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Thermodynamics of ideal gases in quasistatic electromagnetic fields

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The thermodynamics of ideal gases in the presence of quasistatic electromagnetic fields is considered. It is shown that thermodynamic properties of continua, in the presence of these fields, can be characterized by two conjugate sets of variables consisting of three extensive field-independent, and three intensive field-dependent variables. These sets are entropy, volume, and mass, i.e., $\{S,V,N\}$, and field-dependent temperature, pressure, and chemical potential, i.e., $\{\hat{T},\hat{P},\hat{\zeta}\}$, respectively. The second set has the same thermodynamic role as $\{T,P,\zeta\}$ that prevails in the absence of fields. In this context, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ must be uniform at equilibrium and, consequently, T, P, and ζ can have discontinuous jumps across interfaces that separate materials of different electromagnetic properties. Ideal gases that follow the Langevin equation are affected by a fixed $\mathbf{B}$ field, so that $\hat{T}$ increases, whereas both $\hat{P}$ and $\hat{\zeta}$ decrease as compared to their values in the absence of the field. The equation of state of ideal gases in fields has been formulated in terms of $\hat{T}$ and $\hat{P}$. Using this equation, it is shown that the change in the pressure P, which is induced by the field, is positive at fixed $\mathbf{B}$, whereas it is negative, but smaller, if $\mathbf{H}$ is fixed. Magnetic susceptibilities are defined at either fixed density, or at fixed pressure as two distinct and different thermodynamic variables. The susceptibility at fixed density follows the Curie-Wiess law. In contrast, the one defined at fixed pressure, being inversely proportional to the temperature squared, follows a different law. The fundamental equation of ideal gases in the presence of magnetic fields is derived. The field-dependent energy $\hat{U}$ is shown to be a function of S, V, and N and of the field-dependent entropy $\hat{S}$, and vice versa. Both $\hat{U}$ and $\hat{S}$ are functions of S, V, and N and the magnetic induction $\mathbf{B}$. Field-dependent specific heats of ideal gases, and relations between them, have been formulated under different constraints. At fixed $\mathbf{B}$, the field-induced increase in the specific heat is proportional to the ratio of magnetic to thermal energy squared. Ideal gases that are contained in discrete systems, under the action of magnetic fields, follow an equation of state that can be different than the one which is applicable for cases involving continua. This equation of state is not unique in the sense that it consists of field-dependent variables which are functions of the geometry of the discrete system, and their forms vary according to the constraints imposed on the discrete system and its surroundings. In the presence of fixed intensity magnetic fields, mixtures of permeable ideal gases are shown to satisfy the Gibbs theorem, and, at fixed $\mathbf{B}$, their entropy of mixing is larger than the value prevailing when the field is absent. Finally, the formulas and results obtained for ideal gases in magnetic fields can be applied to ideal gases in electric fields, through appropriate replacement of magnetic variables by their electric counterparts. [S1063-651X(96)08110-X]

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INTRODUCTION

Recently the theory of thermodynamics in the presence of electromagnetic fields has been formulated [1]. It was shown that in a lossless ideal system the electromagnetic energy must be a state function that has an exact differential. Furthermore, it is this differential that must be added to the energy differential prevailing in the absence of the field. In this way the sum remains an exact differential of a state function that stands for the overall internal energy. The theory provides different formulations for the field-dependent pressure and chemical potential under different field constraints. The case of discrete systems, where part or all of the field energy can be stored outside the physical boundaries of a thermodynamic system (which is the source of this field), has been defined with respect to the relation between energy and its source. The field energy stored outside the boundaries of a system, which is identified as its sole source, is accounted for as pertaining to this source. This is a consequence of the need to integrate the energy of a field source over the whole space that is energized due to its presence. The theory of thermodynamics in the presence of fields [1] was followed by system analysis of field-dependent thermodynamic variables and Maxwell relations [2]. The analysis of well defined systems provided a direct test and a better insight as to the validity and meaning of the field-dependent pressure and chemical potential. The existence of a field-dependent temperature as the third field-dependent variable was not considered as yet, due to the need to find its physical justification and meaning. In this work an attempt is made to derive a complete set of field-dependent thermodynamic variables (e.g., inclusive of the field-dependent temperature) and then use it to obtain the fundamental equation and equations of state of ideal gases, in a quasistatic electromagnetic field.

THEORY

The theory is first developed for the case of gases that form a continuum in the field, and then for the case of gases contained in a discrete system. The ideal gases are assumed to be electromagnetically linear, and the electromagnetic fields are quasistatic. We develop the theory in detail for gases in magnetoquasistatic fields and then show how to transform the results and formulate the electric counterpart.

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A. Uniform and isotropic continuum

Formulation of variables

In what follows the ideal gas is contained in a system that forms a uniform and isotropic continuum with respect to the field. Such a system can, for example, be a thin hollow toroid that is filled with the gas. The magnetic energy of the system is given by

$$U_M = \tfrac{1}{2} V B^2/\mu = \tfrac{1}{2} V \mu H^2, \tag{1}$$

$$\mathbf{B} = \mu \mathbf{H}, \tag{2}$$

where **H**, μ, and **B** are the magnetic field intensity, permeability, and magnetic induction, respectively. Note that, here and henceforth, vectors are denoted by boldface fonts, whereas their moduli by regular fonts. The magnetic energy U_M is fully contained in the volume V where **H** and μ are uniform and μ is independent of **H**. The permeability μ is a function of the density ρ and temperature T of the gas,

$$\mu = \mu(\rho, T). \tag{3}$$

The temperature is a function of the entropy S, the volume V, and the mole number N,

$$T = T(S, V, N). \tag{4}$$

The density is given by

$$\rho = N/V. \tag{5}$$

By virtue of Eqs. (3), (4), and (5), we have

$$\mu = \mu(S, V, N), \tag{6}$$

and hence

$$d\mu = (\partial \mu/\partial S)_{V,N} dS + (\partial \mu/\partial V)_{S,N} dV + (\partial \mu/\partial N)_{S,V} dN. \tag{7}$$

The differential of U_M can be presented in the following two forms. The first form is obtained from Eq. (1) by selecting V, **B**, and μ as the independent variables,

$$dU_M(V, \mathbf{B}, \mu) = \frac{1}{2} \frac{B^2}{\mu}\, dV + V \frac{B}{\mu}\, dB - \frac{1}{2} V \frac{B^2}{\mu^2}\, d\mu. \tag{8}$$

Combining Eqs. (2) and (8) gives

$$dU_M(V, \mathbf{B}, \mu) = \tfrac{1}{2} \mathbf{H} \cdot \mathbf{B}\; dV + V \mathbf{H} \cdot d\mathbf{B} - \tfrac{1}{2} V H^2 d\mu. \tag{9}$$

The second form is obtained from Eq. (1) by selecting V, **H**, and μ as the independent variables. The result is

$$dU_M(V, \mathbf{H}, \mu) = \tfrac{1}{2} \mathbf{H} \cdot \mathbf{B}\; dV + V \mathbf{B} \cdot d\mathbf{H} + \tfrac{1}{2} V H^2 d\mu. \tag{10}$$

For example, at fixed V and **B**, Eqs. (9) and (10), using $d\mathbf{H} = d(\mathbf{B}/\mu)$, yield $-\tfrac{1}{2} V H^2 d\mu$, whereas at fixed V and **H**, using $d\mathbf{B} = d(\mu \mathbf{H})$, the result is $\tfrac{1}{2} V H^2 d\mu$. Thus at fixed V and **B**, a positive change in μ decreases the magnetic energy, whereas the reverse is true if **H**, instead of **B**, is held fixed. In the absence of the field, the internal energy is given by

$$U = TS - PV + \zeta N. \tag{11}$$

In the presence of the magnetic field (see Appendix A for further details),

$$\hat{U} = U + U_M = TS - PV + \zeta N + U_M, \tag{12}$$

where $\hat{U}$ is the field-dependent overall energy, and T, P, and ζ are the temperature, pressure, and chemical potential in the absence of the field.

The differentials of U and of U_M are both exact, but they are different in the sense that dU is given by

$$dU = T\, dS - P\, dV + \zeta\, dN. \tag{13}$$

Since the Gibbs-Duhem equation holds,

$$-S\, dT + V\, dP - N\, d\zeta = 0, \tag{14}$$

whereas dU_M is given either by Eq. (9) or by (10). Differentiation of Eq. (12) in conjunction with Eqs. (7), (9), and (13) yields

$$d\hat{U} = \hat{T}\, dS - \hat{P}\, dV + \hat{\zeta}\, dN + V \mathbf{H} \cdot d\mathbf{B}, \tag{15}$$

where $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ are field-dependent intensive variables which are defined, at fixed **B**, as follows:

$$\hat{T} = (\partial \hat{U}/\partial S)_{V,N,\mathbf{B}} = T - \tfrac{1}{2} V H^2 (\partial \mu/\partial S)_{V,N}, \tag{16}$$

$$\hat{P} = -(\partial \hat{U}/\partial V)_{S,N,\mathbf{B}} = P + \tfrac{1}{2} V H^2 (\partial \mu/\partial V)_{S,N} - \tfrac{1}{2} \mu H^2, \tag{17}$$

$$\hat{\zeta} = (\partial \hat{U}/\partial N)_{S,V,\mathbf{B}} = \zeta - \tfrac{1}{2} V H^2 (\partial \mu/\partial N)_{S,V}. \tag{18}$$

Expressing these variables in terms of specific entropy s and density ρ gives

$$\hat{T} = T - \frac{1}{2\rho} H^2 (\partial \mu/\partial s)_{V,N}, \tag{19}$$

$$\hat{P} = P - \tfrac{1}{2} H^2 \rho (\partial \mu/\partial \rho)_{S,N} - \tfrac{1}{2} \mu H^2, \tag{20}$$

$$\hat{\zeta} = \zeta - \tfrac{1}{2} H^2 (\partial \mu/\partial \rho)_{S,V}, \tag{21}$$

where

$$s = S/N. \tag{22}$$

The use of the energy differential [in the form given by Eq. (15)] for derivation of Eq. (12) is described in Appendix A.

