Theory and system analysis of field-dependent thermodynamic variables and Maxwell relations

Y. Zimmels
Department of Civil Engineering, Technion–Israel Institute of Technology, Haifa 32000, Israel
(Received 25 September 1995)

Using previously developed principles of thermodynamics in the presence of fields a generalized set of field-dependent, extensive and intensive, thermodynamic variables is formulated. It is shown that extensive variables can depend on field constraints in the same way as the intensive ones do. Using these generalized variables, Maxwell relations are formulated and then tested under different field constraints. Conventional magnetic field systems are used to evaluate directly thermodynamic variables, which are then compared to those predicted by the theory. This provides a direct test and the means to illustrate the validity and significance of the theory in magnetic circuits. These tests involve uniform fields, continua and discrete systems that are subject to different field constraints. In this way the dependence of the thermodynamic variables on the field constraints is verified both directly and by the theory. The case of a sphere in a uniform field is used to show how thermodynamic variables can be defined in discrete systems. To this end an effective thermodynamic permeability of the sphere is defined. This facilitates the use of a model where the field is considered to be entirely within the boundary of the sphere, as if it were an ordinary thermodynamic system. It is shown that for this discrete system, there are more ways to define the magnetic chemical potential as compared to the case of a continuum. This is due to the fact that field constraints can be imposed independently on the sphere and on the uniform field. The significance of the volume of a subsystem that contains the sphere is considered. It is shown that the magnetic energy of this subsystem is a function of the volume of the sphere but not of that of the subsystem. This provides further insight concerning the significance of variables, such as volume, when the thermodynamics of a system is considered in the presence of fields. Finally, it is shown that, for the sphere, the ratio of the work delivered by a current source to build the field to the one that is delivered to an external mechanical work source, that balances quasistatically the magnetic pull, is one-third or less.

PACS number(s): 05.70.Ce, 41.20.Gz

I. INTRODUCTION

In a previous publication [1], fundamental aspects of thermodynamics in the presence of electromagnetic fields were formulated. It was shown that electromagnetic energy cannot be treated by ordinary thermodynamic formulation and consequently, the pressure and chemical potential, in the presence of quasistatic electromagnetic fields, are not unique in the sense that their form depends on constraints set on these fields. The theory has been presented in detail for the case of a linear magnetic material in the form of a continuum and then was extended for the case of discrete systems. In this work we formulate a generalized set of thermodynamic variables and Maxwell relations in the presence of fields and consider their significance. The applicability of the theory is then tested in specific case studies that facilitate unambiguous formulation of the field, transfer of energy, and mass, and of related thermodynamic variables. In this context, an attempt is made to provide an in-depth thermodynamic analysis of magnetic field systems aiming at better understanding of the significance of related field-dependent variables.

II. THEORY

A. Formulation of field-dependent variables

The change of internal energy of a system in the absence of fields can be presented in the following form:

$$dU' = \sum_{i=0}^{n} \xi_i dX_i \ , \tag{1}$$

where U' is the internal energy, X_i is the ith independent extensive variable, and ξ_i is given by

$$\xi_i = (\partial U'/\partial X_i)_{X_{j'}}, \quad j' \neq i, \quad i,j' = 0,1,\ldots,n \ . \tag{2}$$

If the change of internal energy of a system due to the presence of a field is denoted by dU_f, then the change of the total internal energy (i.e., dU'') is given by

$$dU'' = dU' + dU_f = \sum_{i=0}^{n} \xi_i dX_i + dU_f \ . \tag{3}$$

Since both U'' and U' are state functions, it follows that U_f must also qualify as a state function and hence dU_f must be an exact differential [1]. If U_f is a function of m'' independent variables Y_m, $1 \leq m \leq m''$, then

$$U_f = U_f(Y_1, Y_2, \ldots, Y_{m''}) \ . \tag{4}$$

Suppose further that for $m' \leq m < m_0$, $m_0 \leq m''$,

$$Y_m = Y_m(\xi_0, \xi_1, \ldots, \xi_n) \ , \tag{5}$$

whereas for $m_0 \leq m \leq m''$,

$$Y_m = Y_m(X_0, X_1, \ldots, X_n) \ . \tag{6}$$

Hence

$$dU_f = \sum_{m=1}^{m'-1} \frac{\partial U_f}{\partial Y_m} dY_m + \sum_{m=m'}^{m_0-1} \frac{\partial U_f}{\partial Y_m} \sum_{i=0}^{n} \frac{\partial Y_m}{\partial \xi_i} d\xi_i + \sum_{m=m_0}^{m''} \frac{\partial U_f}{\partial Y_m} \sum_{i=0}^{n} \frac{\partial Y_m}{\partial X_i} dX_i \ . \tag{7}$$

Consider the following Legendre transformation of U':

$$U'''(\xi_0, \ldots, \xi_j, X_{j+1}, \ldots, X_n) = U'(X_0, X_1, \ldots, X_n) - \sum_{i=0}^{j} \xi_i X_i \ , \tag{8}$$

$$dU''' = -\sum_{i=0}^{j} X_i d\xi_i + \sum_{i=j+1}^{n} \xi_i dX_i \ , \qquad j = -1, 0, \ldots, n \ , \tag{9}$$

where $j = -1$ denotes the case of the original untransformed energy, i.e., the first sum on the right-hand side of Eq. (9) vanishes and $U''' = U'$. Combining Eqs. (7) and (9) followed by rearrangement of terms gives

$$\begin{aligned} dU &= dU''' + dU_f \\ &= -\sum_{i=0}^{j} \hat{X}_i d\xi_i + \sum_{i=j+1}^{n} \hat{\xi}_i dX_i \\ &\quad + \sum_{i=j+1}^{n} \sum_{m=m'}^{m_0-1} \frac{\partial U_f}{\partial Y_m} \frac{\partial Y_m}{\partial \xi_i} d\xi_i \\ &\quad + \sum_{i=0}^{j} \sum_{m=m_0}^{m''} \frac{\partial U_f}{\partial Y_m} \frac{\partial Y_m}{\partial X_i} dX_i + \sum_{m=1}^{m'-1} \frac{\partial U_f}{\partial Y_m} dY_m \ , \end{aligned} \tag{10}$$

where

$$\hat{X}_i = X_i - \sum_{m=m'}^{m_0-1} \frac{\partial U_f}{\partial Y_m} \frac{\partial Y_m}{\partial \xi_i}, \quad i = 0, \ldots, j \ , \tag{11}$$

$$\hat{\xi}_i = \xi_i + \sum_{m=m_0}^{m''} \frac{\partial U_f}{\partial Y_m} \frac{\partial Y_m}{\partial X_i}, \quad i = j+1, \ldots, n \ . \tag{12}$$

Thus setting $Y_m = \text{const}$ for $m = 1, \ldots, m'-1$, $\xi_i = \text{const}$ for $i = j+1, \ldots, n$, and $X_i = \text{const}$ for $i = 0, \ldots, j$ gives

$$dU = -\sum_{i=0}^{j} \hat{X}_i d\xi_i + \sum_{i=j+1}^{n} \hat{\xi}_i dX_i \tag{13}$$

($Y_m = \text{const}$ for $m = 1, \ldots, m'-1$, $\xi_i = \text{const}$ for $i = j+1, \ldots, n$, and $X_i = \text{const}$ for $i = 0, \ldots, j$). Equation (13) has been derived here with a view to present the counterpart of Eq. (9) in the presence of fields. Note that in the absence of fields, $\hat{X}_i = X_i$ and $\hat{\xi}_i = \xi_i$ and the constraints included in Eq. (13) do not exist. Thus, the unique feature imparted by the presence of fields is that X_i and ξ_i are replaced by $\hat{X}_i$ and $\hat{\xi}_i$, subject to the condition that the constraints set in Eq. (13) be satisfied.

Equation (12) has already been derived for the general case of the jth system under the action of k' fields [1], while here it is given for one field only. In contrast, Eqs. (11) and (13) have not been derived in this general form and their meaning is yet to be elucidated.

Equations (11), (12), and (13) show that in the presence of fields

$$-(\partial U/\partial \xi_i)_{X_l, \xi_k, Y_{m_1}} = \hat{X}_i \neq X_i \ ,$$

$$k, l = 0, 1, \ldots, n, \quad k \neq i \ , \tag{14}$$

$$m_1 = 1, \ldots, m'-1, \quad i = 0, \ldots, j \ .$$

$$(\partial U/\partial X_i)_{\xi_l, X_k, Y_{m_1}} = \hat{\xi}_i \neq \xi_i \ ,$$

$$k, l = 0, 1, \ldots, n, \quad k \neq i \ , \tag{15}$$

$$m_1 = 1, \ldots, m'-1, \quad i = j+1, \ldots, n \ .$$

Furthermore, from Eq. (10),

$$(\partial U/\partial \xi_i)_{X_l, \xi_k, Y_{m_1}} = \sum_{m=m'}^{m_0-1} \frac{\partial U_f}{\partial Y_m} \frac{\partial Y_m}{\partial \xi_i} \ ,$$

$$k, l = 0, 1, \ldots, n, \quad k \neq i \ , \tag{16}$$

$$m_1 = 1, \ldots, m'-1, \quad i = j+1, \ldots, n \ ;$$

$$(\partial U/\partial X_i)_{\xi_l, X_k, Y_{m_1}} = \sum_{m=m_0}^{m''} \frac{\partial U_f}{\partial Y_m} \frac{\partial Y_m}{\partial X_i} \ ,$$

$$k, l = 0, 1, \ldots, n, \quad k \neq i \ , \tag{17}$$

$$m_1 = 1, \ldots, m'-1, \quad i = 0, 1, \ldots, j \ .$$

It follows that for fixed Y_{m_1}, $m_1 = 1, \ldots, m'-1$, where Y_{m_1} is independent of both X_i and ξ_i, $i = 0, \ldots, n$, the partial derivative of the energy with respect to an extensive variable does not yield its intensive conjugate, which prevails in the absence of the field. Similarly the partial derivative of the transformed energy with respect to an intensive variable does not yield the negative of its extensive conjugate that prevails in the absence of the field. This is a unique property of thermodynamic systems in the presence of fields. Alternatively the presence of fields can be the reason for the above effects.

Equations (11) and (12) also show that if $\partial U_f/\partial Y_m$ depends on the field constraints, as indeed is the case with magnetic fields [1], then neither $\hat{X}_i$ nor $\hat{\xi}_i$ is unique, i.e., in the sense that they take different forms under different field constraints. This property is illustrated in the sequel.

Equation (13) appears to be a generalization of Eq. (9) for systems in the presence of fields. It reduces to Eq. (9) if

$$\partial Y_m/\partial \xi_i = 0 \quad (m' \leq m < m_0, \quad i = 0, 1, \ldots, j)$$

and

$$\partial Y_m/\partial X_i = 0 \quad (m_0 \leq m \leq m'', \quad i = j+1, \ldots, n)$$

are satisfied, simultaneously.

The second term on the right-hand side of Eq. (12) was shown to depend on field constraints in the case of magnetoquasistatic fields. The results [1] for a linear magnetizable continuum at fixed **B** and fixed **H** are summarized by the following equations. At fixed **B**,

$$P_{\mathbf{B},N}=P-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}-\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\ , \tag{18}$$

$$\zeta_{\mathbf{B},V}=\zeta-\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\ ; \tag{19}$$

at fixed **H**,

$$P_{\mathbf{H},N}=P-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}+\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\ , \tag{20}$$

$$\zeta_{\mathbf{H},V}=\zeta+\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\ , \tag{21}$$

where μ, ρ, **H**, and **B** are permeability, density, magnetizing field, and magnetic induction, respectively:

$$\mathbf{B}=\mu\mathbf{H}\ . \tag{22}$$

Note that the subscripts in Eqs. (18)–(21) denote the variables held constant when the pressure or chemical potential is evaluated. For example, $\zeta_{\mathbf{B},V}$ is evaluated at constant **B** and V. We show now how Eq. (18) is derived from Eq. (12). In this case $i=1$, X_i denotes the volume V, ξ_i, the pressure $-P$ in the absence of field, and $\hat{\xi}_i$ the pressure $-P_{\mathbf{B},N}$ in the presence of a field that is constrained at fixed **B**. In this case

$$U_f=U_f(\mathbf{B},\mu,V)=\tfrac{1}{2}VB^2/\mu\ , \tag{23}$$

$$\mu=\mu(\rho,T)\ , \tag{24}$$

$$\rho=N/V\ , \tag{25}$$

where N, V, and T are mass, volume, and temperature, respectively.

Note that henceforth vectors and their moduli are denoted by boldface and regular fonts, respectively. This notation has already been used in Eqs. (18)–(25).

In accordance with the convention set by Eqs. (5) and (6) where Y_m is either a function of intensive or extensive variables but not of both, we define $\mu=\mu(T)$ at fixed ρ and $\mu=\mu(\rho)=\mu(N,V)$ at fixed T. This gives

$$U_f=U_f(Y_1,Y_2,Y_3,Y_4)\ , \tag{26}$$

where

$$Y_1=\mathbf{B},\quad Y_2=\mu(T),\quad Y_3=\mu(N,V),\quad Y_4=V\ . \tag{27}$$

In this case, $m'=2$, $m_0=3$, and $m''=4$.

Recall that the entropy was not transformed and hence T must be fixed under the condition of Eq. (13). Furthermore, by definition of $P_{\mathbf{B},N}$, **B** and N are also fixed. Hence

$$\frac{\partial U_f}{\partial Y_1}=\frac{\partial U_f}{\partial Y_2}=0\ , \tag{28}$$

$$\frac{\partial U_f}{\partial Y_3}\frac{\partial Y_3}{\partial V}=\frac{\partial U_f}{\partial\mu}\frac{\partial\mu}{\partial\rho}\left[-\frac{\rho}{V}\right]=\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\ , \tag{29}$$

where here use was made of Eq. (23) and then of Eq. (22).

$$\frac{\partial U_f}{\partial Y_4}\frac{\partial Y_4}{\partial V}=\frac{1}{2}B^2/\mu=\frac{1}{2}\mathbf{H}\cdot\mathbf{B}\ . \tag{30}$$

Combining Eqs. (12), (28), (29), and (30) and using the fact that $\xi_i=-P$ gives

$$\hat{\xi}_i=-\left[P-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}-\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\right]\ . \tag{31}$$

Recall that here $\hat{\xi}_i=-P_{\mathbf{B},N}$, Eq. (18) is obtained.

