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Storage of electromagnetic field energy in matter

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Abstract. The partitioning, uniqueness and form of field energy stored in matter, and its properties as a state function, is established. Consequently, the first and second laws apply to the nonfield and field parts of the internal energy as separate entities. This provides a bridge between thermodynamics and the classical theory of electromagnetism. Presentation of the temperature as the sum of nonfield and field contributions is used to establish field dependent barriers to temperature decrease toward the absolute zero, and the existence of field induced temperature jumps. These temperature jumps appear at the instant the field is switched on, or turned off. The partitioning of field and nonfield energies is illustrated for a specific case of an ideal gas, and the heat absorbed by the field is derived in terms of difference in adiabatic magnetization. Finally, the current, restrictive, form of electromagnetic field energy density is redefined with respect to the effect of field energy stored outside the system boundaries.

PACS. 05.70.-a Thermodynamics – 05.70.Ce Thermodynamic functions and equations of state – 05.90.+m Other topics in statistical physics, thermodynamics, and nonlinear dynamical systems

The establishment of electromagnetic field energy, stored in matter, as internal energy and a state function, which is partitioned from its nonfield counterpart, is of fundamental consequence regarding polarizable and nonuniform systems. Once the form of this energy is determined, then its thermodynamic and related electromagnetic properties are known. The partitioning between nonfield and field components, of the internal energy, warrants the application of the first and second law to each one of them as separate entities, with unique contributions to thermodynamic and field variables characterizing the system (see Appendix A). The process of energy storage in polarizable matter can be treated in the context of thermodynamics in the presence of fields [1–3]. Nevertheless, the effect of field induced changes in temperature, and the exact form of the stored field energy, are not yet known. For example, in adiabatic magnetization, a long standing fundamental problem relates to the effect of a field induced change in temperature on the polarizability and field energy of the system. The question is whether the stored energy is path dependent. This work sets to bridge the gap between the classic theories of thermodynamics and electromagnetism, by establishing the form, uniqueness, and fundamental consequences of field energy stored in matter.

Uniqueness of field energy: the sources of electric, magnetic, and gravitational fields are charges, currents, and masses, respectively. If all charges, currents and masses are specified in space and time, then fields produced by their presence [4] are readily shown to be unique. This is true irrespective of the process, whereby these field generating entities reach their final positions in space and time, and the systems to which they are assigned, *e.g.*, being part of polarizable matter or an independent source. Consequently, there exist, for each field, a function that is determined by the state of the field, *e.g.*, as uniquely expressed by the value of the field variables. This means that in the presence of fields, the internal energy of a system comprises nonfield and field energies that are both state functions.

Uniform magnetic fields: in what follows, we consider conservative, lossless systems that do not include hysteresis, generation of heat, or permanent magnetization. The quasistatic work W_e delivered by a current source of a quasistatic magnetic field, is given by,

$$W_e = \int_\lambda i\mathrm{d}\lambda = \int_{V'} \int_0^{\mathbf{B}} \mathbf{H}\cdot\mathrm{d}\mathbf{B}\delta\mathbf{V}, \quad \mathbf{B} = \mu\mathbf{H} \qquad (1)$$

where $\mathbf{H}$, $\mathbf{B}$, δV, V', i, λ, and μ denote field strength, magnetic induction, infinitesimal volume element, space occupied by the field, current, flux linked by i, and permeability, respectively. In general, V' stands for all space and μ is a function of temperature, density and the field, or alternatively of the fundamental set (defined later): entropy, volume, mass and the field $\mathbf{B}$. It follows that the effect of temperature on W_e is through the permeability of the matter being magnetized. If, as a special case, the field is uniform and confined to a fixed volume V (for example a thin gap between the poles of a yoke magnet,

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where $\mathbf{H} = 0$ except for the gap) then,

$$\mathrm{d}W_e = V\mathbf{H}\cdot\mathrm{d}\mathbf{B}, \qquad W_e = V\int_0^{\mathbf{B}} \mathbf{H}\cdot\mathrm{d}\mathbf{B}. \tag{2}$$

Note that if W_e is delivered subject to the constraint that no heat transfer across the system boundaries or their displacement is allowed, then by virtue of the first law, W_e is transformed (see Appendix A) into energy that can be stored and retrieved exclusively by field interactions. In this respect, this energy can be defined as field energy. However, if the above constraints are not satisfied, as is the case with lossy and electromechanical systems, the work W_e produces energy forms that are different than the one stored by the field.

As equation (1) depends exclusively on field variables, which are integrated over all space, it holds irrespective of the distribution of matter, and the corresponding permeability, in the integration space. This includes the phenomenon of magnetostriction and the change of density due to expansion of matter as the field is changed. In this context and as discussed in the sequel, integration of $\mathbf{H}\cdot\mathrm{d}(\mathbf{B}/\rho)$ (defined as magnetic work per unit mass [1,5,6]) over a mass that is the source of a field outside its own boundaries, does not account for its energy which is stored over all space. Consequently, as this integration does not always agree with equation (1), $\mathbf{H}\cdot\mathrm{d}(\mathbf{B}/\rho)$ cannot be defined, *e.g.* in a general sense, as the magnetic work per unit mass. The proof is straightforward. Integration of $\int_0^{\mathbf{B}}\mathbf{H}\cdot\mathrm{d}(\mathbf{B}/\rho)$ over the mass m gives $\int_m\int_0^{\mathbf{B}}\mathbf{H}\cdot\mathrm{d}(\mathbf{B}/\rho)\mathrm{d}m$. This equation must hold at fixed ρ, so that integration over a fixed mass, with $\mathrm{d}m = \rho\mathrm{d}V$, gives $\int_V\int\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V$. This result differs from equation (1). Here the integration volume is $V = \rho m$, whereas in equation (1), it is all space V'. It follows that the term $\mathbf{H}\cdot\mathrm{d}(\mathbf{B}/\rho)$ does not fulfill the requirement from a magnetic work term per unit mass.

An example of how $\mathrm{d}W_e$ produces terms of field energy storage, electromechanical work and heat, in the context of the first law, is given in Appendix B.

In the presence of the field the temperature [5], denoted by $\hat{T}$, is related to that in its absence $T = \hat{T}(\mathbf{B} = 0)$ by,

$$\begin{aligned}
\hat{T} &= \left(\frac{\partial\hat{U}}{\partial S}\right)_{V,N,\mathbf{B}} = T + \left(\frac{\partial U_M}{\partial S}\right)_{V,N,\mathbf{B}},\\
T &= \left(\frac{\partial U}{\partial S}\right)_{V,N} && (3)\\
\hat{U} &= \hat{U}(S,V,N,\mathbf{B}) = U + U_M\\
U &= \hat{U}(S,V,N,\mathbf{B}=0) = U(S,V,N),\\
U_M &= U_M(S,V,N,\mathbf{B}) && (4)
\end{aligned}$$

where $\hat{U}$, U_M, U, S, V, and N denote internal energy in the presence of the field, energy stored in the magnetic field, nonfield internal energy, nonfield entropy (see its definition below), volume, and mass, respectively. Details on definition of independent variables and related energies are given in Appendix A. Note that establishing U_M as a state function facilitates the application of the first and second law to the stored field energy, see Appendix A.

Equations (3, 4) can be derived as follows: in the absence of fields, the internal energy U of a homogeneous and uniform system is a function of S, V and N. As both U and S are defined in the absence of fields, they are nonfield variables. At fixed S, V, and N, U is invariable as the field $\mathbf{B}$ is increased quasistatically from $\mathbf{B} = 0$ to a finite final value. Furthermore, the imposition of fixed S, V and N means that the increase in $\mathbf{B}$ is done adiabatically (*i.e.* in the sense that only electromagnetic power and no heat flows across the system boundaries) with no mechanical interactions between the system (kept at fixed shape) and its surroundings. Under these conditions and by virtue of the first law, the work done in magnetizing the system is stored as an additional internal energy U_M

$$U_M = \int_{V'}\int_0^{\mathbf{B}}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V, \qquad \text{fixed} \quad S,\,V,\,N \tag{5}$$

where the condition of fixed S, V, N imposes a single unique integration path of $\mathbf{B}$. At the final level of $\mathbf{B}$, the internal energy of the system, being denoted by $\hat{U}$, is

$$\hat{U} = U + U_M. \tag{6}$$

Note that as both U and U_M are state functions, they can be evaluated also along other paths. However, such alternative paths may be more complicated.

