FARADAY

Euler integration of thermodynamic systems in the presence of fields

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The significance and validity of Euler integration and the Gibbs–Duhem equation for thermodynamic systems in the presence of fields is considered. It is shown that the presence of fields can change the fundamental property concerning Euler integrability and applicability of the Gibbs–Duhem equation that underlines classical thermodynamics. In this context, an assembly of charges, current elements or a combination thereof, is not expected to be a first-order homogeneous function of its extensive variables. Consequently, Euler integration of systems that include charges, current elements, or generally involve interaction with electromagnetic fields can be meaningless. This means that, in general, such systems are not expected to satisfy the Gibbs–Duhem equation. Specific examples of capacitors, charged spheres, magnetic circuit of variable gap and a sphere in a uniform field, are used to illustrate the effect of the field on the energy and thermodynamic properties of polarizable systems. It is shown that, apart from limited configurations, these specific systems do not behave as first-order homogeneous functions of their extensive variables and their Euler integration can lead to results of no physical significance. Finally, in the presence of fields, the field-independent part of the energy differential can be Euler integrated, but the field-dependent part must be integrated as an exact differential. Consequently, the sum of the field-independent and field-dependent exact differentials is generally not Euler integrable.

The classical theory of thermodynamics involves the concept of internal energy and entropy as state functions. Either of these state functions can be used, in conjunction with volume and the complete set of masses of a system, to describe its full thermodynamic properties at equilibrium. Furthermore, in the absence of fields, thermodynamic systems are defined as being first- and zero-order homogeneous functions of their extensive, and intensive variables, respectively. This facilitates Euler integration of the internal energy, where all intensive variables are held fixed as their extensive conjugates are increased from zero to their final values. In this sense, the Euler integration is equivalent to building a thermodynamic system from nothing, at prescribed values of its intensive variables. The presence of fields can change this fundamental property of a thermodynamic system. For example, this change can be due to interaction at a distance and partition of energy on both sides of the system boundaries. Recently the theory of thermodynamics in the presence of electromagnetic fields has been formulated,[1] and then followed by system analysis of field-dependent thermodynamic variables and Maxwell relations.[2] It was shown that, in the presence of electromagnetic fields, the differential of the field-dependent internal energy is the sum of two exact differentials. The first exact differential consists of the conventional, 'field-free', differential of the internal energy, while the second one stands exclusively for the energy due to the presence of the field. Expansion of these differentials as functions of the extensive variables and a field vector facilitated formulations of corresponding field-dependent intensive variables. Although the sum of the two differentials, being exact, can be directly integrated, it was not possible to perform a general Euler integration using the field-dependent intensive variables. This was indicated briefly as a general result of the theory without attempting to perform Euler integration on specific examples, or providing a rigorous proof.

In this work we consider the physical significance and the very existence of Euler integrations of thermodynamic systems in the presence of fields. To this end, a theoretical analysis concerning properties of thermodynamic functions and Euler integration in the presence of quasistatic electric and magnetic fields is performed. Following the theory, analyses of specific cases are presented. This is done with a view to elucidating and demonstrating the implications of the theory. A primary consequence of this theory is concerned with the validity of the Gibbs–Duhem equation in the presence of fields.

Theory

In classical thermodynamics that does not involve fields, the internal energy, U, can be presented as a function of $\{X_0, \ldots, X_n\}$ as follows,

$$U = U(X_0, \ldots, X_n) \tag{1}$$

where X_i denotes the ith independent extensive variable, $i = 0, 1, \ldots, n$, of the set consisting of $n + 1$ independent extensive variables. This set is assumed to include all relevant variables that provide the complete thermodynamic information, so that eqn. (1) becomes the fundamental equation. Each extensive variable of this set is a scalar. A one-component, uniform and isotropic bulk system can be characterized by the set $\{S, V, N\}$, where S is entropy, V volume and N mass. In classical thermodynamics, system boundaries have the role of determining the nature and extent of interaction that involve flow of S and N and changes in V. Alternatively, boundaries can be used to set constraints for flow of heat and mass, into and from a system, as well as to determine the size of a system. In classical thermodynamics, systems at equilibrium need not be characterized with respect to their space coordinates or shape. In this context such systems do not involve the need to solve boundary value problems as is the case with fields. A fundamental property of conventional thermodynamic systems is that they are first-order homogeneous functions of the set $\{X_0, \ldots, X_n\}$, and hence they can be Euler integrated. This property can be presented as follows,[3]

$$U(\lambda X_0, \ldots, \lambda X_n) = \lambda U(X_0, \ldots, X_n) \tag{2}$$

where λ is a constant.

Alternatively,

$$\mathrm{d}U = \sum_{i=0}^{n} \xi_i \, \mathrm{d}X_i, \qquad \xi_i = (\partial U/\partial X_i)_{X_j}, \qquad j \neq i, \; i, j = 0, \ldots, n \tag{3}$$

can be integrated, holding ξ_i, $i = 0,\ldots,n$, fixed, so that U takes the following form

$$U = \sum_{i=0}^{n} \xi_i X_i \tag{4}$$

Eqn. (4) shows that U is completely determined if the pair products, $\xi_i X_i$, $i = 0,\ldots,n$, are known. In a uniform and isotropic, one component, bulk system, eqn. (4) reduces to,

$$U = TS - PV + \zeta N \tag{5}$$

where interfacial energy has been neglected and

$$T = (\partial U/\partial S)_{V,N}; \quad -P = (\partial U/\partial V)_{S,N}; \quad \zeta = (\partial U/\partial N)_{S,V}$$

It is clear that the classical theory of thermodynamics is not concerned with the effect of either shape or space coordinates of the system and its contents. Another characteristic of classical thermodynamics, in the absence of fields, is the requirement that the complete set $\{X_0, \ldots, X_n\}$ be assigned to the space enclosed within the boundaries of a system, *e.g.* where U is defined. This means that U must depend only on the contents of a system, for which it is defined.

The presence of fields changes the physical world of thermodynamic systems in several aspects.

1. Fields involve interactions at a distance.
2. A field that is generated by the contents of a system can extend beyond its physical boundaries. Consequently, the energy of this field can be stored on both sides of the system boundaries.
3. Fields are governed by laws that hold irrespective of the thermodynamic systems involved.
4. Fields must satisfy boundary conditions and as such are functions of position and orientation in space and the nature of the relevant boundaries.
5. The energy stored in a field of a system can be changed in a process where all the field independent extensive variables, *e.g.* $\{X_0, \ldots, X_n\}$ of this system are fixed.