Suppose we transform only the entropy so that in Eqs. (8) and (9) $j=0$, the result being the Helmholtz potential. In this case, letting $i=0$, we identify in Eq. (11), $X_0=S$ and $\hat{X}_0=\hat{S}$ so that $\xi_0=T$. The only variable that is a function of T is Y_2. Hence

$$\frac{\partial U_f}{\partial Y_2}\frac{\partial Y_2}{\partial T}=\frac{\partial U_f}{\partial\mu}\frac{\partial\mu}{\partial T}\ ; \tag{32}$$

at fixed **B**,

$$\frac{\partial U_f}{\partial\mu}=-\frac{1}{2}VH^2\ , \tag{33}$$

whereas at fixed **H**,

$$\frac{\partial U_f}{\partial\mu}=\frac{1}{2}VH^2\ . \tag{34}$$

Thus at fixed **B**,

$$\hat{S}_{\mathbf{B}}=S+\frac{1}{2}VH^2\frac{\partial\mu}{\partial T}\ , \tag{35}$$

whereas at fixed **H**,

$$\hat{S}_{\mathbf{H}}=S-\frac{1}{2}VH^2\frac{\partial\mu}{\partial T}\ . \tag{36}$$

Equation (35) is well known [2,3]. It gives the entropy of the system in the presence of a magnetic field, subject to the constraint that no field-related energy exchange, between the system and its surroundings, is allowed. This condition is embodied in **B** being fixed.

Equation (36) gives the entropy under the constraint that there must be such a field-related energy exchange, i.e., with the current source of the field. In this sense the entropy of the current source that is related to its interaction with the system is coupled with that of the system. Assuming that $\partial\mu/\partial T<0$, this gives a larger effective value for the total entropy. This shows that under the conditions where the system does, or receives, temperature-dependent work from an external current source its entropy cannot be isolated from that of this source. If the system does work on the source due to increase in its temperature, then the coupled or effective entropy increases. However, when it receives work from this source, due to a decrease in its temperature, then its effective entropy decreases, i.e., as compared to the entropy in the absence of the field. Note that this coupling of entropy has been defined for discrete systems [1], e.g., regarding the field they generate outside their own boundaries, and here its meaning is extended to coupling between the system and its source of field.

We are in position now to introduce Maxwell relations for systems in the presence of fields, and in particular in the presence of magnetoquasistatic fields.

B. Maxwell relations in the presence of fields

Equation (10) can be used to derive Maxwell relations in the presence of fields. However, at this point, Eq. (13) is used to this end since, despite its narrower scope, it has the same form as Eq. (9), which is its thermodynamic counterpart in the absence of fields. The full scope of Maxwell relations is given in Appendix A.

The following Maxwell relations can be derived from Eq. (13) for its complete range of existence, i.e., $j=-1,0,\ldots,n$. Recall that, by definition, if $j=-1$, Eq. (13) reduces to the original untransformed form of the energy. Similarly if $j=n$, then the last term (i.e., for $i=n+1$) vanishes or simply does not exist. Here the Maxwell relations in the presence of fields is given by three sets of equations:

$$\left[\frac{\partial\hat{\xi}_{i_1}}{\partial X_{i_2}}\right]_{X_{i_3},\xi_{i_5}}=\left[\frac{\partial\hat{\xi}_{i_2}}{\partial X_{i_1}}\right]_{X_{i_4},\xi_{i_5}}, \quad i_3\neq i_2,\quad i_4\neq i_1\ , \tag{37}$$

where

$$i_1,i_2=j+1,\ldots,n,\quad i_3,i_4,i_5=0,\ldots,n\ ,$$

$$\left[\frac{\partial\hat{X}_{i_1}}{\partial\xi_{i_2}}\right]_{\xi_{i_3},X_{i_5}}=\left[\frac{\partial\hat{X}_{i_2}}{\partial\xi_{i_1}}\right]_{\xi_{i_4},X_{i_5}}, \quad i_3\neq i_2,\quad i_4\neq i_1\ , \tag{38}$$

where

$$i_1,i_2=0,\ldots,j,\quad i_3,i_4,i_5=0,\ldots,n\ ,$$

$$-\left[\frac{\partial\hat{X}_{i_1}}{\partial X_{i_2}}\right]_{X_{i_3},\xi_{i_4}}=\left[\frac{\partial\hat{\xi}_{i_2}}{\partial\xi_{i_1}}\right]_{\xi_{i_5},X_{i_6}}, \quad i_3\neq i_2,i_5\neq i_1\ , \tag{39}$$

where

$$i_1=0,\ldots,j,\quad i_2=j+1,\ldots,n\ ,$$

$$i_3,i_4,i_5,i_6=0,\ldots,n\ .$$

In the absence of fields Eqs. (37), (38), and (39) reduce to the conventional Maxwell relations, provided that the constraints set in conjunction with Eq. (13) are lifted, i.e., that ξ_i and X_i are no longer constant for $i=j+1,\ldots,n$ and $i=0,\ldots,j$, respectively. For example, consider the potential $U'''(T,V,\zeta)$ for which

$$dU'''(T,\zeta,V)=-SdT-Nd\zeta-PdV\ . \tag{40}$$

Note that the order of terms in Eq. (40) expresses the convention [see Eq. (9)] that all transformed variables are grouped first. In this case ζ is the chemical potential, $j=1$, and $n=2$.

Letting $i_1=0$, $i_2=1$ (i.e., $X_{i_1}=X_0=S$, $\xi_{i_1}=T$ and $X_{i_2}=X_1=N$, $\xi_{i_2}=\zeta$) and using Eq. (38) gives

$$\left[\frac{\partial S}{\partial\zeta}\right]_{T,V}=\left[\frac{\partial N}{\partial T}\right]_{\zeta,V}\ . \tag{41}$$

Here ξ_{i_3} was found to be T since $i_3=0,1$ (but not 2 since the field is absent and the constraint for $j+1=n=2$ has been lifted) and $i_3\neq i_2=1$, which means that $\xi_{i_3}\neq\xi_{i_2}=\zeta$: Similarly $\xi_{i_4}=\zeta$ and X_{i_5} is found to be V, since $i_5=j+1=2$, which corresponds to the third term on the right-hand side of Eq. (40).

Using Eq. (39) gives

$$\left[\frac{\partial S}{\partial V}\right]_{T,\zeta}=\left[\frac{\partial P}{\partial T}\right]_{V,\zeta}\ . \tag{42}$$

Here the only extensive variable is $X_{i_2}=V$ and hence $i_6=i_2$. Moreover, $i_3\neq i_2$ means that none can be assigned to X_{i_3}. The variable ξ_{i_4} can be either T or ζ since i_4 is either 0 or 1, but not 2 since the constraints of Eq. (13) have been lifted. In contrast, ξ_{i_5} can only be ζ since $i_5\neq i_1$.

Next we show, as an example, the validity of a Maxwell relation, which is derived from the generalized Helmholtz potential for the case of a linear magnetizable continuum. The field-dependent Helmholtz potential $\hat{F}$ is expressed in a differential form as

$$d\hat{F}=-\hat{S}dT-\hat{P}dV+\hat{\zeta}dN \tag{43}$$

and its Maxwell relations are given by

$$-\left[\frac{\partial\hat{P}}{\partial N}\right]_{T,V,\alpha}=\left[\frac{\partial\hat{\zeta}}{\partial V}\right]_{T,N,\alpha}, \tag{44}$$

$$\left[\frac{\partial\hat{S}}{\partial V}\right]_{T,N,\alpha}=\left[\frac{\partial\hat{P}}{\partial T}\right]_{V,N,\alpha}, \tag{45}$$

$$-\left[\frac{\partial\hat{S}}{\partial N}\right]_{T,V,\alpha}=\left[\frac{\partial\hat{\zeta}}{\partial T}\right]_{V,N,\alpha}, \tag{46}$$

where α denotes the three-variable set S,P,ζ.

Note that in Eqs. (44), (45), and (46) all variables held fixed are not field variables. The first two of each five-variable subscript appear also in the absence of the field, whereas the last three that are represented by α are a consequence of its presence. The validity of Eq. (44) is shown here while that of Eqs. (45) and (46) can readily be shown in a similar way.

Equations (44)–(46) must be supplemented with additional information concerning the constraints that are imposed on field variables. The simplest but not the only possible constraints are either fixed **B** or fixed **H**. First consider imposing the constraint that **B** is fixed.

1. Fixed B

In this case we identify $\hat{P}$ as $P_{\mathbf{B},N}$ and $\hat{\zeta}$ as $\zeta_{\mathbf{B},V}$. Combining Eqs. (18), (19), and (44) gives

$$-\left[\partial\left[P-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}-\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\right]\Big/\partial N\right]_{T,V,\alpha}=\left[\partial\left[\zeta-\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\right]\Big/\partial V\right]_{T,N,\alpha}. \quad (47)$$

Equation (47) must be tested if it holds in the presence as well as in the absence of the magnetic field, i.e., $\mathbf{H}=\mathbf{0}$, where α must be excluded from the subscripts of Eq. (47). This gives

$$-(\partial P/\partial N)_{T,V}=(\partial\zeta/\partial V)_{T,N}. \quad (48)$$

Equation (48) is a well-known and valid Maxwell relation. In the presence of fields and under the constraints imposed on Eq. (13), P and ζ are fixed and it remains to be shown that the field-dependent terms, on the right- and left-hand sides of Eq. (47), reduce to the same field-dependent function. Using $N=\rho V$, it is straightforward to show that at fixed $\mathbf{B}$

$$[\partial(\tfrac{1}{2}\mathbf{H}\cdot\mathbf{B})/\partial N]_{T,V,\alpha}=-\frac{1}{2V}H^2\left[\frac{\partial\mu}{\partial\rho}\right], \quad (49)$$

$$\left[\partial\left[\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\right]\Big/\partial N\right]_{T,V,\alpha}=\frac{1}{2V}B^2\rho\frac{\partial^2(1/\mu)}{\partial\rho^2}+\frac{1}{2V}H^2\left[\frac{\partial\mu}{\partial\rho}\right], \quad (50)$$

$$\left[\partial\left[-\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\right]\Big/\partial V\right]_{T,N,\alpha}=\frac{1}{2V}B^2\rho\frac{\partial^2(1/\mu)}{\partial\rho^2}. \quad (51)$$

Thus, as required, both the right- and left-hand sides of Eq. (47) reduce to the same function, i.e., $(1/2V)B^2\rho\partial^2(1/\mu)/\partial\rho^2$. This completes the proof that Eq. (44) holds at fixed $\mathbf{B}$. Note that subscripts T,V,α and T,N,α were dropped from the derivatives of μ since μ is a function of ρ and T, and the meaning of $\partial\mu/\partial\rho$ should be construed henceforth as being evaluated at fixed T.

2. *Fixed H*

In this case we identify $\hat{P}$ as $P_{\mathbf{H},N}$ and $\hat{\zeta}$ as $\zeta_{\mathbf{H},V}$. Combining Eqs. (20), (21), and (44) gives

$$-\left[\partial\left[P-\frac{1}{2}\mathbf{H}\cdot\mathbf{B}+\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\right]\Big/\partial N\right]_{T,V,\alpha}=\left[\partial\left[\zeta+\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\right]\Big/\partial V\right]_{T,N,\alpha}. \quad (52)$$

In this case Eq. (48) holds. Furthermore,

$$[\partial(\tfrac{1}{2}\mathbf{H}\cdot\mathbf{B})/\partial N]_{T,V,\alpha}=\frac{1}{2V}H^2\frac{\partial\mu}{\partial\rho}, \quad (53)$$

$$\left[\partial\left[-\frac{1}{2}H^2\rho\frac{\partial\mu}{\partial\rho}\right]\Big/\partial N\right]_{T,V,\alpha}=-\frac{1}{2V}H^2\frac{\partial\mu}{\partial\rho}-\frac{1}{2V}H^2\rho\frac{\partial^2\mu}{\partial\rho^2}, \quad (54)$$

$$\left[\partial\left[\frac{1}{2}H^2\frac{\partial\mu}{\partial\rho}\right]\Big/\partial V\right]_{T,N,\alpha}=-\frac{1}{2V}H^2\rho\frac{\partial^2\mu}{\partial\rho^2}. \quad (55)$$

It is seen that both sides of Eq. (52) reduce to $-(1/2V)H^2\rho\partial^2\mu/\partial\rho^2$, as required.

Thus Eq. (44) is valid, irrespective of which of the two field constraints is selected, i.e., fixed $\mathbf{B}$ or fixed $\mathbf{H}$. In what follows we present detailed analysis of specific systems under different constraints. This facilitates direct evaluation of thermodynamic variables and subsequently, their comparison with the theory presented in the previous [1] and present work.

As already mentioned, further details on the extended scope of Maxwell relations derivable from Eq. (10), and Legendre transformation of its field terms, are given in Appendix A. This extended scope and the attendant Legendre transformation are shown to include, and agree with, known Maxwell relations that are used to describe phenomena such as the magnetocatoric effect.

III. ANALYSIS OF SPECIFIC SYSTEMS

The systems studied in the following examples are characterized as being rigid with respect to the magnetized space; i.e., they are confined within fixed boundaries. A nonrigid system with a variable magnetized space is considered later as part of the Appendixes. First we consider rigid systems that are constrained to carry fixed flux and are characterized by a uniform $\mathbf{B}$. This is followed by imposing a constraint of uniform $\mathbf{H}$.

A. Uniform field B

Consider the systems shown in Fig. 1. In Fig. 1(a), the geometry is cylindrical, whereas in Fig. 1(b) it is rectangular. In Fig. 1(a) the system is defined within the boundaries of a cylinder of radius R and length L. In Fig. 1(b) the system is defined within the boundaries of the gap. The dimensions of this gap in the x, y, and z directions are L, l, and l' where z is perpendicular to the xy plane. Note that the z axis and the l' dimension are not shown in Fig. 1(b). The cylinder is energized by a solenoid that is wound around it, whereas the magnetic flux in the gap originates from a coil set on the left leg of the yoke. The cylinder is long and the gap is narrow to the extent that end effects can be neglected. The volume V in both systems is set fixed. Furthermore, in Fig. 1(a) L and hence also R are fixed, while in Fig. 1(b) L, l, and hence also l' are fixed. Each system consists of two subsystems, which are denoted by 1 and 2 and henceforth the subscript i ($i=1,2$) denotes the ith subsystem.

