We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



6

Thermodynamics of Electric and Magnetic Systems

Radu Paul Lungu
Department of Physics, University of Bucharest, Măgurele-Bucharest, Romania

1. Introduction

The systems which contain electric or magnetic media have besides the electric (respectively magnetic) properties also the common properties of a thermodynamic systems (that is thermal, volumic, chemical); moreover, there are correlations between the electric (magnetic) properties and the thermal or volumic properties. Because there are a great variety of situations with the corresponding properties, we shall present briefly only the most important characteristics of the simplest electric or magnetic systems. For these systems there are supplementary difficulties (comparing to the simple neutral fluid) because the inherent non-homogeneity of these systems and also because the special coupling between the electric (respectively magnetic) degree of freedom and the volumic degree of freedom. These difficulties have let to the use of different methods of study in the literature, being necessary to modify some standard thermodynamic quantities (introduced in the standard textbooks for the simple thermodynamic systems).

In order to have a relation with the presentations of other works, we shall discuss the electric (respectively the magnetic) systems with many methods and we shall note some improper use of the different concepts which had been introduced initially in the standard thermodynamics. Although the most of the electric or magnetic systems are solid, in order to maintain a short and also an intelligible exposition we shall present explicitly only the case when the system is of the fluid type, and when it contain a single chemical species, therefore neglecting the anisotropy effects and the complications introduced by the theory of elasticity.

We remark that for the thermodynamics of quasi-static processes must be considered only equilibrium states, so that we will deal only with electrostatic or magneto-static fields. Although there are interference effects between the electric and magnetic phenomena, these are very small; therefore, in order to simplify the exposition, we shall study separately the electric and the magnetic systems, emphasizing the formal similitude between these type of systems.

There are many textbooks which present the basic problems of thermodynamics, some of the most important of them used the classical point of new [1-12], and also other used the neo-gibbsian point of view [13-15]; in the following we shall use the last point of view (i.e. we shall use the neo-gibbsian thermodynamics) [16].

2. Electric systems

2.1 General electrodynamic results

Accordingly to the electrodynamics, the electrostatic field created by a distribution of static electric charges, in an electric medium, is characterized by the vectorial fields *the intensity of the electric field* $\boldsymbol{\mathcal{E}}(\mathbf{r})$ and *the intensity of electric induction* $\boldsymbol{\mathcal{D}}(\mathbf{r})$, which satisfy the electrostatic Maxwell equations [17-20]:

$$\text{rot}\ \boldsymbol{\mathcal{E}}(\mathbf{r}) = 0\ , \tag{1a}$$

$$\text{div}\ \boldsymbol{\mathcal{D}}(\mathbf{r}) = \rho(\mathbf{r})\ , \tag{1b}$$

where $\rho(\mathbf{r})$ is the volumic density of the electric free charge (there are excluded the polarization charges).

From Eq. (1a) it follows that $\boldsymbol{\mathcal{E}}(\mathbf{r})$ is an irrotational field, *i.e.* it derives from an electrostatic potential $\Phi(\mathbf{r})$:

$$\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\ \text{grad}\ \Phi(\mathbf{r})\ . \tag{2}$$

Also, on the surface of an conductor having the electric charge, the surface density of electric charge σ is related to the normal component (this is directed towards the conductor) of the electric induction with the relation:

$$\mathcal{D}_n = -\,\sigma\ . \tag{3}$$

Under the influence of the electrostatic field, the dielectric polarizes (it appears polarization charges), and it is characterized by the *electric dipolar moment* $\boldsymbol{\mathcal{P}}$, respectively by the *polarization* (the volumic density of dipolar electric moment) $\boldsymbol{P}(\mathbf{r})$:

$$\boldsymbol{P}(\mathbf{r}) \equiv \lim_{\delta V \to 0} \frac{\delta \boldsymbol{\mathcal{P}}(\mathbf{r})}{\delta V(\mathbf{r})} \quad \Longleftrightarrow \quad \boldsymbol{\mathcal{P}} = \int_V \mathrm{d}^3\mathbf{r}\ \boldsymbol{P}(\mathbf{r})\ . \tag{4}$$

Using the polarization it results the relation between the characteristic vectors of the electrostatic field:

$$\boldsymbol{\mathcal{D}}(\mathbf{r}) = \overline{\varepsilon}_0\, \boldsymbol{\mathcal{E}}(\mathbf{r}) + \boldsymbol{P}(\mathbf{r})\ , \tag{5}$$

where $\overline{\varepsilon}_0$ is the electric permitivity of the vacuum (it is an universal constant depending on the system of units).

The general relation between the intensity of the electric field $\boldsymbol{\mathcal{E}}(\mathbf{r})$ and the polarization $\boldsymbol{P}(\mathbf{r})$ is

$$\boldsymbol{P}(\mathbf{r}) = \overline{\varepsilon}_0\, \hat{\chi}_\mathrm{e}(\mathcal{E}, \mathbf{r}) : \boldsymbol{\mathcal{E}}(\mathbf{r}) + \boldsymbol{P}_0(\mathbf{r})\ , \tag{6a}$$

where $\boldsymbol{P}_0$ is the spontaneous polarization, and $\hat{\boldsymbol{\chi}}_\mathrm{e}$ is the electric susceptibility tensor (generally it is dependent on the electric field).

For simplicity, we shall consider only the particular case when there is no spontaneous polarization (i.e. the absence of ferroelectric phenomena) $\boldsymbol{P}_0 = 0$, and the dielectric is linear and isotropic (then $\hat{\boldsymbol{\chi}}_\mathrm{e}$ is reducible to a scalar which is independent on the electric field); in this last case, Eq. (6a) becomes:

$$\boldsymbol{P} = \overline{\varepsilon}_0\, \chi_\mathrm{e}\, \boldsymbol{\mathcal{E}}\ , \tag{6b}$$

and Eq. (5) allows a parallelism and proportionality relation between the field vectors:

$$\boldsymbol{\mathcal{D}} = \overline{\varepsilon}_0 (1 + \chi_\mathrm{e})\, \boldsymbol{\mathcal{E}}\ . \tag{7}$$

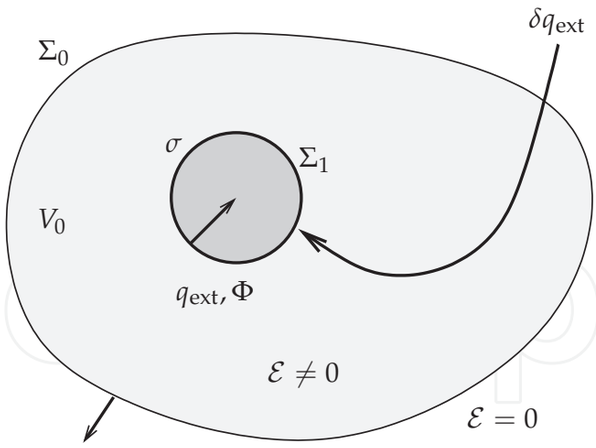


Fig. 1. The system chosen for the evaluation of the electric work.

In the common cases the susceptibility (for the specified types of dielectrics) depends on the temperature and of the particle density (or of the pressure) in the form:

$$\chi_{\text{e}} = \mathfrak{n}\, \overline{\chi}_{\text{e}}(T, \mathfrak{P}) \,, \tag{8}$$

where $\mathfrak{n} \equiv N/V$ is the particle density, $\overline{\chi}_{\text{e}}$ is the specific (per particle) susceptibility, and $\mathfrak{P}$ is the pressure[1].

In the narrow sense, the concrete expression of the electric susceptibility per particle is an empirical information of the thermal state equation type; we shall consider explicitly two simple cases:

– the *ideal* dielectric

$$\overline{\chi}_{\text{e}}(T) = \frac{K}{T} \,, \tag{9a}$$

– the *non-ideal* dielectric

$$\overline{\chi}_{\text{e}}(T, \mathfrak{P}) = \frac{K}{T - \Theta(\mathfrak{P})} \,, \tag{9b}$$

where K is a constant depending on the dielectric (called *Curie constant*), and $\Theta(\mathfrak{P})$ is a function of the pressure, having the dimension of a temperature.

Using the general relations of the electrostatics, we can deduce the expression of the infinitesimal *electric work*, as the energy given to the thermo-isolated dielectric when the electric field varies:

$$\delta\!\!\!^{-}\mathcal{L}_{\text{e}} = \int_{V_0} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \delta \boldsymbol{\mathcal{D}} \,, \tag{10}$$

under the condition that the system is located in the domain with the volume $V_0 =$ constant, so that outside to this domain the electric field *vanishes*.

Proof:

[1] We can define the dipolar electric moment per particle as $\boldsymbol{\mathcal{P}} = N\, \mathfrak{p}$, resulting the susceptibility per particle with an analogous relation to (6b) $\mathfrak{p} = \overline{\varepsilon}_0\, \overline{\chi}_{\text{e}}\, \boldsymbol{\mathcal{E}}$.

The electrostatic field from the dielectric is created by charges located on conductors; we consider the situation illustrated in Fig. 1, where inside the domain with the volume V_0 and fixed external surface Σ_0, there are dielectrics and a conductor (this last has the surface Σ_1) with the electric charge q_{ex} (respectively the charge density σ) which is the source of the electrostatic field[2].

In the conditions defined above, the infinitesimal electric work is the energy given for the transport of the small electric charge δq_{ex} from outside (the region without electric field) until the conductor surface Σ_1, which has the electrostatic potential Φ:

$$\delta\mathcal{L}_{\text{e}} = \Phi\ \delta q_{\text{ex}}\ .$$

In order to express the electric work in terms of the vectors for the electrostatic field, we observe that the charge q_{ex} located on the internal conductor can be written with the normal component of the electric induction, accordingly to Eq. (3):

$$q_{\text{ex}} = \oint_{\Sigma_1} \sigma\ \mathrm{d}\mathcal{A} = -\oint_{\Sigma_1} \mathcal{D}_n\ \mathrm{d}\mathcal{A}\ ,$$

and from previous relation it results that a variation of the charge δq_{ex} implies a variation of the electric induction $\delta\mathcal{D}$ (the surface Σ_1 is fixed); because the electrostatic potential Φ is constant on the surface Σ_1, the expression of the electric work can be written as:

$$\delta\mathcal{L}_{\text{e}} = -\oint_{\Sigma_1} \mathrm{d}\mathcal{A}\ \boldsymbol{n}_1 \cdot \Phi\ \delta\boldsymbol{\mathcal{D}}\ .$$

The integral on the surface Σ_1 can be transformed in a volume integral, using the Gauss' theorem:

$$\int_{\mathcal{D}} \mathrm{d}V\ \operatorname{div}\ \boldsymbol{a} = \oint_{\partial\mathcal{D}} \mathrm{d}\mathcal{A}\ \boldsymbol{n}\cdot\boldsymbol{a}\ ;$$

then we obtain

$$\delta\mathcal{L}_{\text{e}} = -\int_V \mathrm{d}V\ \operatorname{div}\ \left(\Phi\ \delta\boldsymbol{\mathcal{D}}\right) + \oint_{\Sigma_0} \mathrm{d}\mathcal{A}\ \boldsymbol{n}_0 \cdot \Phi\ \delta\boldsymbol{\mathcal{D}}\ .$$

From the defining conditions, on the external surface Σ_0 the electrostatic potential Φ and the electric induction $\mathcal{D}$ vannish, so that the surface integral $\oint_{\Sigma_0} \ldots$ has no contribution.