Note that if the condition of fixed **B** implies that the flux linkage with the current source is also fixed, then no field-related exchange of energy between the current source and the system is allowed. This means that, at fixed magnetic flux, the system is limited to exchange of energy with its surroundings but not with its current source. Equations (19)–(21) show that for materials that are characterized by $(\partial \mu/\partial s)_{V,N} < 0$, $(\partial \mu/\partial \rho)_{S,N} > 0$, $(\partial \mu/\partial \rho)_{S,V} > 0$, and are held at fixed **B**, $\hat{T} > T$, $\hat{P} < P$, and $\hat{\zeta} < \zeta$. If **H** instead of **B** is set fixed, then energy exchanges between the system and current source occurs, the consequence being that the signs of the terms that involve a derivative of μ are reversed. Thus, at fixed **H**,

$$\hat{T}=T+\frac{1}{2\rho}H^2(\partial\mu/\partial s)_{V,N}, \tag{23}$$

$$\hat{P}=P+\tfrac{1}{2}H^2\rho(\partial\mu/\partial\rho)_{S,N}-\tfrac{1}{2}\mu H^2, \tag{24}$$

$$\hat{\zeta}=\zeta+\tfrac{1}{2}H^2(\partial\mu/\partial\rho)_{S,V}. \tag{25}$$

Note that in deriving Eq. (20) from Eq. (17), use was made of

$$\begin{aligned}(\partial\mu/\partial V)_{S,N}&=(\partial\mu/\partial\rho)_{S,N}(\partial\rho/\partial V)_{S,N}\\&=-(\rho/V)(\partial\mu/\partial\rho)_{S,N}.\end{aligned} \tag{26}$$

Equation (15), in conjunction with $\hat{T}$ [see Eqs. (16), (19), and (23) for its alternative forms] shows that in the presence of the field, the heat differential which is delivered to the system is $\hat{T}dS$ and not TdS. Recall that TdS is the heat differential in the absence of fields. It follows that the excess in the heat differential due to the field is $(\hat{T}-T)dS$.

An attempt to identify $\hat{T}d\hat{S}$ [where $\hat{S}$ is the field-dependent entropy [1] which is given below by Eq. (71)] as the heat differential instead of $\hat{T}dS$ will show that, at fixed S, V, N, and **B**, it vanishes. It follows that $\hat{S}$ cannot replace S as the fundamental and independent entropic variable, and $\hat{T}dS$ is indeed the heat differential in the presence of the field; also see the discussion of the more general perspective of Eq. (15) below.

Furthermore, it is important to realize that the set $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ is defined by Eqs. (19)–(21) and by Eqs. (23)–(25), exclusively for the constraints of fixed **B** and **H**, respectively. This limits their use only for those processes that conform with one of the above constraints. For example, if a process simultaneously involves variable **B** and **H**, then Eqs. (19)–(21) and (23)–(25) cannot be applied directly. However, since the energy is a state function it can be analyzed by first holding **B** fixed and letting **H** vary, and then holding **H** fixed and letting **B** vary, so that the final values of **H** and **B** are reached.

In a more general perspective, Eq. (15) gives the differential of the field-dependent internal energy in terms of four distinct and independent differentials. Each of these differentials has a clear physical meaning as follows. The first differential $\hat{T}dS$ stands for the energy change at fixed V, N and **B** (i.e., fixed flux). As no volume, mass, and magnetic flux changes are allowed, this energy change must involve heat exclusively. It follows that $\hat{T}dS$ is indeed the heat differential in the presence of the field. The second differential $-\hat{P}dV$ stands for the energy change at fixed S, N, and **B**. As no entropy, mass, and magnetic flux changes are allowed, this energy change must involve pressure-volume, or, alternatively, mechanical work exclusively. It follows that $-\hat{P}dV$ is indeed the pressure-volume or mechanical work differential in the presence of the field. The third differential $\hat{\zeta}dN$ stands for the energy change at fixed S, V, and **B**. As no entropy, volume, and magnetic flux changes are allowed, this energy change must involve mass transfer exclusively. It follows that $\hat{\zeta}dN$ is indeed the mass transfer energy (or work) differential in the presence of the field. The fourth differential stands for the energy change at fixed S, V, and N. As no entropy, volume, and mass changes are allowed, this energy change must involve change of flux, or alternatively, a change of magnetization due to the exclusive interaction between the current sources and the system being polarized. It follows that $V\mathbf{H}\cdot d\mathbf{B}$ is indeed the magnetization work differential of the current sources.

Although Eq. (15) can be integrated at variables $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ to retrieve Eq. (12), it cannot be Euler integrated, i.e., holding $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ fixed, for the same purpose. It follows that, in general, except for the case $H=0$,

$$\hat{U}\neq\hat{T}S-\hat{P}V+\hat{\zeta}N+\tfrac{1}{2}V\mu H^2. \tag{27}$$

The integration of Eq. (15) can readily be carried out by separating, and then grouping according to type, the field-independent and field-dependent terms, so that each group becomes an exact differential. The field-independent group can be Euler integrated (i.e., holding T, P, and ζ fixed), but the field-dependent differential must be integrated as one exact differential. This integration retrieves Eq. (12).

The analysis presented hitherto includes the contribution of free space to the magnetic energy. Since $\hat{T}$ and $\hat{\zeta}$ are functions of partial derivatives of μ, they give the net effect of the gas (i.e., independent of the energy stored in free space). However, $\hat{P}$ depends on the term $-\frac{1}{2}\mu H^2$, which includes the effect of free space. It follows that the net effect of the gas, i.e., with respect to the field-dependent pressure, is obtained once the term $-\frac{1}{2}\mu H^2$ is replaced either by $-\frac{1}{2}B^2[(1/\mu)-(1/\mu_0)]$, or by $-\frac{1}{2}(\mu-\mu_0)H^2$, for the cases where either **B** or **H** are held fixed, respectively.

Using the variable μ', which is defined by

$$\mu'=\mu-\mu_0, \tag{28}$$

the net effect of the gas is obtained if, in the term $-\frac{1}{2}\mu H^2$, μ is replaced either by $-\mu\mu'/\mu_0$ or by μ' for the cases in which either **B** or **H** is held fixed, respectively. The variables $\hat{P}$ and $\hat{\zeta}$ have been defined elsewhere already [1]. However, $\hat{T}$ has not yet been defined explicitly, and its physical implications need further considerations.

If $(\partial\mu/\partial s)_{V,N}<0$, as is the case with ideal gases, then at fixed **B**, $\hat{T}>T$, whereas at fixed **H**, $\hat{T}<T$. In the former case, a decrease in μ due to an increase in s increases **H** and hence also the entropic part of the magnetic energy. This gives an overall effect of an increased field-dependent temperature. In the latter case, i.e., fixed **H**, the reverse is true. At fixed **B**, which here implies fixed flux, $\hat{T}$ represents the exclusive effect of the field on matter which is under its action. In contrast, at fixed **H**, $\hat{T}$ also involves the effect of the current source. In this respect, the pure effect of the field is to increase the temperature of matter for which $(\partial\mu/\partial s)_{V,N}<0$ holds. Nevertheless, according to the formal definition of temperature, the two different field constraints yield two different field-dependent temperatures. These temperatures reflect the different rates of change of the field-dependent energy with the field-independent entropy. These different rates arise when different field constraints are imposed on the system and its current source. For further details, on derivations and properties of derivatives of $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ with respect to H; see Appendix B. Formally, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ are a set that characterizes the thermodynamic system in the same way that the set T, P, and ζ characterizes this system in the absence of fields. Thus, using this formalism, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ can be considered as the field-dependent temperature, pressure, and chemical potential of the continuum. Using these intensive variables as ordinary thermodynamic variables suggests that, at equilibrium, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ be uniform across the system. This has been stated already for $\hat{P}$ and $\hat{\zeta}$ elsewhere [1], the consequence being that there can be a jump in P and ζ across interfaces separating materials of different magnetic properties. The uniformity of $\hat{T}$ suggests that, in the presence of electromagnetic fields, T may also have a jump across such interfaces. The existence of such jumps, i.e., in each variable of the set T, P, and ζ due to $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ being uniform at equilibrium across interfaces, means that, at the instant the field is removed, T, P, and ζ must be nonuniform across these interfaces. This gives rise to driving forces that act to change the position of the interfaces, and cause a flow of heat and matter across them. This important observation can be formulated as the following corollary.

Systems that have different electromagnetic properties, and share a common interface, are driven to change their equilibrium position and exchange heat and matter across this interface, when the field acting on them is removed. In this sense, removal of the field drives systems, which have different electromagnetic properties and share a common interface, to change the way their field-independent energies are partitioned. The actual realization and outcome of this drive depends on constraints that are imposed on both systems and their common interface. In the same context, if (in the absence of fields) a system is at equilibrium and T, P, and ζ are uniform, then at the instant a field is imposed on this system, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ are nonuniform. It follows that a change in T, P, and ζ must occur if the system is to shift back to equilibrium. When this equilibrium is reached, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ become uniform, while T, P, and ζ turn nonuniform. Having defined the set of field-dependent thermodynamic variables, we next formulate the equations of state and the entropic fundamental equation of gas in the presence of the field.

Formulation of equations of state

The first equation of state involves the energy of the gas. The magnetic energy as given by Eq. (1) includes the contribution of free space. Thus, in order to obtain the net energy due to the gas, it is necessary to subtract the energy stored in free space. The value of this net energy of matter depends on the constraints which are imposed on it, e.g., whether **B** or **H** is held fixed. Thus the net energy $\hat{U}_g$, due to the gas is

$$\hat{U}_g = U + \tfrac{1}{2} V B^2 \left(\frac{1}{\mu} - \frac{1}{\mu_0} \right) = U - \tfrac{1}{2} V \mu' H^2 (\mu/\mu_0) \tag{29a}$$

at fixed **B**, or

$$\hat{u}_g = u - \frac{1}{2\rho} \mu' H^2 (\mu/\mu_0), \tag{29b}$$

$$\hat{U}_g = U + \tfrac{1}{2} V \mu' H^2, \tag{30a}$$

at fixed **H**, or

$$\hat{u}_g = u + \frac{1}{2\rho} \mu' H^2, \tag{30b}$$

where $u = U/N$ and $\hat{u}_g = \hat{U}_g/N$.