For example, masses, charges and current elements (such as loops) interact at a distance. The field generated by a polarized body of finite permeability, which does not form a perfectly closed circuit, extends beyond its physical boundaries. Electromagnetic fields follow the Maxwell equations and gravitational fields Newton's law of gravity, which hold irrespective of the thermodynamic system in question. Electromagnetic fields satisfy boundary conditions subject to Maxwell's equations and, as such, are position dependent. The energy of a polarizable system can be changed gravitationally and electromagnetically without a change in its field-independent entropy, volume or mass. For example, this can be achieved following a change in the shape or orientation of a system, or by holding its position fixed, bringing another mass from infinity and energizing a current source in its vicinity. Systems that must satisfy boundary conditions and are subject to laws such as the Maxwell equations do not possess, in general, the property of being first-order homogeneous functions of their contents and size, and their properties are expected to vary also with shape. We start by considering an elementary electrostatic system consisting of an assembly of charges. The work, W, of assembling a set of m point charges $\{q_1, \ldots, q_m\}$ from infinity (*e.g.* where there is no interaction between them) is given by[1,4]

$$W = \frac{1}{2} \sum_{j=1}^{m} q_j \psi_j \tag{6}$$

where ψ_j is the electric potential at the position occupied by q_j.

If we define our system so that it includes the set of these charges, then its internal energy can be expressed as

$$U = \sum_{i=0}^{n} \xi_i X_i + \frac{1}{2} \sum_{j=1}^{m} q_j \psi_j \tag{7}$$

$$\psi_j = \sum_{k=0}^{j-1} \frac{q_k}{4\pi\varepsilon_0 r_{jk}} + \sum_{k=j+1}^{m+1} \frac{q_k}{4\pi\varepsilon_0 r_{jk}} \tag{8}$$

where r_{jk} is the distance between q_j and q_k, $j \neq k$, $j = 1, \ldots, m$, $k = 0, \ldots, m+1$, and $q_0 = q_{m+1} = 0$. Combining eqn. (7) and (8) gives,

$$U = \sum_{i=0}^{n} \xi_i X_i + \frac{1}{8\pi\varepsilon_0} \times \left(\sum_{j=1}^{m} \sum_{k=0}^{j-1} q_j q_k / r_{jk} + \sum_{j=1}^{m} \sum_{k=j+1}^{m+1} q_j q_k / r_{jk} \right) \tag{9}$$

Eqn. (9) shows that U is a function of the charge squared. For example, if $q_j = q$, $j = 1, \ldots, m$, then U is a function of q^2 and, hence, it cannot be a first-order homogeneous function of the charge. Suppose we express each charge in its fixed position by λq_j, $0 \leqslant \lambda \leqslant 1$, so that as λ is increased from zero to λ, the amount of charge in the system increases from zero to $\lambda \sum_{j=1}^{m} q_j$. In this process q_j, $j = 1, \ldots, m$, are fixed and U is a function of λ^2. This shows that in this process of building the system of charges from nothing, U is not a first-order homogeneous function of the charge. Suppose we duplicate λ such systems and join them together, so that a new system, which is λ times larger than the original system, is obtained. It is clear that, owing to the presence of charges, this information is insufficient to characterize the new system. The energy of the new system is given by

$$U' = \lambda \sum_{i=0}^{n} \xi_i X_i + \frac{1}{8\pi\varepsilon_0} \times \left(\sum_{j=1}^{\lambda m} \sum_{k=0}^{j-1} q_j q_k / r_{jk} + \sum_{j=1}^{\lambda m} \sum_{k=j+1}^{\lambda(m+1)} q_j q_k / r_{jk} \right) \tag{10}$$

Since the intercharge radii change as more charges are added to build the new system, it follows that

$$\frac{1}{2} \sum_{j=1}^{\lambda m} q_j \psi_j \neq \frac{\lambda}{2} \sum_{j=1}^{m} q_j \psi_j \tag{11}$$

Furthermore, U' depends on the way the new system is built, *i.e.* on its final geometry. For example, duplicating the original system λ times in the form of a row, or in the form of a cluster, should yield different values for U'. It follows that a thermodynamic system that contains charges is not expected to be a first-order homogeneous function of its volume and contents. An immediate consequence is that, except for limited idealized cases, a system containing charges, or that charges can be induced in it (as it is being built) through interaction with external charges, cannot be Euler integrated. Therefore, except for limited idealized cases, the conventional Gibbs–Duhem equation is meaningless for charged systems. The differential of U can be obtained directly from eqn. (7) as

$$\mathrm{d}U = \sum_{i=0}^{n} \xi_i \, \mathrm{d}X_i + \mathrm{d}\left(\frac{1}{2} \sum_{j=1}^{m} q_j \psi_j \right) \tag{12}$$

where here use was made of the Gibbs–Duhem equation that holds in the absence of fields

$$\sum_{i=0}^{n} X_i \, \mathrm{d}\xi_i = 0 \tag{13}$$

This is justified since the sum $\sum_{i=0}^{n} \xi_i X_i$ consists exclusively of variables that are field independent, *e.g.* they are defined subject to the conditions that exclude effects of fields. Eqn. (12) accounts for two types of field-related energy changes that can occur in the system. The first energy change involves actual introduction of charges into the system, and the second is due

to charges outside its boundaries that produce a change in the field inside the system. If we restrict the analysis only to the case of actual introduction of charges from infinity into the system, and allow no changes in its field due to redistribution of outside charges, then

$$\mathrm{d}\left(\frac{1}{2}\sum_{j=1}^{m} q_j\psi_j\right) = \sum_{j=1}^{m} \psi_j\,\mathrm{d}q_j \tag{14}$$

Eqn. (14) is the well known differential of electric work that is necessary in order to increase each of the charges $q_1, \ldots, q_m$ (while holding their positions fixed) by a corresponding differential amount of charge that is brought from infinity.

Combining eqn. (12) and (14) gives

$$\mathrm{d}U = \sum_{i=0}^{n} \xi_i\,\mathrm{d}X_i + \sum_{j=1}^{m} \psi_j\,\mathrm{d}q_j \tag{15}$$

Various forms of eqn. (15) are often used, in the literature, to indicate the internal energy differential of systems that include charges. However, eqn. (15) is restrictive, in the sense that it does not account for the part due to charges existing outside the system. This is also seen when an attempt is made to Euler integrate eqn. (15) at fixed ξ_i, $i = 0, \ldots, n$ and fixed ψ_j, $j = 1, \ldots, m$. The integration gives

$$U = \sum_{i=0}^{n} \xi_i X_i + \sum_{j=1}^{m} \psi_j q_j \tag{16}$$

It is clear that such integration has no physical basis. Moreover eqn. (16) violates the correct energy as given by eqn. (7), and hence is not acceptable. In contrast, eqn. (12) facilitates Euler integration of the field-independent part along with direct, *e.g.* non-Eulerian, integration of the exact differential of the electric energy. It follows that thermodynamic systems, that involve or are affected by charges, are fundamentally different from ordinary systems which are free from effects of charges. These systems are not first-order homogeneous functions of the amount of charge. Integration of their energy differential involves a field-independent part that can be Euler integrated and a field-dependent part that must be integrated as an exact differential. In what follows we use simple electrostatic systems to demonstrate and elaborate on these observations.