For the volumic integral we can perform the following transformations of the integrand:

$$\begin{aligned}\operatorname{div}\left(\Phi\ \delta\boldsymbol{\mathcal{D}}\right) &= \operatorname{grad}\Phi\cdot\delta\boldsymbol{\mathcal{D}} + \Phi\ \operatorname{div}\left(\delta\boldsymbol{\mathcal{D}}\right) = -\boldsymbol{\mathcal{E}}\cdot\delta\boldsymbol{\mathcal{D}} + \Phi\ \delta\big(\operatorname{div}\boldsymbol{\mathcal{D}}\big)\\ &= -\boldsymbol{\mathcal{E}}\cdot\delta\boldsymbol{\mathcal{D}}\ ,\end{aligned}$$

because Eq. (2) and the absence of another free charges inside the dielectric:

$$\operatorname{div}\boldsymbol{\mathcal{D}} = \rho_{\text{int}} = 0\ .$$

Finally, by combining the previous results, we get Eq. (10). □

We note that the expression (10) for the electric work, implies a domain for integration with a fixed volume (V_0), and in addition the electric field must vanish outside this domain.

Therefore, there are two methods to deal the thermodynamics of dielectrics on the basis of the electric work (and also the necessary conditions for the validity of the corresponding expression): *the open system method* (when the domain of integration is fixed but it has a fictitious frontier and it contains only a part of the dielectric), and *the closed system method* (when the domain of integration has physical a frontier, possibly located at the infinity, but the dielectric is located in a part of this domain); we observe that the second method is more physical, but in the same time it is more complex, because we must consider a compound system and only a part of this total system is of special interest (this is the dielectric). In addition we shall see that the second method implies the change of the common definitions

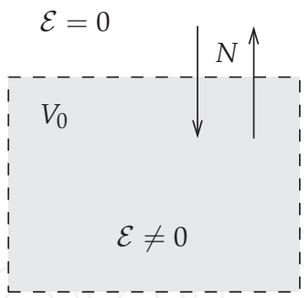


Fig. 2. The open system model.

for the state parameters associated to the electric and volumic degrees of freedom (both the extensive and the intensive).

1. The open system method: we consider a fixed domain (having the volume $V = \text{const.}$) which contains an electrostatic field inside, but outside to this domain the electrostatic field vanishes; the interesting system is the dielectric located inside the above specified domain, as an open thermodynamic system (the dielectric fills completely the domain, but there is a part of this dielectric outside the domain, at vanishing electrostatic field, because the frontier is totally permeable).

We note the following characteristic features of this situation:

– the thermodynamic system (the portion of the dielectric located in electrostatic field) has a fixed volume ($V = V_0 = \text{constant}$), but in the same time, it is an *open* thermodynamic system ($N \neq \text{constant}$);

– the electro-striction effect (this is the variation of the volume produced by the variation of the electric field) in this case leads to the variation of the particle number, or in another words, by variation of the particle density $\mathfrak{n} \equiv N/V_0 \neq$ constant (because the volume is fixed, but the frontier is chemical permeable);

– in the simplest case, when we consider a homogeneous electrostatic field[3], inside the domain with the volume V_0, infinitesimal electric work can be written in the form

$$\delta \mathcal{L}_{\mathrm{e}} = \mathcal{E}\, \delta(V_0\, \mathcal{D})\,, \tag{11}$$

and this implies the following definition for the electric state parameters (the extensive and the intensive ones):

$$\begin{cases} X_{\mathrm{e}} = V_0\, \mathcal{D} = \mathfrak{D} \\ P_{\mathrm{e}} = \mathcal{E} \end{cases} \tag{12}$$

[in this case $V = \text{const.}$, that is the volumic degree of freedom for this system is frozen; but we emphasize that the expression $\delta \mathcal{L}_{\mathrm{e}} = \mathcal{E}\, \delta(V\, \mathcal{D})$ when the volume of the system V can varies is *incorrect*].

[2] In order to have the general situation, we do not suppose particular properties for the dielectrics, so that we consider the non-homogeneous case.

[3] This situation is realized by considering a plane electric condenser having very closed plates, so that it is possible to consider approximately that the electric field vanishes outside the condenser; the space inside and outside the condenser is filled with a fluid dielectric. Accordingly to the previous definitions, the thermodynamic interesting system is only the part of the dielectric which is located inside the plates of the condenser, and the frontier of this system is fictitious.

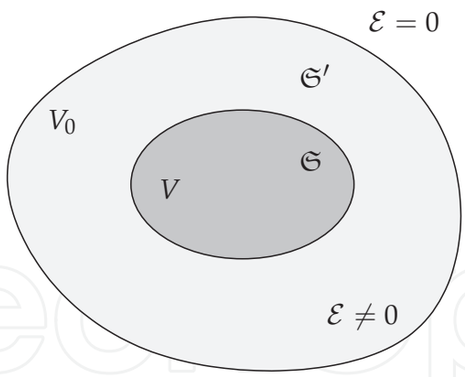


Fig. 3. The model for the closed system.

2. The closed system method: we consider the dielectric surrounded by an non-electric fluid (that is, the dielectric is located on a part of the domain with electric field).
Then it is necessary to define the compound system corresponding to the whole space where exists electric field

$$\mathfrak{S}^{(\tau)} = \mathfrak{S} \bigcup \mathfrak{S}' \,,$$

where $\mathfrak{S}$ is the dielectric system with the volume V, and $\mathfrak{S}'$ is an auxiliary non-electric system having the volume $V' = V_0 - V$, as it is illustrated in Fig. 3.

We must remark that the auxiliary system (having negligible electric properties) is necessary in order to obtain the condition $\mathcal{E} \to 0$ towards the frontier of the domain which have the volume V_0, and also it produces a pressure on the dielectric; thus, the volume of the dielectric is not fixed and we can distinguish directly electro-striction effects.

Because the polarization $\boldsymbol{P}$ is non-vanishing only in the domain V, occupied by the system $\mathfrak{S}$, we transform the expression (10) using Eq. (5), in order to extract the electrization work on the subsystem $\mathfrak{S}$

$$\begin{aligned} \delta\!\!\!^{-}\mathcal{L}_{\mathrm{e}}^{(\tau)} = \int_{V_0} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \delta\boldsymbol{\mathcal{D}} &= \int_{V_0} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \overline{\varepsilon}_0\, \delta\boldsymbol{\mathcal{E}} + \int_{V_0} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \delta\boldsymbol{P} \\ &\equiv \delta W_{\mathcal{E}}^{(\tau)} + \delta\!\!\!^{-}\mathcal{L}_{\mathrm{p}} \,, \end{aligned}$$

where $\delta W_{\mathcal{E}}^{(\tau)}$ is the variation of the energy for the field inside the total volume V_0, and $\delta\!\!\!^{-}\mathcal{L}_{\mathrm{p}}$ is the work for polarize the dielectric.

The first term allows the separation of the contributions corresponding the two subsystems when the energy of the electrostatic field changes:

$$\begin{aligned} \delta W_{\mathcal{E}}^{(\tau)} = \int_{V_0} \mathrm{d}^3\mathbf{r}\, \delta\Big(\frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2}\Big) &= \delta\left\{\int_V \mathrm{d}^3\mathbf{r}\, \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2}\right\} + \delta\left\{\int_{V'} \mathrm{d}^3\mathbf{r}\, \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2}\right\} \\ &= \delta W_{\mathcal{E}} + \delta W'_{\mathcal{E}} \,. \end{aligned}$$

The second term can be interpreted as electric polarization work and it implies only the dielectric; in order to include the possible electro-strictive effects, we shall write this term in the form

$$\delta\!\!\!^{-}\mathcal{L}_{\mathrm{p}} = \int_{V_0} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \delta\boldsymbol{P} = \int_{V_f} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P}_f - \int_{V_i} \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P}_i = \delta\left\{\int_V \mathrm{d}^3\mathbf{r}\, \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P}\right\}\Big|_{\mathcal{E}=\mathrm{const.}}$$

that is, the polarization work implies the variation of the polarization $\delta \boldsymbol{P}$ and of the volume δV of the dielectric with the condition of constant electric field: $\boldsymbol{\mathcal{E}} = \text{constant}$ (during the process).

On the basis of the previous results we can separate the contribution of the electric work on the dielectric ($\text{đ}\mathcal{L}_\text{e}$) from those on the auxiliary non-electric system ($\delta W'_\mathcal{E}$):

$$\text{đ}\mathcal{L}_\text{e}^{(\tau)} = \text{đ}\mathcal{L}_\text{e} + \delta W'_\mathcal{E} \,, \tag{13a}$$

$$\text{đ}\mathcal{L}_\text{e} = \text{đ}\mathcal{L}_\text{p} + \delta W_\mathcal{E} \,. \tag{13b}$$

For the electric work on the dielectric (the subsystem $\mathfrak{S}$) we observe two interpretations in the case when $\mathfrak{S}$ is homogeneous[4]:

1. we take into account only the polarization work $\text{đ}\mathcal{L}_\text{p}$ and we neglect systematically the energy of the electric field inside the dielectric $\delta W_\mathcal{E}$; then the polarization work in the uniform electric field can be expressed with the dipolar electric moment

$$\text{đ}\mathcal{L}_\text{p} = \boldsymbol{\mathcal{E}} \cdot \delta \int_V \text{d}^3\mathbf{r}\, \boldsymbol{P} = \boldsymbol{\mathcal{E}} \cdot \delta \boldsymbol{\mathcal{P}} \,; \tag{14}$$

2. we estimate the contributions of the both terms from Eq. (13b), taking into account the implications due to the homogeneity of the system:

$$\begin{aligned} \text{đ}\mathcal{L}_\text{p} &= \mathcal{E}\, \text{d}\mathcal{P} = \mathcal{E}\, \text{d}(VP) \,, \\ \text{d}W_\mathcal{E} &= \text{d}\Big(\frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2}\, V\Big) = -\,\frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2}\, \text{d}V + \mathcal{E}\, \text{d}(V\, \overline{\varepsilon}_0\, \mathcal{E}) \,, \end{aligned}$$

   so that we obtain the total electric work performed by the dielectric

$$\text{đ}\mathcal{L}_\text{e} = \text{đ}\mathcal{L}_\text{p} + \text{d}W_\mathcal{E} = -\,\frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2}\, \text{d}V + \mathcal{E}\, \text{d}(V\, \mathcal{D}) \,, \tag{15}$$

   and the last expression can be interpreted as an work performed on two degrees of freedom (volumic and electric).

We observe that for isotropic dielectrics the vectors $\boldsymbol{\mathcal{E}}$, $\boldsymbol{\mathcal{D}}$ and $\boldsymbol{P}$ are collinear; therefore, we shall omit the vectorial notation, for simplicity.