Thus Eq. (29) is the ‘‘energy equation of state’’ in a fixed **B** field, whereas Eq. (30) is its counterpart in a fixed **H** field. Equation (29) shows also that in a fixed **B** field, $\hat{U}_g$ is a decreasing function of μ'. The reverse is true in a fixed **H** field [see Eq. (30)].

The pressure of the gas is readily obtained as

$$\begin{aligned} \hat{P}_g &= -(\partial \hat{U}_g / \partial V)_{S,N,\mathbf{B}} \\ &= P - \tfrac{1}{2} H^2 \rho (\partial \mu / \partial \rho)_{S,N} + \tfrac{1}{2} \mu' H^2 (\mu/\mu_0), \quad \mathbf{B} \text{ fixed}, \end{aligned} \tag{31}$$

$$\begin{aligned} \hat{P}_g &= -(\partial \hat{U}_g / \partial V)_{S,N,\mathbf{H}} \\ &= P + \tfrac{1}{2} H^2 \rho (\partial \mu / \partial \rho)_{S,N} - \tfrac{1}{2} \mu' H^2, \quad \mathbf{H} \text{ fixed}. \end{aligned} \tag{32}$$

Equation (31) shows that if $\mu' \mu/\mu_0 > \rho(\partial\mu/\partial\rho)_{S,N}$, then $\hat{P}_g - P > 0$, and the effect of the field is to increase the pressure of the gas. As shown below this indeed is the case for permeable gases. Recalling that in the absence of the field $P = \rho R T$, the second equation of state can be obtained by elimination of T between Eqs. (19) and (31) in a fixed **B** field, and between Eqs. (23) and (32) in a fixed **H** field. The result is

$$\hat{P}_g = \rho R \hat{T} + \tfrac{1}{2} H^2 [R(\partial\mu/\partial s)_{V,N} + \mu' \mu/\mu_0 - \rho(\partial\mu/\partial\rho)_{S,N}] \tag{33}$$

at fixed **B**, and

$$\hat{P}_g = \rho R \hat{T} - \tfrac{1}{2} H^2 [R(\partial\mu/\partial s)_{V,N} + \mu' - \rho(\partial\mu/\partial\rho)_{S,N}] \tag{34}$$

at fixed **H**. At either $\mathbf{H} = \mathbf{0}$ or $\mu = \mu_0$, Eqs. (33) and (34) reduce to $P = \rho R T$, as expected.

For monatomic ideal gases [3],

$$(\partial s/\partial T)_{V,N} = \frac{3}{2} \frac{R}{T}. \tag{35}$$

Hence using

$$(\partial\mu/\partial s)_{V,N} = (\partial\mu/\partial T)_{V,N} / (\partial s/\partial T)_{V,N} \tag{36}$$

gives

$$(\partial\mu/\partial s)_{V,N} = (2T/3R)(\partial\mu/\partial T)_{V,N}. \tag{37}$$

The permeability is a linear function of the susceptibility χ,

$$\mu = \mu_0 (1 + \chi), \tag{38}$$

where χ is defined as the ratio of magnetization **M** and field **H**,

$$\chi = \mathbf{M}/\mathbf{H}, \tag{39}$$

$$\mathbf{M} = \mathbf{B}/\mu_0 - \mathbf{H}. \tag{40}$$

The magnetization of an ideal gas is assumed here to follow the Langevin equation [4]

$$M = M_s(\coth a - 1/a), \tag{41}$$

$$M_s = Nm = \rho \tilde{N} m, \tag{42}$$

where M_s is the saturation magnetization, N is the number density (i.e., per unit volume) of the gas molecules, m is the dipole moment of a single molecule, $\tilde{N}$ is Avogadro's number, and a is defined by

$$a = \mu_0 mH/kT, \tag{43}$$

where k is the Boltzmann constant.

At room temperature, the value of a for ideal gases is expected to be small. This facilitates the use of the following approximation which holds for $a \ll 1$:

$$M = \tfrac{1}{3} M_s a = \tfrac{1}{3} M_s \frac{\mu_0 mH}{kT}, \quad a \ll 1\,. \tag{44}$$

By virtue of Eq. (39), the susceptibility of the gas is obtained from Eq. (44) as

$$\chi = C/T, \tag{45}$$

where C is a function of ρ via its dependence on M_s,

$$C = C(\rho) = \tfrac{1}{3} M_s \mu_0 m/k = \tfrac{1}{3} \rho \tilde{N} \mu_0 m^2/k. \tag{46}$$

Note that by introducing the rightmost side of Eq. (46), it is implied that $m > 0$. If $m < 0$, as is the case for diamagnetic gases, then $C(\rho)$ would be negative. For the sake of simplicity, we assume henceforth that $m > 0$. The Curie-Weiss law can be expressed as [3]

$$\chi = C'/(T - \theta), \tag{47}$$

where C' and θ are constants.

It is seen that the gas follows the Curie-Weiss law if ρ is fixed and if, in Eq. (47), $\theta = 0$. In this case $C' = C$. Since $\rho = 1/v$, setting ρ fixed is equivalent to imposing a fixed specific volume v. Thus, under the condition of fixed ρ, and hence also of fixed v, the susceptibility is defined as one pertaining to matter that is held at fixed v. However, if P instead of ρ is held fixed, and the use of $\rho = P/RT$ as an approximation is justified (as indeed is the case since the field effect in gases is expected to be small) then C becomes an inverse function of T,

$$C(T) = \tfrac{1}{3} P \mu_0 (m/k)^2/T, \quad P = \text{const.} \tag{48}$$

In this case the susceptibility, e.g., at fixed pressure, is an inverse function of T^2,

$$\chi = C''/T^2, \quad P = \text{const}, \tag{49}$$

$$C'' = \tfrac{1}{3} P \mu_0 (m/k)^2. \tag{50}$$

Thus Eqs. (45) and (49) define the susceptibility χ at fixed v, i.e., $\chi = \chi_v$, and at fixed P, i.e., $\chi = \chi_p$, respectively. This seems to offer the magnetic counterpart of the specific heat at fixed v and at fixed P, i.e., c_v and c_p, respectively. In summary, the susceptibility of ideal gases that satisfy the Langevin equation follows two different laws depending on ρ or P being fixed. The Curie-Weiss law is followed only at fixed ρ, but not at fixed P, where the susceptibility varies with $1/T^2$. In what follows we use Eq. (3), and hence the derivatives of μ are evaluated either at fixed ρ or at fixed T,

$$d\mu = (\partial\mu/\partial\rho)_T d\rho + (\partial\mu/\partial T)_\rho dT. \tag{51}$$

Thus Eq. (45) must be used for evaluation of $(\partial\mu/\partial T)_\rho$, as is done below. Furthermore, henceforth, $\partial\mu/\partial\rho$ and $\partial\mu/\partial T$ stand for $(\partial\mu/\partial\rho)_T$ and $(\partial\mu/\partial T)_\rho$,

$$\partial\mu/\partial T = \mu_0 \partial\chi/\partial T = -\mu_0 C/T^2 = -\mu_0 \chi/T = -\mu'/T. \tag{52}$$

Again, by virtue of Eqs. (38), (39), (42), and (44), and at fixed T, μ is a linear function of ρ,

$$\mu = K\rho + \mu_0, \quad K = \tfrac{1}{3} \tilde{N} \frac{(\mu_0 m)^2}{kT}, \tag{53}$$

where at fixed T, K is a constant. Hence

$$\partial\mu/\partial\rho = K = \mu'/\rho\,. \tag{54}$$

Combining Eqs. (31) and (54) gives

$$\hat{P}_g = P + \tfrac{1}{2} \mu' H^2 (\mu/\mu_0 - 1), \quad \mathbf{B} \text{ fixed.} \tag{55}$$

Combining Eqs. (32) and (54) gives

$$\hat{P}_g = P, \tag{56}$$

where $P = \rho RT$ holds. Note that the derivation of Eqs. (55) and (56) [as well as Eqs. (59) and (60) below] implies equality between $(\partial\mu/\partial\rho)_T$ and $(\partial\mu/\partial\rho)_{S,N}$; see Appendix C for proof and details. Equation (55) shows that if **B** is set fixed, then for gases that are permeable $\hat{P}_g > \rho RT$, and hence the field acts so as to increase the pressure; i.e., above its value P at $H = 0$. In contrast, Eq. (56) shows that, at fixed **H**, $\hat{P}_g = \rho RT$, irrespective of the gas permeability and the field. Note that Eq. (55) is an equation of state having the form $\hat{P}_g = \hat{P}_g(\rho, T, \mathbf{H})$. Here the field-dependent pressure is a function of the field-independent temperature T and the field **H**. This constitutes dependence of $\hat{P}_g$ on mixed variables, i.e., on one which is independent of the field and the other which is the field strength.

Combining Eqs. (19), (37), and (52) gives

$$\hat{T} = T + \frac{1}{3\rho R} \mu' H^2, \quad \mathbf{B} \text{ fixed.} \tag{57}$$

Combining Eqs. (23), (37), and (52) gives

$$\hat{T} = T - \frac{1}{3\rho R} \mu' H^2, \quad \mathbf{H} \text{ fixed.} \tag{58}$$

Equations (57) and (58) show that if a monatomic gas is permeable, then, at fixed **B**, $\hat{T} > T$, whereas at fixed **H**, $\hat{T} < T$. For ideal gases that follow the Langevin equation, substitution of Eq. (54) into Eq. (33) for the case of fixed **B**, and into Eq. (34) for the case of fixed **H** give

$$\hat{P}_g=\rho R\hat{T}+\tfrac{1}{2}H^2[R(\partial\mu/\partial s)_{V,N}+\mu'(\mu/\mu_0-1)], \quad \mathbf{B}\ \text{fixed}, \tag{59}$$

$$\hat{P}_g=\rho R\hat{T}-\tfrac{1}{2}H^2R(\partial\mu/\partial s)_{V,N}, \quad \mathbf{H}\ \text{fixed}. \tag{60}$$

If these gases are also monatomic, then Eq. (37) holds, and upon its substitution [in conjunction with Eq. (52)] into Eqs. (59) and (60) we obtain

$$\hat{P}_g=\rho R\hat{T}+\tfrac{1}{2}\mu' H^2[\mu/\mu_0-5/3], \quad \mathbf{B}\ \text{fixed}, \tag{61}$$

$$\hat{P}_g=\rho R\hat{T}+\tfrac{1}{3}\mu' H^2, \quad \mathbf{H}\ \text{fixed}. \tag{62}$$