Capacitors

The electric energy, U_e, stored in a capacitor, consisting of two electrodes (denoted 1 and 2), is given by[4,5]

$$U_e = \frac{1}{2}Qv = \frac{1}{2}Cv^2 = \frac{1}{2}\frac{Q^2}{C} \tag{17}$$

where Q is the total surface free charge on the positive electrode, which here is denoted by the subscript 2,

$$Q = \int_{A_2} \sigma_2\,\mathrm{d}A_2 = -\int_{A_1} \sigma_1\,\mathrm{d}A_1 \tag{18}$$

$v = v_2 - v_1$, is the voltage difference across the electrodes, C is the capacitance that relates Q to v, and A_1, A_2 are the surface area of the first and second electrodes, respectively.

$$Q = Cv \tag{19}$$

It is clear from eqn. (17) that U_e can be presented as a function of either C and v or C and Q. Furthermore, the way U_e varies with C depends on the selection of constraints that can be imposed on the capacitor. Thus, if v is held fixed, then U_e is directly proportional to C, whereas if Q is held fixed, it is inversely proportional to C. The capacitance is a function of geometry, and permittivity, *e.g.* of volume and shape of the capacitor as well as of its contents and their thermodynamic properties. For example, the capacitance of two parallel-plate electrodes with negligible field fringing can be expressed as a function of the volume, V, and distance l between them as follows,

$$C = \varepsilon V/l^2; \qquad V = A_1 l = A_2 l \tag{20}$$

where ε is permittivity.

Combining eqn. (17) and (20) gives the well known dependence of U_e on the field,

$$U_e = \frac{1}{2}V\varepsilon E^2 \tag{21}$$

where E is the electric field intensity,

$$E = v/l \tag{22}$$

Eqn. (21) shows that if the electric energy density $\frac{1}{2}\varepsilon E^2$ is held fixed, then U_e is a first-order homogeneous function of V. In general, the energy stored in an electric field is given by[4–6]

$$U_e = \int_V \int_0^{\boldsymbol{D}} \boldsymbol{E}\cdot\mathrm{d}\boldsymbol{D}\,\mathrm{d}V \tag{23}$$

where

$$\boldsymbol{D} = \varepsilon\boldsymbol{E} \tag{24}$$

is the electric displacement.

Eqn. (23) shows that if the energy density $\boldsymbol{E}\cdot\mathrm{d}\boldsymbol{D}$ varies with position, then U_e is not expected to be a first-order homogeneous function of V. A simple example is a parallel-plate capacitor that has significant fringing, so that eqn. (20) does not hold. As the volume of this capacitor is progressively increased, by increasing the area of its electrodes at fixed l, the relative part of the electric energy stored in the fringing field decreases. Consequently, the electric energy density tends to a constant value, so that U_e can be approximated as a first-order homogeneous function of V.

In what follows we consider a specific case of a capacitor with variable dimensions and contents. Fig. 1 shows a parallel-plate capacitor that consists of two parallel, rectangular and perfectly conducting plate electrodes of area A. The lower part of the space between the plates is occupied by a rectangular solid slab of a dielectric material with permittivity ε_2, whereas the upper part is full of fluid with permittivity ε_1. The lower plate and the slab are fixed together and the upper plate can move so that its distance, x, from the top of the dielectric slab is variable. The voltage difference, v, across the plates, *e.g.* between the points a and b, is set by a source that is connected to them *via* perfectly conducting wires.

$$v = -\int_b^a \boldsymbol{E}\cdot\mathrm{d}\boldsymbol{l} \tag{25}$$

The following equations apply to the capacitor.[7]

$$\varepsilon_1 E_1 = \varepsilon_2 E_2 \tag{26}$$

$$E_1 = -\frac{v}{x + (\varepsilon_1/\varepsilon_2)l} \tag{27}$$

$$Q = -A\varepsilon_1 E_1 = \frac{\varepsilon_1 A v}{x + (\varepsilon_1/\varepsilon_2)l} = C(x)v \tag{28}$$

$$C(x) = \frac{\varepsilon_1 A}{x + (\varepsilon_1/\varepsilon_2)l} \tag{29}$$

$$i = \mathrm{d}Q/\mathrm{d}t = \frac{\varepsilon_1 A}{x + (\varepsilon_1/\varepsilon_2)l}\frac{\mathrm{d}v}{\mathrm{d}t} - \frac{\varepsilon_1 A v}{[x + (\varepsilon_1/\varepsilon_2)l]^2}\frac{\mathrm{d}x}{\mathrm{d}t} \tag{30}$$

The electric energy, U_e, of this capacitor can be transformed into eqn. (21) using

$$V = Ax'; \qquad x' = l + x$$

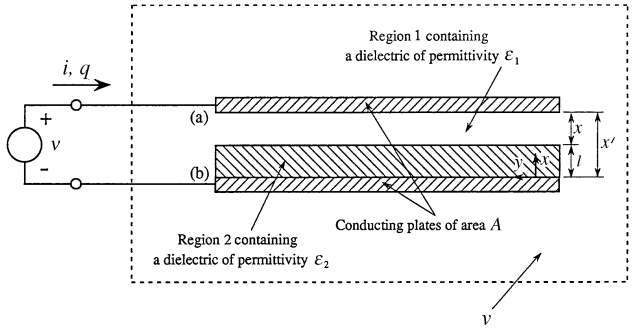

Fig. 1 Parallel-plate capacitor of variable dimensions and contents. After Woodson and Melcher.[7]

and provided that ε and E are defined as follows

$$\frac{x'}{\varepsilon} = \frac{x}{\varepsilon_1} + \frac{l}{\varepsilon_2} \tag{31}$$

$$E = \frac{v}{x'} \tag{32}$$

As already stated with respect to eqn. (21), U_e can be a first-order homogeneous function of V provided that $\frac{1}{2}\varepsilon E^2$ is invariable. This condition is satisfied in a particular process where ε_1, ε_2, x, l and v are held fixed as A is changed. In this process, changing A to λA gives the following changes: V to λV, Q to λQ and hence, by virtue of eqn. (17), also U_e to λU_e. Assuming that the field-independent temperature T, pressure P, and chemical potential, ζ, of all phases involved are also invariable, *e.g.* as A is changed, the corresponding entropies, volume and masses are also duplicated λ times, and hence, the field-independent energy, U'', is changed to $\lambda U''$. Thus the total internal energy, $U'' + U_e$, of the capacitor changes in this process to $\lambda(U'' + U_e)$ and, consequently, it satisfies the conditions required from a first-order homogeneous function.

However, in other processes, where $\frac{1}{2}\varepsilon E^2$ cannot be maintained invariable, *i.e.* as V and Q are changed to λV and λQ, respectively, U_e does not change to λU_e. For example, consider the process in which ε_1, ε_2 and A are held fixed, the pair (x, l) is changed to $(\lambda x, \lambda l)$, and v is changed to $\lambda^2 v$, so that V and Q are changed to λV and λQ, respectively.