2.2 Thermodynamic potentials

We shall discuss, for simplicity, only the case when the electric system is homogeneous and of fluid type, being surrounded by a non-electric environment. Then, the fundamental thermodynamic differential form is:

$$\text{d}\,\mathcal{U} = \text{đ}\mathcal{Q} + \text{đ}\mathcal{L}_V + \text{đ}\mathcal{L}_\text{e} + \text{đ}\mathcal{L}_N \,. \tag{16}$$

For the thermodynamic study of the electric system there are many methods, depending the choice of the fundamental variables (corresponding to the choice of the concrete expression for the electric work $\text{đ}\mathcal{L}_\text{e}$).

[4] The condition of homogeneity implies an uniform electric field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = \text{const.}$ in the subsystem $\mathfrak{S}$, and this property is realized only when the dielectric is an ellipsoid in an uniform external field.

2.2.1 Pseudo-potentials method

We replace the expression (13b) – (14) for the electric work, and also the expression for the other forms of work and for the heat; then, the fundamental thermodynamic differential form has the explicit expression:

$$\mathrm{d}\mathcal{U} = T\ \mathrm{d}\mathcal{S} - \mathfrak{P}\ \mathrm{d}V + \mathcal{E}\ \mathrm{d}\mathcal{P} + \mathrm{d}W_{\mathcal{E}} + \mu\ \mathrm{d}N\ . \tag{17}$$

We observe that the preceding differential form contains a term $\mathrm{d}W_{\mathcal{E}}$ which is a exact total differential (from the mathematical point of view) and it represents the variation of the energy of the electric field located in the space occupied by the dielectric; we put this quantity in the left side of the above equality we obtain:

$$\mathrm{d}\widetilde{\mathcal{U}} = T\ \mathrm{d}\mathcal{S} - \mathfrak{P}\ \mathrm{d}V + \mathcal{E}\ \mathrm{d}\mathcal{P} + \mu\ \mathrm{d}N\ , \tag{18}$$

where $\widetilde{\mathcal{U}} \equiv \mathcal{U} - W_{\mathcal{E}}$ is called the *internal pseudo-energy* of the dielectric[5].

We present some observations concerning the differential form (18):

• $\widetilde{\mathcal{U}}(\mathcal{S}, V, \mathcal{P}, N)$ is equivalent to the fundamental thermodynamic equation of the system, since it contains the whole thermodynamic information about the system (that is, its derivatives are the state equations)[6]; and on the other side, the pseudo-energy has no specified convexity properties (because it was obtained by subtracting a part of the energy from the total internal energy of the system);

• $\widetilde{\mathcal{U}}(\mathcal{S}, V, \mathcal{P}, N)$ is a homogeneous function of degree 1 (because it is obtained as a difference of two homogeneous functions of degree 1);

• by considering the differential form (18) as similar to the fundamental thermodynamic differential form, it follows that the electric state parameters are[7]

$$\begin{cases} \widetilde{X}_e = \mathcal{P}\ =\ P\,V\ , \\ \widetilde{P}_e = \mathcal{E}\ ; \end{cases}$$

• if we perform the Legendre transformations of the function $\widetilde{\mathcal{U}}(\mathcal{S}, V, \mathcal{P}, N)$, then we obtain objects of the thermodynamic potential types (that is, the derivatives of these quantities give the state equations of the dielectric); however, these objects are not true thermodynamic potentials (firstly since they have not the needed properties of convexity-concavity), so that they are usually called *thermodynamic pseudo-potentials*.

In the following we shall present briefly only the most used pseudo-potentials: the *electric pseudo-free energy* and the *electric Gibbs pseudo-potential*.

[5] Because we consider in the expression $W_{\mathcal{E}} = V\,\overline{\varepsilon}_0\mathcal{E}^2/2$ the intensity of the electric field in the presence of the dielectric, this energy is due both to the vacuum and to the dielectric; thus, $\widetilde{\mathcal{U}}$ *is not the internal energy of the dielectric* (without the energy of the electric fields in vacuum), but it is an artificial quantity.

[6] We shall show later that the derivatives of the pseudo-energy (more exactly, the derivatives of the pseudo-potentials deduced from the pseudo-energy) are the correct state equations.

[7] We observe that the use of the internal pseudo-energy implies the modification of the extensive electric state parameter ($V\,\boldsymbol{\mathcal{D}}\ \rightarrow\ V\boldsymbol{P}$), but the intensive electric state parameter ($\boldsymbol{\mathcal{E}}$) had been unmodified.

a.1. The electric pseudo-free energy is the Legendre transformation on the thermal and electric degrees of freedom[8]

$$\widetilde{\mathcal{F}}^* \equiv \widetilde{\mathcal{U}} - T\,\mathcal{S} - \mathcal{E}\,\mathcal{P}\ , \tag{19}$$

having the differential form[9]:

$$\mathrm{d}\widetilde{\mathcal{F}}^* = -\,\mathcal{S}\ \mathrm{d}T - \mathfrak{P}\ \mathrm{d}V - \mathcal{P}\ \mathrm{d}\mathcal{E} + \mu\ \mathrm{d}N\ , \tag{20}$$

so that it allows the deduce the state equations in the representation $(T, V, \mathcal{E}, N)$.
We consider the simplest case, when the dielectric behaves as a neutral fluid, having the free energy $\mathcal{F}_0(T, V, N)$, in the absence of the electric field and when the electric susceptibility is $\chi_e(T, V/N)$; then, we can consider as known the electric state equation (the expression of the dipolar electric moment):

$$\left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial\,\mathcal{E}}\right)_{T,V,N} = -\,\mathcal{P}(T, V, \mathcal{E}, N) = -\,\overline{\varepsilon}_0\,\chi_e(T, V/N)\ \mathcal{E}\ V\ .$$

By partial integration, with respect to the electric field, and taking into account that at vanishing electrical field the electric pseudo-free energy reduces to the proper free energy (the Helmholtz potential):

$$\widetilde{\mathcal{F}}^*\Big|_{\mathcal{E}=0} = \mathcal{U}_0 - T\,\mathcal{S}_0 = \mathcal{F}_0(T, V, N)\ ,$$

we obtain:

$$\widetilde{\mathcal{F}}^*(T, V, \mathcal{E}, N) = \mathcal{F}_0(T, V, N) + \mathcal{F}^*_{\mathrm{el}}(T, V, \mathcal{E}, N)\ , \tag{21a}$$

$$\mathcal{F}^*_{\mathrm{el}}(T, V, \mathcal{E}, N) \equiv -\,\frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\ \chi_e(T, V/N)\ V\ , \tag{21b}$$

that is, the electric pseudo-free energy of the dielectric is the sum of the free energy at null electric field and the electric part $\mathcal{F}^*_{\mathrm{el}}$.

The additivity (factorization) property of the electric pseudo-free energy is transmitted to the non-electric state equations: the entropy, the pressure and the chemical potential (these are sums of the non-electric part, corresponding to vanishing electric field, and the electric part):

$$\mathcal{S}(T, V, \mathcal{E}, N) = -\left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial\,T}\right)_{V,\mathcal{E},N} = \mathcal{S}_0(T, V, N) + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\chi_e}{\partial\,T}\right)_{V,N} V\ , \tag{22a}$$

$$\mathfrak{P}(T, V, \mathcal{E}, N) = -\left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial\,V}\right)_{T,\mathcal{E},N} = \mathfrak{P}_0(T, V, N) + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,(\chi_e V)}{\partial\,V}\right)_{T,N}\ , \tag{22b}$$

$$\mu(T, V, \mathcal{E}, N) = \left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial N}\right)_{T,V,\mathcal{E}} = \mu_0(T, V, N) - \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\chi_e}{\partial N}\right)_{T,V} V\ . \tag{22c}$$

[8] Because the absence of the correct properties of the convexity, we shall use only the classic definition of the Legendre transformation.

[9] In the strictly sense, $\widetilde{\mathcal{F}}^*$ is a simple Gibbs potential, so that the common terminology is criticizable.

a.2. The electric Gibbs pseudo-potential is defined, analogously to the previous case, as the Legendre transformation on the thermal, volumic and electric degrees of freedom[10]

$$\widetilde{\mathcal{G}}^* \equiv \widetilde{\mathcal{U}} - T\,\mathcal{S} + \mathfrak{P}\,V - \mathcal{E}\,\mathcal{P}\ , \tag{23}$$

having the differential form

$$\mathrm{d}\widetilde{\mathcal{G}}^* = -\,\mathcal{S}\,\mathrm{d}T + V\,\mathrm{d}\mathfrak{P} - \mathcal{P}\,\mathrm{d}\mathcal{E} + \mu\,\mathrm{d}N\ , \tag{24}$$

so that it allows the deduction of the state equations in the representation $(T, \mathfrak{P}, \mathcal{E}, N)$.
We consider the simplest case (analogously in the former case), when the dielectric behaves as a neutral fluid, having the proper Gibbs potential (the free enthalpy) $\mathcal{G}_0(T, \mathfrak{P}, N)$ in the absence of the electric field and when the electric susceptibility is $\overline{\chi}_e(T, \mathfrak{P})$; then, we can consider as known the electric state equation (the expression of the dipolar electric moment):

$$\left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,\mathcal{E}}\right)_{T,\mathfrak{P},N} = -\,\mathcal{P}(T, \mathfrak{P}, \mathcal{E}, N) = -\,\overline{\varepsilon}_0\,\overline{\chi}_e(T, \mathfrak{P})\ \mathcal{E}\ N\ .$$

By partial integration, with respect to the electric field, and taking into account that at vanishing electrical field the electric Gibbs pseudo-potential reduces to the proper Gibbs potential:

$$\widetilde{\mathcal{G}}^*\Big|_{\mathcal{E}=0} = \mathcal{U}_0 - T\,\mathcal{S}_0 + \mathfrak{P}\,V_0 = \mathcal{G}_0(T, \mathfrak{P}, N)\ ,$$

we obtain:

$$\widetilde{\mathcal{G}}^*(T, \mathfrak{P}, \mathcal{E}, N) = \mathcal{G}_0(T, \mathfrak{P}, N) + \mathcal{G}^*_{\mathrm{el}}(T, \mathfrak{P}, \mathcal{E}, N)\ , \tag{25a}$$

$$\mathcal{G}^*_{\mathrm{el}}(T, \mathfrak{P}, \mathcal{E}, N) \equiv -\,\frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,\overline{\chi}_e(T, \mathfrak{P})\ N\ , \tag{25b}$$

that is, the electric Gibbs pseudo-potential of the dielectric is the sum of the Gibbs potential at null electric field and the electric part $\mathcal{G}^*_{\mathrm{el}}$.