Note that, as shown in Eq. (52), μ' is an inverse function of T,

$$\mu'=\mu_0 C/T. \tag{63}$$

Thus, eliminating T between Eqs. (57) (at fixed **B**) or (58) (at fixed **H**) and (63), gives the following quadric equations in μ':

$$\frac{1}{3\rho R}H^2(\mu')^2-\hat{T}\mu'+\mu_0 C=0, \quad \mathbf{B}\ \text{fixed}, \tag{64}$$

$$\frac{1}{3\rho R}H^2(\mu')^2+\hat{T}\mu'-\mu_0 C=0, \quad \mathbf{H}\ \text{fixed}. \tag{65}$$

Solution of μ' as a function of ρ, $\hat{T}$, and H gives

$$\mu'=\mu'(\rho,\hat{T},H). \tag{66}$$

Since $\mu=\mu'+\mu_0$, we also have

$$\mu=\mu(\rho,\hat{T},H). \tag{67}$$

Hence Eqs. (61) and (62), in conjunction with Eqs. (66) and (67), present an equation of state where $\hat{P}_g$ is a function of, ρ, $\hat{T}$, and H,

$$\hat{P}_g=\hat{P}_g(\rho,\hat{T},H). \tag{68}$$

Thus, in contrast to Eq. (55), here $\hat{P}_g$ is a function of field-dependent temperature $\hat{T}$ rather than of the field-independent T. This eliminates the dependence of $\hat{P}_g$ on mixed variables, which is characteristic of Eq. (55).

Fundamental equation

In the absence of fields, the fundamental equation can be expressed in the following equivalent forms:

$$U=U(S,V,N), \tag{69}$$

$$S=S(U,V,N). \tag{70}$$

In the presence of the field, U and S are replaced by $\hat{U}$ and $\hat{S}$. However, as shown below, the functional relationship of Eqs. (69) and (70), i.e., $\hat{U}=\hat{U}(\hat{S},V,N)$ and $\hat{S}=\hat{S}(\hat{U},V,N)$, does not hold.

At fixed **B** the field-dependent entropy $\hat{S}$ is given by [1,5,6]

$$\hat{S}=S+\tfrac{1}{2}V\frac{B^2}{\mu^2}\left(\frac{\partial\mu}{\partial T}\right)_\rho. \tag{71}$$

At fixed **H** the sign of the magnetic term is reversed. Multiplying both sides of Eq. (71) by T gives

$$T\hat{S}=TS+\tfrac{1}{2}V\frac{B^2}{\mu^2}T\left(\frac{\partial\mu}{\partial T}\right)_\rho. \tag{72}$$

It is clear that $T(\partial\mu/\partial T)_\rho$ can be presented in terms of μ,

$$T(\partial\mu/\partial T)_\rho=\alpha(S,V,N)\mu(S,V,N)+\beta(S,V,N), \tag{73}$$

where $\alpha(S,V,N)$ and $\beta(S,V,N)$ are factors accounting for the possible nonlinear dependence of μ on T. Note that for ideal gases, using Eq. (52), we find that $T(\partial\mu/\partial T)_\rho=-\mu'$, and hence [see Eq. (28)] in this case, α and β are constants: $\alpha(S,V,N)=-1$ and $\beta(S,V,N)=\mu_0$. By virtue of Eqs. (1), (2), and (12), Eq. (72) can be expressed as

$$T\hat{S}=TS-(\alpha+\beta/\mu)U+(\alpha+\beta/\mu)\hat{U}. \tag{74}$$

Since T, α, β, and U are all functions of S, V, and N, it follows that

$$\hat{S}=\hat{S}(S,V,N,\hat{U}), \tag{75}$$

and hence

$$\hat{U}=\hat{U}(S,V,N,\hat{S}). \tag{76}$$

In the absence of field, $\hat{U}=U$ and $\hat{S}=S$ and Eqs. (75) and (76) reduce to Eqs. (70) and (69), respectively. However, in the presence of the field $\hat{S}$ is a function of four variables, three of which are field independent, and the fourth is $\hat{U}$. Similarly, $\hat{U}$ is a function of the same field-independent variables and $\hat{S}$. The fourth field-dependent variable, by its very nature, is a consequence of the presence of the field. Equations (75) and (76) can be derived using the following different approach. By virtue of Eqs. (6) and (8)

$$U_M=U_M(V,B,\mu)=U_M(S,V,N,B). \tag{77}$$

Hence [see Eqs. (1) and (12)]

$$\hat{U}=\hat{U}(S,V,N,B). \tag{78}$$

Equation (71) in conjunction with Eq. (6) shows that

$$\hat{S}=\hat{S}(S,V,N,B). \tag{79}$$

Eliminating B between Eqs. (78) and (79) yields Eqs. (75) and (76).

Note that, by virtue of Eqs. (16)–(18) in conjunction with Eqs. (76) and (78), the field-dependent variables $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ are also functions of the set S, V, N, and $\hat{S}$ or its equivalent S, V, N, and B. In the absence of the field, the entropic formulation of the fundamental equation for ideal monatomic gas is given by [3]

$$s=s_o+\tfrac{3}{2}R\ \ln\frac{T}{T_o}+R\ \ln\frac{v}{v_o}, \tag{80}$$

where the subscript o indicates a reference state. Hence, in the presence of a magnetic field,

$$\hat{s}=s_o+\tfrac{3}{2}R\ \ln\frac{T}{T_o}+R\ \ln\frac{v}{v_o}+\frac{(-1)^k}{2\rho}H^2\left(\frac{\partial\mu}{\partial T}\right)_\rho, \tag{81}$$

where, at fixed **B**, $k=0$, whereas at fixed **H**, $k=1$.

The energy density of the gas is given by

$$u=\tfrac{3}{2}RT. \tag{82}$$

Solving Eq. (82) for T and substituting the result in Eq. (81) gives

$$\hat{s}=s_o+\frac{3}{2}R\ \ln\frac{u}{u_o}+R\ \ln\frac{v}{v_o}+\frac{(-1)^k}{2\rho}H^2\left(\frac{\partial\mu}{\partial T}\right)_\rho. \tag{83}$$

The information in Eq. (83) will be complete once the functional dependence of $(\partial\mu/\partial T)_\rho$ on μ and u is known. Such a relation is given by Eq. (52), which can be presented [using Eq. (82)] as a function of μ' and u in the following form:

$$(\partial\mu/\partial T)_\rho=-\mu'\bigg/\left(\frac{2}{3}\frac{u}{R}\right). \tag{84}$$

Using Eq. (29b) and combining Eqs. (83) (for $k=0$) and (84) gives

$$\hat{s}=s_0+\frac{3}{2}R\ \ln\frac{u}{u_0}+R\ \ln\frac{v}{v_0}+\left[(\hat{u}_g-u)\bigg/\left(\frac{2}{3}\frac{u}{R}\right)\right]\frac{\mu_0}{\mu},\quad \mathbf{B}\ \text{fixed}, \tag{85}$$

where, by virtue of Eqs. (38), (45), and (82), $\mu=\mu_0(1+C/[\tfrac{2}{3}(u/R)])$. Recalling that $u=u(s,v)$ and $\hat{u}=\hat{u}(s,v,\mathbf{B})$, it is seen that

$$\hat{s}=\hat{s}(s,v,\hat{u})=\hat{s}(s,v,\mathbf{B}). \tag{86}$$

Equation (86) is equivalent to Eqs. (75) and (79). Similar reasoning leads to the same conclusion when **H** instead of **B** is held fixed.

At fixed **B** the energy representation of the fundamental equation can be obtained by combining Eqs. (29b) and (82), and the solution of T, i.e., $T=T(s,v,\hat{s})$, from Eq. (81),

$$\hat{u}=\tfrac{3}{2}RT(s,v,\hat{s})-\frac{1}{2\rho}\mu' H^2(\mu/\mu_0). \tag{87}$$

Since the magnetic term is also a function of s, v, and **B**, and hence also of s, v, and $\hat{s}$, we have

$$\hat{u}=\hat{u}(s,v,\hat{s})=\hat{u}(s,v,\mathbf{B}). \tag{88}$$

Equation (88) is equivalent to Eqs. (76) and (78).

Specific heat in the presence of field

The specific heat at fixed volume is defined by

$$C_v=\frac{1}{N}\left(\frac{dQ}{dT}\right)_V. \tag{89}$$

For the case of an ideal gas,

$$du=c_v dT, \tag{90}$$

where in the case of a monatomic gas,

$$c_v=\tfrac{3}{2}R. \tag{91}$$

It follows that [see Eq. (1)]

$$d\hat{u}=c_v dT+d\left(\frac{1}{2\rho}\mu H^2\right). \tag{92}$$

At fixed **B** and ρ (since $v=1/\rho$ is fixed),

$$d\hat{u}_{\mathbf{B}}=\left[c_v-\frac{1}{2\rho}H^2(\partial\mu/\partial T)_\rho\right]dT. \tag{93}$$

Equation (93) facilitates the definition of the following field-dependent specific heat at fixed **B** and v,

$$\hat{c}_{v,\mathbf{B}}=c_v-\frac{1}{2\rho}H^2(\partial\mu/\partial T)_\rho=c_v+\tfrac{1}{6}R(\mu_0 mH/kT)^2. \tag{94}$$

The counterpart of $\hat{c}_{v,\mathbf{B}}$ at fixed **H** and v is

$$\hat{c}_{v,\mathbf{H}}=c_v+\frac{1}{2\rho}H^2(\partial\mu/\partial T)_\rho=c_v-\tfrac{1}{6}R(\mu_0 mH/kT)^2, \tag{95}$$

where, in deriving the right-hand side of Eqs. (94) and (95), use was made of Eqs. (45), (46), and (52). It follows that

$$d\hat{u}=\hat{c}_{v,\beta}dT, \tag{96}$$

where $\beta\equiv\mathbf{B}$ at fixed **B**, whereas $\beta\equiv\mathbf{H}$ at fixed **H**. Note that $\hat{c}_{v,\mathbf{B}}$ is larger than $\hat{c}_{v,\mathbf{H}}$ by $-(1/\rho)H^2(\partial\mu/\partial T)_\rho$. This reflects the fact that when matter is heated by dT, at fixed **B**, its energy increases by $-(1/2\rho)H^2(\partial\mu/\partial T)_\rho dT$, whereas the reverse applies when **H** is held fixed.