As a result of this process, the capacitance C is changed to C/λ and hence, by virtue of eqn. (17), U_e is changed to $\lambda^3 U_e$. Representing, for this case, the total internal energy U as

$$U = U(S_1, S_2, V_1, V_2, N_1, N_2, Q) \tag{33}$$

it is clear that, in general,

$$\lambda U = U(\lambda S_1, \lambda S_2, \lambda V_1, \lambda V_2, \lambda N_1, \lambda N_2, \lambda Q) \tag{34}$$

does not hold.

It follows that U is not a homogeneous first-order function of the set $\{S_1, S_2, V_1, V_2, N_1, N_2, Q\}$ since its field-dependent part, U_e, is not a first-order homogeneous function of V and Q (where $V = V_1 + V_2$).

The next example is a uniformly charged sphere, in a medium of permittivity ε. The charge density, ρ_e, and the permittivity, ε, are uniform and fixed across the volume, V, of the sphere. The total charge of the sphere is $Q = \rho_e V$. The field E_r, which is radial, is given by[4]

$$E_r = \begin{cases} \dfrac{Qr}{4\pi\varepsilon R^3}; & r < R \\ \dfrac{Q}{4\pi\varepsilon r^2}; & r > R \end{cases} \tag{35}$$

where R is the radius of the sphere and r is the radial distance from its centre. The corresponding energy density, u_e, is given by

$$u_e = \frac{1}{2}\varepsilon E_r^2 = \begin{cases} \dfrac{Q^2 r^2}{32\pi^2\varepsilon R^6}; & r < R \\ \dfrac{Q^2}{32\pi^2\varepsilon r^4}; & r > R \end{cases} \tag{36}$$

The total stored electric energy is obtained as

$$U_e = \int_{r=0}^{\infty} u_e \, dV = \frac{3}{20}\frac{Q^2}{\pi\varepsilon R} = \left(\frac{3}{4\pi}\right)^{2/3} \frac{\rho_e^{1/3}}{5\varepsilon} Q^{5/3} \tag{37}$$

and hence the capacitance of the sphere is

$$C = \frac{10}{3}\pi\varepsilon R \tag{38}$$

It is clear that, in this case, since ρ_e is fixed, changing V to λV changes Q to λQ and *vice versa*. However, changing Q to λQ results in a change of U_e to $\lambda^{5/3} U_e$. This shows that a uniformly charged sphere is not a first-order homogeneous function of either V or Q. If the sphere carries a surface charge of fixed density σ_0, then the electric energy, U_σ, exclusively stored due to this surface charge is given by[4]

$$U_\sigma = \frac{Q^2}{8\pi\varepsilon R} = \frac{Q^{3/2}\sigma_0^{1/2}}{2(4\pi)^{1/2}\varepsilon}; \qquad Q = 4\pi R^2\sigma_0 \tag{39}$$

Hence, in this case, a change of Q to λQ produces a change of U_σ to $\lambda^{3/2} U_\sigma$, and U_σ is not a first-order homogeneous function of Q. Consequently, the total energy due to bulk and surface charges, *e.g.* $U_e + U_\sigma$, and hence also the total internal energy U of the sphere, are not first-order homogeneous functions of Q.

Duplication of the sphere system λ times can be done also by assembling λ identical spheres as a new system. In this case, it is clear that different geometries of the group of spheres yield different electric energies, and that this energy is not expected to be a linear function of λ, irrespective of the geometry chosen.

We turn next to consider the energy stored in a magnetic field using the work required to assemble a current distribution.

Magnetic Fields

Current distributions. The stored energy, U_I, of a current distribution, consisting of m current elements is given by,[4]

$$U_I = \frac{1}{2}\sum_{j=1}^{m} I_j \, d\Phi_j = \frac{1}{2}\sum_{j=1}^{m} \boldsymbol{I}_j \cdot \boldsymbol{A}_j \; dl_j \tag{40}$$

where $\boldsymbol{I}_j$ is the current carried by the jth current element with flux $d\Phi_j$, vector potential $\boldsymbol{A}_j$ and length dl_j.

If the current is distributed continuously over a line, surface, or volume, then U_I is given by[4]

$$U_I = \begin{cases} \dfrac{1}{2}\displaystyle\int_L \boldsymbol{I}_l \cdot \boldsymbol{A} \, dl; & \text{line current} \\ \dfrac{1}{2}\displaystyle\int_\Omega \boldsymbol{I}_\Omega \cdot \boldsymbol{A} \, d\Omega; & \text{surface current} \\ \dfrac{1}{2}\displaystyle\int_V \boldsymbol{I}_V \cdot \boldsymbol{A} \, dV; & \text{volume current} \end{cases} \tag{41}$$

where $\boldsymbol{I}_l$, $\boldsymbol{I}_\Omega$ and $\boldsymbol{I}_V$ are line, surface and volume currents, respectively, and Ω is surface area. The vector potential, $\boldsymbol{A}$, is given by[4]

$$\boldsymbol{A} = \frac{\mu_0}{4\pi}\int_\beta \frac{\boldsymbol{I}_\beta \, d\beta}{r_{QP}}; \qquad P \neq Q, \quad r_{QP} \neq 0 \tag{42}$$

where μ_0 is the permeability of free space, r_{QP} is the distance between the position P where $\boldsymbol{A}$ is evaluated and the position Q of the current element contributing to it, and β is l, Ω or V, depending on the type of current (*e.g.* line, surface, or volume) involved. Using eqn. (42), eqn. (41) can be presented in the following form:

$$U_I = \frac{\mu_0}{8\pi}\int_\beta \boldsymbol{I}_\beta \cdot \left(\int_\beta \frac{\boldsymbol{I}_\beta \, d\beta}{r_{QP}}\right) d\beta; \qquad P \neq Q, \qquad r_{PQ} \neq 0 \quad (43)$$

Eqn. (43) expresses the effect of interaction between the current elements on the energy, *e.g.* through the vector potential, $\boldsymbol{A}$, that has contributions from all of them. This is similar to the way U [see eqn. (7) and (9)] is affected by the interactions between all charges, *e.g. via* the electric potntial ψ_j. This shows that, in general, U_I is not expected to be a homogeneous first-order function of the current. An alternative form for the energy that arises due to volume currents [see eqn. (41)], is given by

$$U_I = \frac{1}{2}\int_V \boldsymbol{H} \cdot \boldsymbol{B} \, dV \quad (44)$$

where $\boldsymbol{H}$ and $\boldsymbol{B}$ are magnetic field strength and magnetic induction, respectively.

$$\boldsymbol{B} = \mu \boldsymbol{H} \quad (45)$$

and μ is magnetic permeability.