In Fig. 1(a), subsystem 1 consists of a relatively thin section of the whole cylinder while subsystem 2 consists of the rest of the system. Both subsystems have the same radius and cross-sectional area A that is set perpendicular to their common axis. The respective volumes are $V_1=Ax$ and $V_2=A(L-x)$ subject to the condition $x\ll R$. In Fig. 1(b) the planar boundary between subsystems 1 and 2 is set at a distance x from the lower planar face of the yoke, which is also the $x=0$ boundary of the system.

Note that in Figs. 1(a) and 1(b), the only variable coordinate is x, and it is assumed that the permeability of the yoke as well as that of the material outside the cylinder are practically infinite. In both systems boundary conditions dictate that the field **B** be uniform across the whole system. The analysis presented in what follows applies equally well to both systems and this is the reason for bringing them up together in the first place. Therefore, in what follows, the term "system" serves to indicate both systems. The practically infinite permeability of the yoke material [Fig. 1(b)] and also of the surroundings of the cylinder [marked as phase 3 in Fig. 1(a)] guarantees that the magnetic energy is confined solely to the system. This simplifies the analysis considerably.

The effective (weighted average) permeability μ of the system is given by

$$\frac{L}{\mu}=\frac{x}{\mu_1}+\frac{L-x}{\mu_2}\ , \tag{56}$$

$$d\mu=-(\mu^2/L)\{(1/\mu_1-1/\mu_2)dx-(x/\mu_1^2)d\mu_1 -[(L-x)/\mu_2^2]d\mu_2\}\ . \tag{57}$$

This variable is defined so that the magnetic energy stored in the gap is the same, had the gap been made of a uniformly permeable matter, e.g., at the value of μ.

The magnetic energy, $U_M=U_f$, of the system is given by Eq. (23). Note that here the symbol U_M is used so as to clearly distinguish the case of a magnetic field from the general case of fields, which is denoted by U_f.

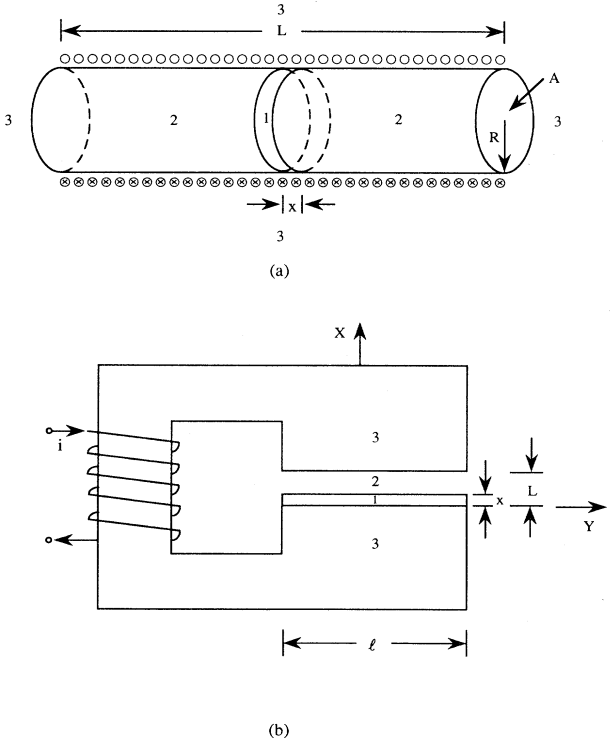


FIG. 1. Magnetic field system at fixed field **B**. (a) Cylindrical geometry; (b) rectangular geometry.

Differentiating Eq. (23), at fixed **B**, and combining the result with Eq. (57) gives

$$dU_{M,\mathbf{B}}=\tfrac{1}{2}AB^2\{(1/\mu_1-1/\mu_2)dx-(x/\mu_1^2)d\mu_1 -[(L-x)/\mu_2^2]d\mu_2\}\ , \tag{58}$$

where subscript **B** denotes that **B** is fixed. At fixed temperature the permeability $\mu(\rho,T)$ is a function of the density ρ. This can be expressed as

$$\mu(\rho,T=\text{const})=K(\rho)\rho+\mu_0\ , \tag{59}$$

where μ_0 is permeability of free space. If $K(\rho)=K$ is fixed then,

$$\mu(\rho,T=\text{const})=K\rho+\mu_0\ , \tag{60}$$

whereas if the Clausius Mossotti model of magnetostriction can be applied then [1]

$$K(\rho)=\frac{3\mu_0K_1}{1-K_1\rho}\ , \tag{61}$$

$$\mu(\rho,T=\text{const})=\frac{3\mu_0K_1}{1-K_1\rho}\rho+\mu_0\ , \tag{62}$$

where K_1 denotes a constant. Suppose the material in each subsystem satisfies Eq. (60). In this case it can readily be shown that

$$d\mu_1=\frac{K}{Ax}\left[dN_1-\frac{N_1}{x}dx\right]\ , \tag{63}$$

$$d\mu_2=\frac{K}{A(L-x)}\left[dN_2+\frac{N_2}{L-x}dx\right]\ . \tag{64}$$

Combining Eqs. (58), (60), (63), and (64), at fixed total mass, i.e., $d(N_1+N_2)=0$, gives

$$dU_{M,\mathbf{B}}=\frac{1}{2}AB^2\left\{\left[\frac{1}{\mu_1}-\frac{1}{\mu_2}\right]\left[2-\mu_0\left[\frac{1}{\mu_1}+\frac{1}{\mu_2}\right]\right]dx -\frac{K}{A}\left[\frac{1}{\mu_1^2}-\frac{1}{\mu_2^2}\right]dN_1\right\}\ . \tag{65}$$

Hence

$$(\partial U_{M,\mathbf{B}}/\partial x)_{N_1}=\frac{1}{2}AB^2\left[\frac{1}{\mu_1}-\frac{1}{\mu_2}\right]\left[2-\mu_0\left[\frac{1}{\mu_1}+\frac{1}{\mu_2}\right]\right]\ , \tag{66}$$

$$(\partial U_{M,\mathbf{B}}/\partial N_1)_x=-\frac{1}{2}B^2\left[\frac{\mu_1-\mu_0}{\rho_1\mu_1^2}-\frac{\mu_2-\mu_0}{\rho_2\mu_2^2}\right]\ , \tag{67}$$

where here use was made of Eq. (60) in the form $\mu_i=K\rho_i+\mu_0$, $i=1,2$. The physical meaning of the partial derivatives, given by Eqs. (66) and (67) is that they provide the difference of force and chemical potential, existing across the boundary between subsystems 1 and 2, respectively. The difference in the magnetic pressure across this boundary is readily obtained by manipulating Eq. (66) as

$$(P_{\mathbf{B},N_1}-P)-(P_{\mathbf{B},N_2}-P)=-\frac{1}{A}\left[\frac{\partial U_{M,\mathbf{B}}}{\partial x}\right]_{N_1}$$
$$=(\tfrac{1}{2}\mu_0 H_1^2-\mathbf{H}_1\cdot\mathbf{B}_1)$$
$$-(\tfrac{1}{2}\mu_0 H_2^2-\mathbf{H}_2\cdot\mathbf{B}_2)\ , \quad (68)$$

where here use was made of

$$\mathbf{B}_i=\mu_i\mathbf{H}_i,\quad i=1,2\ . \quad (69)$$

For materials that satisfy Eq. (60), Eq. (18) takes the following form [1]

$$P_{\mathbf{B},N}-P=\tfrac{1}{2}\mu_0 H^2-\mathbf{H}\cdot\mathbf{B}\ . \quad (70)$$

Thus Eq. (68) agrees with Eq. (70) when the latter is applied to subsystems 1 and 2. Equation (66) shows that $-(\partial U_{M,\mathbf{B}}/\partial x)_{N_1}>0$ if $\mu_1>\mu_0$, $\mu_2\geq\mu_0$, and $\mu_1>\mu_2$. Hence under this condition the magnetic force tends to increase x. Equation (67) can readily be manipulated to give

$$(\zeta_{\mathbf{B},V_1}-\zeta)-(\zeta_{\mathbf{B},V_2}-\zeta)=(\partial U_{M,\mathbf{B}}/\partial N_1)_x$$
$$=-\frac{1}{2\rho_1}\mu_0\mathbf{M}_1\cdot\mathbf{H}_1$$
$$-\left[-\frac{1}{2\rho_2}\mu_0\mathbf{M}_2\cdot\mathbf{H}_2\right]\ . \quad (71)$$

In this way the variable $\zeta_{\mathbf{B},V_i}-\zeta$ can be defined as

$$\zeta_{\mathbf{B},V_i}-\zeta=-\frac{1}{2\rho_i}\mu_0(\mathbf{M}\cdot\mathbf{H})_i,\quad i=1,2\ . \quad (72)$$

Equation (19) takes the form of Eq. (72) when the former is applied to the ith subsystem that satisfies Eq. (60). Hence the pressure and chemical potential as given by Eqs. (18) and (19) agree with the ones evaluated in this specific example.

In the system shown in Fig. 1, the constraint of uniform $\mathbf{B}$ is a consequence of the boundary conditions as set by the geometry of subsystems 1 and 2. This implies that $\mathbf{B}$ is fixed in space; i.e., it is position independent. The condition that $\mathbf{B}$ is also made independent of the permeability, i.e., by adjusting the current source, fixes its value in both space and time. Under this condition no magnetic energy is exchanged between the system and the current source of its field. However, this constraint is not the only one that can be imposed on the system. For example, at the same boundary conditions that impose a uniform $\mathbf{B}$ the system can be constrained to have a fixed magnetic energy. In this case

$$U_M=\frac{1}{2}V\mu H^2=\frac{1}{2}VB^2/\mu=K_2'\ , \quad (73)$$

where K_2' is a constant and U_M is the magnetic energy of the whole system. In Eq. (73), μ is the permeability of the system as given by Eq. (56) and H is given by

$$H=[xH_1+(L-x)H_2]/L=(2K_2/\mu)^{1/2},\quad K_2=K_2'/V\ . \quad (74)$$

Note that H is defined as the total ampere turns per unit width L of the gap; see Fig. 1(b).

The first part of Eq. (74) is a consequence of Ampere's Law and the second comes from Eq. (73). Differentiation of Eq. (74) in conjunction with Eqs. (56) and (57) gives

$$dH=\frac{1}{2L}(2K_2\mu)^{1/2}\{(1/\mu_1-1/\mu_2)dx-(x/\mu_1^2)d\mu_1$$
$$-[(L-x)/\mu_2^2]d\mu_2\}\ . \quad (75)$$

The corresponding change in B is readily obtained using Eq. (73) as

$$dB=\tfrac{1}{2}Hd\mu=-\mu dH\ , \quad (76)$$

where H and dH are given by Eqs. (74) and (75), respectively. Note that dB is subject to $\mathbf{B}$ being uniform across the whole system. In what follows we evaluate the change of magnetic energy, U_{M1}, of subsystem 1. The result will then be used to evaluate related thermodynamic variables. The change in U_{M1} consists of two parts, which we denote as a change in U_{M1}' and U_{M1}''. In the first part the change dU_{M1}' is due to changes in system variables, i.e., dx and dN_1, whereas in the second, i.e., dU_{M1}'', the change, dB, is imposed by the current source so as to satisfy the constraint of fixed U_M. Thus

$$dU_{M1}=dU_{M1}'+dU_{M1}''\ , \quad (77)$$
$$dU_{M1}'=\tfrac{1}{2}\mu_1 H_1^2 dV_1-\tfrac{1}{2}V_1 H_1^2 d\mu_1\ , \quad (78)$$
$$dU_{M1}''=V_1 H_1 dB=\tfrac{1}{2}V_1 H_1 Hd\mu\ , \quad (79)$$

where here use was made of Eq. (76).

Combining Eqs. (77)–(79) gives

$$dU_{M1}=\tfrac{1}{2}V_1 H_1(Hd\mu-H_1 d\mu_1)+\tfrac{1}{2}\mu_1 H_1^2 dV_1\ . \quad (80)$$

Combining Eqs. (63), (64), (75), (76), and (80) gives

$$dU_{M1}=\frac{1}{2}V_1 H_1\left\{-\frac{1}{L}(2K_2\mu)^{1/2}\mu\left[(1/\mu_1-1/\mu_2)dx-(x/\mu_1^2)\frac{K}{Ax}\left[dN_1-\frac{N_1}{x}dx\right]\right.\right.$$
$$\left.\left.-[(L-x)/\mu_2^2]\frac{K}{A(L-x)}\left[dN_2+\frac{N_2}{L-x}dx\right]\right]-H_1\frac{K}{Ax}\left[dN_1-\frac{N_1}{x}dx\right]\right\}$$
$$+\frac{1}{2}\mu_1 H_1^2 A dx\ , \quad (81)$$

where in Eq. (80) use was made of $dV_1 = Adx$.

We are now in a position to define the pressure and chemical potential of the material in subsystem 1 as follows:

$$P_{\mathbf{B},N_1}(U_M=\text{const}) = -\frac{1}{A}(\partial U_{M1}/\partial x)_{N_1,U_M} , \tag{82}$$

$$(\partial U_{M1}/\partial x)_{N_1,U_M} = \frac{1}{2}V_1H_1\left[-\frac{1}{L}(2K_2\mu)^{1/2}\mu(1/\mu_1-1/\mu_2)[2-\mu_0(1/\mu_1+1/\mu_2)] + \frac{H_1}{x}(\mu_1-\mu_0)\right]+\frac{1}{2}\mu_1H_1^2A , \tag{83}$$

$$\zeta_{\mathbf{B},V_1}(U_M=\text{const}) = (\partial U_{M1}/\partial N_1)_{x,U_M} , \tag{84}$$

$$(\partial U_{M1}/\partial N_1)_{x,U_M} = \frac{1}{2}V_1H_1\left[\frac{K}{V}(2K_2\mu)^{1/2}\mu(1/\mu_1^2-1/\mu_2^2)-H_1(\mu_1-\mu_0)/N_1\right] , \tag{85}$$

where here use was made of $dN_1+dN_2=0$ and $V=AL$.