The additivity (factorization) property of the electric Gibbs pseudo-potential is transmitted to the non-electric state equations: the entropy, the volume and the chemical potential (these are sums of the non-electric part, corresponding to vanishing electric field, and the electric part):

$$\mathcal{S}(T, \mathfrak{P}, \mathcal{E}, N) = -\left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,T}\right)_{\mathfrak{P},\mathcal{E},N} = \mathcal{S}_0(T, \mathfrak{P}, N) + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\overline{\chi}_e}{\partial\,T}\right)_{\mathfrak{P}} N\ , \tag{26a}$$

$$V(T, \mathfrak{P}, \mathcal{E}, N) = \left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,\mathfrak{P}}\right)_{T,\mathcal{E},N} = V_0(T, \mathfrak{P}, N) - \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\overline{\chi}_e}{\partial\,\mathfrak{P}}\right)_{T} N\ , \tag{26b}$$

$$\mu(T, \mathfrak{P}, \mathcal{E}, N) = \left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial N}\right)_{T,\mathfrak{P},\mathcal{E}} = \mu_0(T, \mathfrak{P}, N) - \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,\overline{\chi}_e(T, \mathfrak{P})\ . \tag{26c}$$

We observe, in addition, that the electric Gibbs pseudo-potential is a maximal Legendre transformation, so that with the Euler relation we obtain

$$\widetilde{\mathcal{G}}^*(T, \mathfrak{P}, \mathcal{E}, N) = \mu(T, \mathfrak{P}, \mathcal{E})\ N\ . \tag{27}$$

[10] Because the absence of the correct properties of the convexity, we shall use only the classic definition of the Legendre transformation (like in the preceding case).

2.2.2 The method of modified potentials

We use the expression (15) for the electric work, without extracting terms with total exact differential type from the internal energy of the dielectric; then, the differential form (16) can be written in the following explicit manner:

$$\begin{aligned} \mathrm{d}\mathcal{U} &= T\,\mathrm{d}\mathcal{S} - \left(\mathfrak{P} + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\right)\mathrm{d}V + \mathcal{E}\,\mathrm{d}(\mathcal{D}\,V) + \mu\,\mathrm{d}N \\ &= T\,\mathrm{d}\mathcal{S} - \pi\,\mathrm{d}V + \mathcal{E}\,\mathrm{d}\mathfrak{D} + \mu\,\mathrm{d}N\,. \end{aligned} \tag{28}$$

We observe that in this case the electric work has contributions on two thermodynamic degrees of freedom, so that we must redefine the electric and volumic state parameters:

$$X_V = V\,, \qquad P'_V = -\,\pi \equiv -\left(\mathfrak{P} + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\right)\,, \tag{29a}$$

$$X'_{\mathcal{E}} = \mathfrak{D} \equiv \mathcal{D}\,V\,, \qquad P_{\mathcal{E}} = \mathcal{E}\,. \tag{29b}$$

In this last case it appears some peculiarities of the electric state parameters (both for the extensive and for the intensive), so that there are needed cautions when it is used this method:

– V and $\mathfrak{D} \equiv \mathcal{D}\,V$ must be considered as independent variables,

– the effective pressure has an supplementary electric contribution $\overline{\varepsilon}_0\,\mathcal{E}^2/2$.

Although the modified potential method implies the employment of some unusual state parameters, however it has the major advantage that $\mathcal{U}(\mathcal{S}, V, \mathfrak{D}, N)$ is the true fundamental energetic thermodynamic equation, and it is a *convex* and *homogeneous of degree* 1 function; thus, it is valid the Euler equation:

$$\mathcal{U} = T\,\mathcal{S} - \pi\,V + \mathcal{E}\,\mathfrak{D} + \mu\,N\,, \tag{30}$$

and it is possible to define true thermodynamic potential with Legendre transformations. From the Euler relation (30) and passing to the common variables, it results

$$\mathcal{U} = T\,\mathcal{S} - \mathfrak{P}\,V + \mathcal{E}\,P\,V + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,V + \mu\,N\,,$$

so that it is ensured that $\widetilde{\mathcal{U}} \equiv \mathcal{U} - W_{\mathcal{E}}$ is a homogeneous function of degree 1 with respect to the variables $(\mathcal{S}, V, \mathcal{P}, N)$.

In order to compare the results of the method of modified potentials with those of the method of the pseudo-potentials we shall present only *the electric free energy* and *the electric Gibbs potential* as energetic thermodynamic potentials.

b.1. The electric free energy is the Legendre transformation on the thermal and electric degrees of freedom

$$\mathcal{F}^*(T, V, \mathcal{E}, N) \equiv \inf_{\mathcal{S},\mathfrak{D}} \left\{\, \mathcal{U}(\mathcal{S}, V, \mathfrak{D}, N) - T\,\mathcal{S} - \mathcal{E}\,\mathfrak{D} \,\right\}\,, \tag{31}$$

and it has the following differential form[11]:

$$\mathrm{d}\mathcal{F}^* = -\,\mathcal{S}\,\mathrm{d}T - \pi\,\mathrm{d}V - \mathfrak{D}\,\mathrm{d}\mathcal{E} + \mu\,\mathrm{d}N\,. \tag{32}$$

[11] In the strictly sense, $\mathcal{F}^*$ is a simple Gibbs potential, so that the common terminology is criticizable.

We shall emphasize some important properties of the above defined electric free energy $\mathcal{F}^*(T,V,\mathcal{E},N)$.

1. When the electric field vanishes it becomes the proper free energy (the Helmholtz potential)

$$\mathcal{F}^*(T,V,0,N) = \mathcal{U}_0(T,V,N) - T\,\mathcal{S}_0(T,V,N) = \mathcal{F}_0(T,V,N)\ .$$

2. The electric state equation is

$$\left(\frac{\partial\,\mathcal{F}^*}{\partial\,\mathcal{E}}\right)_{T,V,N} = -\,\mathfrak{D}(T,V,\mathcal{E},N) = -\,\overline{\varepsilon}_0\,\left[1+\chi_e(T,V/N)\right]\,\mathcal{E}\,V\ .$$

3. By partial integration with respect to the electric field and the use of the condition of null field, we obtain the general expression of the electric free energy (for a linear and homogeneous dielectric)

$$\mathcal{F}^*(T,V,\mathcal{E},N) = \mathcal{F}_0(T,V,N) - \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,\left[\,1+\chi_e(T,V/N)\,\right]\,V\ . \tag{33}$$

4. $\mathcal{F}^*(T,V,\mathcal{E},N)$ is a function *concave* in respect to the variables T and $\mathcal{E}$; as a result we get the relation

$$\left(\frac{\partial^2\mathcal{F}^*}{\partial\,\mathcal{E}^2}\right)_{T,V,N} = -\,\overline{\varepsilon}_0\,\left[1+\chi_e\right]\,V<0\ ,$$

and it follows "the stability condition" $\chi_e > -1$. (We note that actually is realized a more strong condition $\chi_e > 0$, but this has no thermodynamic reasons).

5. The state equations, deduced from Eq. (33) are:

$$\mathcal{S}(T,V,\mathcal{E},N) = -\left(\frac{\partial\,\mathcal{F}^*}{\partial\,T}\right)_{V,\mathcal{E},N} = \mathcal{S}_0(T,V,N) + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\chi_e}{\partial\,T}\right)_{V,N} V\ , \tag{34a}$$

$$\pi(T,V,\mathcal{E},N) = -\left(\frac{\partial\,\mathcal{F}^*}{\partial\,V}\right)_{T,\mathcal{E},N} = \mathfrak{P}_0(T,V,N) + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left[1+\left(\frac{\partial\,(\chi_e V)}{\partial\,V}\right)_{T,N}\right]\ , \tag{34b}$$

$$\mu(T,V,\mathcal{E},N) = \left(\frac{\partial\,\mathcal{F}^*}{\partial N}\right)_{T,V,\mathcal{E}} = \mu_0(T,V,N) - \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\chi_e}{\partial N}\right)_{T,V} V\ . \tag{34c}$$

Because $\pi = \mathfrak{P} + \overline{\varepsilon}_0\,\mathcal{E}^2/2$, it results that the state equations (34) are identical with Eqs. (22), and this shows that $\widetilde{\mathcal{F}}^*$ (the correspondent pseudo-potential to $\mathcal{F}^*$) gives correct state equations.

From Eq. (33) it result that the free energy (Helmholtz potential) is

$$\mathcal{F} = \mathcal{F}^* + \mathcal{E}\,\mathfrak{D} = \mathcal{F}_0 + \frac{\mathcal{E}\,\mathcal{D}}{2}\,V\ ,$$

so that the electric part of the volumic density of free energy is:

$$\mathfrak{f}_{\mathrm{el}} \equiv \frac{\mathcal{F}-\mathcal{F}_0}{V} = \frac{\mathcal{E}\,\mathcal{D}}{2}\ .$$

We emphasize that in many books the previous expression for the electric part of the free energy density is erroneously considered as electric part of the internal energy density.

Correctly, the internal energy has the expression

$$\mathcal{U} = \mathcal{F}^* + T\,\mathcal{S} + \mathcal{E}\,\mathfrak{D} = \left(\mathcal{F}_0 + T\,\mathcal{S}_0\right) + \left(\frac{\mathcal{E}\,\mathcal{D}}{2} + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,T\,\frac{\partial\,\chi_e}{\partial\,T}\right)\,V\,,$$

so that the electric part of the volumic density of internal energy is

$$\mathfrak{u}_{\rm el} = \frac{\mathcal{U} - \mathcal{U}_0}{V} = \frac{\mathcal{E}\,\mathcal{D}}{2} + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,T\,\frac{\partial\,\chi_e}{\partial\,T} \neq \frac{\mathcal{E}\,\mathcal{D}}{2}\,.$$

b.2. The electric Gibbs potential is defined analogously, as the Legendre transformation on the thermal, volumic and electric degrees of freedom

$$\mathcal{G}^*(T,\pi,\mathcal{E},N) \equiv \inf_{\mathcal{S},V,\mathfrak{D}} \left\{\,\mathcal{U}(\mathcal{S},V,\mathfrak{D},N) - T\,\mathcal{S} + \pi\,V - \mathcal{E}\,\mathfrak{D}\,\right\}\,, \tag{35}$$

and it has the differential form

$$\mathrm{d}\mathcal{G}^* = -\,\mathcal{S}\,\mathrm{d}T + V\,\mathrm{d}\pi - \mathfrak{D}\,\mathrm{d}\mathcal{E} + \mu\,\mathrm{d}N\,. \tag{36}$$

According to the definition, $\mathcal{G}^*$ is a maximal Legendre transform, so that the Euler relation leads to:

$$\mathcal{G}^* = \mu\,N\,. \tag{37}$$

On the other side, by replacing the variables π and $\mathfrak{D}$, accordingly to the definitions (29), we obtain the *the electric Gibbs potential is equal to the electric Gibbs pseudo-potential*[12] (but they have different variables):

$$\mathcal{G}^*(T,\pi,\mathcal{E},N) = \widetilde{\mathcal{G}}^*(T,\mathfrak{P},\mathcal{E},N)$$
$$\pi = \mathfrak{P} + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\,.$$

From the preceding properties it follows that the equations deduced from the potential $\mathcal{G}^*$ are identical with Eqs. (22); we observe, however, that it is more convenient to use the pseudo-potential $\widetilde{\mathcal{G}}^*$, because this has more natural variables than the corresponding potential $\mathcal{G}^*$.