Here, eqn. (44) is restrictive to current elements, and the general expression for the energy, U_M, stored in a magnetic field, is given[4,6,8,9] by

$$U_M = \int_V \int_0^{\boldsymbol{B}} \boldsymbol{H} \cdot d\boldsymbol{B} \, dV \quad (46)$$

Eqn. (46) is the magnetic counterpart of eqn. (23). If μ is independent of $\boldsymbol{H}$ throughout V, then eqn (46) reduces to eqn. (44). As is the case with electric fields, U_M can be a first-order homogeneous function of V provided that $\int_0^{\boldsymbol{B}} \boldsymbol{H} \cdot d\boldsymbol{B}$ is uniform, fixed and independent of V. If μ is independent of $\boldsymbol{H}$ this means that $\frac{1}{2}\mu H^2$ must have this property, similar to the requirement from $\frac{1}{2}\varepsilon E^2$ in the case of an electric field.

We proceed to consider a variable gap magnetic circuit. Fig. 2 shows the system that consists of a fixed core and a plunger.[2,7] This system is characterized by the following equations.[7]

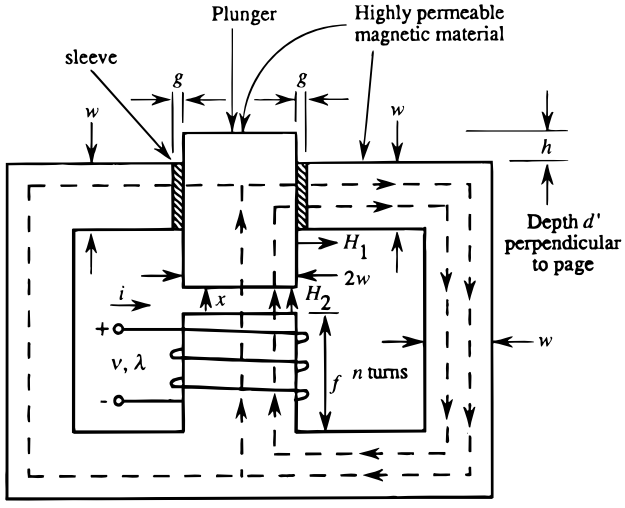

Fig. 2 Variable gap magnetic circuit consisting of a fixed core and a plunger. After Woodson and Melcher.[7]

$$H_1 = H_2 = \frac{ni}{g + x} \quad (47)$$

$$\Phi = L(x)i \quad (48)$$

$$L(x) = \frac{a\mu n^2}{g + x} \quad (49)$$

$$v = \frac{a\mu n^2}{g + x}\frac{di}{dt} - \frac{a\mu n^2 i}{(g + x)^2}\frac{dx}{dt} \quad (50)$$

$$a = 2wd' \quad (51)$$

where i is the current which is forced through n turns at voltage difference v, x is the width of the gap, g is the width of one sleeve, $L(x)$ is the system inductance, Φ is the flux linkage, μ is the permeability of the contents of the gap and the sleeves, and a is the cross-sectional area of the plunger which has dimensions $2w$ and d'.

Since the core and plunger are highly permeable, their capacity to store magnetic energy can be neglected. It follows that the magnetic energy is stored in the gap and in the fringing field around it. Similar to the case of capacitors, the ratio of the energy stored in the fringing field to that stored in the gap decreases as x decreases. This ratio is rather complex and hence, on these grounds, the magnetic energy is not expected to be a first-order homogeneous function of the volume of the gap. However, as shown below, this can be concluded also by considering the energy of the gap and sleeves and neglecting the fringing effect. The magnetic energy that is stored in the gap is given by

$$U_M = \frac{1}{2}L(x)i^2 = \frac{1}{2}\frac{\Phi^2}{L(x)} \quad (52)$$

Using $x = V/a$ and combining eqn. (49) and (52) gives

$$U_M = \frac{1}{2}\frac{a^2\mu n^2}{ga + V}i^2 = \frac{1}{2}\frac{ga + V}{a^2\mu n^2}\Phi^2 \quad (53)$$

Eqn. (53) clearly shows that $U_M = U_M(V, i) = U_M(V, \Phi)$ is not a first-order homogeneous function of either (V, i) or (V, Φ). It follows that the total energy of the variable gap system also cannot be a first-order homogeneous function of V. This agrees with the fact that the energy density in the gap depends on x and hence also on V (*e.g.* when the latter is a sole function of x).

The only way to change V at fixed energy density is by changing the cross-sectional area a at fixed g, x and i, through a change in d'. However, if x and Φ are held fixed as d' is changed, then the energy density becomes variable. Next we consider the case of a sphere in a uniform field.

Sphere in a uniform field

Fig. 3 shows a sphere in a field $\boldsymbol{H}_0$ existing between two planar and parallel pole faces. The permeability of the pole faces, which are set perpendicular to the plane of the figure and to the z axis, is practically infinite so that $\boldsymbol{H}_0$ is perpendicular to them. The gap has a volume V that is shared by the volume V_1 of the sphere and volume V_2 of the material surrounding it, so that $V = V_1 + V_2$. As shown in the figure, the corresponding permeabilities are μ_1 and μ_2 and they are assumed to be magnetically linear. The sphere radius is small compared to the distance L between the faces of the poles, so that neglecting end effects the field $\boldsymbol{H}_0$ can be approximated as being uniform. The magnetic energy U'_{M1} that exists due to the presence of the sphere, *e.g.* the sphere is its sole source, is given by,[2]

$$U'_{M1} = \frac{1}{2}V_1\mu_2\frac{\mu_1 - \mu_2}{\mu_1 + 2\mu_2}H_0^2 \quad (54)$$

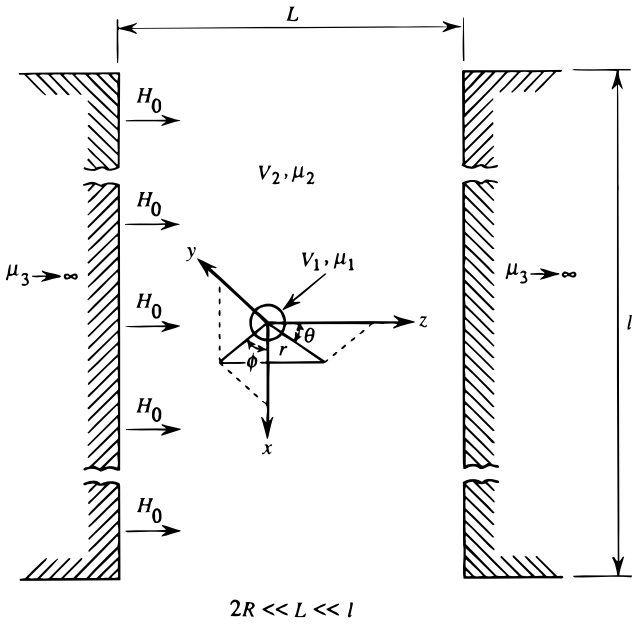

Fig. 3 Magnetizable sphere in a magnetic field between two planar and parallel pole faces. The field in the absence of the sphere is virtually uniform. After Zimmels.[2]