The value of U_M depends on the levels of S, V, N at which equation (5) is evaluated. This reflects the dependence of U_M on the permeability, which is a function of the temperature $T = T(S,V,N)$, density $\rho = N/V$ and $\mathbf{B}$. This gives $\mu = \mu(T,\rho,\mathbf{B}) = \mu(S,V,N,\mathbf{B})$. Consequently U_M is a function of the set S, V, N, $\mathbf{B}$, which comprises four independent variables. It follows that similar to the presentation of $\mathrm{d}U(S,V,N)$ as

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \zeta\mathrm{d}N \tag{7}$$

the functional dependence of $\mathrm{d}U_M$, on the set S, V, N, $\mathbf{B}$ can be expressed as,

$$\mathrm{d}U_M = T_M\mathrm{d}S - p_M\mathrm{d}V + \zeta_M\mathrm{d}N + \left(\frac{\partial U_M}{\partial\mathbf{B}}\right)_{S,V,N}\mathrm{d}\mathbf{B}. \tag{8}$$

Differentiation of equation (6) in conjunction with equations (7, 8), and using $(\partial U_M/\partial\mathbf{B})_{S,V,N}\mathrm{d}\mathbf{B} = \int_{V'}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V$, gives

$$\mathrm{d}\hat{U} = \hat{T}\mathrm{d}S - \hat{p}\mathrm{d}V + \hat{\zeta}\mathrm{d}N + \int_{V'}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V \tag{9}$$

where $\hat{T} = T + T_M$, $\hat{p} = p + p_M$, $\hat{\zeta} = \zeta + \zeta_M$ are temperature, pressure and chemical potential, which are functions of the set S, V, N, $\mathbf{B}$. The volume differential, $\mathrm{d}V$, is used in two different ways: as change in the system's volume in $\hat{p}\mathrm{d}V$, and as an integration variable in the integral term of equations (9, 5). Note that T, p and ζ and T_M, p_M and ζ_M (see their definitions in Eqs. (11, 12)) are the nonfield and field components of $\hat{T}$, $\hat{p}$ and $\hat{\zeta}$, and in this work "fixed V" means that the volume is fixed with respect to both size and shape. The question, what is the magnetic work term, can now be resolved by analysis of equation (8) in the context of the first law, see Appendix A for proof of applicability of the first law to U, U_M and $\hat{U}$.

Similar to the definition of the heat differential as $\mathrm{d}Q = T\mathrm{d}S$ in the absence of fields, the magnetic heat differential is defined as $\mathrm{d}Q_M = T_M\mathrm{d}S$. The next three terms in equation (8), which are not associated with the change of S, are readily identified as work terms. Hence their sum is the long sought magnetic work term. It follows that

$$\mathrm{d}U_M = \mathrm{d}Q_M + \mathrm{d}W_M \tag{10}$$

$$\mathrm{d}Q_M = T_M\mathrm{d}S \tag{11}$$

$$\mathrm{d}W_M = -p_M\mathrm{d}V + \zeta_M\mathrm{d}N + \int_{V'} \mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V \tag{12}$$

where

$$T_M = \left(\frac{\partial U_M}{\partial S}\right)_{V,N,\mathbf{B}},$$
$$-p_M = \left(\frac{\partial U_M}{\partial V}\right)_{S,N,\mathbf{B}},$$
$$\zeta_M = \left(\frac{\partial U_M}{\partial N}\right)_{S,V,\mathbf{B}},$$

and $\mathrm{d}\mathbf{B}$ is constrained to a path of fixed S, V, N. Recall that U_M is a state function, so that other paths for evaluation of $\mathrm{d}Q_M$ and $\mathrm{d}W_M$ are equally valid. However, they may be more complicated.

Equations (3, 4) are a direct consequence of equations (6–9), and the definition given for T_M in equation (11).

Equation (12) shows that the general magnetic work term consists of three terms. Consequently, the use of the third integral term, as the complete magnetic work term (as often encountered in literature) is justified only at fixed S, V, and N. Otherwise the effect of the other two terms must be accounted for. Note that if the integral term is evaluated only at variable S, V, and N, then $\mathrm{d}\mathbf{B}$ can be expanded in terms of these three variables, in contrast to the declared independence of all variables in the set S, V, N and $\mathbf{B}$.

A fundamental problem is to determine U_M. By virtue of the first law, and excluding nonfield interactions, U_M can be evaluated as the adiabatic magnetization work. Therefore, the problem is how to calculate this work. Being a state function U_M can be evaluated along any path that leads to the state defined by the set $\{S, V, N, \mathbf{B}\}$. As this set consists of four independent variables, an adiabatic path at fixed S, V, N, that sets U fixed, is selected to this end. This path, being free from the effect of changes in nonfield variables on the magnetization process, involves an adiabatic field induced change in T_M, which translates to a change in the temperature $\hat{T}$. The question is, if the effect of this change on the permeability, and in turn on U_M, is significant.

In isothermal magnetization of linear matter at fixed density, integration of equation (2) (holding the permeability μ fixed) yields $W_e = (1/2)VB^2/\mu$. As U_M is defined in an adiabatic rather than isothermal process (Eq. (5)), the question is whether $W_e = (1/2)VB^2/\mu$ can be used as a good estimate for U_M. The purpose of the following analysis is to show that for linear matter, the deviation of U_M from W_e is negligibly small. Assuming that indeed this is the case, it is beneficial to maintain the form of W_e in the analysis of U_M.

The permeability (at room temperature) of linear matter, such as paramagnetic compounds, is a monotonic decreasing function of temperature. A well-known example are materials that follow the Langevin equation

$$\mathbf{M} = \mathbf{M}_s[\coth a - 1/a],$$
$$\mathbf{M}_s = N\mathbf{m},\ a = \mu_0\mathbf{m}\cdot\mathbf{H}_0/kT \tag{13}$$

where $\mathbf{M}$, $\mathbf{M}_s$, N, $\mathbf{m}$, μ_0, $\mathbf{H}_0$ and k denote magnetization, saturation magnetization, number of dipoles per unit volume, dipole moment, permeability of free space, field strength, and Boltzmann's constant, respectively. At room temperature, a is typically small $a \ll 1$, so that in this limiting case, $\mathbf{M}$ reduces to

$$\mathbf{M} = \frac{\mu_0 m^2 N}{3kT}\mathbf{H}. \tag{14}$$

In this case,

$$\mu = \mu_0\left(1 + \frac{\mu_0 m^2 N}{3kT}\right), \quad a \ll 1. \tag{15}$$

Equation (15) was derived using the temperature as a given variable. The question is whether the Boltzmann statistics holds in the presence of fields was not yet addressed, and is outside the scope of this work. If it does, then the temperature must be $\hat{T}$, where $\hat{T} = T + T_M$. If however, it holds only for the nonfield part of $\hat{T}$, then the use of T is justified. In the latter case, μ is not a function of T_M, so that it is invariable in adiabatic magnetization, where T is fixed and $\hat{T}$ changes with $\mathbf{B}$ *via* T_M. We shall consider the implication of the case where $\hat{T}$ applies instead of T in equation (15). In this case, the susceptibility can be presented as $\chi = K(\rho)/\hat{T}$, $K(\rho) = \mu_0 m^2 N/3k$.

As shown in Appendix C, U_M of linear matter can be presented in the same form of W_e as,

$$U_M = \frac{1}{2}VB^2/\mu(\overline{B}), \tag{16}$$

where the dependence of μ on B is exclusively *via* the temperature $\hat{T} = \hat{T}(B)$, $\overline{B}$ and $\mu(\overline{B})$ denote intermediate values of the field between 0 and B and of the permeability between $\mu(B = 0)$ and $\mu(B)$, the field is assumed uniform within V, and no energy is stored outside V (for example by enclosing the system with infinitely permeable matter).

If the permeability is a monotonic decreasing function of temperature, and the temperature rises in adiabatic magnetization of a linearly permeable material, then

$$\frac{1}{2}VB^2/\mu(B=0) < U_M < \frac{1}{2}VB^2/\mu(B). \tag{17}$$

Hence, holding S, V and N fixed in adiabatic magnetization of permeable linear matter, the maximum range of U_M depends on $1/\mu(B) - 1/\mu(B=0)$.