2.2.3 Thermodynamic potentials for open systems

Previously we have shown that the electric work implies two methods for treating the dielectrics: either as a closed subsystem of a compound system (this situation was discussed above), or as an open system located in a fixed volume (and the electric field is different from zero only inside the domain with fixed volume).

[12] The equality $\mathcal{G}^* = \widetilde{\mathcal{G}}^*$ (as quantities, but not as functions) can be obtained directly by comparing the consequences of the Euler equation (27) and (37).

If we use the second method, then the electric work has the expression (11) and the dielectric system has only 3 thermodynamic degrees of freedom: thermal, electric and chemical (the volumic degree of freedom is frozen); then, the fundamental differential form is

$$\mathrm{d}\mathcal{U} = T\ \mathrm{d}\mathcal{S} + \mathcal{E}\ \mathrm{d}(V_0\,\mathcal{D}) + \mu\ \mathrm{d}N\ . \tag{38}$$

Among the thermodynamic potentials, that can be obtained by Legendre transformations of the energetic fundamental thermodynamic equation, denoted as $\mathcal{U}(\mathcal{S}, V_0\,\mathcal{D}, N) \equiv \mathcal{U}(\mathcal{S}, \mathcal{D}, N; V_0)$, we shall present only the electric free energy:

$$\mathcal{F}^*(T, \mathcal{E}, N; V_0) \equiv \inf_{\mathcal{S},\mathfrak{D}} \left\{ \mathcal{U}(\mathcal{S}, \mathfrak{D}, N; V_0) - T\,\mathcal{S} - \mathcal{E}\,\mathfrak{D} \right\}, \tag{39}$$

which has the following properties:

1. the differential form:

$$\mathrm{d}\mathcal{F}^* = -\,\mathcal{S}\ \mathrm{d}T - V_0\,\mathcal{D}\ \mathrm{d}\mathcal{E} + \mu\ \mathrm{d}N\ ; \tag{40}$$

2. it reduces to the free energy (the Helmholtz potential) at vanishing electric field

$$\mathcal{F}^*(T, 0, N; V_0) = \mathcal{U}_0(T, N; V_0) - T\,\mathcal{S}_0(T, N; V_0) = \mathcal{F}_0(T, N; V_0)\ ;$$

3. by integrating the electric state equation $V_0\,\mathcal{D}(T, \mathcal{E}, N) = V_0\,[1 + \chi_e]\,\overline{\varepsilon}_0\,\mathcal{E}$, we obtain

$$\mathcal{F}^*(T, \mathcal{E}, N; V_0) = \mathcal{F}_0(T, N; V_0) - V_0\,\frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\ \left[1 + \chi_e(T, V/N)\right]\ . \tag{41}$$

We note that the results are equivalent to those obtained by the previous method, but the situation is simpler because the volumic degree of freedom is frozen.

2.3 Thermodynamic coefficients and processes

2.3.1 Definitions for the principal thermodynamic coefficients

Because the dielectric has 4 thermodynamic degrees of freedom (in the simplest case, when it is fluid), there are a great number of simple thermodynamic coefficients; taking into account this complexity, we shall present only the common coefficients, corresponding to closed dielectric systems (N = constant). In this case it is convenient to use reduced extensive parameters with respect to the particle number; thus, we shall use the specific entropy $s = \dfrac{\mathcal{S}}{N}$ and the specific volume $v = \dfrac{V}{N}$.

a.1. The sensible specific heats are defined for non-isothermal processes "φ":

$$c_\varphi \equiv \frac{C_\varphi}{N} = \frac{1}{N}\ T\left(\frac{\partial\,\mathcal{S}}{\partial\,T}\right)_\varphi = T\left(\frac{\partial\,s}{\partial\,T}\right)_\varphi\ . \tag{42}$$

In the case, when the process φ is simple, we obtain the following specific isobaric/isochoric and iso-polarization/iso-field heats: $c_{V,\mathfrak{p}}$, $c_{V,\mathcal{E}}$, $c_{P,\mathfrak{p}}$, $c_{P,\mathcal{E}}$.

a.2. The latent specific heats are defined for isothermal processes "ψ":

$$\lambda_\psi^{(a)} = \frac{1}{N}\ T\left(\frac{\partial\,\mathcal{S}}{\partial\,a}\right)_\psi = T\left(\frac{\partial\,s}{\partial\,a}\right)_\psi\ . \tag{43}$$

The most important cases (for "ψ" and a) are the isothermal-isobaric process with $a = \mathcal{E}$ when we have *the isobaric electro-caloric coefficient* λ and the conjugated isothermal-isofield process with $a = \mathfrak{P}$, when we have *the iso-field piezo-caloric coefficient* $\lambda_{\mathcal{E}}^{(P)}$:

$$\lambda = T\left(\frac{\partial s}{\partial \mathcal{E}}\right)_{T,\mathfrak{P}} , \qquad \lambda_{\mathcal{E}}^{(P)} = T\left(\frac{\partial s}{\partial \mathfrak{P}}\right)_{T,\mathcal{E}} . \tag{44}$$

a.3. The thermodynamic susceptibilities are of two types: for the volumic degree of freedom (in this case they are called *compressibility coefficients*) and for the electric degree of freedom (these are called *electric susceptibilities*):

$$\varkappa_{\varphi} = \frac{-1}{V}\left(\frac{\partial V}{\partial \mathfrak{P}}\right)_{\varphi} = \frac{-1}{v}\left(\frac{\partial v}{\partial \mathfrak{P}}\right)_{\varphi} , \tag{45}$$

$$\chi_{\psi}^{(\mathrm{el})} = \frac{1}{V}\left(\frac{\partial \mathcal{P}}{\partial \mathcal{E}}\right)_{\psi} = \left(\frac{\partial P}{\partial \mathcal{E}}\right)_{\psi} . \tag{46}$$

In the simple cases "φ" is an isothermal/adiabatic and iso-polarization/iso-field processes; it results the following simple compressibility coefficients: $\varkappa_{T,\mathcal{P}}$, $\varkappa_{T,\mathcal{E}}$, $\varkappa_{s,\mathcal{P}}$ and $\varkappa_{s,\mathcal{E}}$. Analogously "$\psi$" as simple process is isothermal/adiabatic and isobaric/isochoric, resulting the following simple electric susceptibilities: $\chi_{T,v}^{(\mathrm{el})}$, $\chi_{T,\mathfrak{P}}^{(\mathrm{el})}$, $\chi_{s,v}^{(\mathrm{el})}$ and $\chi_{s,\mathfrak{P}}^{(\mathrm{el})}$.

From Eq. (6b) we observe that the isothermal electric susceptibility is proportional to the susceptibility used in the electrodynamics:

$$\chi_{T,v}^{(\mathrm{el})} = \left(\frac{\partial P}{\partial \mathcal{E}}\right)_{T,v} = \overline{\varepsilon}_0\, \chi_e(T,v) .$$

a.4. The thermal coefficients are of two types, corresponding to the two non-thermal and non-chemical degrees of freedom (the volumic and the electric ones). If we consider only thermal coefficients for extensive parameters, then we can define the following types of simple coefficients:

- the *isobaric thermal expansion coefficients* (also iso-polarization/iso-field)

$$\alpha_y = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathfrak{P},y,N} = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_{\mathfrak{P},y} , \tag{47}$$

  where the index y is $\mathcal{P}$ or $\mathcal{E}$;

- the *pyro-electric coefficients* (also isochoric/isobaric)

$$\pi_a = \frac{1}{N}\left(\frac{\partial \mathcal{P}}{\partial T}\right)_{\mathcal{E},a,N} = \left(\frac{\partial \mathfrak{p}}{\partial T}\right)_{\mathcal{E},a} , \tag{48}$$

  where the index a is V (for the volume V) or P (for the pressure $\mathfrak{P}$).

a.5. The mixed coefficients express correlations between the volumic and the electric degrees of freedom; we mention the following simple coefficients:

- the *electro-strictive coefficient*

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial \mathcal{E}}\right)_{T,\mathfrak{P},N} = \frac{1}{v}\left(\frac{\partial v}{\partial \mathcal{E}}\right)_{T,\mathfrak{P}} \ ; \tag{49}$$

- the *piezo-electric coefficient*

$$\varrho = \frac{1}{N}\left(\frac{\partial \mathcal{P}}{\partial \mathfrak{P}}\right)_{T,\mathcal{E},N} = \left(\frac{\partial \mathfrak{p}}{\partial \mathfrak{P}}\right)_{T,\mathcal{E}} . \tag{50}$$

2.3.2 Relations between simple coefficients

Because the great number of thermodynamic coefficients, corresponding to the dielectrics, we must select among all possible relations between the simple coefficients; therefore, we shall present only the most important relations: the symmetry relations (consequences of some Maxwell relations) and special relations (of the type Reech or Mayer).

In order to emphasize symmetry relations expressed by the temperature, the pressure and the electric field $(T, \mathfrak{P}, \mathcal{E})$, as variables, for an closed system (N = constant), we use the differential form of the reduced Gibbs pseudo-potential $\widetilde{g}^*(T, \mathfrak{P}, \mathcal{E}) \equiv \mathcal{G}^*/N$, which is obtained with the general reduction formulae from Eqs. (23) – (24):

$$\mathrm{d}\widetilde{g}^* = -\, s\, \mathrm{d}T + v\, \mathrm{d}\mathfrak{P} - \mathfrak{p}\, \mathrm{d}\mathcal{E} \ . \tag{51}$$

From the above differential form it results 3 Maxwell relations, which can be expressed by simple coefficients, resulting symmetry relations between these coefficients:

$$\left(\frac{\partial s}{\partial \mathfrak{P}}\right)_{T,\mathcal{E}} = -\left(\frac{\partial v}{\partial T}\right)_{\mathfrak{P},\mathcal{E}} \qquad \Longrightarrow \qquad \lambda_{\mathcal{E}}^{(P)} = -\, T\, v\, \alpha_{\mathcal{E}} \ , \tag{52a}$$

(the relation between the iso-field piezo-caloric coefficient and the isobaric-isofield thermal expansion coefficient);

$$\left(\frac{\partial s}{\partial \mathcal{E}}\right)_{T,\mathfrak{P}} = \left(\frac{\partial \mathfrak{p}}{\partial T}\right)_{\mathfrak{P},\mathcal{E}} \qquad \Longrightarrow \qquad \lambda = T\, \pi_P \ , \tag{52b}$$

(the relation between the isobaric electro-caloric coefficient and the isobaric pyro-electric coefficient);

$$\left(\frac{\partial v}{\partial \mathcal{E}}\right)_{T,\mathfrak{P}} = -\left(\frac{\partial \mathfrak{p}}{\partial \mathfrak{P}}\right)_{T,\mathcal{E}} \qquad \Longrightarrow \qquad v\, \gamma = -\, \varrho \ , \tag{52c}$$

(the relation between the electro-strictive coefficient and the piezo-electric coefficient).