The energy U'_{M1} can be expressed also in terms of the field $\boldsymbol{H}_1$ existing within the sphere as follows,

$$U'_{M1} = \frac{1}{2} V_1 \mu_s H_1^2 = \frac{1}{2} V_1 B_1^2/\mu'_s \tag{55}$$

$$\mu_s = \mu_1\left[\frac{1}{9}(\mu_1/\mu_2 - 2\mu_2/\mu_1 + 1)\right] \tag{56}$$

$$\frac{1}{\mu'_s} = \frac{1}{\mu_1}\left[\frac{1}{9}\left(\frac{\mu_1}{\mu_2} - 2\frac{\mu_2}{\mu_1} + 1\right)\right] = \frac{\mu_s}{\mu_1^2} \tag{57}$$

where

$$\boldsymbol{H}_1 = \boldsymbol{B}_1/\mu_1 = \frac{3\mu_2 H_0}{\mu_1 + 2\mu_2}\boldsymbol{i}_z \tag{58}$$

The energy U'_{M1} consists of two parts which reflect the energy stored within and outside the sphere. If $\mu_1 \to \infty$, then only the part outside the boundaries of the sphere is significant.

$$U'_{M1}(\mu_1 \to \infty) = \frac{1}{2} V_1 \mu_2 H_0^2 \tag{59}$$

Eqn. (59) shows that the energy of the infinitely permeable sphere can be presented as if the field, H_0, were completely confined within its volume, V_1, and the permeability of the contents of V_1 were μ_2. In general, permeability, μ, is a function of density, ρ, temperature T and field $\boldsymbol{H}$.

$$\mu = \mu(\rho, T, \boldsymbol{H}) \tag{60}$$

The temperature is a function of the set $\{S, V, N\}$ and $\rho = N/V$. It follows that

$$\mu = \mu(S, V, N, \boldsymbol{H}) \tag{61}$$

This shows that U'_{M1}, as given by eqn. (54), is a function of the set $\{S_1, S_2, V_1, V_2, N_1, N_2, \boldsymbol{H}_0\}$.

$$U'_{M1} = U'_{M1}(S_1, S_2, V_1, V_2, N_1, N_2, \boldsymbol{H}_0) \tag{62}$$

It is clear that, owing to the structure of eqn. (54) (see also discussion below) U'_{M1} cannot be a first-order homogeneous function of the set $\{S_1, V_1, N_1, \boldsymbol{H}_1\}$, exclusively, *i.e.* only of variables that are defined within the boundaries of the sphere. For example, in eqn. (59), it is a function of the set $\{V_1, S_2, V_2, N_2, \boldsymbol{H}_0\}$. It is only when μ_1, μ_2 and $\boldsymbol{H}_0$ are held fixed, and the sphere does not change into another shape as its volume varies, that U'_{M1} becomes a first-order homogeneous function of V_1. Under these constraints, the energy density $\frac{1}{2}\mu_s H_1^2 = \frac{1}{2}B_1^2/\mu'_s$ is fixed and independent of V_1, as required. Consider the differential of U'_{M1}.

$$\begin{aligned} dU'_{M1} = {} & (\partial U'_{M1}/\partial V_1)_{\mu_1, \mu_2, \boldsymbol{H}_0}\, dV_1 \\ & + (\partial U'_{M1}/\partial \mu_1)_{V_1, \mu_2, \boldsymbol{H}_0}\, d\mu_1 \\ & + (\partial U'_{M1}/\partial \mu_2)_{V_1, \mu_1, \boldsymbol{H}_0}\, d\mu_2 \\ & + (\partial U'_{M1}/\partial \boldsymbol{H}_0)_{V_1, \mu_1, \mu_2}\, d\boldsymbol{H}_0 \end{aligned} \tag{63}$$

From eqn. (61), $d\mu_1$ and $d\mu_2$ can be expanded as follows,

$$\begin{aligned} d\mu_i = {} & [(\partial\mu/\partial S)_{V, N, \boldsymbol{H}}\, dS + (\partial\mu/\partial V)_{S, N, \boldsymbol{H}}\, dV \\ & + (\partial\mu/\partial N)_{S, V, \boldsymbol{H}}\, dN \\ & + (\partial\mu/\partial \boldsymbol{H})_{S, V, N}\, d\boldsymbol{H}]_i; \qquad i = 1, 2 \end{aligned} \tag{64}$$

Combining eqn. (63) and (64) gives

$$\begin{aligned} dU'_{M1} = {} & T_{11}\, dS_1 - P_{11}\, dV_1 + \zeta_{11}\, dN_1 + T_{12}\, dS_2 \\ & - P_{12}\, dV_2 + \zeta_{12} dN_2 + \eta_{11}\, d\boldsymbol{H}_0 \end{aligned} \tag{65}$$

where the index $1j$, $j = 1,2$ indicates that the source is in V_1 and the variable is due to energy stored in V_j.

$$T_{11} = (\partial U'_{M1}/\partial \mu_1)_{V_1, \mu_2, \boldsymbol{H}_0}(\partial \mu_1/\partial S_1)_{V_1, N_1, \boldsymbol{H}_1} \tag{66}$$

$$\begin{aligned} -P_{11} = {} & (\partial U'_{M1}/\partial V_1)_{\mu_1, \mu_2, \boldsymbol{H}_0} \\ & + (\partial U'_{M1}/\partial \mu_1)_{V_1, \mu_2, \boldsymbol{H}_0}(\partial \mu_1/\partial V_1)_{S_1, N_1, \boldsymbol{H}_1} \end{aligned} \tag{67}$$

$$\zeta_{11} = (\partial U'_{M1}/\partial \mu_1)_{V_1, \mu_2, \boldsymbol{H}_0}(\partial \mu_1/\partial N_1)_{S_1, V_1, \boldsymbol{H}_1} \tag{68}$$

$$T_{12} = (\partial U'_{M1}/\partial \mu_2)_{V_1, \mu_1, \boldsymbol{H}_0}(\partial \mu_2/\partial S_2)_{V_2, N_2, \boldsymbol{H}_2} \tag{69}$$

$$-P_{12} = (\partial U'_{M1}/\partial \mu_2)_{V_1, \mu_1, \boldsymbol{H}_0}(\partial \mu_2/\partial V_2)_{S_2, N_2, \boldsymbol{H}_2} \tag{70}$$

$$\zeta_{12} = (\partial U'_{M1}/\partial \mu_2)_{V_1, \mu_1, \boldsymbol{H}_0}(\partial \mu_2/\partial N_2)_{S_2, V_2, \boldsymbol{H}_2} \tag{71}$$

$$\begin{aligned} \eta_{11} = {} & (\partial U'_{M1}/\partial \boldsymbol{H}_0)_{V_1, \mu_1, \mu_2} \\ & + (\partial U'_{M1}/\partial \mu_1)_{V_1, \mu_2, \boldsymbol{H}_0}(\partial \mu_1/\partial \boldsymbol{H}_1)_{S_1, V_1, N_1}\, d\boldsymbol{H}_1 \\ & + (\partial U'_{M1}/\partial \mu_2)_{V_1, \mu_1, \boldsymbol{H}_0}(\partial \mu_2/\partial \boldsymbol{H}_2)_{S_2, V_2, N_2}\, d\boldsymbol{H}_2 \end{aligned} \tag{72}$$

Recall that here, $(\partial\mu_1/\partial \boldsymbol{H}_1)_{S_1, V_1, N_1} = (\partial\mu_2/\partial \boldsymbol{H}_2)_{S_2, V_2, N_2} = 0$, since μ_1 and μ_2 are assumed to be magnetically linear.