Note that the subscript **B** in Eqs. (82) and (84) indicates the uniformity of **B** and not that it is fixed in magnitude. The total magnetic energy of the system comprises the energies of the two subsystems,

$$U_M = U_{M1}+U_{M2} . \tag{86}$$

By virtue of U_M being fixed

$$dU_{M1} = -dU_{M2} . \tag{87}$$

Hence using the fact that N is fixed and hence $dN_1=-dN_2$, we find that

$$\zeta_{\mathbf{B},V_2}(U_M=\text{const}) = \zeta_{\mathbf{B},V_1}(U_M=\text{const}) . \tag{88}$$

The same relation holds for the pressure. Thus under the constraint of fixed N and fixed U_M there is no magnetic drive for mass transfer between the two subsystems that originates from differences in $\zeta_{\mathbf{B},V_i}(U_M=\text{const})$, $i=1,2$.

Equations (83)–(85) and (88) show that because U_M is held fixed, the pressure and chemical potential of the matter in subsystems 1 and 2 become functions of variables that pertain to both subsystems, as well as to the whole system. In particular they depend on the dimensions of the subsystems. If we focus on subsystem 1 and consider subsystem 2 to be its environment, then the above results verify the dependence of thermodynamic variables of subsystem 1 on this environment. This is a unique property of thermodynamics in the presence of fields. Consider the following two cases.

In the first case $\mu_1\to\mu_2$, and hence the magnetic chemical potential takes the following familiar form:

$$\zeta^{\alpha}_{\mathbf{B},V_1}(U_M=\text{const}) = -\tfrac{1}{2}V_1H_1^2(\mu_1-\mu_0)/N_1 = -\frac{1}{2}KH_1^2 = -\frac{\mu_0}{2\rho_1}H_1M_1 . \tag{89}$$

In the second case $\mu_1\to\mu_0$. This gives

$$\zeta^{\beta}_{\mathbf{B},V_1}(U_M=\text{const}) = \frac{1}{2}\frac{V_1}{V}KHH_1\mu^2[1/\mu_0^2-1/\mu_2^2) . \tag{90}$$

Note the superscripts α and β denote the first and second cases, respectively.

Equations (89) and (90) show that the magnetic chemical potential is a function of the variables pertaining to both subsystems and it is only when their permeabilities are the same that the chemical potential appears to depend on variables of one subsystem.

Hitherto we have considered materials that satisfy Eq. (60). Using the same analysis that led to Eqs. (68) and (71), it can readily be shown that for materials that satisfy Eqs. (59), (61), and (62), the magnetic pressure and chemical potential can be presented as

$$P'_{\mathbf{B},N_i} = -\frac{1}{2}(\mathbf{H}\cdot\mathbf{B})_i-\frac{\mu_0}{2}(\mathbf{H}\cdot\mathbf{M})_i/(1-K_1\rho_i), \quad i=1,2 , \tag{91}$$

$$\zeta'_{\mathbf{B},V_i} = -\frac{\mu_0}{2\rho_i}(\mathbf{M}\cdot\mathbf{H})_i/(1-K_1\rho_i), \quad i=1,2 . \tag{92}$$

Equations (91) and (92) agree with the magnetic terms of Eqs. (18) and (19) when the latter are subject to Eq. (62).

B. Uniform field H

Figure 2 shows two systems in which the boundary conditions between their subsystems facilitate the condition of uniform **H**. In Fig. 2(a) the system consists of two concentric cylinders having the same length L. The inner cylinder is designated as subsystem 1 and the annular region extending from its surface to the outer cylinder is marked subsystem 2. The radii of the cylinders are R_1 and R_2 and their cross-sectional areas are A_1 and A_2, respectively. The system is long enough, i.e., $L \gg R_2$, so that end effects can be neglected. A solenoid wound around the system produces a steady uniform field **H**. The permeability of the material in region 3 surrounding the system is practically infinite.

In Fig. 2(b) the gap opened in the yoke is defined as the system. The length of this gap is L, its thickness is l, and the width in the z direction (not shown) is l'. The dimensions L and l' are large compared to l so that end effects can be neglected.

The yoke, which has practically infinite permeability, is energized by a coil wound around its left leg. The boundaries between subsystems 1 and 2 are set parallel to the y axis, i.e., perpendicular to the boundaries of the gap. In this way the field $\mathbf{H}$ within the gap must be parallel to these boundaries. Subsystem 2 extends from the boundaries of subsystem 1 at $(0,x)$ up to the edges of the gap so that its length is $L-x$. In what follows the "system" refers equally well to that depicted either in Fig. 2(a) or in Fig. 2(b). In this case, the effective (weighted average) permeability μ of the system is given by

$$\mu=\frac{1}{V}(V_1\mu_1+V_2\mu_2)\ , \tag{93}$$

where the volume V is fixed:

$$V=V_1+V_2\ . \tag{94}$$

Hence

$$Vd\mu=V_1d\mu_1+(V-V_1)d\mu_2+(\mu_1-\mu_2)dV_1\ . \tag{95}$$

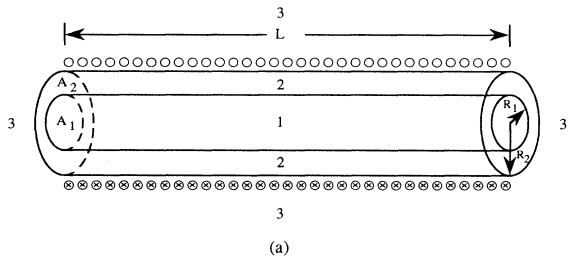
At fixed temperature,

$$d\mu_i=\alpha(\rho_i)d\rho_i,\quad i=1,2\ , \tag{96}$$

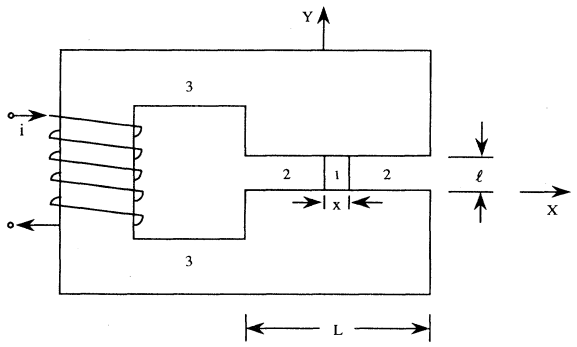
where $\alpha(\rho_i)=K$, when Eq. (60) applies and $\alpha(\rho_i)=K(\rho_i)/(1-K_1\rho_i)$, when Eqs. (59), (61), and (62) prevail.

If Eq. (60) applies then

$$d\mu_1=(K/V_1)(dN_1-\rho_1dV_1)\ , \tag{97}$$



(a)



(b)

FIG. 2. Magnetic field system at fixed field $\mathbf{H}$. (a) Cylindrical geometry; (b) rectangular geometry.

$$d\mu_2=(K/V_2)(dN_2-\rho_2dV_2)$$
$$=-(K/V_2)(dN_1-\rho_2dV_1)\ . \tag{98}$$

Combining Eqs. (95), (97), and (98) gives

$$Vd\mu=K(dN_1+dN_2)+(-K\rho_1+K\rho_2+\mu_1-\mu_2)dV_1\ . \tag{99}$$

The first and second terms on the right-hand side of Eq. (99) vanish due to the fact that $N=N_1+N_2$ is fixed and $K\rho_i=\mu_i-\mu_0$, $i=1,2$. Thus at fixed V, N, and $\mathbf{H}$, the magnetic energy ($\frac{1}{2}V\mu H^2$) of a system that satisfies Eq. (60) is fixed with respect to changes in V_1 or N_1. This shows (as indeed is verified below) that both the pressure and chemical potential must be uniform across the system. The magnetic energy of the ith subsystem is given by

$$U_{Mi}=\tfrac{1}{2}V_iH_i^2\mu_i,\quad \mathbf{H}_i=\mathbf{H},\quad i=1,2\ . \tag{100}$$

Hence the corresponding magnetic chemical potential can be obtained as

$$\zeta''_{\mathbf{H},V_i}=(\partial U_{Mi}/\partial N_i)_{V_i}=\frac{1}{2}KH_i^2=\frac{\mu_0}{2\rho_i}\mathbf{M}_i\cdot\mathbf{H}_i\ . \tag{101}$$

Equation (101) is in agreement with the magnetic term of Eq. (21) when it is subject to Eq. (60). The chemical potential, as defined by Eq. (101), is the same in both subsystems. Similarly the magnetic pressure is obtained as

$$P''_{\mathbf{H},N_i}=-(\partial U_{Mi}/\partial V_i)_{N_i}=-\frac{1}{2}\mu_0H_i^2,\quad \mathbf{H}_i=\mathbf{H}\ . \tag{102}$$

Equation (102), which is in agreement with the magnetic terms of Eq. (20), verifies that the magnetic pressure is also uniform across the system when it satisfies Eq. (60). If Eqs. (59), (61), and (62) prevail, then the counterparts of Eqs. (101) and (102) become

$$\zeta''_{\mathbf{H},V_i}=\frac{1}{2}\alpha'(\rho_i)H_i^2=\frac{\mu_0}{2\rho_i}\mathbf{M}_i\cdot\mathbf{H}_i/(1-K_1\rho_i),\quad i=1,2\ , \tag{103}$$

$$P''_{\mathbf{H},N_i}=-\frac{1}{2}\mathbf{H}_i\cdot\mathbf{B}_i+\frac{\mu_0}{2}\mathbf{M}_i\cdot\mathbf{H}_i/(1-K_1\rho_i),\quad i=1,2\ , \tag{104}$$

where $\alpha'(\rho_i)=3\mu_0K_1/[\rho_i(1-K_1\rho_i)^2]$.

Equations (103) and (104) are in agreement with the magnetic terms in Eqs. (21) and (20) when the latter are subject to Eq. (62). Equations (103) and (104) show that for systems that obey the Clausius Mossotti law, neither the chemical potential nor the pressure is expected to be the same in subsystems 1 and 2. As $\alpha'(\rho_i)$ is inversely proportional to $(1-K_1\rho_i)^2$, $\zeta''_{\mathbf{H},V_i}$ is an increasing function of ρ_i. This suggests the existence of a magnetic driving force for mass transfer from the denser subsystem to that of the lower density. Manipulating Eq. (104) in conjunction with Eq. (62) gives

$$P''_{\mathbf{H},N_i}=-\tfrac{1}{2}\mu_0H_i^2+\tfrac{1}{6}\mu_0M_i^2,\quad i=1,2\ . \tag{105}$$

Comparing Eqs. (102) and (105) shows that under the

Clausius Mossotti law, the pressure depends on the magnetization of the material through the term $\frac{1}{6}\mu_0 M_i^2$. In this case the magnetic pressure increases with density, and there is a net jump in this pressure which amounts to $\frac{1}{6}\mu_0(M_1^2-M_2^2)$, i.e., when the boundary from subsystem 2 to 1 is crossed.

IV. DISCRETE SYSTEMS

Equations (10)–(13) hold for continua, as well as for discrete systems. In the case of a continuum the energy U_f due to the field can be ascribed solely to the space within the boundaries of the system. However, in the general case of discrete systems U_f consists of energy that is stored inside as well as outside the system. The implication of this split energy storage is examined next for the illustrative case of a single isotropic sphere in a uniform magnetic field.

A. Sphere in uniform magnetic field

1. Energy and thermodynamic permeability

Consider a sphere of radius R that is placed in a uniform field $H_0\mathbf{i}_z$ where $\mathbf{i}_z$ is the unit vector in the z direction; see Fig. 3. A spherical coordinate system (r,θ,φ) is placed with its origin at the center of the sphere and the axis $\theta=0$ coinciding with the z axis. The triplet (r,θ,φ) has the corresponding triplet unit vectors $(\mathbf{i}_r,\mathbf{i}_\theta,\mathbf{i}_\varphi)$. In this coordinate system

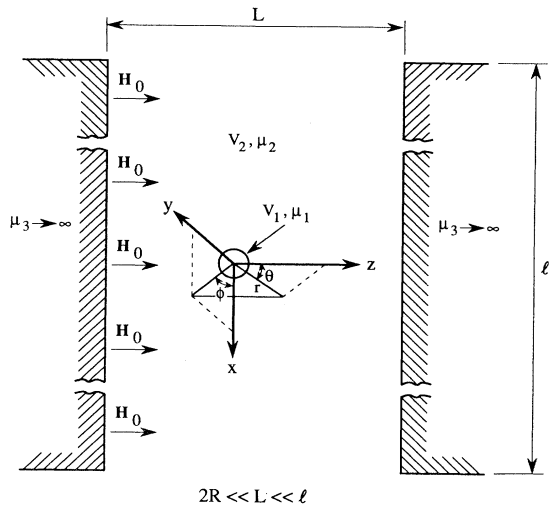


FIG. 3. Details of a sphere in a uniform field. The sphere is defined as subsystem 1 and the rest of the gap as subsystem 2.

$$\mathbf{i}_z=\mathbf{i}_r\cos\theta-\mathbf{i}_\theta\sin\theta\ . \tag{106}$$

Note that variables pertaining to the sphere and to its surroundings are marked by subscripts 1 and 2, respectively. In what follows we evaluate the magnetic energy stored in the sphere and its surroundings and then use the result to evaluate relevant thermodynamic variables.