In the case of ideal gases, μ can be presented as a function of P and T, instead of ρ and T as given by Eq. (51). Using this form of μ gives

$$d\mu=(\partial\mu/\partial P)_T dP+(\partial\mu/\partial T)_P dT. \tag{97}$$

Thus in order to define a specific heat at fixed pressure in the presence of the field, it is sufficient to replace, in Eqs. (94) and (95), c_v by c_P and $(\partial\mu/\partial T)_\rho$ by $(\partial\mu/\partial T)_P$. Substitution of Eqs. (49) and (50) in Eq. (38) and then differentiating the result at fixed P gives

$$(\partial\mu/\partial T)_P=-\tfrac{2}{3}\rho R(\mu_0 m/kT)^2. \tag{98}$$

Hence the counterparts of Eqs. (94) and (95) for the case of fixed P are

$$\hat{c}_{P,\mathbf{B}}=c_P+\tfrac{1}{3}R(\mu_0 mH/kT)^2, \tag{99}$$

$$\hat{c}_{P,\mathbf{H}}=c_P-\tfrac{1}{3}R(\mu_0 mH/kT)^2. \tag{100}$$

Subtracting Eq. (94) from Eq. (99), and recalling that $c_P-c_v=R$, gives

$$\hat{c}_{P,\mathbf{B}}-\hat{c}_{v,\mathbf{B}}=c_P-c_v+\tfrac{1}{6}R(\mu_0 mH/kT)^2 =R[1+\tfrac{1}{6}(\mu_0 mH/kT)^2], \tag{101}$$

$$\hat{c}_{P,\mathbf{H}}-\hat{c}_{v,\mathbf{H}}=c_P-c_v-\tfrac{1}{6}R(\mu_0 mH/kT)^2 =R[1-\tfrac{1}{6}(\mu_0 mH/kT)^2]. \tag{102}$$

Equations (94) and (99) show that a fixed **B** field increases the field-dependent heat capacities at either fixed v or fixed P. The reverse is true if **H** instead of **B** is held fixed. The effect of the field at fixed pressure is twice as large as compared to the one at fixed specific volume.

B. Discrete systems

A hollow sphere, consisting of a thin spherical shell that contains the gas and is placed in a uniform external field $\mathbf{H}_0$, is used here as an illustrative discrete system. The sphere is denoted by subscript 1, and its surroundings by subscript 2.

It is shown elsewhere [2] that the net magnetic energy U'_{M1} of this sphere (i.e., in excess of that prevailing in its absence) is given by

$$U'_{M1}=\tfrac{1}{2}V_1\mu_2\,\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\,H_0^2. \tag{103}$$

This energy of the sphere consists of two parts that are stored within and outside its boundaries. The spherical shell that encloses the gas has the permeability μ_2, and is thin to the extent that any effect it might have on the field can be neglected. The volume of the gas is V_1, and its permeability is μ_1. The permeability outside the sphere is μ_2. The sphere maintains its shape irrespective of its volume. This is a constraint related to the shape of a discrete system, and here the sphere volume can only be changed at fixed shape, i.e., no distortion in the latter is allowed. Differentiation of Eq. (103) followed by collection of terms gives

$$\begin{aligned} dU'_{M1}={}&\tfrac{1}{2}\mu_2\,\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\,H_0^2dV_1+\tfrac{1}{2}\,V_1\,\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\,H_0^2d\mu_1\\ &+\tfrac{1}{2}V_1\,\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\,H_0^2d\mu_2\\ &+V_1\mu_2\,\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\,H_0dH_0. \end{aligned} \tag{104}$$

The change in the permeability μ_i, $i=1$ and 2, can be expressed as [1]

$$d\mu_i=\left(\frac{\partial\mu_i}{\partial\rho_i}\right)_T\frac{1}{V_i}\,(dN_i-\rho_i dV_i)+\left(\frac{\partial\mu_i}{\partial T_i}\right)_\rho dT_i,\qquad i=1\quad\text{and}\quad 2, \tag{105}$$

where subscripts T and ρ mean that the temperature and density are held fixed in the region for which the derivative is evaluated.

Combining Eqs. (104) and (105), and letting $dV_2=(\partial V_2/\partial V_1)dV_1$, $dN_2=(\partial N_2/\partial N_1)dN_1$, and $dT_2=(\partial T_2/\partial T_1)dT_1$, gives dU'_{M1} as a function of V_1, N_1, T_1, and H_0:

$$\begin{aligned} dU'_{M1}={}&\left[\frac{1}{2}\,\mu_2\,\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}-\frac{1}{2}\,\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\,\rho_1\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T-\frac{1}{2}\,\frac{V_1}{V_2}\,\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\,\rho_2\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T\frac{\partial V_2}{\partial V_1}\right]H_0^2dV_1\\ &+\left[\frac{1}{2}\,\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T+\frac{1}{2}\,\frac{V_1}{V_2}\,\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T\frac{\partial N_2}{\partial N_1}\right]H_0^2dN_1+\left[\frac{1}{2}\,V_1\,\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_1}{\partial T_1}\right)_\rho\right.\\ &\left.+\frac{1}{2}\,V_1\,\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_2}{\partial T_2}\right)_\rho\frac{\partial T_2}{\partial T_1}\right]H_0^2dT_1+V_1\mu_2\,\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}\,H_0dH_0. \end{aligned} \tag{106}$$

Note that the use of partial derivatives, in the expressions [preceding Eq. (106)] for dV_2, dN_2, and dT_2, is due to the option to hold different system variables fixed as these expressions vary. Specific cases, such as holding $V=V_1+V_2$ fixed, when evaluating dV_2, are specified below.

Equation (106) facilitates the definition of the following counterparts of Eqs. (19)–(21) for the case of a sphere in a fixed H_0 field,

$$\hat{T}_D=T+(\partial U'_{M1}/\partial S_1)_{V_1,N_1,\mathbf{H}_0}, \tag{107}$$

$$\hat{P}_D=P-(\partial U'_{M1}/\partial V_1)_{S_1,N_1,\mathbf{H}_0}, \tag{108}$$

$$\hat{\zeta}_D=\zeta+(\partial U'_{M1}/\partial N_1)_{S_1,V_1,\mathbf{H}_0}, \tag{109}$$

where subscript D indicates that the system is discrete:

$$(\partial U'_{M1}/\partial S_1)_{V_1,N_1,\mathbf{H}_0}=\frac{1}{2}V_1\left[\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_1}{\partial T_1}\right)_\rho+\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_2}{\partial T_2}\right)_\rho\frac{\partial T_2}{\partial T_1}\right]\times H_0^2\left(\frac{\partial T_1}{\partial S_1}\right)_{V_1,N_1,\mathbf{H}_0}, \tag{110}$$

$$(\partial U'_{M1}/\partial V_1)_{S_1,N_1,\mathbf{H}_0}=\frac{1}{2}\left[\mu_2\frac{\mu_1-\mu_2}{\mu_1+2\mu_2}-\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\rho_1\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T-\frac{V_1}{V_2}\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\times\rho_2\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T\frac{\partial V_2}{\partial V_1}\right]H_0^2, \tag{111}$$

$$(\partial U'_{M1}/\partial N_1)_{S_1,V_1,\mathbf{H}_0}=\frac{1}{2}\left[\frac{3\mu_2^2}{(\mu_1+2\mu_2)^2}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T+\frac{V_1}{V_2}\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{(\mu_1+2\mu_2)^2}\times\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T\frac{\partial N_2}{\partial N_1}\right]H_0^2, \tag{112}$$

where in deriving Eq. (110) use was made of $dT_1=(\partial T_1/\partial S_1)_{V_1,N_1,\mathbf{H}_0}dS_1$.

There are several combinations of constraints that can be imposed on the sphere and the field that surrounds it. For example, consider the following sets of constraints:

(a) *Fixed* V, N, *and uniform temperature*:

$$V=V_1+V_2=\text{const}, \tag{113}$$

$$N=N_1+N_2=\text{const}, \tag{114}$$

$$T=T_1=T_2. \tag{115}$$

From Eqs. (113) and (114), $\partial V_2/\partial V_1=\partial N_2/\partial N_1=-1$, and Eq. (115) gives $\partial T_2/\partial T_1=1$. Note that in the first, second, and third partial derivatives, V, N, and T are held fixed, respectively.

(b) *Fixed* V_2, N, *and uniform temperature*:
In this case, $\partial V_2/\partial V_1=0$, $\partial N_2/\partial N_1=-1$, and $\partial T_2/\partial T_1=1$.

(c) *Fixed* V, N_2, *and uniform temperature*:
In this case, $\partial V_2/\partial V_1=-1$, $\partial N_2/\partial N_1=0$, and $\partial T_2/\partial T_1=1$.

If the sphere is insulated, then T_2 may be held at an arbitrary level compared to T_1. Thus holding T_2 fixed at variable T_1 gives $\partial T_2/\partial T_1=0$, and the above sets can be repeated subject to changing $\partial T_2/\partial T_1$ from 1 to 0.