As dU'_{M1} is an exact differential, integration of all terms from $S_1 = V_1 = N_1 = S_2 = V_2 = N_2 = H_0 = 0$ to their final value must retrieve eqn. (54). In the course of this integration, each member of the set $\{T_{11}, P_{11}, \zeta_{11}, T_{12}, P_{12}, \zeta_{12}, \eta_{11}\}$ must be variable. In contrast, an Euler integration of eqn. (65), *e.g.* holding each member of the above set fixed gives,

$$\begin{aligned} U''_{M1} = {} & T_{11}S_1 - P_{11}V_1 + \zeta_{11}N_1 + T_{12}\, S_2 - P_{12}\, V_2 + \zeta_{12}\, N_2 \\ & + \eta_{11}\boldsymbol{H}_0 \end{aligned} \tag{73}$$

Clearly $U''_{M1} \neq U'_{M1}$ and apparently U''_{M1} has no physical meaning. This also verifies that U'_{M1} is neither a first-order homogeneous function of the set $\{S_1, V_1, N_1, \boldsymbol{H}_1\}$ nor of the set $\{S_1, V_1, N_1, S_2, V_2, N_2, \boldsymbol{H}_0\}$.

In contrast to systems (*e.g.* capacitors and magnetic circuits) in which virtually the complete field can be confined within a finite and prescribed volume, the sphere involves an inherent partition of the field between the part stored in its own volume, V_1, and the part stored in the space outside V_1. Suppose the sphere is a part of another system of volume $V' > V_1$, so that its energy U'_{M1} is part of the energy U of this system.

$$U = \sum_{i=0}^{n}\sum_{j=1}^{2} \xi_{ij} X_{ij} + U'_{M1} \tag{74}$$

where $i1$, and $i2$ denote that the ith variable pertains to the sphere ($j = 1$), and to the space of V' outside the sphere

($j = 2$), respectively. It is clear that if V_1, μ_1, μ_2 and $\boldsymbol{H}_0$ are held fixed, U'_{M1} is also fixed, and under this constraint, U cannot be a first-order homogeneous function of the set $\{X_{ij}\}$, $i = 0, \ldots, n$, $j = 1, 2$. However, if V_1 is set variable, while holding μ_1, μ_2 and $\boldsymbol{H}_0$ fixed, then U'_{M1} becomes a first-order homogeneous function of V_1 and hence, in this case,

$$U(\lambda\{X_{ij}\}, \lambda V_1) = \lambda U \tag{75}$$

$$\mathrm{d}U = \sum_{i=0}^{n} \sum_{j=1}^{2} \xi_{ij}\, \mathrm{d}X_{ij} + \xi'_{M1}\, \mathrm{d}V_1 \tag{76}$$

where

$$\xi'_{M1} = \frac{1}{2}\, \mu_2\, \frac{\mu_1 - \mu_2}{\mu_1 + 2\mu_2}\, H_0^2 \tag{77}$$

Eqn. (76) does not have the same properties and degrees of freedom as is the case in the absence of the field, *i.e.* at $\boldsymbol{H}_0 = 0$. This is due to the requirement that it will satisfy the condition that μ_1 and μ_2 be held fixed. According to eqn. (60) and (61), this condition can be satisfied provided that part or all of the set $\{\xi_{ij}\}$ is set fixed. If this were not so, then independent variability of all members of $\{\xi_{ij}\}$ would have rendered μ_1 and μ_2 variable, thus violating the condition that they must be fixed. This means that eqn. (76) is restrictive and as shown below, it cannot provide the grounds for a field-dependent Gibbs–Duhem equation. Integration of eqn. (76) at fixed $\xi_{ij}(i = 0, \ldots, n, j = 1, 2)$ gives eqn. (74), with $U'_{M1} = \xi'_{M1} V_1$. Thus, differentiation of eqn. (74) gives,

$$\mathrm{d}U = \sum_{i=0}^{n} \sum_{j=1}^{2} \xi_{ij}\, \mathrm{d}X_{ij} + X_{ij}\, \mathrm{d}\xi_{ij} + \xi'_{M1}\, \mathrm{d}V_1 + V_1\, \mathrm{d}\xi'_{M1} \tag{78}$$

Subtraction of eqn. (76) from eqn. (78) gives

$$\sum_{i=0}^{n} \sum_{j=1}^{2} X_{ij}\, \mathrm{d}\xi_{ij} + V_1\, \mathrm{d}\xi'_{M1} = 0. \tag{79}$$

Eqn. (79) appears to have the form of a Gibbs–Duhem equation. However, since μ_1, μ_2 and $\boldsymbol{H}_0$ are fixed, ξ'_{M1} is invariable, $\mathrm{d}\xi'_{M1} = 0$, and the rightmost term of eqn. (79) vanishes. Furthermore, as explained above, at least part of the set $\{\xi_{ij}\}$ must be fixed so that eqn. (79) cannot even have the full scope of a Gibbs–Duhem equation in the absence of the field. At most we can retrieve the 'field-independent' Gibbs–Duhem equation as

$$\sum_{i=0}^{n} \sum_{j=1}^{2} X_{ij}\, \mathrm{d}\xi_{ij} = 0 \tag{80}$$

Eqn. (80) agrees with the fact that, for a given j, $(\sum_{i=0}^{n} X_i\, \mathrm{d}\xi_i)_j = 0; j = 1, 2$, holds.

Note that for objects in a uniform field, $\boldsymbol{H}_0$, that have non-spherical geometries, we expect to be able to present U'_{M1} as the product of ξ'_{M1} and V_1. Clearly, for these objects $\xi'_{M1}(\mu_1, \mu_2, \boldsymbol{H}_0)$ will have a different form from eqn. (77), but the implications of eqn. (74)–(76) and (78)–(80) remain unchanged.