The field within and outside the sphere is given by [4]

$$\mathbf{H}=\begin{cases}\dfrac{3\mu_2 H_0}{\mu_1+2\mu_2}\mathbf{i}_z, & r<R \qquad (107)\\[2ex] H_0\left\{\left[1+\dfrac{2R^3}{r^3}\left(\dfrac{\mu_1-\mu_2}{\mu_1+2\mu_2}\right)\right]\cos\theta\mathbf{i}_r-\left[1-\dfrac{R^3}{r^3}\left(\dfrac{\mu_1-\mu_2}{\mu_1+2\mu_2}\right)\right]\sin\theta\mathbf{i}_\theta\right\}, & r>R\ . \qquad (108)\end{cases}$$

Hence, assuming that all materials involved are linear, the following energies can be defined relative to those prevailing in the absence of the sphere:

$$U_{M1}=\frac{1}{2}V_1\mu_1\left[\frac{3\mu_2}{\mu_1+2\mu_2}\right]^2H_0^2-\frac{1}{2}V_1\mu_2H_0^2\ , \tag{109}$$

$$U_{M2}=\frac{1}{2}\mu_2\int_{V_2}H^2dV_2+\frac{1}{2}V_1\mu_2H_0^2\ . \tag{110}$$

Note that Eqs. (109) and (110) are structured with a view to satisfy the convention [1] that, in the absence of the sphere or when $\mu_1=\mu_2$, U_{M1} vanishes and the energy in V_1 pertains to the source of the field, and not to the space occupied by the sphere. Solution of the integral on the right-hand side of Eq. (110) gives

$$U_{M2}=\frac{1}{2}V_2\mu_2H_0^2+V_1\mu_2\left[\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\right]^2H_0^2+\frac{1}{2}V_1\mu_2H_0^2\ . \tag{111}$$

The first term on the right-hand side of Eq. (111) is the energy stored outside the boundaries of the sphere due to the source of the uniform field, while the second term gives the energy stored there due to the sphere. Thus the energy stored outside the sphere due to its own material is proportional to its volume. The total magnetic energy that is stored in the sphere and its surroundings is obtained as

$$\begin{aligned}U_M=U_{M2}+U_{M1}&=\frac{1}{2}V\mu_2H_0^2+\frac{1}{2}V_1\mu_1\left[\frac{2\mu_2}{\mu_1}\left(\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\right)^2+\left[\frac{3\mu_2}{\mu_1+2\mu_2}\right]^2-\frac{\mu_2}{\mu_1}\right]H_0^2\\&=\frac{1}{2}V\mu_2H_0^2+\frac{1}{2}V_1\mu_1\left[\left(\frac{\mu_2}{\mu_1}\right)\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\right]H_0^2\ ,\end{aligned} \tag{112}$$

where $V=V_1+V_2$ and the second term on the right-hand side of Eq. (112) stands for the overall net effect of the sphere. Combining Eqs. (107) and (112) gives

$$U_M=\tfrac{1}{2}V\mu_2 H_0^2+\tfrac{1}{2}V_1\mu_s H_1^2 , \tag{113}$$

$$\mu_s=\mu_1\{\tfrac{1}{9}[(\mu_1/\mu_2)-2(\mu_2/\mu_1)+1]\} , \tag{114}$$

where μ_s is defined as the effective "thermodynamic" permeability that would have given the same overall net energy due to the sphere, had its own field been uniform and confined to the region within its boundaries only, at the level of the field $\mathbf{H}_1$ prevailing there. In this sense, μ_s (which is a transformation of μ_1) can be considered an ordinary thermodynamic variable of the sphere system. This is due to the fact that μ_s facilitates the use of a model where the overall field due to the sphere is considered as being effectively confined within its boundaries. In order to define other thermodynamic variables of the sphere it is necessary to evaluate partial derivatives of its overall net energy (U'_{M1}), which according to Eq. (113) is defined by

$$U'_{M1}=\tfrac{1}{2}V_1\mu_s H_1^2 . \tag{115}$$

In what follows, we define thermodynamic variables of the sphere at fixed T, N, and V and either fixed $\mathbf{B}_1$ or fixed $\mathbf{H}_1$. This means that all changes of volume and mass are done under the field $\mathbf{H}_0$ and internal to V and no exchange of mass or volume with regions outside V can occur.

2. *Thermodynamic variables under different constraints*

a. Fixed $\mathbf{B}_1$, *T, N, and V.* Combining Eqs. (114), (115), and (69) for $i=1$ gives

$$U'_{M1}=\tfrac{1}{2}V_1 B_1^2/\mu'_s , \tag{116}$$

$$\frac{1}{\mu'_s}=\frac{1}{9}\left[\frac{1}{\mu_2}-\frac{2\mu_2}{\mu_1^2}+\frac{1}{\mu_1}\right] , \tag{117}$$

where here μ'_s is defined as the effective "thermodynamic" permeability for the energy formulation in terms of $\mathbf{B}_1$. Notice that unlike the case of a continuum, here $\mu'_s\neq\mu_s$.

Thus at fixed $\mathbf{B}_1$

$$dU'_{M1}=\frac{1}{2}\frac{B_1^2}{\mu'_s}dV_1+\frac{1}{2}V_1 B_1^2 d(1/\mu'_s) , \tag{118}$$

$$d(1/\mu'_s)=\frac{1}{9}\left[-\left[\frac{1}{\mu_2^2}+\frac{2}{\mu_1^2}\right]d\mu_2+\left[\frac{4\mu_2}{\mu_1^3}-\frac{1}{\mu_1^2}\right]d\mu_1\right] , \tag{119}$$

where here $dV_1=4\pi r^2 dr$ is constrained to be a spherical shell. For linear materials

$$\mu_i=\mu_i(\rho_i,T_i),\quad i=1,2 , \tag{120}$$

$$d\mu_i=(\partial\mu_i/\partial\rho_i)_{T_i}d\rho_i+(\partial\mu_i/\partial T_i)_{\rho_i}dT_i,\quad i=1,2 . \tag{121}$$

At fixed temperature $T_i=T$,

$$d\mu_i=\frac{1}{V_i}(\partial\mu_i/\partial\rho_i)_{T_i}(dN_i-\rho_i dV_i),\quad i=1,2 . \tag{122}$$

Combining Eqs. (118), (119), and (122) and using $dV_2=-dV_1$ and $dN_2=-dN_1$ gives dU'_{M1} in terms of pressure and chemical potential as

$$dU'_{M1}=-P_{\mathbf{B}_1,N_1}dV_1+\zeta_{\mathbf{B}_1,V_1}dN_1 , \tag{123}$$

where

$$P_{\mathbf{B}_1,N_1}=\frac{-1}{18}B_1^2\left[\frac{9}{\mu'_s}-\frac{V_1}{V_2}\alpha_1\left[\frac{\partial\mu_2}{\partial\rho_2}\right]_T\rho_2-\beta_1\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T\rho_1\right] , \tag{124}$$

$$\zeta_{\mathbf{B}_1,V_1}=\frac{1}{18}B_1^2\left[\frac{V_1}{V_2}\alpha_1\left[\frac{\partial\mu_2}{\partial\rho_2}\right]_T+\beta_1\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T\right] , \tag{125}$$

$$\alpha_1=\frac{1}{\mu_2^2}+\frac{2}{\mu_1^2},\quad \beta_1=\frac{4\mu_2}{\mu_1^3}-\frac{1}{\mu_1^2} .$$

Consider the two following extreme cases. In the first one, $\rho_1\to\rho_2$, $\mu_1\to\mu_2$ and hence $1/\mu'_s\to 0$ and $(\partial\mu_1/\partial\rho_1)_T\to(\partial\mu_2/\partial\rho_2)_T$. This and the fact that $V_1/V_2\ll 1$, and hence related terms can be neglected, gives

$$P_{\mathbf{B}_1,N_1}=\frac{1}{6}H_1^2\rho_1\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T,\quad \mu_1\to\mu_2 ,\quad \mathbf{H}_1\to\mathbf{H}_0,\quad V_1/V_2\ll 1 , \tag{126}$$

$$\zeta_{\mathbf{B}_1,V_1}=\frac{1}{6}H_1^2\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T,\quad \mu_1\to\mu_2 ,\quad \mathbf{H}_1\to\mathbf{H}_0,\quad V_1/V_2\ll 1 . \tag{127}$$

Using the first term on the right-hand side of Eq. (113), it is straightforward to show that for matter that is uniformly distributed in V at a fixed and uniform $\mathbf{H}_0$, one obtains

$$P_{\mathbf{H}_0,N}=-\frac{1}{2}\mu_2 H_0^2+\frac{1}{2}H_0^2\rho\left[\frac{\partial\mu}{\partial\rho}\right]_T , \tag{128}$$

$$\zeta_{\mathbf{H}_0,V}=\frac{1}{2}H_0^2\left[\frac{\partial\mu}{\partial\rho}\right]_T \tag{129}$$

where the subscripts 2 in the derivatives were dropped, due to the fact that V, rather than V_2, is involved and here $(\partial\mu_1/\partial\rho_1)_T=(\partial\mu_2/\partial\rho_2)_T=(\partial\mu/\partial\rho)_T$. Equations (128) and (129) are in agreement with the magnetic terms in Eqs. (20) and (21), respectively. It is seen that holding $\mathbf{B}_1$ fixed within the sphere affects only its own thermodynamic variables but not the ones pertaining to the source of the uniform field, as indeed should be the case. Comparison of Eqs. (127) and (129) shows that if $\partial\mu_1/\partial\rho_1=\partial\mu/\partial\rho$ and the sphere consists of the same matter that surrounds it uniformly but at slightly different density, then $\zeta_{\mathbf{B}_1,V_1}<\zeta_{\mathbf{H}_0,V}$ is expected. This suggests that, magnetically, there is a force driving

matter into the sphere when the latter is held at fixed $\mathbf{B}_1$.

In the second case $\mu_1 \to \infty$ and μ_2 is finite. Here, $1/\mu_s' = 1/(9\mu_2)$, $\alpha_1 = 1/\mu_2^2$, $\beta_1 = 0$, and hence recalling that $V_1/V_2 \ll 1$, Eqs. (124) and (125) reduce to

$$P_{\mathbf{B}_1,N_1} = -\tfrac{1}{2}\mu_2 H_0^2, \quad \mu_1 \to \infty, \quad V_1/V_2 \ll 1 , \tag{130}$$

$$\zeta_{\mathbf{B}_1,V_1} = 0, \quad \mu_1 \to \infty, \quad V_1/V_2 \ll 1 . \tag{131}$$

Thus, at $\mu_1 \to \infty$ and μ_2 finite, the magnetic chemical potential of matter within the sphere vanishes, and hence the force driving matter into the sphere increases as compared to the case where μ_1 is finite. In what follows the constraint of fixed $\mathbf{B}_1$ is replaced by that of fixed $\mathbf{H}_1$.

b. Fixed $\mathbf{H}_1$, *T, N, and V.* Differentiating Eq. (115) and combining the result with Eq. (122) gives

$$dU_{M1}' = \frac{1}{18}H_1^2\left[9\mu_s - \frac{V_1}{V_2}\alpha_1'\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T\rho_2 - \beta_1'\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T\rho_1\right]dV_1 + \frac{1}{18}H_1^2\left[\frac{V_1}{V_2}\alpha_1'\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T + \beta_1'\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T\right]dN_1 ,$$

$$\alpha_1' = \mu_1^2/\mu_2^2 + 2, \quad \beta_1' = 2\mu_1/\mu_2 + 1 . \tag{132}$$

Consider, once again, the following two extreme cases. In the first one $\rho_1 \to \rho_2$, $\mu_1 \to \mu_2$, and hence $\mu_s \to 0$. Furthermore, in the limit $\alpha_1' = 3$ and $\beta_1' = 3$. Recalling that $V_1/V_2 \ll 1$, this gives

$$dU_{M1}' = \frac{-1}{6}H_1^2\rho_1\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T dV_1 + \frac{1}{6}H_1^2\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T dN_1 . \tag{133}$$

Thus, the same pressure and chemical potential [compare to Eqs. (126) and (127)] is obtained under this extreme condition, irrespective of $\mathbf{B}_1$ or $\mathbf{H}_1$ being fixed.

In the second case where $\mu_1 \to \infty$ and μ_2 is finite, the result, i.e., $dU_{M1}' = \frac{1}{2}\mu_2 H_0^2 dV_1$ and the corresponding pressure, is identical with that of Eq. (130). Note that here [see Eq. (107)], the fixed level of $\mathbf{H}_1$ must be $\mathbf{H}_1 \to \mathbf{0}$. Similar to the case of fixed $\mathbf{B}_1$, the difference in chemical potential for the same material when it is within or [see Eq. (129)] outside the sphere suggests its tendency to concentrate in the sphere.

Comparing Eqs. (127) and (129) at $\mu_1 = \mu_2 = \mu$, $\rho_1 = \rho_2 = \rho$, and $\mathbf{H}_1 = \mathbf{H}_0$ shows that the latter gives a result that is larger by a factor of 3. This seems to be a discrepancy. However, the two equations are subject to different constraints regarding the way matter is accumulated. In Eq. (127) matter can accumulate only in a spherical space of volume V_1, whereas in Eq. (129) it must be dispersed uniformly in V_2 outside this sphere. In the absence of restoring dispersive forces, this difference in chemical potential is another manifestation of the system being magnetically unstable and of its tendency to form, or else collapse into, denser regions. In the above example, the denser region happens to be a sphere. However, as is well known, it does not provide the lowest possible state of energy that is attained rather in elongated needle like forms that are uniformly dispersed and aligned with the field.

Hitherto we have imposed constraints that are characterized by holding either $\mathbf{B}_1$ or $\mathbf{H}_1$ fixed simultaneous with the overall condition that $\mathbf{H}_0$, N, and V are invariable. These constraints, which are imposed only on the field within the sphere, can be realized by superimposing a hypothetical current source in the form of a flux ball on the sphere. The field $\mathbf{H}_b$ of such a flux ball is given by [5]

$$\mathbf{H}_b = \begin{cases} \dfrac{ni}{3R}(\mathbf{i}_r\cos\theta - \mathbf{i}_\theta\sin\theta), & r < R \\ \dfrac{ni}{6R}\left(\dfrac{R}{r}\right)^3(\mathbf{i}_r 2\cos\theta + \mathbf{i}_\theta\sin\theta), & r > R , \end{cases} \tag{134}$$

where ni are ampere turns.