Using $\mu = \mu_0(1+\chi)$, $\chi = K(\rho)/\hat{T}$ gives

$$1/\mu(B) - 1/\mu(B=0) = \left(\frac{\mu_0 K(\rho)}{\mu(B)\mu(B=0)}\right)\left(\frac{\hat{T}(B)-\hat{T}(B=0)}{\hat{T}(B)\hat{T}(B=0)}\right) \tag{18}$$

where $K(\rho)$ is a sole function of density, and use was made of the fact that at fixed S, V, N, $\hat{T} = \hat{T}(S, V, N, \mathbf{B}) = \hat{T}(\mathbf{B})$, and $\rho = N/V$ is also fixed.

Note that the dependence of χ, and hence, also μ, on $\mathbf{B}$ is through the field dependent temperature $\hat{T} = \hat{T}(\mathbf{B})$.

We continue to focus the discussion on linear materials, which are characterized by fixed permeability in isothermal and isodensity magnetization, whose magnetic energy follows equation (16). Nonlinear matter, such as ferromagnetic substances are discussed later in a different context. The susceptibility, χ, of paramagnetic materials is ordinarily less than 10^{-4}. Hence, $\mu(B)$ and $\mu(B=0)$ are $O(\mu_0)$ so that $\mu(B)\ \mu(B=0) = O(\mu_0^2)$. Recall that here $\mu(B)$ means $\mu[\hat{T}(B)]$ in adiabatic magnetization and not field dependent permeability, as is the case with ferromagnetic materials. In the range of available fields, and as is known from low temperature physics, the change in temperature due to a change of the field, from 0 to B, is expected to be less than 1 K so that at $\hat{T} > 100$ K,

$$\frac{\hat{T}(B)-\hat{T}(B=0)}{\hat{T}(B)} \quad \text{is} \quad O(10^{-2}) \quad \text{or less.}$$

It follows that $1/\mu(B) - 1/\mu(B=0)$ is $O(10^{-6})/O(\mu_0)$, and the relative change *e.g.*,

$$[1/\mu(B) - 1/\mu(B=0)]/[1/\mu(B)],$$
$$\text{is } [O(10^{-6})/O(\mu_0)]/[1/O(\mu_0)] = O(10^{-6}).$$

In the range $\hat{T} > 1$ K, the result is $O(10^{-4})$. This shows that the effect of change of the field on U_M, in adiabatic magnetization, *e.g.*, *via* the change in $\hat{T}$ of permeable linear matter, can be neglected, provided that $\hat{T}$ does not approach the absolute zero. Thus, within this margin of error, it is justified to use a fixed permeability for evaluation of U_M, in adiabatic magnetization.

Hence, assuming that μ is fixed, subject to the negligible error mentioned above, the field energy and the temperature are readily obtained as

$$U_M = W_e = \frac{1}{2}V\mathbf{H}\cdot\mathbf{B} = \frac{1}{2}VB^2/\mu \tag{19}$$

$$\hat{T} = T - \frac{1}{2\rho}H^2\left(\frac{\partial\mu}{\partial s}\right)_{V,N,\mathbf{B}},\ s = S/N,\ \rho = N/V. \tag{20}$$

Equations (3, 20) describe the field dependent temperature $\hat{T}$ in terms of two parts, the field independent part T that arises due to nonfield energy, and the part that exists exclusively due to the presence of the field and its stored energy. This is in accordance with the partition of $\hat{U}$ into the field and nonfield parts, U_M and U, respectively. If $(\partial\mu/\partial s)_{V,N,\mathbf{B}} < 0$ as expected from paramagnetic materials (such as permeable ideal monatomic gases), then $\hat{T} \geq \hat{T}(\mathbf{B}=0) = T$.

Monoatomic gases that follow the Langevin equation provide a simple example of the properties of $(\partial\mu/\partial s)_{V,N,\mathbf{B}}$. In this case [5], $(\partial s/\partial T)_{V,N,\mathbf{B}} = 3R/2T$. Hence [5] using

$$(\partial\mu/\partial s)_{V,N,\mathbf{B}} = (\partial\mu/\partial T)_{V,N,\mathbf{B}}/(\partial s/\partial T)_{V,N,\mathbf{B}},$$

$\mu = \mu_0(1+\chi)$, and $\chi = K(\rho)/\hat{T}$, $K(\rho) = (1/3)\mu_0\mathbf{M}_s\cdot\mathbf{m}/k$ gives

$$\begin{aligned}(\partial\mu/\partial s)_{V,N,\mathbf{B}} &= -(2\mu_0 K(\rho)/3R)/\hat{T}\\ &= -2(\mu-\mu_0)/(3R)\end{aligned} \tag{21}$$

where, as before, $\mathbf{M}_s$ denotes saturation magnetization, $\mathbf{m}$ is the dipole moment of a single molecule and k the Boltzmann's constant. Paramagnetic gases are characterized by $\mu - \mu_0 > 0$, so that $(\partial\mu/\partial s)_{V,N,\mathbf{B}} < 0$ holds. Note that the imposition of a fixed $\mathbf{B}$ does not affect the result, as in this case, V and N can be varied independently of the field.

The physical meaning of equations (3, 20) can be illustrated by an example of heat delivered reversibly, at $\hat{T}$, by a heat reservoir, to the system at fixed V, N, and $\mathbf{B}$. Assuming the surface that links the flux is fixed in position, orientation and shape, a fixed $\mathbf{B}$ implies that λ is fixed, so that no energy exchange between the system and the current sources is allowed. In this case,

$$\mathrm{d}\hat{Q}_{\text{rev}} = \hat{T}\,\mathrm{d}S, \quad \text{fixed} \quad V, N, \mathbf{B}. \tag{22}$$

Combining equations (3, 22) gives,

$$\mathrm{d}\hat{Q}_{\text{rev}} = T\,\mathrm{d}S + \left(\frac{\partial U_M}{\partial S}\right)_{V,N,\mathbf{B}}\mathrm{d}S,\ \text{fixed } V, N, \mathbf{B}. \tag{23}$$

Equation (23) shows that $\mathrm{d}\hat{Q}_{\text{rev}}$ is divided into nonfield, $\mathrm{d}Q_{\text{rev}} = T\,\mathrm{d}S$, and field,

$$\mathrm{d}Q_M = \left(\frac{\partial U_M}{\partial S}\right)_{V,N,\mathbf{B}}\mathrm{d}S = T_M\mathrm{d}S,$$

heat flows. The part $\mathrm{d}Q_{\text{rev}}$ is the well-known reversible nonfield heat flow that prevails in the absence of the field, and $\mathrm{d}Q_M$ is the reversible heat flow taken up as field energy. Note that $\mathrm{d}Q_M = T_M\mathrm{d}S$ is the field counterpart of $\mathrm{d}Q_{\text{rev}} = T\mathrm{d}S$, and as the latter is reversible so must the former be.

Removal of the field produces different results, depending on the constraints set on the system. Isothermal ($\hat{T}$ constant) decrease in the field strength, changes T at fixed

$\hat{T}$. Heat, $\hat{T}\mathrm{d}S$, flows into the system, and at the end of the process $\mathbf{B} = 0$, and $\hat{T} = T$. Adiabatic decrease in the field strength, changes $\hat{T}$ at fixed T. At the end of the process $\mathbf{B} = 0$, and $\hat{T} = T$. Thus, if at the outset (for $\mathbf{B} > 0$) $\hat{T} > T$, then in an isothermal demagnetization of permeable matter, T increases to the level set by the heat reservoir, whereas in adiabatic demagnetization, $\hat{T}$ decreases to the level T, see equation (20), at $H = 0$. The adiabatic effect can be obtained, either by insulating the system, prior to the change in field strength, or by adjusting a fast rate of change of the field at a level that is high enough to secure a negligible heat flow in the time interval where the field decreases to zero. This fast removal of the field produces an effect of adiabatic temperature jump $\hat{T} > T$, across the diathermal wall separating the system from the heat reservoir. This jump becomes the driving force for subsequent irreversible heat flow, that can last a prolonged time at $\mathbf{B} = 0$. As $T \geq 0$ holds in the absence as well as in the presence of the field, equations (3, 20) show that, for permeable matter, the temperature $\hat{T}$ must satisfy the following inequalities,

$$\hat{T} \geq \left(\frac{\partial U_M}{\partial S}\right)_{V,N,\mathbf{B}},$$
$$\hat{T} \geq -\frac{1}{2\rho}H^2\left(\frac{\partial \mu}{\partial s}\right)_{V,N,\mathbf{B}} \quad \text{for linear permeable matter.} \tag{24}$$

This sets a barrier for decrease of the temperature of permeable matter toward the absolute zero, in the presence of a magnetic field. Note that the case of polarization by an electric field, is obtained by replacing the set $\{\mu, \mathbf{H}, \mathbf{B}\}$ by the set $\{\varepsilon, \mathbf{E}, \mathbf{D}\}$, and the subscript M by P_e, where ε, $\mathbf{E}$, and $\mathbf{D}$, are electric permitivity, field strength, and displacement, respectively, and P_e denotes polarization.