Relations of Reech type can be obtained from the general relation (see [16], Eq. (3.25)), resulting the equality between the ratios of the isobaric specific heats, of the compressibility coefficients, and of the electric susceptibilities (isothermal, and respectively adiabatic):

$$\frac{c_{P,\mathfrak{p}}}{c_{P,\mathcal{E}}} = \frac{\varkappa_{s,\mathcal{E}}}{\varkappa_{T,\mathcal{E}}} = \frac{\chi^{(\mathrm{el})}_{s,\mathfrak{P}}}{\chi^{(\mathrm{el})}_{T,\mathfrak{P}}} \ . \tag{53}$$

Analogously, from the general Mayer relation for the specific heats (see [16] Eq. (3.28)) we obtain in this case

$$c_{P,\mathcal{E}} - c_{P,\mathfrak{p}} = T\, v\, \frac{\alpha_{\mathcal{E}}^2}{\chi_{T,\mathfrak{P}}^{(\mathrm{el})}} \,. \tag{54}$$

Similar relations with Eqs. (53) – (54) can be obtained for the coefficients associated to another sets of simple processes (*e.g.* isochoric, iso-polarization processes).

2.3.3 The factorization of some simple coefficients

An important characteristics of some thermodynamic coefficients is *the factorization property*: the expression of the considered coefficient is the sum of the part corresponding to the absence of the electric field (similarly as for the neutral fluid) and the "electric part", and this result comes from the factorization of the state equations.

We shall present the factorization of some coefficients using the variables of the electric Gibbs representation[13] $(T, \mathfrak{P}, \mathcal{E}, N)$; in this case the state equations are Eqs. (26).

The entropy is given by Eq. (26a), and here we write it without the variables (for simplicity), and for using later the convenient variables

$$\mathcal{S} = \mathcal{S}_0 + \mathcal{S}_{\mathrm{el}} \,, \tag{55}$$

where $\mathcal{S}_0$ is the entropy of the dielectric as a neutral fluid, in the absence of the electric field, and $\mathcal{S}_{\mathrm{el}}$ is the electric part of the entropy:

$$\mathcal{S}_{\mathrm{el}} = \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2} \left(\frac{\partial\, \overline{\chi}_e}{\partial\, T} \right)_{\mathfrak{P}} N = \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2} \left(\frac{\partial\, \chi_e}{\partial\, T} \right)_{v} V \,. \tag{56}$$

Accordingly to the general definition (42), we obtain a factorization of the specific heats:

$$c_\varphi = c_\varphi^{(0)} + c_\varphi^{(\mathrm{el})} \,, \tag{57}$$

where $c_\varphi^{(0)} = T(\partial s^{(0)}/\partial\, T)_\varphi$ is the specific heat of the dielectric in the absence of the electric field, and $c_\varphi^{(\mathrm{el})} = T(\partial s^{(\mathrm{el})}/\partial\, T)_\varphi$ is the electric part of the specific heat.

For the isobaric processes there are the specific heat at constant electric field or at constant polarization. From Eq. (56) it results

$$c_{P,\mathcal{E}}^{(\mathrm{el})} = T \left(\frac{\partial\, \overline{\chi}_e}{\partial\, T} \right)_{\mathfrak{P}} \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2} \,. \tag{58}$$

To obtain $c_{P,\mathfrak{p}}^{(\mathrm{el})}$ we express the electric entropy $\mathcal{S}_{\mathrm{el}}$ in terms of the dipolar electric moment (instead the electric field), using Eq. (6b):

$$\mathcal{S}_{\mathrm{el}} = \frac{\mathfrak{p}^2}{2\, \overline{\varepsilon}_0\, \overline{\chi}_e^2} \left(\frac{\partial\, \overline{\chi}_e}{\partial\, T} \right)_{\mathfrak{P}} N = \frac{-\mathfrak{p}^2}{2\, \overline{\varepsilon}_0} \left(\frac{\partial\, (\overline{\chi}_e)^{-1}}{\partial\, T} \right)_{\mathfrak{P}} N \,;$$

[13] We remark that some coefficients need the use of other thermodynamic representations.

then it results for the electric part of the isobaric-isopolarization specific heat the expression:

$$c_{P,\mathfrak{p}}^{(\mathrm{el})} = \frac{-\mathfrak{p}^2}{2\,\overline{\varepsilon}_0}\; T \left(\frac{\partial^2 \left(\overline{\chi}_e\right)^{-1}}{\partial\, T^2} \right)_{\mathfrak{P}} \; . \tag{59}$$

We observe that for an ideal dielectric $\left(\overline{\chi}_e\right)^{-1} \sim T$, so that we obtain $c_{P,\mathfrak{p}}^{(\mathrm{el})} = 0$, that is $c_{P,\mathfrak{p}} = c_P^{(0)}$ (the iso-polarization specific heat is independent of the electric field)[14].
It is interesting to emphasize that for the ideal dielectrics the internal energy has also particular properties. The electric part of the volumic density of internal energy for an arbitrary dielectric has the expression

$$\mathfrak{u}^{(\mathrm{el})} = \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2} \left(1 + \chi_e + T\, \frac{\partial\, \chi_e}{\partial\, T} \right) .$$

For an ideal dielectric we obtain that this energy density is equal to the energy density of the electric field $\mathfrak{u}^{(\mathrm{el})} = \overline{\varepsilon}_0\, \mathcal{E}^2/2 = w_{\mathrm{el}}$, that is the whole electric energy is given only by the electric field, without any contribution from the processes of the electric polarization. The behavior of the iso-polarization specific heats and of the internal energy are similar to the neutral fluids which satisfy the Clapeyron - Mendeleev equations, so that it is justified the terminology "ideal" for the dielectrics which have Curie susceptibility.

In contrast with the specific heats, the isobaric electro-caloric coefficient has contribution only from the electric part of the entropy:

$$\lambda = \overline{\varepsilon}_0\, \mathcal{E}\; T \left(\frac{\partial\, \overline{\chi}_e}{\partial\, T} \right)_{\mathfrak{P}} \; .$$

The volume is given by Eq. (26b), that is it can be expressed in the form:

$$V = V_0 + V_{\mathrm{el}} \, ,$$

where V is the volume of the dielectric as neutral fluid, in the absence of the electrical field, and V_{el} is the electric part of the volume:

$$V_{\mathrm{el}} = -\, \frac{\overline{\varepsilon}_0\, \mathcal{E}^2}{2} \left(\frac{\partial\, \overline{\chi}_e}{\partial\, \mathfrak{P}} \right)_T N \, . \tag{60}$$

Accordingly to the general definitions (45) and respectively (47), the isothermal compressibility coefficients $\varkappa_{T,\mathcal{E}}$ and the isobaric thermal expansion coefficient $\alpha_{\mathcal{E}}$ (both of them at constant field) factorize in non-electric part (corresponding to null electric field, when the dielectric behaves as a neutral fluid) and electric part:

$$\varkappa_{T,\mathcal{E}} = \varkappa_T^{(0)} + \varkappa_{T,\mathcal{E}}^{(\mathrm{el})} \, , \tag{61a}$$

$$\alpha_{\mathcal{E}} = \alpha^{(0)} + \alpha_{\mathcal{E}}^{(\mathrm{el})} \, , \tag{61b}$$

[14] For the corresponding isochoric specific heat we obtain the same result $c_{V,\mathfrak{P}}^{(\mathrm{el})} = c_V$.

where[15]

$$\varkappa^{(\mathrm{el})}_{T,\mathcal{E}} = \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2\,v_0}\left(\frac{\partial^2\overline{\chi}_e}{\partial\mathfrak{P}^2}\right)_T\,, \tag{62a}$$

$$\alpha^{(\mathrm{el})}_{\mathcal{E}} = -\frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2\,v_0}\,\frac{\partial^2\overline{\chi}_e}{\partial\,T\,\partial\mathfrak{P}}\,. \tag{62b}$$

In contrast with the previous coefficients, the electro-strictive coefficient is obtained only from the electric part of the volumic state equation[16]

$$\gamma \approx -\frac{\overline{\varepsilon}_0\,\mathcal{E}}{v_0}\left(\frac{\partial\,\overline{\chi}_e}{\partial\mathfrak{P}}\right)_T\,. \tag{63}$$

2.3.4 Thermodynamic processes

Using the previous results we shall present the most significant thermodynamic processes for the dielectrics as closed system (we shall choose the variable set T, $\mathfrak{P}$, $\mathcal{E}$, N = constant).

d.1. The isothermal electrization: we consider that initially the dielectric is in null electric field $(T,\mathfrak{P},\mathcal{E}_i=0,N)$ and we apply the electric field with an isothermal-isobaric process, so that the final state has the parameters: $(T,\mathfrak{P},\mathcal{E}_f=\mathcal{E},N)$.

Using Eq. (26a) for the entropy, the heat transfered in this process is

$$\begin{aligned}\mathcal{Q}_{if} = T\,\Delta\,\mathcal{S}_{if} &= T\left\{\,\mathcal{S}(T,\mathfrak{P},\mathcal{E},N) - \mathcal{S}(T,\mathfrak{P},0,N)\,\right\}\\ &= \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\;T\left(\frac{\partial\,\overline{\chi}_e}{\partial\,T}\right)_{\mathfrak{P}}\;N\,.\end{aligned} \tag{64}$$

Since $\overline{\chi}_e(T,\mathfrak{P})$ is in general a decreasing function with respect to the temperature, it results that in the electrization process the dielectric yields heat: $\mathcal{Q}_{if}<0$.

d.2. The adiabatic-isobaric depolarization: we consider that initially the dielectric is in the presence of the electric field $\mathcal{E}$ and it has the temperature T_i; then, by a quasi-static adiabatic-isobaric process the electric field is decreasing to vanishing value.

Since the equation of this process is $\mathcal{S}(T,\mathfrak{P},\mathcal{E},N)$ = constant , with the supplementary conditions $\mathfrak{P}$ = constant and N = constant, then by using Eq. (26a), we obtain the equation of the temperature:

$$\mathcal{S}(T_i,\mathfrak{P},\mathcal{E},N) + \mathcal{S}(T_f,\mathfrak{P},0,N)\;;$$

that is, after simple algebraical operations, we get:

$$s^0(T_i,\mathfrak{P}) + \frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\overline{\chi}_e}{\partial\,T}\right)_{\mathfrak{P}} = s^0(T_f,\mathfrak{P})\,. \tag{65}$$

Because the electric susceptibility is in general an decreasing function in respect to the temperature $(\partial\overline{\chi}_e/\partial T)_{\mathfrak{P}} < 0$ and the entropy $s^0(T,\mathfrak{P})$ is an increasing function of

[15] In fact, the factorization is obtained only if we consider small electric effects, so that we could approximate $v\approx v_0$ at the denominators.

[16] We consider that the electro-strictive effects are small, so that we can use the approximation $v\approx v_0$, at the denominator.

temperature, it results $s_i < s_f$, that is the dielectric gets cool during the adiabatic depolarization: $T_f < T_i$.

d.3. The electro-strictive and piezo-electric effects

The *electro-strictive effect* means the variation of the volume (of the dielectric) due to the variation of the electric field, in conditions isothermal-isobaric (also the dielectric is a closed system)[17]; and the electro-strictive coefficient is defined by Eq. (49).

