

(8) The effect of charges on the internal energy of a system must be presented in the form of an exact differential, i.e., of the electric potential energy of all the charges included within its boundaries.

(9) The energy of a magnetoquasistatic field, which is generated by a discrete magnetized system, can be assigned exclusively to this system irrespective of this energy being inside or outside the system's boundaries. This is a unique property of magnetized systems unknown in ordinary thermodynamics, i.e., in the absence of the field.

(10) A fundamental property that governs thermodynamics in the presence of quasistatic electromagnetic fields is that the field dependent energy and entropy existing in a given region of space, or within a well defined system, cannot be separated from their sources. Hence, in general, this energy and entropy cannot be assigned exclusively to this region or system and, as such, be treated by conventional thermodynamic formulations.

(11) Intensive thermodynamic variables can be formulated for discrete systems, in electroquasistatic and magnetoquasistatic fields. This can be done provided that the partial derivatives by which these variables are defined involve the entire energy stored in the field, inside as well as outside the system. As for the case of a continuum, different pairs of pressure and chemical potentials correspond to different constraints that can be imposed on the field.

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APPENDIX: THE FORMULATION OF THE CHEMICAL POTENTIAL USING THE ELECTRIC WORK AT THE TERMINALS OF THE SOURCE OF THE FIELD

Haus and Melcher [8] state that the increments of electrical energy put into the magnetoquasistatic system go either into the total energy or into work on the external mechanical system. We apply this statement to a process in which dN moles of a linear matter are introduced into a system which is depicted schematically in Fig. 1. The system, which is kept at fixed temperature and pressure, contains N moles of this matter that is uniformly dispersed inside a long solenoid. The solenoid has n turns and carries a current i . The cross-sectional area A of the system and its length l are fixed. The dN moles are brought along the symmetry axis of the coil from infinity into the system, where they are dispersed evenly throughout its fixed volume. Along the path of dN , a balancing force to df (not shown in Fig. 1) is maintained, i.e., by the external mechanical source, so that its approach to the system is quasistatic. For this process (which is done at fixed temperature and pressure), the differential electric work at the terminals, dW_t , is given by [8,10]

$$dW_t = id\lambda = dW_m + \int_{-\infty}^x df d\xi, \quad (\text{A1})$$

where λ is the flux linkage at the terminals, ξ denotes the coordinate of dN , and x is the position of dN at which dW_t is evaluated. The mass dN is small and, without reducing the generality of the analysis, it is assumed to be initially in the form of a cube or a sphere. For this mass df is proportional to dN ,

$$df = \alpha dN, \quad (\text{A2})$$

where α is the proportionality constant defined here as

$$\alpha = \partial f / \partial N, \quad f = f(\xi, N). \quad (\text{A3})$$

At a fixed coordinate, f is a sole function of N and, hence, this gives

$$df = (\partial f / \partial N) dN, \quad (\text{A4})$$

$$id\lambda = dW_m + \int_{-\infty}^x \frac{\partial f}{\partial N} d\xi dN. \quad (\text{A5})$$

At fixed i the field \mathbf{H} within the system is also fixed and in this case

$$id\lambda = id(BAn) = AniHd\mu. \quad (\text{A6})$$

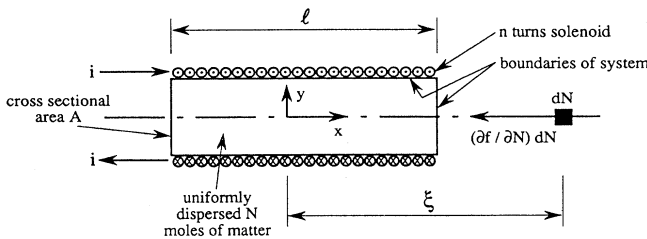


FIG. 1. A system of uniformly dispersed matter excited by a solenoid.

Note that multiplying A and dividing ni simultaneously by l and recalling that $H = ni/l$ gives

$$id\lambda = VH \cdot dB. \quad (\text{A7})$$

Equation (A7) shows that the addition of mass into the system at fixed \mathbf{H} requires that electric work $id\lambda$ be performed at the terminals. This electric work, in terms of field variables, is $VH \cdot dB$ and we are set to show how it is divided between the energy stored in the field, and that delivered to the external mechanical source.