Thus, the temperature of permeable matter, in the simultaneous presence of quasistatic electric and magnetic fields must satisfy the following relation,

$$\hat{T} \geq \left(\frac{\partial U_M}{\partial S}\right)_{V,N,\mathbf{B}} + \left(\frac{\partial U_{P_e}}{\partial S}\right)_{V,N,\mathbf{D}} \cdot \tag{25}$$

The right-hand-side of equation (25) stands for the barrier set by the presence of the fields for further decrease of the temperature toward the absolute zero. This barrier is defined as the lower limit of the temperature $\hat{T}$.

Energy stored in monatomic ideal gas: the internal energy of a monatomic ideal gas, in the absence of the field, is given by,

$$U = \frac{3}{2}NRT, \quad \mathbf{B} = 0 \tag{26}$$

where R is the gas constant.

Combining equations (20, 26) gives,

$$U = \frac{3}{2}NR\left[\hat{T} + \frac{1}{2\rho}H^2\left(\frac{\partial \mu}{\partial s}\right)_{\rho,\mathbf{B}}\right] \cdot \tag{27}$$

Equation (27) facilitates the evaluation of U (the field independent part of $\hat{U}$) in terms of the measurable temperature $\hat{T}$ and field $\mathbf{H}$, prevailing in the system when the field is on. In this context, recalling that the expression in brackets is equal to the field independent T, it remains invariable for $\mathbf{B} \geq 0$, at fixed S, V and N.

Combining equations (6, 19, 27) gives,

$$\hat{U} = \frac{3}{2}NR\left[\hat{T} + \frac{1}{2\rho}H^2\left(\frac{\partial \mu}{\partial s}\right)_{\rho,\mathbf{B}}\right] + \frac{1}{2}VB^2/\mu,$$
$$\mathbf{H} = \mathbf{B}/\mu. \tag{28}$$

Equation (28) expresses $\hat{U}$, in terms of measurable field dependent variables, that characterize the system when the field is on.

Recalling that the monatomic gas is ideal with linear magnetization, gives

$$\frac{1}{2\rho}H^2\left(\frac{\partial \mu}{\partial s}\right)_{\rho,\mathbf{B}} = -\frac{1}{3\rho R}(\mu - \mu_0)H^2 = -\frac{1}{3\rho R}\mu_0\mathbf{H}\cdot\mathbf{M},$$
$$\mu_0\mathbf{M} = (\mu - \mu_0)\mathbf{H}. \tag{29}$$

Equation (29) can be used to estimate levels of $T_M = -(1/2\rho)H^2(\partial\mu/\partial s)_{V,N,\mathbf{B}}$, that can be expected from ideal paramagnetic gases. Substitution of $\mu - \mu_0 = \mu_0\chi$ in equation (29) gives $T_M = (3\rho R)^{-1}\mu_0\chi H^2$. In order to estimate the order of magnitude expected from T_M, we apply the results obtained for monatomic gases also to oxygen, which is diatomic. In doing so, we assume that magnetic effects due to the internal modes of each molecule are small, compared to those arising from orientation.

For example, the molar susceptibility of oxygen is given by $0.993/T$, being $3\,390 \times 10^{-6}$ at 20 °C [6]. The corresponding volume susceptibility is $\chi = 0.143 \times 10^{-6}$ at 760 mm pressure. Using $\rho = 1.3536$ kg/m^3 = 42.3 mole/m^3, $R = 8.3143$ J mole^{-1} K^{-1}, $\mu_0 = 4\pi \times 10^{-7}$, and field intensity of $(5 \times 10^8)/4\pi$ A m^{-1} (equivalent to $50T$) gives $T_M = 0.270$ K. Thus, notwithstanding the use of an extremely high field intensity, $T_M < 1$ K holds in this example of oxygen.

The significance of T_M increases as the zero absolute temperature is approached. For example, given $\mathrm{d}S$, $\mathrm{d}Q_M/\mathrm{d}Q_{\mathrm{rev}} = T_M/T$ (see the paragraph following Eq. (23)), and using $T_M < 1$ K, $\mathrm{d}Q_M/\mathrm{d}Q_{\mathrm{rev}}$ is expected to be small unless the value of T is constrained to be sufficiently close to the absolute zero.

Combining equations (28, 29) gives,

$$U = \frac{3}{2}NR\hat{T} - \frac{1}{2}\mu_0V\mathbf{H}\cdot\mathbf{M}. \tag{30}$$

Combining equations (6, 19, 30) gives:

$$\hat{U} = U + U_M = \frac{3}{2}NR\hat{T} - \frac{1}{2}\mu_0V\mathbf{H}\cdot\mathbf{M} + \frac{1}{2}V\mathbf{H}\cdot\mathbf{B}$$
$$= \frac{3}{2}NR\hat{T} + \frac{1}{2}\mu_0VH^2.$$

It follows that in isothermal, $\hat{T} = \hat{T}(\mathbf{B} = 0)$, magnetization of an ideal gas,

$$\hat{U} = \hat{U}(\mathbf{B} = 0) + \frac{1}{2}\mu_0 V H^2. \tag{31}$$

Equations (19, 30, 31) show that isothermal magnetization changes the nonfield part of the internal energy U by $-(1/2)\mu_0 V\mathbf{H}\cdot\mathbf{M}$, the field energy U_M by $(1/2)V\mathbf{H}\cdot\mathbf{B}$, and the internal energy $\hat{U}$ by $(1/2)\mu_0 VH^2$.

An example of isothermal compression of an ideal paramagnetic gas, in a uniform and fixed field, follows.

Isothermal compression of an ideal paramagnetic gas in a uniform and fixed B field

An ideal paramagnetic gas that follows the Langevin equation, is compressed isothermally in a uniform and fixed $\mathbf{B}$ field from an initial volume V_0 to a final volume V. It is required to determine:

a. the magnetic heat and work terms of the gas;
b. the change in U_M of the gas;
c. the ratio of the magnetic pressure volume work and heat delivered to the gas holding its mass fixed.

In this case [2,7],

$$P_M = -\frac{1}{2}\mathbf{H}\cdot\mathbf{B} - \frac{1}{2}H^2\rho\left(\frac{\partial\mu}{\partial\rho}\right)_{S,\mathbf{B}}, \quad \rho = N/V \tag{32}$$

$$T_M = -\frac{1}{2\rho}H^2\left(\frac{\partial\mu}{\partial s}\right)_{\rho,\mathbf{B}}, \quad s = S/N \tag{33}$$

$$\zeta_M = -\frac{1}{2}H^2\left(\frac{\partial\mu}{\partial\rho}\right)_{S,V,\mathbf{B}}. \tag{34}$$

a. The heat and work terms, $\mathrm{d}Q_M$ and $\mathrm{d}W_M$, are given by equations (11, 12), respectively.

Hence,

$$\mathrm{d}Q_M = -\frac{1}{2\rho}H^2\left(\frac{\partial\mu}{\partial s}\right)_{\rho,\mathbf{B}}\mathrm{d}S \tag{35}$$

$$\mathrm{d}W_M = \left[\frac{1}{2}\mathbf{H}\cdot\mathbf{B} + \frac{1}{2}H^2\rho\left(\frac{\partial\mu}{\partial\rho}\right)_{S,\mathbf{B}}\right]\mathrm{d}V - \frac{1}{2}H^2\left(\frac{\partial\mu}{\partial\rho}\right)_{S,V,\mathbf{B}}\mathrm{d}N + \int_{V'}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V \tag{36}$$

where the last term on the right-hand-side of equation (36) vanishes at fixed $\mathbf{B}$.