The *piezo-electric effect* means the variation of the dipolar electric moment (of the dielectric), due to the variation of the pressure, in conditions isothermal and at constant electric field (also the dielectric is a closed system)[18] and the piezo-electric effect coefficient is defined by Eq. (50).

Between coefficients of the two effects it is the symmetry relation (53), and the corresponding expressions can be put in explicit forms using the electric susceptibility:

$$\gamma = -\frac{1}{v}\,\varrho = \frac{-\overline{\varepsilon}_0\,\mathcal{E}}{v}\left(\frac{\partial\,\overline{\chi}_e}{\partial\,\mathfrak{P}}\right)_T . \tag{66}$$

We observe that the necessary condition to have an electro-strictive effect and an piezo-electric effect is that $\overline{\chi}_e$ depends on the pressure; accordingly to Eqs. (9), it results that only the non-ideal dielectrics can have these effects.

Using the volumic equation of state (26b), we can evaluate the global electro-strictive effect, that is the variation of the volume (of the dielectric) at the isothermal-isobaric electrization:

$$\Delta\,V_{if}(\mathcal{E}) = V(T,\mathfrak{P},\mathcal{E},N) - V(T,\mathfrak{P},0,N) = -\,\frac{\overline{\varepsilon}_0\,\mathcal{E}^2}{2}\left(\frac{\partial\,\overline{\chi}_e}{\partial\,\mathfrak{P}}\right)_T N\,. \tag{67}$$

From the previous expression it results that when the electric susceptibility is a decreasing function of the pressure $(\partial\,\overline{\chi}_e/\partial\mathfrak{P})_T < 0$, then it follows a contraction (a reduction of the volume) at the electrization of the dielectric.

3. Magnetic systems

The thermodynamics of magnetic systems has many formal similitude with the thermodynamics of electric systems; in fact, we shall show that it is possible to obtain the most of the results for magnetic systems by simple replacements from the corresponding relations for dielectric systems.

Because this similitude is only formal, and there are physical differences, and on the other side, in order to have an autonomy with respect to the previous section, we shall present briefly the thermodynamics of the magnetic systems independently of the results obtained for the dielectrics. However, for emphasizing the formal similitude between the electric and the magnetic systems, we shall do this presentation analogously to the previous one (which corresponds to dielectrics).

[17] In other words, the electro-strictive effect can be considered as the volumic response of the dielectric to an electric perturbation.

[18] We observe that the piezo-electric effect can be considered as the electric response of the dielectric to a volumic perturbation, being conjugated to the electro-strictive effect.

3.1 General electrodynamic results

Accordingly to the electrodynamics, the magneto-static field created by a distribution of stationary electric currents, in an magnetic medium is characterized by the vectorial fields *the intensity of magnetic induction* $\boldsymbol{\mathcal{B}}(\mathbf{r})$ and *the intensity of the magnetic field* $\boldsymbol{\mathcal{H}}(\mathbf{r})$ (called also the magnetic excitation) which satisfy the magneto-static Maxwell equations [17-20]:

$$\text{rot}\ \boldsymbol{\mathcal{H}}(\mathbf{r}) = \boldsymbol{j}(\mathbf{r})\ , \tag{68a}$$

$$\text{div}\ \boldsymbol{\mathcal{B}}(\mathbf{r}) = 0\ , \tag{68b}$$

where $\boldsymbol{j}(\mathbf{r})$ is the volumic density of the conduction currents (there are excluded the magnetization currents).

Under the influence of the magneto-static field the medium becomes magnetized (it appears magnetization currents), and it is characterized by the *magnetic dipolar moment* $\boldsymbol{\mathcal{M}}$, respectively by the *magnetization* (the volumic density of dipolar magnetic moment) $\boldsymbol{M}(\mathbf{r})$:

$$\boldsymbol{M}(\mathbf{r}) \equiv \lim_{\delta V \to 0} \frac{\delta \boldsymbol{\mathcal{M}}(\mathbf{r})}{\delta V(\mathbf{r})} \quad \Longleftrightarrow \quad \boldsymbol{\mathcal{M}} = \int_V \mathrm{d}^3\mathbf{r}\ \boldsymbol{M}(\mathbf{r})\ . \tag{69}$$

Using the magnetization it results the relation between the characteristic vectors of the magneto-static field:

$$\boldsymbol{\mathcal{H}}(\mathbf{r}) = \frac{1}{\overline{\mu}_0}\ \boldsymbol{\mathcal{B}}(\mathbf{r}) - \boldsymbol{M}(\mathbf{r})\ , \tag{70}$$

where $\overline{\mu}_0$ is the magnetic permeability of the vacuum (it is an universal constant depending on the system of units).

The general relation between the intensity of the magnetic field $\boldsymbol{\mathcal{H}}(\mathbf{r})$ and the magnetization $\boldsymbol{M}(\mathbf{r})$ is

$$\boldsymbol{M}(\mathbf{r}) = \hat{\chi}_{\mathrm{m}}(\mathcal{H}, \mathbf{r}) : \boldsymbol{\mathcal{H}}(\mathbf{r}) + \boldsymbol{M}_0(\mathbf{r})\ , \tag{71a}$$

where $\boldsymbol{M}_0$ is the spontaneous magnetization, and $\hat{\chi}_{\mathrm{m}}$ is the magnetic susceptibility tensor (generally it is dependent on the magnetic field).

For simplicity, we shall consider only the particular case when there is no spontaneous magnetization (that is the absence of ferromagnetic phenomena) $\boldsymbol{M}_0 = 0$, and the magnetic medium is linear and isotropic (then $\hat{\chi}_{\mathrm{m}}$ is reducible to a scalar which is independent on the magnetic field); in this last case, Eq. (71a) becomes:

$$\boldsymbol{M} = \chi_{\mathrm{m}}\ \boldsymbol{\mathcal{H}}\ , \tag{71b}$$

and Eq. (70) allows a parallelism and proportionality relation between the field vectors:

$$\boldsymbol{\mathcal{B}} = \overline{\mu}_0(1 + \chi_{\mathrm{m}})\ \boldsymbol{\mathcal{H}}\ . \tag{72}$$

In the common cases the susceptibility (for the specified types of magnetic media) depends on the temperature and of the particle density (or of the pressure) in the form:

$$\chi_{\mathrm{m}} = \mathfrak{n}\ \overline{\chi}_{\mathrm{m}}(T, \mathfrak{P})\ , \tag{73}$$

where $\mathfrak{n} \equiv N/V$ is the particle density, and $\overline{\chi}_{\mathrm{m}}$ is the specific (per particle) susceptibility[19].

[19] We can define the dipolar magnetic moment per particle as $\boldsymbol{\mathcal{M}} = N\ \mathfrak{m}$, resulting the susceptibility per particle with an analogous relation to (71b) $\mathfrak{m} = \overline{\chi}_{\mathrm{m}}\ \boldsymbol{\mathcal{H}}$.

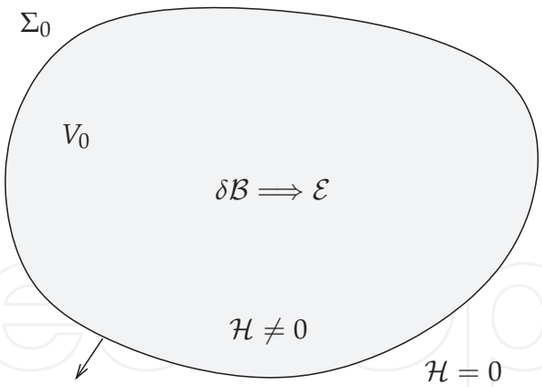


Fig. 4. The system chosen for the evaluation of the magnetic work.

In the strictly sense, the concrete expression of the magnetic susceptibility per particle is an empirical information of the thermal state equation type. On the basis of the type of specific susceptibility, the linear magnetic media are divided in two classes:

a. the *diamagnetic* media, which have negative specific susceptibilities, depending very little of the temperature and the pressure[20]

$$\overline{\chi}_{\mathrm{m}}(T, \mathfrak{P}) \approx \text{constant} \; < \; 0 \; ; \tag{74a}$$

b. the *paramagnetic* media, which have positive specific susceptibilities, with small values; in addition, there are two types of para-magnets:

– *ideal* para-magnets, having susceptibilities of the Curie type and independent of the pressure

$$\overline{\chi}_{\mathrm{m}}(T) = \frac{K}{T} \; , \tag{74b}$$

– *non-ideal* para-magnets, having susceptibilities of the Curie - Weiss type

$$\overline{\chi}_{\mathrm{m}}(T, \mathfrak{P}) = \frac{K}{T - \Theta(\mathfrak{P})} \; , \tag{74c}$$

where K is a constant depending on the paramagnet, called *Curie constant*), and $\Theta(\mathfrak{P})$ is a function of the pressure, having the dimension of a temperature.

Using the general relations of the magneto-statics, we can deduce the expression of the infinitesimal *magnetic work*, as the energy given to the thermo-isolated magnetic medium when the magnetic field varies:

$$\delta\mathcal{L}_{\mathrm{m}} = \int_{V_0} \mathrm{d}^3\mathbf{r} \; \boldsymbol{\mathcal{H}} \cdot \delta\boldsymbol{\mathcal{B}} \; , \tag{75}$$

under the condition that the system is located in the domain with the volume $V_0 = \text{constant}$, so that outside to this domain the magnetic field *is null*.

[20] In this case the magnetization is in the opposite direction to the magnetic field [see Eq. (71)].

Proof:

The magneto-static field from the magnetic medium is created by conduction electric currents; we consider the situation illustrated in Fig. 4, where inside the domain with the volume V_0 and fixed external surface Σ_0, there are magnetic media and electric conductors[21].

In contrast to the electric case, the magnetic work cannot be evaluated directly, since the magnetic forces are not conservative, and also because the variation of the magnetic field produces an electric field through the electro-magnetic induction, accordingly to the Maxwell – Faraday equation

$$\mathrm{rot}\,\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\frac{\partial\,\boldsymbol{\mathcal{B}}(\mathbf{r},t)}{\partial t}\ . \tag{76}$$

For this reasons, the magnetic work, as the variation of the energy corresponding to the magnetic field inside the considered domain, will be evaluated from the electric work on the currents (as sources of the magnetic field) produced by the electric field which was induced at the variation of the magnetic field.