Combining Eqs. (31) and (A6), at fixed volume, gives

$$id\lambda = H^2(\partial\mu/\partial\rho)dN \quad (\text{A8})$$

and, by virtue of Eq. (49),

$$id\lambda = H^2(\mu - \mu_0)dN/\rho. \quad (\text{A9})$$

The work dW_m done in magnetizing the dN moles is the difference between the magnetic energy stored in the volume dN/ρ (which is occupied by dN) after and before its introduction into the system,

$$dW_m = \frac{1}{2}(\mu - \mu_0)H^2dN/\rho. \quad (\text{A10})$$

It follows from Eqs. (A5), (A9), and (A10) that

$$\int_{-\infty}^x \frac{\partial f}{\partial N} d\xi dN = \frac{1}{2}(\mu - \mu_0)H^2dN/\rho. \quad (\text{A11})$$

Thus, the addition of the mass dN to the system at fixed \mathbf{H} results in an equal split of the electric work done at the terminals. This split is between the work required to magnetize the mass dN and that delivered to an external mechanical source used to counterbalance, quasistatically, the pull of the field.

If we elect to hold λ instead of \mathbf{H} fixed, then no electric work is done at the terminals and the work delivered to the mechanical source is at the expense of the magnetic energy stored in the field within the system. In this case, combining Eqs. (A1) and (A11) gives

$$dW_m = -\frac{1}{2}(\mu - \mu_0)H^2dN/\rho. \quad (\text{A12})$$

The internal energy of the system can be expressed as

$$dU' = TdS - PdV + \xi dN + id\lambda - \int_{-\infty}^x \frac{\partial f}{\partial N} d\xi dN, \quad (\text{A13})$$

where the first three terms on the right-hand side of Eq. (A13) have their usual nonmagnetic significance. At fixed S , V , and \mathbf{H} , combining Eqs. (A9), (A11), and (A13) gives

$$dU'_{S,V,H} = \left[\xi + \frac{\mu_0}{2\rho} \mathbf{M} \cdot \mathbf{H} \right] dN, \quad (\text{A14})$$

where use was made of $(\mu - \mu_0)\mathbf{H} = \mu_0\mathbf{M}$.

Hence, $(\partial U' / \partial N)_{S,V,H}$ can be defined as the chemical potential $\zeta_{H,V}$ given by Eq. (53). At fixed S , V , and λ , which here is equivalent to fixed S , V , and \mathbf{B} , combining Eqs. (A11) and (A13) gives

$$dU'_{S,V,B} = \left[\xi - \frac{\mu_0}{2\rho} \mathbf{M} \cdot \mathbf{H} \right] dN. \quad (\text{A15})$$

Hence, $(\partial U' / \partial N)_{S,V,B}$ can be defined as the chemical potential $\zeta_{B,V}$ given by Eq. (51).

- [1] E. A. Guggenheim, *Thermodynamics, An Advanced Treatment for Chemists and Physicists* (North-Holland, Amsterdam, 1967).
- [2] S. R. De Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
- [3] I. Prigogine, P. Mazur, and R. Defay, *J. Chem. Phys.* **50**, 146 (1953).
- [4] R. Defay and P. Mazur, *Bull. Soc. Chim. Belg.* **63**, 562 (1954).
- [5] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).
- [6] M. Modell and R. C. Reid, *Thermodynamics and its Applications*, 2nd ed. (Prentice Hall, Englewood Cliffs, New Jersey, 1983).
- [7] R. E. Rosensweig, in *Thermodynamics*, edited by Gianni Astarita (Plenum, New York, 1989), Chap. 13.
- [8] H. A. Haus and J. R. Melcher, *Electromagnetic Fields and Energy* (Prentice Hall, Englewood Cliffs, New Jersey, 1989).
- [9] J. W. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).
- [10] M. Zahn, *Electromagnetic Field Theory, a Problem Solving Approach* (Krieger, Malabar, FL, 1987).
- [11] W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill, New York, 1950).
- [12] G. N. Hatsopoulos and J. H. Keenan, *Principles of General Thermodynamics* (Wiley, New York, 1965).
- [13] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, 2nd ed. (Pergamon, Oxford, 1984).