In this case ($\hat{T}$ fixed), the susceptibility is a linear function of density,

$$\mu = \mu_0 + \mu_0\chi, \qquad \mu_0\chi = \kappa\rho \tag{37}$$

where $\kappa = \kappa(\hat{T})$ is a sole function of temperature, or alternatively of S

$$(\partial\mu/\partial\rho)_{S,\mathbf{B}} = \kappa = (\mu - \mu_0)/\rho = \mu_0\,\chi/\rho. \tag{38}$$

Equation (21) reads,

$$(\partial\mu/\partial s)_{\rho,\mathbf{B}} = -2\mu_0\,\chi/3R, \qquad \chi = K(\rho)/\hat{T}. \tag{39}$$

Hence,

$$\mathrm{d}Q_M = \frac{1}{3\rho R}\mu_0\chi H^2\mathrm{d}S \tag{40}$$

$$\mathrm{d}W_M = \left[\frac{1}{2}\mu H^2 + \frac{1}{2}\mu_0\chi H^2\right]\mathrm{d}V - \frac{1}{2\rho}\mu_0\chi H^2\mathrm{d}N, \quad \mathbf{B}\ \text{fixed}. \tag{41}$$

Note that if the system is open and $\mathrm{d}N = \rho\mathrm{d}V$ holds, then $\mathrm{d}W_M = (1/2)\mu H^2\mathrm{d}V$, as expected. In this case, the size of the system is simply extended at fixed density and temperature, or else at fixed energy density $(1/2)\mu H^2$.

b. Equation (10) reads,

$$\mathrm{d}U_M = \mathrm{d}Q_M + \mathrm{d}W_M \tag{42}$$

where $\mathrm{d}Q_M$ and $\mathrm{d}W_M$ are given by equations (40, 41) and $H = B/\mu$, with μ being defined as a function of ρ in equation (37).

There is no need to evaluate $\mathrm{d}U_M$ through equation (8), or equations (11, 12), which can turn rather complex. Instead, we use equation (19) directly, as follows:

$$\begin{aligned} U_{M_2} - U_{M_1} &= \frac{1}{2}B^2(V_2/\mu_2 - V_1/\mu_1) \\ &= \frac{1}{2}\frac{B^2}{\mu_1\mu_2}[\mu_0(V_2 - V_1) + \kappa(V_2\rho_1 - V_1\rho_2)] \end{aligned} \tag{43}$$

where use was made of equation (37).

If N is fixed, then manipulation of equation (43) gives,

$$U_{M_2} - U_{M_1} = \frac{1}{2}\frac{B^2}{\mu_1}(V_2 - V_1)\left(\frac{\mu_0}{\mu_2}\right)[1 + \chi(1 + V_1/V_2)], \quad \text{fixed } N \tag{44}$$

where subscripts 1 and 2 denote the initial and final state of the system. Note that if $\mu_1 = \mu_2 = \mu_0$, so that $\chi = 0$, the right-hand-side of equation (44) reduces to $(V_2 - V_1)B^2/2\mu_0$, as expected.

c. At fixed N, $\mathrm{d}W_M = -P_M\mathrm{d}V$. In this case, the required ratio, α, is defined as,

$$\alpha = \frac{-P_M\mathrm{d}V}{T_M\mathrm{d}S} = \frac{P_M\mathrm{d}\rho/\rho^2}{T_M\mathrm{d}s} \tag{45}$$

where use was made of $\mathrm{d}V = -V\mathrm{d}\rho/\rho$ and $\mathrm{d}S = N\mathrm{d}s$ at fixed N.

Combining equations (32, 33, 45) gives

$$\alpha = \frac{\mu/\rho + \partial\mu/\partial\rho}{\partial\mu/\partial s}\frac{\mathrm{d}\rho}{\mathrm{d}s}\cdot \tag{46}$$

Using equations (37, 38), the value of $\partial\mu/\partial s$ given by equation (21) and following equation (29), and $\partial\rho/\partial s = \rho/R$ for monatomic ideal gases, in conjunction with equation (46) gives,

$$\alpha = 3 + 3/2\chi. \tag{47}$$

Equation (46) shows that large values of α are expected, *e.g.* in view of the small values of χ, which are typical of paramagnetic gases. This shows that the magnetic pressure volume work dominates by far the corresponding heat, which is delivered to the gas. This agrees with the observation that under ambient conditions, the effect associated with T_M is expected to be negligibly small, compared to other effects of the field.

Isothermal compression of an ideal paramagnetic gas in a uniform and fixed H field

In this case [2,5],

$$P_M = -\frac{1}{2}\mathbf{H}\cdot\mathbf{B} + \frac{1}{2}H^2\rho\left(\frac{\partial\mu}{\partial\rho}\right)_{S,\mathbf{H}} \tag{48}$$

$$T_M = \frac{1}{2\rho}H^2\left(\frac{\partial\mu}{\partial s}\right)_{\rho,\mathbf{H}} \tag{49}$$

$$\zeta_M = \frac{1}{2}H^2\left(\frac{\partial\mu}{\partial\rho}\right)_{S,V,\mathbf{H}}. \tag{50}$$

a. The heat and work terms take the following forms:

$$\mathrm{d}Q_M = \frac{1}{2\rho}H^2\left(\frac{\partial\mu}{\partial s}\right)_{\rho,\mathbf{H}}\mathrm{d}S \tag{51}$$

$$\begin{aligned}\mathrm{d}W_M = {}&\left[\frac{1}{2}\mathbf{H}\cdot\mathbf{B} - \frac{1}{2}H^2\rho\left(\frac{\partial\mu}{\partial\rho}\right)_{S,\mathbf{H}}\right]\mathrm{d}V\\ &+\frac{1}{2}H^2\left(\frac{\partial\mu}{\partial\rho}\right)_{S,V,\mathbf{H}}\mathrm{d}N + \int_{V'}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V\end{aligned} \tag{52}$$

$$\mathrm{d}Q_M = -\frac{1}{3\rho R}\mu_0\chi H^2\mathrm{d}S \tag{53}$$

$$\begin{aligned}\mathrm{d}W_M &= \left[\frac{1}{2}\mu H^2 - \frac{1}{2}\mu_0\chi H^2\right]\mathrm{d}V + \frac{1}{2\rho}\mu_0\chi H^2\mathrm{d}N\\ &\quad+\int_{V'}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V\\ &= \frac{1}{2}\mu_0H^2\mathrm{d}V + \frac{1}{2}\mu_0\chi H^2\mathrm{d}N + \int_{V'}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\mathrm{d}V.\end{aligned} \tag{54}$$

b. $$U_{M_2} - U_{M_1} = \frac{1}{2}H^2(V_2\mu_2 - V_1\mu_1). \tag{55}$$

Combining equations (37, 55) gives

$$U_{M_2} - U_{M_1} = \frac{1}{2}H^2[\mu_0(V_2 - V_1) + \kappa(V_2\rho_2 - V_1\rho_1)]. \tag{56}$$

At fixed N, $V_2\rho_2 - V_1\rho_1 = 0$, and equation (56) reduces to,

$$U_{M_2} - U_{M_1} = \frac{1}{2}\mu_0(V_2 - V_1)H^2. \tag{57}$$

Equation (57) shows that the magnetic energy of uniformly magnetized ideal gases that follow equation (37) is a sole function of the volume V, provided that $\mathbf{H}$ and N are held fixed as V is changed. This agrees with the presentation of U_M as, $U_M = (1/2)\mu H^2V = (1/2)\mu_0(1 + \kappa\rho)H^2V$, so that $\mathrm{d}U_M = (1/2)\mu_0H^2\mathrm{d}V$, at fixed $\mathbf{H}$ and N, where $V\mathrm{d}\rho + \rho\mathrm{d}V = 0$ holds.

c. $$\alpha = \frac{\mu/\rho - \partial\mu/\partial\rho}{-\partial\mu/\partial s}\frac{\mathrm{d}\rho}{\mathrm{d}s} = -3/2\chi. \tag{58}$$

Thus at fixed $\mathbf{H}$, the flow of heat is reversed. Moreover, α changes from $3 + 3/2\chi$ at fixed $\mathbf{B}$ to $-3/2\chi$ at fixed $\mathbf{H}$.