Suppose that no change is allowed in the surroundings of the sphere as its own variables change. This means that V_2, N_2, and T_2 and hence also ρ_2 and μ_2 are held fixed, as V_1, N_1, and T_1 are varied. In this case it can readily be shown that

$$(\partial U'_{M1}/\partial S_1)_{V_1,N_1,\mathbf{H}_0}=\frac{1}{6\rho_1}H_1^2\left(\frac{\partial\mu_1}{\partial s_1}\right)_{V_1,N_1,\mathbf{H}_0}, \tag{116}$$

$$-(\partial U'_{M1}/\partial V_1)_{S_1,N_1,\mathbf{H}_0}=\tfrac{1}{6}H_1^2\rho_1\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T-\tfrac{1}{18}\mu_1\left[\frac{(\mu_1-\mu_2)(\mu_1+2\mu_2)}{\mu_1\mu_2}\right]H_1^2, \tag{117}$$

$$(\partial U'_{M1}/\partial N_1)_{S_1,V_1,\mathbf{H}_0}=\tfrac{1}{6}H_1^2\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T, \tag{118}$$

where $\mathbf{H}_1$ is the field within the sphere [4],

$$\mathbf{H}_1=\frac{3\mu_2}{\mu_1+2\mu_2}\mathbf{H}_0. \tag{119}$$

Comparing Eqs. (116)–(118) and the respective magnetic terms in Eqs. (23)–(25) shows that they have similar forms. The factor $\frac{1}{2}$ in Eqs. (23) and (25) is replaced by $\frac{1}{6}$ in Eqs. (116) and (118). The same applies to the first magnetic term on the right-hand side of Eq. (24), where the factor $\frac{1}{2}$ is replaced by $\frac{1}{6}$ in the respective term of Eq. (117). In the second magnetic term, the $\frac{1}{2}$ is replaced by $\frac{1}{18}[(\mu_1-\mu_2)(\mu_1+2\mu_2)]/\mu_1\mu_2$. These changes are a reflection of the effect of the geometry of the sphere. Suppose that we relax the constraint that no change in the surroundings of the sphere is allowed. Instead we impose set a of constraints, according to which V and N are fixed and $T_1=T_2=T$ is uniform. Recalling that for this set of constraints $\partial V_2/\partial V_1=\partial N_2/\partial N_1=-1$, we obtain

$$(\partial U'_{M1}/\partial S_1)_{V_1,N_1,\mathbf{H}_0}=\frac{1}{6\rho_1}H_1^2\left(\frac{\partial\mu_1}{\partial s_1}\right)_\rho+\frac{1}{18\rho_1}\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{\mu_2^2}\left(\frac{\partial\mu_2}{\partial T_2}\right)_\rho\left(\frac{\partial T}{\partial s_1}\right)_{\rho,\mathbf{H}_0}H_1^2, \tag{120}$$

$$-(\partial U'_{M1}/\partial V_1)_{S_1,N_1,\mathbf{H}_0}=\tfrac{1}{6}H_1^2\rho_1\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T-\tfrac{1}{18}\left\{\mu_1\left[\frac{(\mu_1-\mu_2)(\mu_1+2\mu_2)}{\mu_1\mu_2}\right]+\frac{V_1}{V_2}\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{\mu_2^2}\rho_2\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T\right\}H_1^2, \tag{121}$$

$$(\partial U'_{M1}/\partial N_1)_{S_1,V_1,\mathbf{H}_0}=\frac{1}{6}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T H_1^2-\frac{1}{18}\frac{V_1}{V_2}\frac{\mu_1^2-2\mu_1\mu_2-2\mu_2^2}{\mu_2^2}\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_T H_1^2. \tag{122}$$

It is seen that changing the constraints results in a significant change in Eqs. (116)–(118). For example, if μ_1/μ_2 is sufficiently large, then Eq. (122) is expected to yield a result that is smaller than the one predicted by Eq. (118).

The equation of state of the gas in the sphere can be obtained by elimination of T between Eqs. (107) and (108) following the substitution of $P=\rho RT$ in Eq. (108). This gives

$$\hat{P}_D=\rho R\hat{T}_D-\rho R(\partial U'_{M1}/\partial S_1)_{V_1,N_1,\mathbf{H}_0}-(\partial U'_{M1}/\partial V_1)_{S_1,N_1,\mathbf{H}_0}, \tag{123}$$

where the first and second partial derivatives are given by Eqs. (110) and (111), respectively. Since these derivatives depend on the constraints that are imposed on the sphere and its surroundings, so does the equation of state of the gas which is confined inside the sphere. In this sense this equation of state is not unique.

Equations (107), (108), and (123) are general in form. Therefore, in the presence of the field, the equation of state of the gas (which is confined within a discrete system) involves effects due to the contents and constraints set on both the system and its surroundings. Equations (116)–(118) and (120)–(122) are specific examples how different sets of constraints (e.g., which are imposed on the sphere and its surroundings) produce different results for the partial derivatives of Eq. (123), and hence also different equations of state.

C. Mixture of ideal gases

If an ideal gas consists of a mixture of ideal gases, then, according to the Gibbs theorem, each gas in the mixture behaves as if it were alone and independent of the other gases. In such a mixture, the gases do not interact with each other. In what follows, the validity of the Gibbs theorem in the presence of electromagnetic fields is considered.

The permeability of a mixture consisting of n different gases is given by

$$\mu=\mu_0\left(1+\sum_{i=1}^{n}\chi_i\right), \tag{124}$$

where χ_i is the susceptibility of the ith gas at the given temperature and pressure, $i=1,2,\ldots,n$.

Applying Eqs. (28) and (38) to the ith gas shows that $\mu_0\chi_i=\mu'_i$, and hence Eq. (124) takes the following convenient form:

$$\mu'=\sum_{i=1}^{n}\mu'_i. \tag{125}$$

Equation (125) indicates that, as regards permeabilities, the net contributions of the gases are additive, as expected.

The same applies to the additivity of densities in the mixture,

$$\rho=\sum_{i=1}^{n}\rho_i. \tag{126}$$

Since $\mu'=K\rho$ and $\mu'_i=K_i\rho_i$, it follows that

$$K=\sum_{i=1}^{n}K_i\rho_i\bigg/\sum_{i=1}^{n}\rho_i. \tag{127}$$

Equation (30) holds for this gas mixture, since it can be treated as a uniform and continuous phase. This gives

$$\hat{U}=U+\tfrac{1}{2}V\mu' H^2,$$

where μ' satisfies Eq. (125).

Using this result and the Gibbs theorem for the additivity of energy in the absence of fields, i.e., $U=\Sigma_{i=1}^{n}U_i$, in conjunction with Eq. (125), gives

$$\hat{U}=\sum_{i=1}^{n}\hat{U}_i,\quad \hat{U}_i=U_1+\tfrac{1}{2}V\mu'_i H^2. \tag{128}$$

At fixed **H**, the entropy of the mixture is given by Eq. (71) with the sign of the magnetic term reversed [2]. Hence, using Eq. (125) in conjunction with Eq. (28) and applying the Gibbs theorem for the additivity of entropy in the absence of fields, i.e., $S=\Sigma_{i=1}^{n}S_i$, gives

$$\hat{S}=\sum_{i=1}^{n}\hat{S}_i,\quad \hat{S}_i=S_i-\tfrac{1}{2}VH^2(\partial\mu_i/\partial T)_\rho, \tag{129}$$

where here subscript ρ implies that ρ_i is fixed.

It follows from Eqs. (128) and (129) that the Gibbs theorem for a mixture of ideal gases holds in the absence as well as in the presence of fixed intensity quasistatic magnetic fields. The effect of the field on the entropy of mixing is considered next.

Combining Eqs. (45), (46), (52), and (71) for a one-component ideal gas that is in a fixed **B** field, and using $R=Nk$, gives

$$\hat{S}=S-\tfrac{1}{6}RN(\mu_0 mH/kT)^2. \tag{130}$$

Suppose a rectangular container is divided into n compartments by $n-1$ planar, very thin, parallel partitions. The ith compartment contains N_i moles of the ith gas, and the field there is H_i. The container is placed in the field so that $\mathbf{B}_i=\mathbf{B}$ is satisfied for all i, where **B** is uniform and fixed. This is achieved by setting the partitions perpendicular to **B** and by making the distance between partitions small as compared to their other dimensions, thus minimizing end effects, so that they can be neglected.

The total entropy of these separately held gases under a fixed **B** field is

$$\hat{S}=\sum_{i=1}^{n}\left[S_i-\tfrac{1}{6}RN_i(\mu_0 m_i H_i/kT)^2\right]. \tag{131}$$

Upon removal of the partitions and completion of mixing of all gases into one homogeneous and uniform mixture of volume $V=\Sigma_{i=1}^{n}V_i$, the system aquires a different overall permeability. The susceptibility of the mixture is the sum of the susceptibilities of the individual gases. This gives [see Eqs. (45) and (46)]

$$\chi=\sum_{i=1}^{n}C(\rho_i)/T=\frac{1}{3V}R\mu_0\sum_{i=1}^{n}N_i(m_i/k)^2/T. \tag{132}$$

Combining Eqs. (38) and (132) gives the permeability of the mixture as

$$\mu=\mu_0+\frac{1}{3V}R\sum_{i=1}^{n}N_i(\mu_0 m_i/k)^2/T. \tag{133}$$

Evaluation of $(\partial\mu/\partial T)_\rho$ by differentiation of Eq. (133), and then combining Eqs. (2) and (71) for the mixture, yields

$$\hat{S}_m=S_m-\tfrac{1}{6}R\sum_{i=1}^{n}N_i(\mu_0 m_i H/kT)^2, \tag{134}$$

where the subscript m denotes a property of the mixture, and H is the modulus of the field in V.

The entropy of mixing, at fixed **B**, is obtained by subtracting Eq. (131) from Eq. (134). The result is

$$\hat{S}_m-\sum_{i=1}^{n}\hat{S}_i=S_m-\sum_{i=1}^{n}S_i+\tfrac{1}{6}R\sum_{i=1}^{n}N_i(\mu_0 m_i H/kT)^2 \times(H_i^2/H^2-1). \tag{135}$$

At uniform and fixed **B**, $H_i^2/H^2=\mu^2/\mu_i^2$, $i=1,2,\ldots,n$. It follows that if $\Sigma_{i=1}^{n}\mu^2/\mu_i^2>1$, then the magnetic part of the entropy of mixing is positive; otherwise it either vanishes or it is negative. In what follows we investigate the change in permeabilities due to the mixing effect. Since each gas behaves as if it were alone (i.e., irrespective of the presence of the other gases), it is sufficient to show that the expansion of the ith gas (e.g., from V_i into the space $V-V_i$, which is initially free of this gas) results in an increase of the permeability of V. Thus, disregarding the other gases, the problem reduces to expansion of the ith gas from V_i into the space which is free of it in $V-V_i$.