The conditions set on $\mathbf{H}_b$ by the constraints can be summarized as follows:

$$\mathbf{H}_b = \mathbf{H}_1' - \frac{3\mu_2}{\mu_1 + 2\mu_2}H_0\mathbf{i}_z, \quad r < R , \tag{135}$$

where at fixed $\mathbf{B}_1$,

$$\mathbf{H}_1' = \mathbf{B}_1/\mu_1$$

and at fixed $\mathbf{H}_1$,

$$\mathbf{H}_1' = \mathbf{H}_1 .$$

The adjustment of $\mathbf{H}_b$, i.e., according to Eq. (134), is via the current i at fixed number of turns n. This in turn produces the field outside the flux ball as per Eq. (134). Thus the resultant field outside the sphere is the sum of the contributions from the sphere [Eq. (108)] and the flux ball [Eq. (134)]. This resultant field varies as μ_1 is changed, thus producing a change in the flux linkage with the current source of the $\mathbf{H}_0$ field. Therefore, the latter must exchange energy (however small) with the sphere. At fixed $\mathbf{B}_1$ the flux passing through the sphere is fixed; there is no energy exchange between the sphere and the flux ball, but there is such an exchange with the current source of $\mathbf{H}_0$. At fixed $\mathbf{H}_1$, the sphere exchanges energy with both current sources, the primary exchange being with the flux ball and the minor one with the current source of $\mathbf{H}_0$. It follows that the constraint of fixed flux through the current source of $\mathbf{H}_0$ can be fundamentally different from the constraints imposed only on the sphere. In what follows we consider the implications of this constraint, which allows no energy exchange between the sphere and the current sources of $\mathbf{H}_0$. As μ_1 is

changed, this constraint can be satisfied by adjusting $\mathbf{H}_0$, V_1, or μ_2, so as to maintain the energy U_M fixed.

Using Eq. (112) this condition can be expressed as follows:

$$\frac{1}{2}V\mu_2\left[1+\frac{V_1}{V}\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\right]H_0^2=U_M=\text{const} . \quad (136)$$

Hence, recalling that V is fixed,

$$(\partial U_M/\partial\mu_1)_{V_1,\mu_2,H_0}d\mu_1+(\partial U_M/\partial\mu_2)_{V_1,\mu_1,H_0}d\mu_2+(\partial U_M/\partial V_1)_{\mu_1,\mu_2,H_0}dV_1+(\partial U_M/\partial H_0)_{V_1,\mu_1,\mu_2}dH_0=0 . \quad (137)$$

For example, at fixed μ_2 and V_1 it can readily be shown that

$$dH_0=-\frac{3}{4}\frac{H_0^3}{U_M}\left[\frac{\mu_2}{\mu_1+2\mu_2}\right]^2\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T dN_1=-\frac{H_0}{12U_M}H_1^2\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T dN_1 \quad (138)$$

and hence

$$dU'_{M1}=\frac{1}{6}H_1^2\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T\left[1-\frac{U'_{M1}}{U_M}\right]dN_1 . \quad (139)$$

Equation (139) facilitates the definition of the following magnetic chemical potential:

$$\zeta_{U_M,V_1}=\frac{1}{6}H_1^2\left[\frac{\partial\mu_1}{\partial\rho_1}\right]_T\left[1-\frac{U'_{M1}}{U_M}\right] . \quad (140)$$

Comparing Eqs. (127) and (140) shows that replacing the constraint of fixed $\mathbf{B}_1$ with fixed U_M decreases the magnetic chemical potential by a factor of $1-U'_{M1}/U_M$. At $\mu_1\to\infty$, $\mathbf{H}_1\to\mathbf{0}$ and ζ_{U_M,V_1} vanishes, as expected.

It is clear from Eq. (137) that there are three combinations of pairs of variables that can be constrained while μ_1 and the remaining unconstrained variable are allowed to change. Although we have chosen to show one such possibility, the option to choose another indicates the existence of two additional forms of related magnetic chemical potential. It follows that in discrete systems such as the sphere, the number of forms that the magnetic chemical potential can assume is expected to be larger than those that can be defined for corresponding cases of continua. We digress briefly to consider the significance of volume of subsystem 1 with respect to that of the sphere.

c. Significance of volume enclosing the sphere. In previous cases the volume V_1 of subsystem 1 was identified as that of the sphere. However, as pointed out elsewhere [1], V_1 need not be the same volume V_M of the magnetizable matter. If V_1 coincides with V_M, then identical changes must occur in both. However, if this constraint is lifted then V_1 and V_M become independent. Note that henceforth properties that pertain to isotropic magnetic matter are denoted by subscript M. Figure 4 shows the same system that is depicted in Fig. 3 with the exception that the volume V_M of the sphere is part of V_1.

In the system of Fig. 3, any change in mass of the sphere at fixed volume $V_1=V_M$ or a change in its volume at fixed mass N_M must result in a change in the corresponding density $\rho_1=\rho_M$, and permeability $\mu_1=\mu_M$. In Fig. 4, ρ_1 is a function of ρ_M as well as of ρ_2.

$$\rho_1=\phi_M\rho_M+(1-\phi_M)\rho_2 ,$$
$$\phi_M=V_M/V_1, \quad N_M=\rho_M V_M . \quad (141)$$

It follows that subject to Eq. (141), ρ_M, and hence also μ_M, can be held fixed as V_M (or alternatively N_M) is varied at fixed V_1 and vice versa. Now we seek to find the form of the magnetic chemical potential for the case in which $\mathbf{B}_M$ and ρ_M are kept fixed while simultaneously maintaining the condition that temperature and the overall mass N and volume V of the system are invariable. The condition of fixed $\mathbf{B}_M$ and μ_M (which follows from holding ρ_M fixed) imposes also a fixed $\mathbf{H}_M$. Thus the result at fixed $\mathbf{H}_M$ and ρ_M must be identical with the one at fixed $\mathbf{B}_M$ and ρ_M. Next, the magnetic chemical potential is evaluated under these constraints.

d. Fixed $\mathbf{B}_M$ and ρ_M or $\mathbf{H}_M$ and ρ_M. In this case the induction and density of the sphere are kept fixed but they are variable within V_1. Here the energy U'_{M1} is

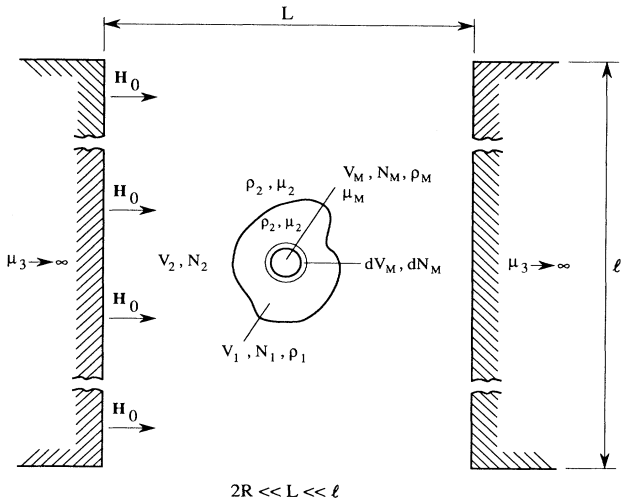


FIG. 4. Details of a sphere contained in subsystem 1 that is part of a system in a uniform field.

given by

$$U'_{M1}=\frac{1}{2}V_M B_M^2/\mu'_M \ , \qquad \frac{1}{\mu'_M}=\frac{1}{9}\left[\frac{1}{\mu_2}-\frac{2\mu_2}{\mu_M^2}+\frac{1}{\mu_M}\right] . \tag{142}$$

Equation (142) agrees with the convention that the magnetic field pertains to its source. Since the only source of field within V_1 is the sphere, it is also the sole contributor to U'_{M1}. Once again μ'_M accounts for the field inside as well as outside the sphere including the space outside V_M and V_1, i.e., the one in $V-V_M$. In this respect, the choice of V_1 has no effect on U'_{M1}, apart from the fact that it must facilitate the constraints set here. At fixed temperature μ_M is a sole function of ρ_M [see Eq. (120)], and hence it is also fixed. Furthermore, using the fact that $V \gg V_M$, μ_2 can be considered effectively invariable as a differential amount of mass and volume are exchanged between the sphere and the rest of the system. This means that, effectively, μ'_M is also invariable. It follows that V_M or alternatively N_M are the only possible magnetic variables in Eq. (142) that are not fixed:

$$dV_M=dN_M/\rho_M \ , \tag{143}$$

$$dU'_{M1}=\frac{1}{2}\frac{B_M^2}{\mu'_M}dV_M=\frac{1}{2\rho_M}\frac{B_M^2}{\mu'_M}dN_M \ . \tag{144}$$

Equation (144) facilitates the definition of the following magnetic chemical potential:

$$\zeta_{\mathbf{B}_M,\mu_M}=\left[\frac{\partial U'_{M1}}{\partial N_M}\right]_{\mathbf{B}_M,\rho_M}=\frac{1}{2\rho_M}\frac{B_M^2}{\mu'_M} \ . \tag{145}$$

The partial derivative in Eq. (145) is not marked with a subscript V_1 along side $\mathbf{B}_M,\rho_M$, since U'_{M1} is not a function of V_1. This is a fundamental difference as compared to ordinary, field free, thermodynamics where a fixed V_1 must be imposed when evaluating the chemical potential. This is also the reason for not including subscripts that denote uniformly dispersed masses that contribute to μ_2 but not to μ_M, since the overall mass and μ_2 are fixed and their field is due to the current sources of $\mathbf{H}_0$. Hence, if they exist, they contribute nothing to dU'_{M1}. Note that although the sphere (which is maintained at fixed $\mathbf{B}_M$ and μ_M) decreases the energy in the space it progressively occupies as it expands (assuming that $\mu_M>\mu_2$), it increases simultaneously its own energy, which is stored outside its boundaries. The net result is reflected in the positive chemical potential of the material within the sphere. Equation (145) has the same form that was obtained elsewhere for the case of a continuum at fixed induction $\mathbf{B}$, density ρ, and permeability μ. This chemical potential, i.e., $\zeta_{\mathbf{B},\mu}$, was defined as [1]

$$\zeta_{\mathbf{B},\mu}=\frac{1}{2\rho}\frac{B^2}{\mu} \ . \tag{146}$$

Equation (145) suggests that if the effective "thermodynamic" permeability of an isotropic discrete system is found, then provided that it is uniformly magnetized, it behaves essentially as if it were a continuum. In Eq. (145) this effective permeability is μ'_M.

The constraint of fixed $\mathbf{H}_0$ throughout the system means that changes in volume or mass of the sphere are carried out under a constant external field $\mathbf{H}_0$. If this constraint is lifted, then exchange of mass between the system and its surroundings, where the field is not uniform, becomes possible. In what follows, we consider the process of introducing a sphere into the system from an initial position outside the field, i.e., where its intensity vanishes. Such position is taken as "infinity." The magnetic work done on this sphere as it approaches the system consists of contributions from the field and the current source. As shown elsewhere [1], at fixed $\mathbf{H}$, and when the mass is spread uniformly in the system, this work is split between the one delivered to a mechanical work source that balances the magnetic pull quasistatically, and the one needed to magnetize the matter as it progressively enters regions of higher field intensity. At fixed flux linkage, no energy exchange between the sphere and the current source can occur. Hence, in this case the only work delivered is by the existing field. It follows that, at fixed $\mathbf{H}$ and variable flux, additional energy is delivered by the current sources in magnetizing the sphere. Thus the decrease in the energy of the field is due to the work delivered to the mechanical source, whereas the buildup of the energy stored in this field is due to the current sources. The work delivered, in a quasistatic process, by the field to the work source, at fixed flux, can be evaluated as follows. Assuming that μ_2 prevails outside the sphere and the variation of the field gradient across its volume can be neglected, the force acting on it is given by

$$\mathbf{F}_M=\mu_0 V_M \mathbf{M}\cdot\nabla\mathbf{H}_e \ , \tag{147}$$

$$\mu_0\mathbf{M}=(\mu_M-\mu_0)\mathbf{H}_i=(\mu_M-\mu_0)\frac{3\mu_2}{\mu_M+2\mu_2}\mathbf{H}_e \ , \tag{148}$$

where $\mathbf{H}_e=\mathbf{H}_e(\mathbf{r},t)$ is the "unperturbed" field (i.e., in the absence of the sphere) at the position $\mathbf{r}$ and time t and $\mathbf{H}_i=\mathbf{H}_i(\mathbf{r},t)$ is the corresponding field inside the sphere. The condition of fixed flux means that both $\mathbf{H}_e$ and $\mathbf{H}_i$ must change as the sphere changes its position outside the system. These changes are due to the adjustment of the current source so as to maintain the flux linkage fixed. However, the geometry of the field set by the current source is invariable. Thus as the sphere is introduced into the field, only its intensity changes while its shape remains the same. At $t=0$ when the sphere is outside the field, the current source produces the field $\mathbf{H}_{e0}=\mathbf{H}_e(\mathbf{r},0)$ and at $t>0$, it changes to $\mathbf{H}_e(\mathbf{r},t)$. Thus it is $\mathbf{H}_{e0}$ that provides the time invariable geometry of the field. Using the fact that $\mathbf{H}_e/\mathbf{H}_{e0}$ is independent of position, Eq. (147) can be expressed in terms of $\mathbf{H}_{e0}$ as follows:

$$\mathbf{F}_M=\frac{1}{2}V_M(\mu_M-\mu_0)\frac{3\mu_2}{\mu_M+2\mu_2}\left[\frac{H_e}{H_{e0}}\right]^2\nabla H_{e0}^2 \ , \tag{149}$$

where $(H_e/H_{e0})^2$ accounts for the effect of the variable current.

Hence the differential mechanical work (dW_λ) delivered by the field to a mechanical work source, as the position of the sphere is changed by $d\mathbf{r}$, holding λ fixed, is

$$dW_\lambda=\frac{1}{2}V_M(\mu_M-\mu_0)\frac{3\mu_2}{\mu_M+2\mu_2}\left[\frac{H_e}{H_{e0}}\right]^2 dH_{e0}^2 . \quad (150)$$

Integration of Eq. (150) from $\mathbf{H}_{e0}=\mathbf{0}$ to $\mathbf{H}_{e0}=\mathbf{H}_0$ gives

$$W_\lambda=\frac{1}{2}V_M(\mu_M-\mu_0)\frac{3\mu_2}{\mu_M+2\mu_2}\overline{\left[\frac{H_e}{H_{e0}}\right]^2}H_0^2$$
$$=\frac{\mu_0}{2}V_M\overline{\left[\frac{H_e}{H_{e0}}\right]^2}\mathbf{M}_1\cdot\mathbf{H}_0 , \quad (151)$$

where $\overline{(H_e/H_{e0})^2}$ and $\mathbf{M}_1$ are defined by

$$\overline{\left[\frac{H_e}{H_{e0}}\right]^2}=\int_0^{H_0}\left[\frac{H_e}{H_{e0}}\right]^2 dH_{e0}^2 , \quad (152a)$$

$$\mu_0\mathbf{M}_1=(\mu_M-\mu_0)\frac{3\mu_2}{\mu_M+2\mu_2}\mathbf{H}_0=(\mu_M-\mu_0)\mathbf{H}_1 . \quad (152b)$$

If $\mu_M>\mu_2$, then $\overline{(H_e/H_{e0})^2}<1$.