Suppose the magnetic moment, m_1, that is induced by the field, is locked in the frame of reference of the sphere both in magnitude and direction. Thus, rotation of the sphere results in rotation of this moment relative to $\boldsymbol{H}_0$. The work W_θ required to rotate m_1 (in the field $\boldsymbol{H}_0$), from an angle $\theta = 0$ to $\theta > 0$, is given by[4]

$$W_\theta = \mu_0\, m_1 H_0 (1 - \cos\theta) \tag{81}$$

where, using eqn. (58), it can readily be shown that at $\theta = 0$

$$m_1 = V_1\, \frac{\mu_1 - \mu_0}{\mu_0}\, \frac{3\mu_2}{\mu_1 + 2\mu_2}\, H_0 \tag{82}$$

Combining eqn. (81) and (82) gives

$$W_\theta = V_1\, \frac{3\mu_2(\mu_1 - \mu_0)}{\mu_1 + 2\mu_2}\, H_0^2 (1 - \cos\theta) \tag{83}$$

The work, W_θ, is stored as a potential magnetic energy so that the magnetic energy of the sphere, *e.g.* with its locked in moment m_1, takes the following form

$$U'_{M1}(\theta) = U'_{M1}(\theta = 0) + W_\theta = \frac{1}{2} V_1 \mu_2 H_0^2\, \frac{\mu_1 - \mu_2 + 6(\mu_1 - \mu_0)\cos\theta}{\mu_1 + 2\mu_2} \tag{84}$$

It follows that, in this case, the energy U as given by eqn. (74) is also a function of θ. Hence U cannot be a first-order homogeneous function of the set $\{X_{ij}\}$ and V_1, see eqn. (75), unless θ is fixed.

Eqn. (66)–(68) provide the formal definition of the magnetic component of the temperature (T_{11}), pressure (P_{11}) and chemical potential (ζ_{11}) of the contents of the sphere. By virtue of eqn. (84), T_{11}, P_{11} and ζ_{11} are all functions of θ. Hence, the temperature, pressure and chemical potential of the sphere, which are functions of T_{11}, P_{11} and ζ_{11}, respectively, must also be functions of θ. This result is striking in the sense that the field dependent temperature, pressure and chemical potential can be also orientation dependent.

Summary and Conclusions

Classical thermodynamics deals with systems that are first- and zero-order functions of their extensive and intensive variables, respectively. This is the basis for the fact that ordinary thermodynamic systems, which are free from effect of fields, can be Euler integrated and they follow the Gibbs–Duhem equation. The presence of fields can change the physical grounds which are the reason for these basic properties of thermodynamic systems.

Classical thermodynamics is concerned with scalar variables such as entropy, volume and mass, and their intensive conjugates, *e.g.* temperature, pressure and chemical potential. Classical thermodynamics is not concerned with interactions at a distance, effect of position in space, effect of geometry and shape, and partition of energy of the system on both sides of its own boundaries. The presence of fields subjects thermodynamic systems to laws that govern the fields. These laws affect the way energy is stored and distributed. This subjects the thermodynamic systems to additional constraints that are imposed on the fields. Such constraints can be due to boundary conditions and the interaction of the field with its sources. In this context, the source of the field can change the field-dependent energy of a system holding all its extensive variables fixed. This would not be possible in classical thermodynamics, where the energy of a system is a function of the complete set of its extensive variables.

An assembly of charges provides an example of the fundamental difference between a thermodynamic system in the absence and in the presence of an electric field. The energy of a thermodynamic system that contains an assembly of charges depends on the distances between the charges and on their quantities. Furthermore, the energy depends on charges that exist outside the system. The consequence of the presence of charges is that the system is no longer a first order homogeneous function of its extensive variables (the amount of charge being counted as one of them), it cannot be Euler integrated and the Gibbs–Duhem equation does not hold. However, the energy differential can be separated into field-independent and field-dependent exact differentials that can be integrated separately. The field-independent differential possesses the properties of an ordinary 'field-free' differential of a classical thermodynamic system, and as such, can be Euler integrated.

The field-dependent differential can be integrated directly but, in general, it cannot be Euler integrated to give a meaningful physical result. This means that the sum of the field-independent and field-dependent differentials cannot be, as a rule, Euler integrated as stated above.

There are limited cases in which the electric energy that is stored in the field can be a first-order homogeneous function of the extensive variables, *e.g.* entropy, volume and mass, of the system. In these cases, the energy density of the field must be fixed throughout the space where the field of the system exists. A parallel-plate capacitor sets a good example for conditions that permit or prohibit its definition as being a first order homogeneous function of its extensive variables. For a capacitor that has variable surface area of its plates at fixed distance between them and fixed voltage and composition, the condition that it can be reasonably approximated as, a first-order homogeneous function of its volume, is that its fringing field be small. The smaller the fringing effect the better is the approximation. However, if the volume changes due to a change in the distance between the plates at fixed area, then the electric energy density, stored in the field, no longer remains fixed as the volume and capacitance change. This means that such capacitors are not first-order homogeneous functions of their extensive variables. Other examples, such as charged spheres, support the conclusion that thermodynamic systems, in the presence of electric fields, cannot be defined in general terms as being first-order homogeneous functions of their extensive variables, *e.g.* apart from very specific and limited cases.

In electric fields, charges interact at a distance. In magnetic fields, currents interact at a distance. The magnetic work required to assemble current elements from infinity is half the sum of the scalar product between the current element, times its length, and the vector potential existing there. In case of volume currents, the differential magnetic energy stored in the field is the magnetic energy density in a given position times the volume differential assigned to this position. As is the case with an electric field, the condition that a thermodynamic system, in the presence of a magnetic field, be a first-order homogeneous function of its extensive variables is that the magnetic energy density be fixed and independent of the size and geometry of the system. This condition can be satisfied in limited classes of cases only. The case of a magnetic circuit with a variable gap serves as the magnetic counterpart of the parallel-plate capacitor. The magnetic energy that is stored in the gap and its fringing field can be a first-order homogeneous function of its volume, provided that the fringing effect can be neglected and the composition of the gap, and the distance between the pole faces that form it, are held fixed. In any case, the magnetic energy being proportional to the current squared, or the flux squared, cannot be a first-order homogeneous functions of these variables.

Discrete thermodynamic systems that are energized by a current source produce fields that extend beyond their own physical boundaries. A sphere in a uniform magnetic field serves as a classic example to the partition of its own energy, between the part outside and the part inside its boundary. The magnetic energy pertaining to such a sphere depends on its own extensive variables as well as on extensive variables of its surroundings. The result is that, in general, the magnetic energy of the sphere is not a first order homogeneous function of its own extensive variables and consequently, it cannot be Euler integrated, and the Gibbs–Duhem equation does not hold. If the magnetic moment of the sphere is locked in the frame of reference of the sphere, then the magnetic energy of the sphere depends also on the orientation of the sphere in the frame of reference of the external field. This shows that, even in the limited cases where magnetic energy of the sphere can be a first-order homogeneous function of its volume, its orientation must be fixed. Otherwise, a variable orientation in the process of Euler integration would render the result meaningless. This work shows that thermodynamic systems in the presence of fields are not expected, apart from limited cases, to possess the same properties that characterize them in the absence of the fields. This concerns their Euler integrability and consequently the applicability of the Gibbs–Duhem equation to the complete set of variables that characterize the energy of a system in the presence of fields.

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