Before the expansion, the averaged effective permeability of the container system (i.e., of V) with respect to the exclusive contribution of the ith gas, μ_i^a, is given by

$$\frac{1}{\mu_i^a}=\frac{x_i}{\mu_i}+\frac{1-x_i}{\mu_0},\quad x_i=V_i/V. \tag{136}$$

Manipulating Eq. (136) in conjunction with Eq. (53) for the ith gas, and using $\rho_i=N_i/V_i$, gives

$$\frac{1}{\mu_i^a}=\frac{K_iN_i/V_i+\mu_0-x_iK_iN_i/V_i}{(K_iN_i/V_i+\mu_0)\mu_0}. \tag{137}$$

After expansion, the permeability of V, e.g., with respect to the exclusive contribution of the ith gas, has changed to μ_i^b,

$$\mu_i^b=K_iN_i/V+\mu_0. \tag{138}$$

Hence

$$\mu_i^b/\mu_i^a=\left[\frac{(1-x_i)K_iN_i/V_i+\mu_0}{K_iN_i/V_i+\mu_0}\right]\left[\frac{K_iN_i/V+\mu_0}{\mu_0}\right]. \tag{139}$$

Equation (139) shows that if $x_i\rightarrow 0$, then $\mu_i^b/\mu_i^a=K_iN_i/(\mu_0 V)+1$, and hence (recalling that for permeable gases $K_i>0$) $\mu_i^b>\mu_i^a$. It follows that if we divide each gas into j_1 infinitesimally thin layers of thickness $\Delta x_j\rightarrow 0$, so that $x_i=\Sigma_{j=1}^{j_1}\Delta x_j$, then [by Eq. (139)] upon expansion, each thin layer contributes to the increase of the permeability of V. Thus, at fixed **B**, the expansion of all the n gaseous layers increases the permeability of the container system and, hence, in the presence of the magnetic field, the entropy of mixing at fixed **B** is larger than in its absence. However, if **H**, instead of **B**, is held fixed, then the magnetic entropy of mixing vanishes.

D. Transformation of the results to electroquasistatic fields

The results obtained hitherto for continuum and discrete systems in magnetoquasistatic fields can be transformed to electroquasistatic fields by replacing the set μ, **H**, and **B** by ε, **E**, and **D**, respectively. Here, ε is electric permittivity, **E** is the electric field strength, and **D** is the electric displacement. The electric polarization $\mathbf{P}_E$ should replace $\mu_0\mathbf{M}$. Furthermore, variables that are functions of the magnetic set must also be replaced by appropriate electric notation. For example U_M, U'_{M1}, μ', χ, and m can be replaced by U_e, U'_{e1}, ε', χ_e, and m_e, where the subscript e denotes that the variable expresses an electric quantity.

SUMMARY AND CONCLUSIONS

(1) The thermodynamic properties of a continuum in the presence of electromagnetic fields, at either fixed **B** or **H**, can be described by two conjugate sets of variables. These two

sets consist of the variables S, V, and N and $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$. The first set, i.e., S,V,N, prevails in the absence of fields and in this respect, it is ''field independent.'' The variables of the second set are functions of the first set as well as of the field, and in this respect they are ''field dependent.'' In the absence of fields, the set $\hat{T},\hat{P},\hat{\zeta}$ reduces to T,P,ζ.

(2) The field-dependent energy $\hat{U}$ cannot be obtained by Euler integration of $d\hat{U}$ holding $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ fixed. However, if $d\hat{U}$ is separated into field-independent and field-dependent exact differentials, then it can be Euler integrated holding T, P, and ζ fixed.

(3) In the presence of electromagnetic fields, the set $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ has the same thermodynamic role which is characteristic of the set T, P, and ζ prevailing when the fields are absent. It follows that, at equilibrium, $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ must be uniform in continua that are under the action of fields. This can result in the occurrence of discontinuous jumps in T, P, and ζ across interfaces that separate materials of different electromagnetic properties. Systems that have different magnetic properties and share a common interface are driven by the field to change their equilibrium values of T, P, and ζ which prevail in its absence.

(4) If $(\partial\mu/\partial s)_{V,N}<0$ and $(\partial\mu/\partial\rho)_{S,N}>0$, as is the case with ideal gases and the majority of liquids and solids, then, at fixed **B**, $\hat{T}>T$, $\hat{P}<P$, and $\hat{\zeta}<\zeta$. If **H**, instead of **B**, is held fixed, then for ideal gases, $\hat{T}<T$, $\hat{P}=P$ and $\hat{\zeta}>\zeta$. For gases that follow the Langevin equation in a fixed **B** field $\hat{P}_g>P$, whereas if **H** is fixed $\hat{P}_g=P$.

(5) Equations of state of an ideal gas in the presence of fields have been derived. In the absence of fields, these equations reduce to the ordinary equation of state of an ideal gas.

(6) Two different magnetic susceptibilities can be defined for ideal gases that follow the Langevin equation. One susceptibility χ_v is defined at fixed density, or fixed specific volume v, and the other, χ_P, is defined at fixed pressure P. The first susceptibility, i.e., χ_v, is proportional to $1/T$, and consequently it follows the Curie-Weiss law. The second susceptibility, i.e., χ_P, follows a different law since it is proportional to $1/T^2$. These susceptibilities are the consequence of imposing the above constraints on the gas, i.e., in the same way that they give rise to the well-known heat capacities at fixed volume c_v and fixed pressure c_P.

(7) The fundamental equation of an ideal gas in the presence of fields can be presented in the following alternative formulations: energy formulation $\hat{U}=\hat{U}(S,V,N,\hat{S})$ and entropic formulation $S=\hat{S}(S,V,N,\hat{U})$. These formulations are also a consequence of the fact that $\hat{U}$ and $\hat{S}$ are both functions of S, V, N, and **B**.

(8) Specific heats of ideal gases, with positive susceptibility in the presence of fields, have been formulated. At fixed **B**, the field increases c_v (which prevails in its absence) by (1/6) $R(\mu_0 mH/kT)^2$, whereas at fixed **H**, c_v is decreased by the same amount. If the gases have negative susceptibilities, then the reverse of the above applies. The following relations between field-dependent heat capacities have also been established:

$$\hat{c}_{v,\mathbf{B}}-\hat{c}_{v,\mathbf{H}}=\tfrac{1}{2}(\hat{c}_{P,\mathbf{B}}-\hat{c}_{P,\mathbf{H}})=\tfrac{1}{3}R(\mu_0 mH/kT)^2,$$

$$\hat{c}_{p,\mathbf{B}}-\hat{c}_{v,\mathbf{B}}=R[1+\tfrac{1}{6}(\mu_0 mH/kT)^2]=\hat{c}_{p,\mathbf{H}}-\hat{c}_{v,\mathbf{H}}+\tfrac{1}{3}R(\mu_0 mH/kT)^2.$$

(9) Ideal gases that are contained in discrete systems and are placed under the action of electromagnetic fields, can be characterized thermodynamically by the sets S, V, and N and $\hat{T}_D$, $\hat{P}_D$, and $\hat{\zeta}_D$. The set $\hat{T}_D$, $\hat{P}_D$, and $\hat{\zeta}_D$ depends on the geometry of the system and the constraints imposed on it. This set is expected to be different from the set $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ that characterizes a continuum.

(10) The equation of state of an ideal gas that is contained in a discrete system has been formulated. This equation of state depends on the geometry and constraints of the system and its surroundings and in this sense it is not unique.

(11) The Gibbs theorem, with respect to ideal gases, holds in the presence as well as in the absence of fixed intensity electromagnetic fields.

(12) The expansion of permeable ideal gases, within a confined space of volume V, increases the permeability of V.

(13) The entropy of mixing of permeable ideal gases, in the presence of a uniform and fixed **B** magnetic field, is larger than the entropy of mixing of these gases in the absence of the field. In this sense the effect of a fixed **B** field is to increase the entropy of mixing of permeable ideal gases. However, if **H** instead of **B** is held fixed in the mixing process, then no increase of entropy of mixing due to the field is expected to occur.

APPENDIX A: VERIFICATION OF EQ. (12)

We express (in addition to U_M) the hypothetical effect of the field, on each of the ordinary thermodynamic variables, by adding a hypothetical field-dependent increment in the form ΔZ, where Z is T, S, P, V, ζ, and N. In the absence of the field $\Delta Z=0$, and Eq. (11) prevails, whereas in the presence of the field where $\Delta Z\neq 0$ we have

$$\begin{aligned}\hat{U}&=(T+\Delta T)(S+\Delta S)-(P+\Delta P)(V+\Delta V)\\&\quad+(\zeta+\Delta\zeta)(N+\Delta N)+U_M\\&=TS-PV+\zeta N+U_M(\Delta Z)+U_M,\end{aligned}\tag{A1}$$

where

$$\begin{aligned}U_M(\Delta Z)&=\Delta T(S+\Delta S)+T\Delta S-\Delta P(V+\Delta V)-P\Delta V\\&\quad+\Delta\zeta(N+\Delta N)+\zeta\Delta N.\end{aligned}\tag{A2}$$

However the total magnetic energy that is stored in the field is known to be exactly equal to U_M, so that

$$U_M+U_M(\Delta Z)=U_M\tag{A3}$$

must be satisfied, and hence

$$U_M(\Delta Z)=0.\tag{A4}$$

This shows that $\hat{U}$ is given by

$$\hat{U}=TS-PV+\zeta N+U_M.\tag{A5}$$

Equation (A5) agrees with Eq. (12) to the extent that even if we hypothesize that the field changes the conventional thermodynamic variables, apart from the effect of U_M, then the overall effect cancels out. This justifies using these variables as being independent of the field.

Furthermore, the result expressed by Eq. (A5) and the fact [see Eqs. (12)–(14)] that

$$d\hat{U}=dU+dU_M=T\,dS-P\,dV+\zeta\,dN+dU_M \qquad \text{(A6)}$$

show that S, V, and N, and hence also U, T, P, and ζ must indeed be independent of U_M. The very existence of the field does not change variables that prevail in its absence. If it were not so, then U_M cannot be arbitrarily changed holding the set S, V, and N fixed, and vice versa. Recalling that $U_M=U_M(S,V,N,\mathbf{B})$, it follows that, at fixed S, V, and N, $U_M=U_M(\mathbf{B})$ can be changed independently and by magnetic means only, i.e., as a sole function of $\mathbf{B}$. It must be clear that $U_M=U_M(\mathbf{B})$ implies its exclusive dependence on the source of the field $\mathbf{B}$ and not on the contents and volume of the system where U_M is evaluated.