It can readily be shown that if the constraint of fixed λ is replaced by that of a fixed current in the source of the field $\mathbf{H}_{e0}$, then $H_e/H_{e0}=1$ and the work W_H delivered to the mechanical work source is

$$W_H=\frac{\mu_0}{2}V_M\mathbf{M}_1\cdot\mathbf{H}_0 . \quad (153)$$

Thus for materials that are characterized by $\mu_M>\mu_2$, $W_\lambda<W_H$.

Since, at fixed λ, there is no exchange of energy with the current source the change in the energy of the field (i.e., $-W_\lambda$) is given by

$$U_M-U_{M0}=-\frac{\mu_0}{2}V_M\overline{\left[\frac{H_e}{H_{e0}}\right]^2}\mathbf{M}_1\cdot\mathbf{H}_0 , \quad (154)$$

where U_{M0} denotes the initial energy, i.e., when the sphere is outside the field.

In the next step, the field is increased by the current source to its original value $\mathbf{H}_{e0}$ that prevailed in the absence of the sphere. At the end of this process the excess of the magnetic energy, i.e., relative to its value in the absence of the sphere, is simply U'_{M1} [see Eq. (115)]. Recall that when the sphere is introduced quasistatically into the field at fixed $\mathbf{H}_0$ and variable λ, the work done by the field on the mechanical work source is W_H [see Eq. (153)]. It follows that the work done by the current sources in reestablishing the field and magnetizing the sphere is $W_H+U'_{M1}$. Thus, in this case, the ratio of work delivered to build the field of the sphere to that delivered to the mechanical work source is

$$\frac{U'_{M1}}{W_H}=\frac{1}{3}\frac{\mu_M-\mu_2}{\mu_M-\mu_0} .$$

If the sphere is small enough that the error introduced by assuming $(H_e/H_{e0})^2=1$ is negligible then using $W_\lambda=W_H$ is justified. If $\mu_2=\mu_0$, then $U'_{M1}/W_H=\frac{1}{3}$. However, if $\mu_2>\mu_0$, then $U'_{M1}/W_H<\frac{1}{3}$. Thus at fixed $\mathbf{H}_0$ the work delivered by the current source to the mechanical work source is at least three times the work it delivers in magnetizing the sphere. This result is a consequence of the geometry of the sphere. If the sphere is magnetized directly in the field by increasing its intensity from $\mathbf{H}_e=0$ to $\mathbf{H}_e=\mathbf{H}_0$, then the magnetic energy of the sphere is U'_{M1} [see Eqs. (107), (114), and (115)] and no work is delivered to an external mechanical source:

$$U'_{M1}=\frac{1}{2}V_M(\mu_M-\mu_2)\frac{\mu_2}{\mu_M+2\mu_2}H_0^2 . \quad (155)$$

Thus the magnetic chemical potential of matter in the form of a small sphere, with respect to the process in which it is introduced into the field, can be defined as follows: At fixed λ and $\overline{(H_e/H_{e0})^2}=1$,

$$\zeta_{\lambda,V}=-\frac{\mu_0}{2\rho_M}\mathbf{M}_1\cdot\mathbf{H}_0$$
$$=-\frac{1}{2\rho_M}(\mu_M-\mu_0)\frac{3\mu_2}{\mu_M+2\mu_2}H_0^2 , \quad (156)$$

whereas, at fixed $\mathbf{H}_0$, considering only changes of energy in the field, and excluding those occurring in the current sources, the result is

$$\zeta_{\mathbf{H}_0,V}=\frac{1}{2\rho_M}(\mu_M-\mu_0)\frac{\mu_2}{\mu_M+2\mu_2}H_0^2 . \quad (157)$$

The analysis presented hitherto involves rigid systems. An example of a nonrigid, variable inductance system is discussed briefly below.

B. Variable inductance system

Detailed analysis of a variable inductance magnetic field system that is characterized by a fixed core and a plunger (see Fig. 5) is given in Appendix B. This analysis provides additional insight regarding the effect of con-

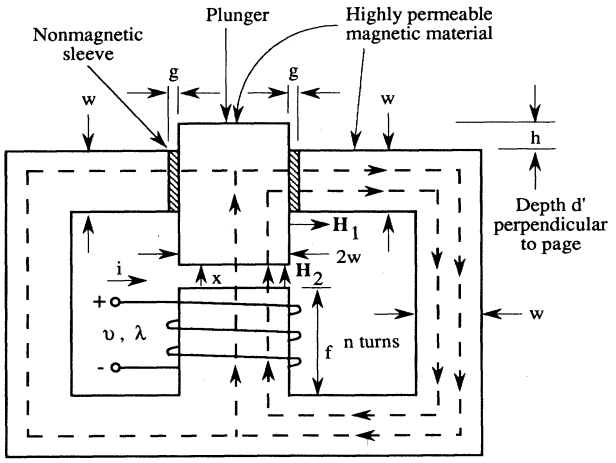


FIG. 5. A magnetic field system consisting of a circuit with a stationary core and a movable plunger, after Woodson and Melcher [7].

straints on the nature of the magnetic chemical potential and the work delivered to the mechanical work source, to the field, or by the field.

Furthermore, the thermodynamic significance of a variable gap system is illustrated. This variable gap circuit is used to show the conditions that yield positive as well as negative magnetic chemical potential at the same fixed flux (i.e., fixed **B**). When the plunger is free to move and hence the gap is variable, the energy of the system builds up when an incompressible matter (of finite and fixed permeability) is pushed, at fixed flux, against the plunger, thus opening the gap. This results in a positive magnetic chemical potential $\zeta_{\mathbf{B}_2,V}$, which is a reflection of the higher energy density of the matter in the field.

However, when the plunger is not free to move and the gap becomes fixed as part of a rigid structure, then as permeable matter enters the gap, at fixed flux, the energy of the system decreases. This results in a negative chemical potential $\zeta_{\mathbf{B}_2,x}$ which is a reflection of the attraction of the matter into the field. The reference magnetic chemical potential of permeable matter can be defined as the one prevailing in its absence. In the former case, the reference chemical potential corresponds to a closed gap (or else a gap full of infinitely permeable matter), whereas in the latter it corresponds to a gap full of nonpermeable matter, i.e., $\zeta_{\mathbf{B}_2,V}=0$ and $\zeta_{\mathbf{B}_2,x}=(1/2\rho_M)B_2^2/\mu_0$, respectively. It follows that the minimum and maximum values of the reference level are obtained for the variable and fixed gap conditions, respectively.

V. SUMMARY AND CONCLUSIONS

(1) Field-dependent thermodynamic variables of a continuum depend on constraints that are imposed on the field. In particular this applies to field-dependent extensive variables, which is a new consequence of the theory. The generalized intensive, as well as extensive variables that are functions of field and nonfield variables, can be used as ordinary thermodynamic variables. This concerns expressions for the differential of the internal energy and potentials that are derivable therefrom. Comparisons of the generalized variables with those that were previously defined elsewhere, show a complete agreement.

(2) The entropy of the current source is coupled with that of the system having a common flux linkage. This gives rise to different forms of the entropy according to the imposed field constraint. At fixed **B**, where no energy exchange exists with the current source, the entropy of the system is lower compared to its value in the absence of the field. At fixed **H**, the current source exchanges energy with the system and their related entropies are thus coupled. The value of this coupled entropy is larger than that of the system in the absence of the field.

(3) The generalized field-dependent variables facilitate the formulation of generalized Maxwell relations, which must hold irrespective of the field constraints.

(4) Analyses of conventional and simple magnetic field systems show that direct evaluation of thermodynamic variables, that characterize these systems, agree with those set by the general theory. This provides a validation test for the generalized variables, in systems of known magnetic properties that can be subjected to different field constraints.

(5) The thermodynamic properties of a sphere in a uniform field can be expressed in terms of an effective thermodynamic permeability. This permeability facilitates the use of a model where the effect of the field, due to the sphere, is considered as if it were completely stored within its boundaries. In this way, the sphere can be treated using the principles of ordinary thermodynamics that, otherwise, does not handle energies stored outside the boundaries of systems.

(6) Field-dependent thermodynamic variables of a sphere in a uniform field can be defined using the larger number of available field constraints, i.e., as compared to the case of a continuum. These constraints can be defined independently, either for the uniform field, or for the sphere.

(7) If the volume of the sphere (representing a discrete system) is different from the volume of the subsystem in which it is contained, then the volume of the latter may not be a field-dependent thermodynamic variable. If the sphere is the only source of field in the subsystem, then it is the volume of this sphere and not that of the subsystem that is the field-dependent thermodynamic variable (i.e., which characterizes the subsystem with respect to the field).

(8) When a magnetizable sphere is introduced quasistatically from infinity into a uniform field, the work delivered to a mechanical work source (which balances quasistatically the pull of the field) is the same irrespective of its source being the field or the current source. The ratio of the work done by the current source in establishing the field of the sphere to that delivered to the mechanical work source, is one-third or less, depending on the field constraints and the permeability prevailing outside the sphere.

(9) The variable gap magnetic circuit demonstrates the effect of field and geometrical constraints on the magnetic chemical potential, and the choice of its reference level. This reference level ranges from 0 to $(1/2\rho_M)B^2/\mu_0$ for the cases of variable and fixed gaps, respectively.

(10) In a variable gap magnetic circuit that is held at fixed flux, the magnetic chemical potential of an incompressible permeable matter is positive. However, if the gap is maintained as part of a rigid and fixed structure, then at the same fixed flux, the sign of the magnetic chemical potential is reversed.

ACKNOWLEDGMENTS

The basic ideas of this paper were formulated while the author visited with Professor Markus Zahn at the Department of Electrical Engineering, MIT. The valuable comments and suggestions made by Professor Zahn are hereby gratefully acknowledged.

APPENDIX A: FORMULATION OF MAXWELL RELATIONS

Equation (10) can be expressed in the following concise form:

$$dU=-\sum_{i=0}^{n}\hat{X}_i d\xi_i+\sum_{i=0}^{n}\hat{\xi}_i dX_i+\sum_{m=1}^{m'-1}\frac{\partial U_f}{\partial Y_m}dY_m\ , \quad \text{(A1)}$$

where

$$\hat{X}_i=\begin{cases} X_i-\sum_{m=m'}^{m_0-1}\frac{\partial U_f}{\partial Y_m}\frac{\partial Y_m}{\partial \xi_i}, & i=0,\ldots,j \\ -\sum_{m=m'}^{m_0-1}\frac{\partial U_f}{\partial Y_m}\frac{\partial Y_m}{\partial \xi_i}, & i=j+1,\ldots,n\ , \end{cases} \quad \text{(A2)}$$

$$\hat{\xi}_i=\begin{cases} \sum_{m=m_0}^{m''}\frac{\partial U_f}{\partial Y_m}\frac{\partial Y_m}{\partial X_i}, & i=0,\ldots,j \\ \xi_i+\sum_{m=m_0}^{m''}\frac{\partial U_f}{\partial Y_m}\frac{\partial Y_m}{\partial X_i}, & i=j+1,\ldots,n\ . \end{cases} \quad \text{(A3)}$$

Equation (A1) facilitates the formulation of Maxwell relations that are listed below:

$$\left[\frac{\partial \hat{\xi}_{i_1}}{\partial X_{i_2}}\right]_{X_{i_3},\xi_{i_5},Y_m}=\left[\frac{\partial \hat{\xi}_{i_2}}{\partial X_{i_1}}\right]_{X_{i_4},\xi_{i_6},Y_m}\ , \quad \text{(A4)}$$

$i_1,i_2,i_3,i_4,i_5,i_6=0,\ldots,n,\quad i_3\neq i_2,\quad i_4,i_5\neq i_1,\quad i_6\neq i_2,$ $m=1,\ldots,m'-1;$

$$\left[\frac{\partial \hat{X}_{i_1}}{\partial \xi_{i_2}}\right]_{\xi_{i_3},X_{i_5},Y_m}=\left[\frac{\partial \hat{X}_{i_2}}{\partial \xi_{i_1}}\right]_{\xi_{i_4},X_{i_6},Y_m}\ , \quad \text{(A5)}$$

$i_1,i_2,i_3,i_4,i_5,i_6=0,\ldots,n,\quad i_3\neq i_2,\quad i_4,i_5\neq i_1,\quad i_6\neq i_2,$ $m=1,\ldots,m'-1;$

$$-\left[\frac{\partial \hat{X}_{i_1}}{\partial X_{i_2}}\right]_{X_{i_3},\xi_{i_4},Y_m}=\left[\frac{\partial \hat{\xi}_{i_2}}{\partial \xi_{i_1}}\right]_{\xi_{i_5},X_{i_6},Y_m}\ , \quad \text{(A6)}$$

$i_1,i_2,i_3,i_4,i_5,i_6=0,\ldots,n,\ i_3\neq i_2,\ i_3\neq i_1,\ i_5\neq i_1,\ i_5\neq i_2,$ $m=1,\ldots,m'-1;$

$$-\left[\frac{\partial \hat{X}_{i_1}}{\partial Y_m}\right]_{X_{i_2},\xi_{i_2},Y_{i_3}}=\left[\frac{\partial(\partial U_f/\partial Y_m)}{\partial \xi_{i_1}}\right]_{X_{i_2},\xi_{i_4},Y_{i_5}}\ , \quad \text{(A7)}$$

$i_1,i_2,i_4=0,\ldots,n,\quad m,i_3,i_5=1,\ldots,m'-1,\quad i_3\neq m,$ $i_4\neq i_1;$

$$\left[\frac{\partial \hat{\xi}_{i_1}}{\partial Y_m}\right]_{X_{i_2},\xi_{i_2},Y_{i_3}}=\left[\frac{\partial(\partial U_f/\partial Y_m)}{\partial X_{i_1}}\right]_{X_{i_4},\xi_{i_2},Y_{i_5}}\ ,$$

$i_1,i_2,i_4=0,\ldots,n,\quad m,i_3,i_5=1,\ldots,m'-1,\quad i_3\neq m,$ $i_4\neq i_1.$

If we hold Y_m, $m=m',\ldots,m''$, fixed so that only Y_m, which are independent of ξ_i and X_i, contribute to dU in Eq. (A1), then this equation becomes

$$dU=-\sum_{i=0}^{j}X_i d\xi_i+\sum_{i=j+1}^{n}\xi_i dX_i+\sum_{m=1}^{m'-1}\eta_m dY_m\ , \quad \text{(A8)}$$

where $\eta_m=\partial U_f/\partial Y_m$, $m=1,\ldots,m'-1$.