Formulation of intensive energy storage. The work, W_e, equation (1), can be expressed as,

$$\begin{aligned}W_e &= W_{e,V} + W_{e,V'-V},\\ W_{e,V} &= \int_V\int_0^{\mathbf{B}}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\delta V,\\ W_{e,V'-V} &= \int_{V'-V}\int_0^{\mathbf{B}}\mathbf{H}\cdot\mathrm{d}\mathbf{B}\delta V\end{aligned} \tag{59}$$

where $W_{e,V}$, and $W_{e,V'-V}$, denote the work transformed into energy stored within (in V), and outside (in $V' - V$), the system, respectively.

Note that W_e is delivered exclusively to the contents of the system. This can be realized if one uses the point of view of the work required to turn all the system's dipoles to their final orientation. An observer that evaluates this work, by recording all the driving forces and their displacements, is bound to conclude that it is done exclusively on the contents of the system. This conforms with the fact that the turning process of each and every dipole occurs within the boundaries of the system, *i.e.* inside V. The existence of the field, and the way the field energy is stored, may be immaterial to this observer. Furthermore, if W_e is delivered adiabatically at fixed volume, V, and mass, N, then, by virtue of the first law, this observer may safely conclude that the internal energy of the system increases exactly by W_e. Thus, the ability of the contents of the system to store their field energy over all space does not change the observation that this energy pertains exclusively to them. The point of view, used by the observer to evaluate W_e, can be applied to define work per unit volume as $w_e = W_e/V$, so that volume integration of w_e over V produces the correct result for the work. However, if $\mathbf{H}\cdot\mathrm{d}\mathbf{B}$ is defined as the work per unit volume, from the field point of view, then its integration must be done over all space V' and not over V. In this sense, the meaning of $\mathbf{H}\cdot\mathrm{d}\mathbf{B}$ as work per unit volume cannot be assigned in general to a system but to all space. Consequently, and as shown below, the statement that the magnetization work per unit volume of the system is $\mathbf{H}\cdot\mathrm{d}\mathbf{B}$ can turn to be meaningless.

If the field is uniform in a fixed volume V, but nonuniform in $V' - V$, then,

$$\mathrm{d}W_e = V\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathrm{d}\left(\int_{V'-V}\int_0^{\mathbf{B}} \mathbf{H}\cdot \mathrm{d}\mathbf{B}\delta V\right), \text{ fixed } V. \tag{60}$$

Hence, the work per unit volume, V, delivered to the system, takes the following form,

$$\begin{aligned}\mathrm{d}w_e &= \mathrm{d}W_e/V \\ &= \mathbf{H}\cdot \mathrm{d}\mathbf{B} + \frac{1}{V}\mathrm{d}\left(\int_{V'-V}\int_0^{\mathbf{B}} \mathbf{H}\cdot \mathrm{d}\mathbf{B}\delta V\right), \text{ fixed } V.\end{aligned} \tag{61}$$

Equations (60, 61) show that unless the field vanishes at all points of $V' - V$, the work delivered and hence also the energy stored per unit volume, V, of the system, is different then $\mathbf{H}\cdot\mathrm{d}\mathbf{B}$. Alternatively, the statement that the work per unit volume w_e is equal to $\mathbf{H}\cdot \mathrm{d}\mathbf{B}$ is generally false. This stems from the fact that the integration domains of w_e (which is V) and $\mathbf{H}\cdot \mathrm{d}\mathbf{B}$ (which is all space, V') are fundamentally different. Similarly, in electric polarization, the energy density, per unit volume, V, is generally different than $\mathbf{E}\cdot \mathrm{d}\mathbf{D}$. It follows that the common way of expressing the internal energy density, per unit mass, in the form,

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v + \sum_{i=1}^{n}\zeta_i \mathrm{d}m_i + \mathbf{H}\cdot \mathrm{d}(\mathbf{B}/\rho) + \mathbf{E}\cdot \mathrm{d}(\mathbf{D}/\rho) \tag{62}$$

is restrictive, in the sense that it does not hold in cases where the field, due to the contents of the system, in V, does not vanish outside its boundaries, *e.g.*, in $V' - V$.

As already shown (see discussion following Eq. (2)), the proof is by integration over the mass (assumed to be finite) of the system. As this integration does not include all space, it cannot be generally correct. Note that, in equation (62), m_i, and ζ_i, stands for mass fraction, and chemical potential of the ith species, u, s, and v, are internal energy, entropy, and volume, per unit mass, ρ is density, T is temperature and P is pressure. The observation regarding the restrictive nature of equation (62), applies also to the general case of nonuniform fields that extend beyond the system boundaries. This can be realized by considering each volume element, δV, as a subsystem surrounded by a nonuniform field.

Equation (63) gives the general formulation of the internal energy per unit mass, $\hat{u}$, as

$$\begin{aligned}\mathrm{d}\hat{u} &= \hat{T}\mathrm{d}s - \hat{p}\mathrm{d}v + \sum_{i=1}^{n}\hat{\zeta}_i \mathrm{d}m_i \\ &\quad + \frac{1}{\rho}(\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathbf{E}\cdot \mathrm{d}\mathbf{D}) \\ &\quad + \frac{1}{V\rho}\mathrm{d}\left[\int_{V'-V}\int_0^{\mathbf{B}} (\mathbf{H}\cdot \mathrm{d}\mathbf{B} + \mathbf{E}\cdot \mathrm{d}\mathbf{D})\delta V\right]\end{aligned} \tag{63}$$

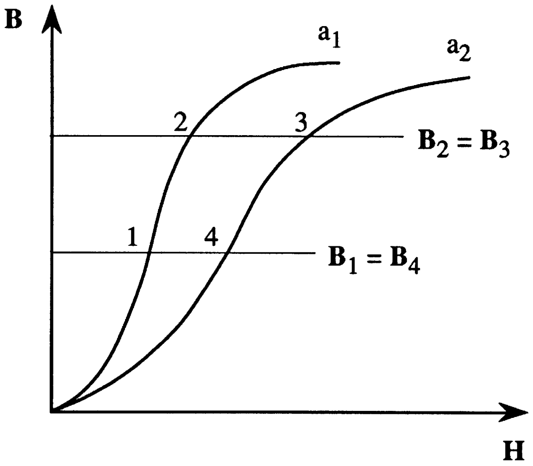

Fig. 1. Nonlinear adiabatic magnetization curves. The two different curves, denoted by a_1 and a_2, indicate magnetization under two different conditions (such as different temperatures).

where the set $\{\hat{T}, \hat{p}, \hat{\zeta}\}$ denotes [2,7] field dependent temperature, pressure, and chemical potential, see equation (9).

Field energy work and heat. Figure 1 shows two nonlinear adiabatic magnetization curves, a_1 and a_2, and two levels of fixed $\mathbf{B}$, intersecting a_1 at points 1 and 2, and a_2 at points 3 and 4. The volume V and mass N are fixed throughout. Assuming that fixed $\mathbf{B}$ implies that no work is exchanged with the current sources, the horizontal section $2 \rightarrow 3$ and $1 \rightarrow 4$ involve only heat flow, whereas sections $1 \rightarrow 2$ and $3 \rightarrow 4$ involve adiabatic work. Equation (1) gives the work done in establishing the field, and hence, its stored energy, provided that W_e is performed at fixed S, V and N. Adiabatic (fixed S) magnetization curves of a given material, at fixed volume and mass, are not expected to intersect except at the ($\mathbf{H} = 0$, $\mathbf{B} = 0$) origin. Consequently, each point that exists physically in the $\mathbf{BH}$ plane lies on a single magnetization curve (at fixed S, V, and N), and hence its field energy, U_M, is unique. Since, at $H = B = 0$, $U_M = 0$, we have

$$W_e(0 \rightarrow 2) + Q_M(2 \rightarrow 3) + W_e(3 \rightarrow 0) = 0 \tag{64}$$

$$W_e(0 \rightarrow 1) + Q_M(1 \rightarrow 4) + W_e(4 \rightarrow 0) = 0. \tag{65}$$