We turn now to examine an alternative analysis, that uses the energy differential, as a starting point, to derive Eq. (12). Suppose Eq. (15) is not known and we seek a general expression for the field-dependent energy differential. We start by writing the energy differential $d\hat{U}$ in a form that makes a clear distinction between the part due to system variables, and the part due to the effect of the current sources (denoted by subscript C) of the field,

$$d\hat{U}=\sum_{i=0}^{n}\hat{\xi}_i dX_i+dU_{MC}. \qquad \text{(A7)}$$

By definition, the variables $\hat{\xi}_i$ are functions of the extensive variables $X_0,\ldots,X_n$ and the field, and dU_{MC} is the change in the magnetic energy due to the exclusive action of the current sources of the field. Since the current sources are, by definition, independent of the system variables all terms of Eq. (A7) are independent, as required.

Thus $\hat{\xi}_i dX_i$ represents the change in energy due to a change in X_i, at the conditions set by the current sources of the field. These conditions, and the constraints set on the field, determine the way $\hat{\xi}_i$ depends on the field. Similarly, dU_{MC} expresses the net effect of the current sources on the system, which is characterized by a given set of extensive variables, i.e., at fixed X_i, $i=0,1,\ldots,n$.

It follows that this differential must express the magnetic work done by the current sources on the system, e.g., at fixed X_i, $i=0,\ldots,n$, and hence it is given by

$$dU_{MC}=V\mathbf{H}\cdot d\mathbf{B}, \qquad \text{(A8)}$$

where $d\mathbf{B}$ is set (at fixed X_i, $i=0,\ldots,n$) by the current sources only.

Combining Eqs. (A7) and (A8) gives

$$d\hat{U}=\sum_{i=0}^{n}\hat{\xi}_i dX_i+V\mathbf{H}\cdot d\mathbf{B}, \quad \hat{\xi}_i=(\partial\hat{U}/\partial X_i)_{X_j,\mathbf{B}}, \qquad j\neq i, \quad i,j=0,\ldots,n. \qquad \text{(A9)}$$

Since the variables $\hat{\xi}_i$ are state variables, they must be separable into field-independent and field-dependent parts

$$\hat{\xi}_i=\xi_i+\xi_{Mi}, \qquad \text{(A10)}$$

where

$$\xi_i=(\partial U/\partial X_i)_{X_j}, \quad j\neq i, \quad i,j=0,\ldots,n \qquad \text{(A11)}$$

is the partial derivative of the energy $U=\hat{U}(\mathbf{B}=\mathbf{0})$, that prevails in the absence of the field (e.g., at $\mathbf{B}=\mathbf{0}$), with respect to X_i, and

$$\xi_{Mi}=(\partial U_M/\partial X_i)_{X_j,\mathbf{B}}, \quad j\neq i, \quad i,j=0,\ldots,n \qquad \text{(A12)}$$

is the partial derivative of the magnetic energy U_M with respect to X_i, at fixed $\mathbf{B}$.

Suppose $\hat{\xi}_i$ were not separable, in the form specified by Eq. (A10). Then removal of the field would not yield $\hat{\xi}_i(\mathbf{B}=\mathbf{0})=\xi_i$, and turning the field on, at fixed ξ_i, would not increase $\hat{\xi}_i$ from its value at $\mathbf{B}=\mathbf{0}$ by ξ_{Mi}, as required.

Combining Eqs. (A9)–(A12), followed by rearrangement of terms, gives

$$d\hat{U}=\sum_{i=0}^{n}(\partial U/\partial X_i)_{X_j}dX_i+\sum_{i=0}^{n}(\partial U_M/\partial X_i)_{X_j,\mathbf{B}}dX_i+V\mathbf{H}\cdot d\mathbf{B}. \qquad \text{(A13)}$$

The first sum on the right-hand side of Eq. (A13) is readily identified as the energy differential dU that prevails in the absence of the field. The second sum combined with the third term, on the right-hand side of Eq. (A13), gives the total differential of the magnetic energy dU_M. Hence

$$d\hat{U}=dU+dU_M. \qquad \text{(A14)}$$

Upon integration of Eq. (A14), Eq. (12) is obtained. Combining Eqs. (A10), (A11), and (A12) gives

$$\hat{\xi}_i=(\partial\hat{U}/\partial X_i)_{X_j,\mathbf{B}}=(\partial U/\partial X_i)_{X_j}+(\partial U_M/\partial X_i)_{X_j,\mathbf{B}}, \qquad j\neq i, \quad i,j=0,\ldots,n. \qquad \text{(A15)}$$

Equation (A15) is equivalent to Eqs. (16)–(18).

APPENDIX B: DERIVATIVES OF $\hat{T}$, $\hat{P}$, AND $\hat{\zeta}$ WITH RESPECT TO THE FIELD

Differentiation of Eq. (19) at fixed ρ and T gives

$$\left(\frac{\partial\hat{T}}{\partial H}\right)_{\rho,T}=-\frac{1}{\rho}H\left(\frac{\partial\mu}{\partial s}\right)_{V,N}. \qquad \text{(B1)}$$

Differentiation of Eq. (20) at fixed ρ, T, and P gives

$$\left(\frac{\partial\hat{P}}{\partial H}\right)_{\rho,T,P}=-\rho H\left(\frac{\partial\mu}{\partial\rho}\right)_{S,N}-\mu H. \qquad \text{(B2)}$$

Differentiation of Eq. (21) at fixed ρ and T gives

$$\left(\frac{\partial\hat{\zeta}}{\partial H}\right)_{\rho,T}=-H\left(\frac{\partial\mu}{\partial\rho}\right)_{S,V}. \qquad \text{(B3)}$$

Equations (B1)–(B3) can be derived as Maxwell relations using the Legendre transformation [see Eq. (15)]

$$\begin{aligned}d(\hat{U}-VHB)&=\hat{T}\,dS-\hat{P}\,dV+\hat{\zeta}\,dN-VB\,dH-HB\,dV\\&=\hat{T}\,dS-(\hat{P}+HB)dV+\hat{\zeta}\,dN-VB\,dH.\end{aligned} \qquad \text{(B4)}$$

From Eq. (B4) we have

$$\left(\frac{\partial \hat{T}}{\partial H}\right)_{S,V,N} = -\left[\frac{\partial (VB)}{\partial S}\right]_{V,N,H} = -\frac{H}{\rho}\left(\frac{\partial \mu}{\partial s}\right)_{V,N,H}, \quad s = S/N. \tag{B5}$$

Since μ has been assumed to be independent of H, it can be dropped from the subscript V,N,H of the rightmost derivative of Eq. (B5). Holding S, V, and N fixed means that ρ and T are also fixed. This shows that Eq. (B5) verifies Eq. (B1),

$$\left[\frac{\partial (\hat{P} + HB)}{\partial H}\right]_{S,V,N} = \left[\frac{\partial (VB)}{\partial V}\right]_{S,N,H} = \mu H - \rho H\left(\frac{\partial \mu}{\partial \rho}\right)_{S,N,H}. \tag{B6}$$

Using $HB = \mu H^2$, and the assumption that μ is fixed when S, V, and N are fixed, gives

$$\left(\frac{\partial \hat{P}}{\partial H}\right)_{S,V,N} = -\rho H\left(\frac{\partial \mu}{\partial \rho}\right)_{S,N} - \mu H. \tag{B7}$$

If S, V, and N are fixed, then ρ, T, and P are also fixed, so that Eq. (B7) verifies Eq. (B2):

$$\left(\frac{\partial \hat{\zeta}}{\partial H}\right)_{S,V,N} = -\left[\frac{\partial (VB)}{\partial N}\right]_{S,V,H} = -VH\left(\frac{\partial \mu}{\partial N}\right)_{S,V,H}$$

$$= -H\left(\frac{\partial \mu}{\partial \rho}\right)_{S,V,H}. \tag{B8}$$

Hence Eq. (B8) verifies Eq. (B3).

Equation (B1) shows that if $(\partial \mu/\partial s)_{V,N} < 0$, as is the case with gases and many other materials, then, at fixed ρ and T, $\hat{T}$ is an increasing function of H. Equations (B2) and (B3) show that if $(\partial \mu/\partial \rho)_{S,N} > 0$, as is the case with permeable gases and other liquids and solids then, at fixed **B**, S, V, and N, $\hat{P}$ and $\hat{\zeta}$ are decreasing functions of H.

APPENDIX C

Equation (4) shows that T can be presented as a function of ρ and s as follows:

$$T = T(S,V,N) = T(s,v) = T(\rho,s), \quad v = 1/\rho. \tag{C1}$$

Combining Eqs. (3) and (C1) gives

$$\mu = \mu(\rho,s). \tag{C2}$$

Differentiation of Eqs. (3) and (C2) gives

$$d\mu = (\partial \mu/\partial \rho)_T d\rho + (\partial \mu/\partial T)_\rho dT, \tag{C3}$$

$$d\mu = (\partial \mu/\partial \rho)_s d\rho + (\partial \mu/\partial s)_\rho ds. \tag{C4}$$

Subtraction of Eq. (C4) from (C3) gives

$$0 = [(\partial \mu/\partial \rho)_T - (\partial \mu/\partial \rho)_s] d\rho + (\partial \mu/\partial T)_\rho dT - (\partial \mu/\partial s)_\rho ds. \tag{C5}$$

By virtue of Eqs. (C3) and (C4), ρ must be independent of T and s, and vice versa. This constraint sets T as a sole function of s. It follows that the coefficient of $d\rho$ in Eq. (C4) must vanish, and hence

$$(\partial \mu/\partial \rho)_T = (\partial \mu/\partial \rho)_s = (\partial \mu/\partial \rho)_{S,N}, \tag{C6}$$

where here use was made of the equivalence between fixing $s = S/N$ and fixing the pair S and N. Furthermore using, at fixed ρ (or also the constraint that T is independent of ρ), $T = T(s)$ gives $dT = (\partial T/\partial s)_\rho ds$ and $(\partial \mu/\partial T)_\rho dT = (\partial \mu/\partial T)_\rho (\partial T/\partial s)_\rho ds = (\partial \mu/\partial s)_\rho ds$, the result being that the second and third terms in Eq. (C5) cancel out.

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