Equation (A8) facilitates the following Legendre transformation:

$$dU_\eta=d\left[U-\sum_{m=1}^{m_1}\eta_m Y_m\right]=-\sum_{i=0}^{j}X_i d\xi_i+\sum_{i=j+1}^{n}\xi_i dX_i-\sum_{m=1}^{m_1}Y_m d\eta_m+\sum_{m=m_1+1}^{m'-1}\eta_m dY_m,\quad 1\le m_1\le m'-1\ . \quad \text{(A9)}$$

Equation (A9) can be used to formulate Maxwell relations between variables that are either field independent or field dependent; i.e., they do not involve both types as $\hat{X}_i$ and $\hat{\xi}_i$ do,

$$\frac{\partial X_{i_1}}{\partial \eta_{i_2}}=\frac{\partial Y_{i_2}}{\partial \xi_{i_1}},\quad i_1=0,\ldots,j,\quad i_2=1,\ldots,m_1\ , \quad \text{(A10)}$$

$$-\frac{\partial X_{i_1}}{\partial Y_{i_2}}=\frac{\partial \eta_{i_2}}{\partial \xi_{i_1}},\quad i_1=0,\ldots,j,\quad i_2=m_1+1,\ldots,m'-1\ , \quad \text{(A11)}$$

$$-\frac{\partial \xi_{i_1}}{\partial \eta_{i_2}}=\frac{\partial Y_{i_2}}{\partial X_{i_1}},\quad i_1=j+1,\ldots,n,\quad i_2=1,\ldots,m_1\ , \quad \text{(A12)}$$

$$\frac{\partial \xi_{i_1}}{\partial Y_{i_2}}=\frac{\partial \eta_{i_2}}{\partial X_{i_1}},\quad i_1=j+1,\ldots,n,$$

$$i_2=m_1+1,\ldots,m'-1\ . \quad \text{(A13)}$$

In Eqs. (A10)–(A13) all variables that are not part of the derivative are held fixed. The use of Eqs. (A8)–(A13) can be illustrated in the following example concerning the internal energy. In the case of a magnetizable continuum, the internal energy is given by [1]

$$dU=TdS-PdV+\zeta dN+\tfrac{1}{2}\mathbf{H}\cdot\mathbf{B}dV_M+V_M\mathbf{H}\cdot d\mathbf{B}$$
$$-\tfrac{1}{2}V_M H^2 d\mu_M\ . \quad \text{(A14)}$$

Equation (A14), which has the form of Eq. (A8), can be transformed into that of Eq. (A9) if V_M and μ_M are held constant. The result is

$$dU(H)=TdS-PdV+\zeta dN-V_M\mathbf{B}\cdot d\mathbf{H}\ , \quad \text{(A15)}$$

where $U(H)=U-V_M\mathbf{H}\cdot\mathbf{B}$.

Application of Eq. (A12) in conjunction with Eq. (A15) gives

$$\left[\frac{\partial T}{\partial H}\right]_{S,V,N}=-\left[\frac{\partial(V_M B)}{\partial S}\right]_{H,V,N}\ . \quad \text{(A16)}$$

Since $\mathbf{B}=\mu_0(\mathbf{H}+\mathbf{M})$ and $\mathbf{H}$ is fixed it follows that

$$\left[\frac{\partial(V_M B)}{\partial S}\right]_{H,V,N}=\mu_0\left[\frac{\partial I_M}{\partial S}\right]_{H,V,N}, \tag{A17}$$

where $\mathbf{I}_M=V_M\mathbf{M}$ is the magnetic moment of the material in V_M.

Combining Eqs. (A16) and (A17) yields

$$\left[\frac{\partial T}{\partial H}\right]_{S,V,N}=-\mu_0\left[\frac{\partial I_M}{\partial S}\right]_{H,V,N}, \quad V_M=\text{const}, \quad \mu_M=\text{const}. \tag{A18}$$

Similarly, using the enthalpy [i.e., replacing in Eq. (A15) $-PdV$ by VdP], one obtains

$$\left[\frac{\partial T}{\partial H}\right]_{S,P,N}=-\mu_0\left[\frac{\partial I_M}{\partial S}\right]_{H,P,N}. \tag{A19}$$

Equation (A19) is known [6] for its use in the analysis of the magnetocaloric effect. However, here it is derived from the general theory. This is done by first specifying field-related variables that must be held constant (i.e., in the general equation) and then applying a Legendre transformation from which the required Maxwell relation is obtained.

APPENDIX B: ANALYSIS OF A MAGNETIC FIELD SYSTEM

Figure 5 shows a magnetic field system [7] consisting of a circuit with a fixed structure (i.e., core) and a plunger. The variables of this system are as follows: the current i, which is forced through the n turns windings and the width of the air gap, x, between the plunger and the central leg of the core. This system is characterized by the following equations [7]:

$$H_1=H_2=\frac{ni}{g+x}, \tag{B1}$$

$$\lambda=L(x)i, \tag{B2}$$

$$L(x)=\frac{a\mu n^2}{g+x}, \tag{B3}$$

$$v=\frac{a\mu n^2}{g+x}\frac{di}{dt}-\frac{a\mu n^2 i}{(g+x)^2}\frac{dx}{dt}, \tag{B4}$$

where

$$a=2wd' \tag{B5}$$

denotes the cross-sectional area of the plunger, which is $2w$ wide and d' long, i.e., perpendicular to the plane of Fig. 5. The permeability μ is the same in the gap and in the sleeves. H_1 and H_2 are the field intensities in the gap of the right-hand side sleeve and between the plunger and the central leg of the core, respectively, λ is the flux linkage through the windings, $L(x)$ is the inductance of the circuit and v is voltage across the terminals. Note that the field in the left-hand side sleeve is $-H_1$.

The core and the plunger are made from the same highly permeable material that is considered here to be practically infinite, so that the field intensity and hence also the energy stored there vanish. The magnetic energy of this system is

$$U_M=\frac{1}{2}L(x)i^2=\frac{1}{2}\frac{\lambda^2}{L(x)}. \tag{B6}$$

Next we define the magnetic chemical potential at fixed μ and different constraints. The permeability is held fixed by changing the amount of matter with x, at fixed temperature T, so that the density ρ_M and consequently, $\mu=\mu(\rho_M,T)$ are invariable.

1. Fixed λ

In this case $B_2=\lambda/(an)$ and $H_2=B_2/\mu$ are also fixed

$$\zeta_{\mathbf{B}_2,V}=(\partial U_M/\partial N_M)_{\lambda,V}, \tag{B7}$$

$$(\partial U_M/\partial N_M)_{\lambda,V}=(\partial U_M/\partial x)_{\lambda,V}/(\partial N_M/\partial x)_{\lambda,V}, \tag{B8}$$

$$(\partial U_M/\partial x)_{\lambda,V}=-\frac{1}{2}i^2\frac{\partial L(x)}{\partial x}, \tag{B9}$$

$$(\partial N_M/\partial x)_{\lambda,V}=a\rho_M. \tag{B10}$$

Note that here V denotes the volume enclosing the whole magnetic circuit. This volume includes that of the gap, i.e., $V_e=ax$. Thus the mass filling the gap at fixed density and temperature can be varied, while holding V fixed.

Differentiating Eq. (B3), substituting the result in Eq. (B9) and combining Eqs. (B7)–(B10), in conjunction with Eq. (B1), gives

$$\zeta_{\mathbf{B}_2,V}=\frac{\mu}{2\rho_M}H_2^2. \tag{B11}$$

The same result applies at fixed $\mathbf{H}_2$ and variable x, since μ of the added matter is also fixed. However, at fixed $\mathbf{B}_2$ and x, i.e., holding the plunger fixed in position as matter is added into an empty gap, the sign of the chemical potential reverses so that $\zeta_{\mathbf{B}_2,x}=-\zeta_{\mathbf{B}_2,V}$.

2. Fixed i

In this case

$$(\partial U_M/\partial x)_i=\frac{1}{2}i^2\frac{\partial L(x)}{\partial x}$$

and the corresponding magnetic chemical potential is obtained as

$$\zeta_{i,V}=(\partial U_M/\partial N_M)_i=-\frac{\mu}{2\rho_M}H_2^2. \tag{B12}$$

It follows that

$$(\partial U_M/\partial N_M)_\lambda+(\partial U_M/\partial N_M)_i=\zeta_{\mathbf{B}_2,V}+\zeta_{i,V}=0 \tag{B13}$$

and

$$\zeta_{i,V}=\zeta_{\mathbf{B}_2,x}.$$

Note that the magnetic chemical potential functions given by Eqs. (B11) and (B12) are for the field that exists outside its source material but is defined as part of the system. Had we chosen the core and the plunger as our system, i.e., excluding the gaps, the results would have

remained the same. This is due to the fact that the field in the gaps pertains to its source, which is the core and plunger system, irrespective of this field being outside its boundaries.

3. Fixed U_M

In this case, differentiating Eq. (B6) followed by rearrangement of terms gives

$$\frac{\partial \ln L(x)}{\partial x} = -\frac{2}{i}\frac{\partial i}{\partial x} . \tag{B14}$$

Since U_M is held fixed as mass enters or leaves the system, the magnetic chemical potential vanishes:

$$\zeta_{U_M,V} = (\partial U_M/\partial N_M)_{U_M} = 0 . \tag{B15}$$

The different constraints imposed on the system affect the proportion of work delivered to the mechanical work source by the current source and by the field, and whether the field delivers or gains energy. In what follows the work delivered by the current source is considered.

4. Work delivered by the current source

The work done at the terminals in a time differential dt is obtained from Eq. (B4) as

$$dW(i,x) = vidt = \frac{1}{2}L(x)di^2 - \mu a n^2 i^2 \frac{dx}{(g+x)^2} . \tag{B16}$$

5. Fixed λ

In this case $i = \lambda/L(x)$ and hence by virtue of

$$di = -\frac{\lambda}{[L(x)]^2}\frac{\partial L(x)}{\partial x}dx = \frac{\lambda}{a\mu_0 n^2}dx , \tag{B17}$$

we obtain

$$dW_\lambda(i,x) = \lambda di - a\mu H_2^2 dx = \lambda di - \frac{\lambda^2}{a\mu_0 n^2}dx = 0 . \tag{B18}$$

Thus, as expected, at fixed λ no work is delivered by the current source and energy exchange can only take place between the field and the mechanical work source.

6. Fixed i

In this case

$$dW_i(i,x) = -\mu a H_2^2 dx . \tag{B19}$$

Hence, using Eq. (B10) gives

$$dW_i(i,x) = -\frac{\mu}{\rho_M}H_2^2 dN_M , \tag{B20}$$

$$[\partial W(i,x)/\partial N_M]_i = -\frac{\mu}{\rho_M}H_2^2 = 2\zeta_{i,V} . \tag{B21}$$

It follows that at fixed i, the work delivered by the current source (i.e., as x decreases at fixed i) splits equally between the field and the mechanical work source. Note that when the mechanical work source is disconnected from the plunger, the excess energy that remains in the system due to the added mass can be recovered by turning the current off.

7. Fixed U_M

In this case, combining Eqs. (B10), (B14), and (B16) gives

$$dW_{U_M}(i,x) = -\frac{\mu}{2\rho_M}H_2^2 dN_M , \tag{B22}$$

$$[\partial W(i,x)/\partial N_M]_{U_M} = -\frac{\mu}{2\rho_M}H_2^2 . \tag{B23}$$

Thus, as mass is withdrawn from the gap, at fixed U_M, the current source delivers work to the mechanical work source (e.g., the one connected to this mass) with the field acting as a transmission agent only, i.e., with no change in its own energy. If the electric energy of the current source is U_e, then

$$(\partial U_e/\partial N_M)_{U_M} = -[\partial W(i,x)/\partial N_M]U_M = \frac{\mu}{2\rho_M}H_2^2 . \tag{B24}$$

Equation (B24) facilitates the definition of the following electromagnetic chemical potential:

$$\zeta_{U_{EM},V} = \frac{\mu}{2\rho_M}H_2^2 . \tag{B25}$$

This chemical potential is defined with respect to the system coupled with the current source, or simply with respect to the current source. Thus, at fixed U_M, the magnetic chemical potential with respect to the system vanishes, but the one with respect to the current source is positive and equal to that prevailing at fixed λ.

The results obtained here verify that the rate of change of the work delivered to the mechanical work source with mass is $(\mu/2\rho_M)H_2^2$. This is true irrespective of this work being delivered by the current source or by the field.

[1] Y. Zimmels, Phys. Rev. E **52**, 1452 (1995).
[2] L. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media,* 2nd ed. (Pergamon, Oxford, 1984).
[3] E. A. Guggenheim, *Thermodynamics, An Advanced Treatment for Chemists and Physicists* (North-Holland, Amsterdam, 1967).
[4] M. Zahn, *Electromagnetic Field Theory, a Problem Solving Approach* (Krieger, Malabar, FL, 1987), reprint edition.
[5] H. A. Haus and J. R. Melcher, *Electromagnetic Fields and Energy* (Prentice-Hall, Englewood Cliffs, NJ, 1989).
[6] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).
[7] H. H. Woodson and J. R. Melcher, *Electromechanical Dynamics, Pt. 1: Discrete Systems* (Krieger, Malabar, FL, 1968).