Subtracting equation (65) from equation (64) gives

$$W_e(1 \rightarrow 2) + Q_M(2 \rightarrow 3) = Q_M(1 \rightarrow 4) + W_e(4 \rightarrow 3) \tag{66}$$

where Q_M denotes heat delivered and used to build up the field, and use was made of the relations

$$\begin{aligned}W(i \rightarrow j) &= W(0 \rightarrow j) - W(0 \rightarrow i), \\ W(i \rightarrow j) &= -W(j \rightarrow i), \quad i, j = 1, 2 \text{ or } 3, 4.\end{aligned}$$

Any, physically existent, two points in the $\mathbf{BH}$ plane can be connected by a combination of two segments comprising adiabatic work and heat flow at fixed $\mathbf{B}$. For example see points 0 and 3, and 1 and 3. By virtue of equation (66), this proves the existence of a state function of a field energy, at every physical point of the **BH** plane, irrespective of linearity or nonlinearity of the material being magnetized. The heat used to build the field up can be related to changes in the adiabatic magnetization curves, at fixed V, N and $\mathbf{B}$, as follows. At point 3, see Figure 1, the field energy U_{M_3} is expressible in two alternative ways,

$$U_{M_3} = \left[\int_{V'} \int_0^{\mathbf{B}_3} \mathbf{H} \cdot \mathrm{d}\mathbf{B} \delta V\right]_{a_2}, \text{ adiabatic path } a_2 \quad (67)$$

$$U_{M_3} = \left[\int_{V'} \int_0^{\mathbf{B}_2} \mathbf{H} \cdot \mathrm{d}\mathbf{B} \delta V\right]_{a_1} + Q_M(2 \to 3), \quad (68)$$

adiabatic path a_1 and then fixed $\mathbf{B}$. Hence

$$Q_M = \Delta\left(\int_{V'} \int_0^{\mathbf{B}} \mathbf{H} \cdot \mathrm{d}\mathbf{B} \delta V\right), \text{ fixed } V, N, \mathbf{B} \quad (69)$$

where use was made of $\mathbf{B} = \mathbf{B}_2 = \mathbf{B}_3$, the symbol $2 \to 3$ was dropped, and Δ denotes the change in the adiabatic magnetization work, *e.g.* due to the shift from a_1 to a_2. Equation (69), being general in nature, facilitates evaluation of heat taken up or released by the field, using predetermined data of adiabatic magnetization curves.

Appendix A: Application of the first law to $\hat{\mathrm{U}}$, U and $\mathrm{U_M}$

We postulate the existence of a magnetic internal energy for a single component system of entropy S, volume V and mass N, that is energized by a uniform induction field $\mathbf{B}$ across V. It follows that the internal energy $\hat{U}$, of this system is a function of the set $\{S, V, N, \mathbf{B}\}$. The meaning of S depends on constraints imposed on this set. If, by definition, this set consists of four independent variables, then S, being under this constraint independent of $\mathbf{B}$, stands for the nonmagnetic part of the entropy. Otherwise, if S includes (in addition to the nonfield entropy) the part arising exclusively due to the field, it must be a function of $\mathbf{B}$, contrary to the statement of its independence. Thus, it is $\mathbf{B}$ that gives rise to an additional field entropy, S_M, and the total entropy, $\hat{S}$, is obtained as $\hat{S} = S + S_M$

$$\hat{U} = \hat{U}(S, V, N, \mathbf{B}). \quad (A.1)$$

Note that the selection of $\mathbf{B}$, as the independent field variable, conforms with the form of the differential magnetic work term, as given by equation (2). The option to use $\mathbf{H}$ or $\mathbf{M}$ instead of $\mathbf{B}$ exists in view of the constitutive relations that relate these variables. For example, using $\mathbf{B} = \mu\mathbf{H}$, with μ being defined as $\mu = \mu(S, V, N, \mathbf{B})$, facilitates the replacement of the set S, V, N, $\mathbf{B}$ by S, V, N, $\mathbf{H}$. However in doing so, the form and meaning of the work term becomes more complicated, as the conditions of fixed $\mathbf{H}$ allow energy transfer between the current sources of the field and the system.

In the absence of the field, $\hat{U}$ must reduce to the well-known internal energy U that is a function of the set (S, V, N),

$$\hat{U}(S, V, N, \mathbf{B} = 0) = U(S, V, N). \quad (A.2)$$

It follows that the energy difference arising from the presence of the field, $\hat{U}(S, V, N, \mathbf{B}) - U(S, V, N)$, is a function of the set $\{S, V, N, \mathbf{B}\}$. This energy difference is denoted by $U_M = U_M(S, V, N, \mathbf{B})$, and named “magnetic internal energy” or in short “magnetic energy”

$$U_M(S, V, N, \mathbf{B}) = \hat{U}(S, V, N, \mathbf{B}) - U(S, V, N). \quad (A.3)$$

As both $\hat{U}(S, V, N, \mathbf{B})$ and $U(S, V, N)$ are state functions, *e.g.* by the very definition of their being internal energies in the presence and absence of the field, respectively, $U_M(S, V, N, \mathbf{B})$ must also be a state function [2]. This agrees with the functional form of U_M as given by equation (19).

Rearranging equation (A.3) gives

$$\hat{U} = U + U_M. \quad (A.4)$$

Equation (A.4) shows that $\hat{U}$ is the sum of two state functions: U, the nonfield part that arises in the absence of the field, and U_M that is a consequence of its presence. Furthermore, $\hat{U}$ can be evaluated by first calculating U at $U_M = 0$, and then evaluating U_M with U held fixed. In terms of the set $\{S, V, N, \mathbf{B}\}$, U is evaluated at $B = 0$ using the set $\{S, V, N\}$, and then holding this set fixed, $\mathbf{B}$ is increased to its final level. Recalling that the initial and final values of state functions are path independent, other integration paths are equally valid.

The set $\{S, V, N, \mathbf{B}\}$ comprises four independent variables. Consequently, $\mathbf{B}$ must be independent of the subset $\{S, V, N\}$ and *vice versa*. This presentation, which imposes a variable field strength $\mathbf{H}$, has the following advantage. At fixed $\{S, V, N\}$, a change in $\mathbf{B}$ produces a change in U_M, but not in U. This specific change in U_M guarantees that the work done on the system by the sources that give rise to $\mathbf{B}$, at fixed $\{S, V, N\}$, is completely converted into energy that is stored in the field. The definition of U_M, as given by equation (A.3), does not specify where is the field energy stored. However, equation (A.3) does require that U_M be associated with the contents of the system that exist in V. This means that although the field and its energy U_M can exist on both sides of the boundaries enclosing V, both must pertain to the contents of V. This is a unique property of U_M that does not apply to U.

By virtue of equation (A.4)

$$\mathrm{d}\hat{U} = \mathrm{d}U + \mathrm{d}U_M. \quad (A.5)$$

In equation (A.5) both $\hat{U}$ and U are proper internal energy functions in the presence and absence of the field, respectively. Consequently, both must satisfy the first law as,

$$\mathrm{d}\hat{U} = \mathrm{d}\hat{W} + \mathrm{d}\hat{Q}, \qquad \mathbf{B} > 0, \quad (A.6)$$

$$\mathrm{d}U = \mathrm{d}W + \mathrm{d}Q, \qquad \mathbf{B} = 0. \quad (A.7)$$

Subtraction of equation (A.7) from equation (A.6) gives,

$$\mathrm{d}\hat{U} - \mathrm{d}U = (\mathrm{d}\hat{W} - \mathrm{d}W) + (\mathrm{d}\hat{Q} - \mathrm{d}Q). \qquad (A.8)$$

Combining equations (A.5, A.8) gives,

$$\begin{aligned} \mathrm{d}U_M &= \mathrm{d}W_M + \mathrm{d}Q_M, \\ \mathrm{d}W_M &= \mathrm{d}\hat{W} - \mathrm{d}W, \\ \mathrm{d}Q_M &= \mathrm{d}\hat{Q} - \mathrm{d}Q. \end{aligned} \qquad (A.9)$$

The meaning of $\mathrm{d}W_M$ and $\mathrm{d}Q_M$ is given by equations (10–12), as the work and heat terms that effect the change $\mathrm{d}U_M$. Equation (11) shows that $\mathrm{d}Q_M$ is a function of the nonfield entropy S with T_M replacing T, as the integrating factor. Equation (12) shows that $\mathrm{d}W_M$ is a function of the differentials of V, N, and $\mathbf{B}$, as expressed by the three terms on its right-hand-side. The first term relates to mechanical pressure volume work, the second to mass transfer work, and the third to magnetization work (at fixed S, V, N).

Equations (A.6, A.7, A.9) show that the first law applies to $\hat{U}$, U and U_M without exception. This result conforms with the uniqueness of field energy, which suggests the existence of internal field energy, *e.g.*, in the sense that this field energy, although stored over all space, pertains to the contents of the system. This is also the case with the nonfield internal energy U, as it is stored, by its very definition, within the system boundaries.

Appendix B: Mechanical and thermal coupling of fixed mass polarizable systems

Electromechanical systems are used to transform electric into mechanical work, and *vice versa.* This transformation involves energy that is stored or delivered by, or to, electromagnetic fields. The work delivered by current sources to an electromechanical system, of fixed mass, that is thermally coupled to a heat source, can be expressed as,

$$\mathrm{d}W_e = \mathrm{d}W_{\mathrm{mag}} + \mathrm{d}W_x + \mathrm{d}W_Q, \quad \text{fixed mass} \qquad (B.1)$$

where W denotes work, and subscripts mag and x, and Q, characterize the part converted into energy stored in magnetic field and mechanical work, and heat, delivered by the field, respectively.

All four terms of equation (B.1) involve field interactions. For example $\mathrm{d}W_x$ and $\mathrm{d}W_Q$ are mechanical work and heat delivered by the field, and $\mathrm{d}W_e$ is the work delivered to the field by the current sources. Equation (B.1) can be expressed as follows,

$$i\mathrm{d}\lambda = \mathrm{d}W_{\mathrm{mag}} + f\mathrm{d}x - \mathrm{d}Q_M \qquad (B.2)$$

where $\mathrm{d}Q_M$ denotes heat delivered to the field as per equation (11), $i\mathrm{d}\lambda = \mathrm{d}W_e$, $f\mathrm{d}x = \mathrm{d}W_x$, $-\mathrm{d}Q_M = \mathrm{d}W_Q$, and i, λ, f, and x are: current, flux linked by i, force, and position of f, respectively. The work, $\mathrm{d}W_e = i\mathrm{d}\lambda$, delivered (adiabatically, $\mathrm{d}Q = 0$, at fixed x) by the current sources to the field, is related to field variables as follows,

$$i\mathrm{d}\lambda = \int_{V'} \mathbf{H}\cdot\mathrm{d}\mathbf{B}\delta V, \quad \text{fixed } x, \qquad \text{adiabatic magnetization } (\mathrm{d}Q = 0) \qquad (B.3)$$

where $\mathbf{H}$, $\mathbf{B}$, δV and V' are magnetic field strength, magnetic induction, volume element, and volume occupied by the field, respectively.

The energy, U_M, stored in the field is a state function so that $\mathrm{d}U_M = \mathrm{d}W_{\mathrm{mag}}$ must be satisfied. Hence, by virtue of equation (B.2),

$$\mathrm{d}U_M = i\mathrm{d}\lambda - f\mathrm{d}x + \mathrm{d}Q_M \qquad (B.4)$$

where $i\mathrm{d}\lambda - f\mathrm{d}x$ and $\mathrm{d}Q_M$ are readily identified as the net work and heat delivered to the field.

Equation (B.4) is the first law of thermodynamics that is exclusively associated with the field. This equation corroborates the fundamental concept that the internal energy can be split into nonfield and field parts, *e.g.* U and U_M, respectively. An alternative derivation of equation (B.4), using a two-step process follows. Initially the system is at equilibrium. The first step (subscript 1) is adiabatic at fixed x, so that

$$i\mathrm{d}\lambda = \mathrm{d}U_{M_1}, \qquad \mathrm{d}x = \mathrm{d}Q_M = 0 \qquad (B.5)$$

where $\mathrm{d}U_{M_1}$ is the change in the energy stored in the field in the first step.

In the second step (subscript 2), λ is kept fixed so that no work is delivered by the current source, heat is allowed to flow, and x is variable.

$$\mathrm{d}U_{M_2} = -f\mathrm{d}x + \mathrm{d}Q_M, \quad \text{fixed } \lambda. \qquad (B.6)$$

Combining equations (B.5, B.6) gives equations (B.4).

Note that $\mathrm{d}U_M = \mathrm{d}U_{M_1} + \mathrm{d}U_{M_2}$ is the total change of energy stored in the field, $i\mathrm{d}\lambda - f\mathrm{d}x$ is the net work, and $\mathrm{d}Q_M$ heat, delivered to the system in the two step process. Combining equations (B.3, B.4) gives,

$$\mathrm{d}U_M = \int_{V'} H\mathrm{d}B\delta V - f\mathrm{d}x + \mathrm{d}Q_M. \qquad (B.7)$$

Note that when equation (B.7) is applied to the analysis of field energy, work and heat, given in the section following equation (63), no external mechanical work exists so that $f = 0$. In the adiabatic path (Eqs. (64, 65)) $\mathrm{d}Q_M = T_M\mathrm{d}S = 0$, whereas at fixed $\mathbf{B}$, the work term vanishes and the only contribution to $\mathrm{d}U_M$ is from $\mathrm{d}Q_M$. This agrees with the analysis of equations (64–69).

Appendix C: Derivation of equation (16)

Let $\mu(\mathbf{B})$ and $\mu(\mathbf{B} = 0)$ be defined as the adiabatic value of the permeability, which is obtained in a magnetization process from 0 to $\mathbf{B}$, at $\mathbf{B}$ and $\mathbf{B} = 0$, respectively.

If in adiabatic magnetization at fixed, S, V, N, μ is a decreasing monotonic function of $\mathbf{B}$ (*e.g. via* its dependence on the temperature $\hat{T}$, as in paramagnetic materials), then $\mu(\mathbf{B}) < \mu(\overline{\mathbf{B}}) < \mu(\mathbf{B} = \mathbf{0})$, where $\mathbf{B} > \overline{\mathbf{B}} > 0$ and $\overline{\mathbf{B}}$ denotes an intermediate value between 0 and $\mathbf{B}$. If μ is an increasing monotonic function of $\mathbf{B}$, as may be the case in adiabatic magnetization of diamagnetic materials, then, $\mu(\mathbf{B} = 0) < \mu(\overline{\mathbf{B}}) < \mu(\mathbf{B})$.

Let the functional differences, d_1 and d_2, be defined as follows:

$$d_1 = \frac{1}{2}B^2/\mu(\mathbf{B}) - \int_0^{\mathbf{B}} \mathbf{H}\cdot \mathrm{d}\mathbf{B}$$

$$\mathbf{H} = \mathbf{B}/\mu, \quad \text{fixed } S,\ V,\ N \tag{C.1}$$

$$d_2 = \frac{1}{2}B^2/\mu(\mathbf{B} = 0) - \int_0^{\mathbf{B}} \mathbf{H}\cdot \mathrm{d}\mathbf{B},$$

$$\mathbf{H} = \mathbf{B}/\mu, \quad \text{fixed } S,\ V,\ N. \tag{C.2}$$

As the complete adiabatic integration path (involving paramagnetic materials) is characterized by $\mu(\mathbf{B}) \le \mu \le \mu(\mathbf{B} = 0)$, $d_1 > 0$ and $d_2 < 0$ hold. Consequently, recalling that μ is a monotonic function of $\mathbf{B}$, there exists an intermediate value $\overline{\mathbf{B}}$, between 0 and $\mathbf{B}$, for which

$$\frac{1}{2}B^2/\mu(\overline{\mathbf{B}}) - \int_0^{\mathbf{B}} \mathbf{H}\cdot \mathrm{d}\mathbf{B} = 0,$$

so that

$$V\int_0^{\mathbf{B}} \mathbf{H}\cdot \mathrm{d}\mathbf{B} = \frac{1}{2}VB^2/\mu(\overline{\mathbf{B}}) = U_M.$$

This verifies equation (16).

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