We consider an infinitesimal variation of the magnetic field $\delta\boldsymbol{\mathcal{B}}(\mathbf{r})$ produced in the infinitesimal time interval δt; the induced electric field performs in the time interval δt, on the currents, the work

$$\delta\mathcal{L}_{\mathrm{el}} = \delta t \int_{V_0} \mathrm{d}^3\mathbf{r}\ \boldsymbol{j}\cdot\boldsymbol{\mathcal{E}}\ . \tag{77}$$

Using Eq. (68a) we transform the integrand in the following form:

$$\boldsymbol{j}\cdot\boldsymbol{\mathcal{E}} = \boldsymbol{\mathcal{E}}\cdot\mathrm{rot}\,\boldsymbol{\mathcal{H}} = \mathrm{div}\left(\boldsymbol{\mathcal{H}}\times\boldsymbol{\mathcal{E}}\right) + \boldsymbol{\mathcal{H}}\cdot\mathrm{rot}\,\boldsymbol{\mathcal{E}}\ ,$$

and it results for the electric work the expression

$$\delta\mathcal{L}_{\mathrm{el}} = \delta t \int_{V_0} \mathrm{d}^3\mathbf{r}\ \mathrm{div}\left(\boldsymbol{\mathcal{H}}\times\boldsymbol{\mathcal{E}}\right) + \delta t \int_{V_0} \mathrm{d}^3\mathbf{r}\ \boldsymbol{\mathcal{H}}\cdot\mathrm{rot}\ \boldsymbol{\mathcal{E}}\ .$$

We transform the first term in a surface integral, using the Gauss' theorem, and this integral vanishes, because the hypothesis that the magnetic field is null on the frontier of the domain

$$\int_{V_0} \mathrm{d}^3\mathbf{r}\ \mathrm{div}\left(\boldsymbol{\mathcal{H}}\times\boldsymbol{\mathcal{E}}\right) = \oint_{\Sigma_0} \mathrm{d}\mathcal{A}\ \boldsymbol{n}_0\cdot\left(\boldsymbol{\mathcal{H}}\times\boldsymbol{\mathcal{E}}\right) = 0\ ;$$

in the second term we use the Maxwell - Faraday equation (76) and we introduce the variation of the magnetic induction with the relation $(\partial\boldsymbol{\mathcal{B}}/\partial t)\,\delta t = \delta\boldsymbol{\mathcal{B}}$, so that it results

$$\delta t \int_{V_0} \mathrm{d}^3\mathbf{r}\ \boldsymbol{\mathcal{H}}\cdot\mathrm{rot}\,\boldsymbol{\mathcal{E}} = -\int_{V_0} \mathrm{d}^3\mathbf{r}\ \boldsymbol{\mathcal{H}}\cdot\frac{\partial\,\boldsymbol{\mathcal{B}}}{\partial t}\ \delta t = -\int_{V_0} \mathrm{d}^3\mathbf{r}\ \boldsymbol{\mathcal{H}}\cdot\delta\,\boldsymbol{\mathcal{B}}\ .$$

We observe that the electric work, determined previously, must be compensated by an additional work supplied from outside; therefore the magnetic work given to the system for an infinitesimal variation of the magnetic field is $\delta\mathcal{L}_{\mathrm{m}} = -\,\delta\mathcal{L}_{\mathrm{el}}$, and it results Eq. (75). □

We note that the expression (75) for the magnetic work, implies a domain for integration with a fixed volume (V_0), and in addition the magnetic field must vanish outside this domain.

[21] In order to have the general situation, we do not suppose particular properties for the magnetic medium inside the chosen domain, so that we consider the non-homogeneous case.

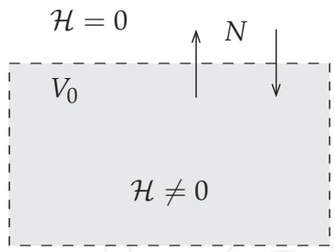


Fig. 5. The open system model.

By comparing the expressions of the magnetic work and electric work (10) we observe the formal similitude between these formula, and this leads to the following substitution rule to obtain the magnetic results from the electric ones:

$$\begin{cases} \boldsymbol{\mathcal{E}} \longrightarrow \boldsymbol{\mathcal{H}} \\ \boldsymbol{\mathcal{D}} \longrightarrow \boldsymbol{\mathcal{B}} \, . \end{cases}$$

However this similitude is only formal, since from the physical point of view, the correspondence between the electrical field vectors and the magnetic ones is $\boldsymbol{\mathcal{E}} \leftrightarrow \boldsymbol{\mathcal{B}}$ and $\boldsymbol{\mathcal{D}} \leftrightarrow \boldsymbol{\mathcal{H}}$.

In the following we shall present the consequences derived from the expression of the magnetic work (75) in an analog manner as the electric case; therefore we shall consider two methods to deal with the thermodynamics of the magnetic media, based on the expression of the magnetic work (and of the necessary conditions for the validity of this expression).

1. The open system method: we consider a fixed domain (having the volume $V =$ constant) which contains an magneto-static field inside, but outside to this domain the magneto-static field vanishes; the interesting system is the magnetic medium located inside the above specified domain, as an open thermodynamic system (the magnetic medium fills completely the domain, but there is a part of this medium, outside the domain at vanishing magneto-static field, because the frontier is totally permeable).

We note the following characteristic features of this situation:

– the thermodynamic system (the portion of the magnetic medium located in magneto-static field) has a fixed volume ($V = V_0 =$ constant), but it is an *open* thermodynamic system ($N \neq$ constant);

– the magneto-striction effect (this is the variation of the volume produced by the variation of the magnetic field) in this case leads to the variation of the particle number, or in another words, by variation of the particle density $\mathfrak{n} \equiv N/V_0 \neq$ constant;

– in the simplest case, when we consider a homogeneous magneto-static field[22], inside the domain with the volume V_0, infinitesimal magnetic work can be written in the form

$$\delta\mathcal{L}_{\mathrm{m}} = \mathcal{H} \, \delta(V_0 \mathcal{B}) \, , \tag{78}$$

[22] This situation is realized by considering a very long cylindrical solenoid, so that it is possible to consider approximately that the magnetic field vanishes outside the solenoid; the space inside and outside the solenoid is filled with a fluid paramagnet (or diamagnet). Accordingly to the previous definitions, the thermodynamic interesting system is only the part of the magnetic medium which is located inside the solenoid, and the frontier of this system is fictitious.

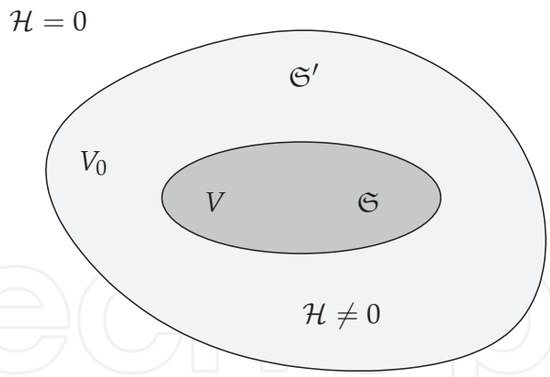


Fig. 6. The model for the closed system.

and this implies the following definition for the magnetic state parameters

$$\begin{cases} X_{\mathrm{m}} = V_0 \mathcal{B} \equiv \mathfrak{B} \, , \\ P_{\mathrm{m}} = \mathcal{H} \, ; \end{cases} \tag{79}$$

[in this case $V =$ constant, that is the volumic degree of freedom for this system is frozen; but we emphasize that the expression $\delta\!\!\!^{-}\mathcal{L}_{\mathrm{m}} = \mathcal{H} \ \delta(V\mathcal{B})$ when the volume of the system V can varies is *incorrect*].

2. The closed system method: we consider the magnetic medium surrounded by an non-magnetic medium, so that the magnetic medium does not occupy the whole space where is present the magnetic field.
In this case it is necessary to define the compound system corresponding to the domain with magnetic field

$$\mathfrak{S}^{(\tau)} = \mathfrak{S} \bigcup \mathfrak{S}' \, ,$$

where $\mathfrak{S}$ is the magnetic system with the volume V, and $\mathfrak{S}'$ is an auxiliary non-magnetic system having the volume $V' = V_0 - V$, as it is illustrated in Fig. 6.

We must remark that the auxiliary system (having negligible magnetic properties) is necessary in order to obtain the condition $\mathcal{H} \to 0$ towards the frontier of the domain which have the volume V_0, and also it produces a pressure on the magnetic medium; thus, the volume of the magnetic medium is not fixed and we can distinguish directly magneto-striction effects.

Because the magnetization $\boldsymbol{M}$ is non-vanishing only in the domain V, occupied by the system $\mathfrak{S}$, we transform the expression (75) using Eq. (70), in order to extract the magnetization work on the subsystem $\mathfrak{S}$

$$\begin{aligned} \delta\mathcal{L}_{\mathrm{m}}^{(\tau)} = \int_{V_0} \mathrm{d}^3\mathbf{r} \ \boldsymbol{\mathcal{H}} \cdot \delta \boldsymbol{\mathcal{B}} = \int_{V_0} \mathrm{d}^3\mathbf{r} \ \boldsymbol{\mathcal{H}} \cdot \overline{\mu}_0 \, \delta \boldsymbol{\mathcal{H}} + \int_{V_0} \mathrm{d}^3\mathbf{r} \ \boldsymbol{\mathcal{H}} \cdot \overline{\mu}_0 \, \delta \boldsymbol{M} \\ \equiv \delta W_{\mathcal{H}}^{(\tau)} + \delta\mathcal{L}_{\mathrm{M}} \, , \end{aligned}$$

where $\delta W_{\mathcal{H}}^{(\tau)}$ is the variation of the energy for the field inside the total volume V_0, and $\delta\!\!\!^{-}\mathcal{L}_{\mathrm{p}}$ is the work for magnetize the magnetic medium.

The first term allows the separation of the contributions corresponding the two subsystems when the energy of the magneto-static field changes:

$$\delta W_{\mathcal{H}}^{(\tau)} = \int_{V_0} \mathrm{d}^3\mathbf{r}\, \delta\Big(\frac{\overline{\mu}_0\mathcal{H}^2}{2}\Big) = \delta\left\{\int_V \mathrm{d}^3\mathbf{r}\, \frac{\overline{\mu}_0\mathcal{H}^2}{2}\right\} + \delta\left\{\int_{V'} \mathrm{d}^3\mathbf{r}\, \frac{\overline{\mu}_0\mathcal{H}^2}{2}\right\}$$
$$= \delta W_{\mathcal{H}} + \delta W'_{\mathcal{H}}\,.$$

The second term can be interpreted as magnetization work and it implies only the magnetic medium; in order to include the possible magneto-strictive effects, we shall write this term in the form

$$\eth\mathcal{L}_{\mathrm{M}} = \int_{V_0} \mathrm{d}^3\mathbf{r}\, \overline{\mu}_0\, \boldsymbol{\mathcal{H}}\cdot\delta\boldsymbol{M} = \int_{V_f} \mathrm{d}^3\mathbf{r}\, \overline{\mu}_0\, \boldsymbol{\mathcal{H}}\cdot\boldsymbol{M}_f - \int_{V_i} \mathrm{d}^3\mathbf{r}\, \overline{\mu}_0\, \boldsymbol{\mathcal{H}}\cdot\boldsymbol{M}_i$$
$$= \delta\left\{\int_V \mathrm{d}^3\mathbf{r}\, \overline{\mu}_0\, \boldsymbol{\mathcal{H}}\cdot\boldsymbol{M}\right\}\Big|_{\mathcal{H}=\text{const.}}$$

that is, the magnetization work implies the variation of the magnetization $\delta\boldsymbol{M}$ and also the variation of the volume δV of the magnetic medium, with the condition of constant magnetic field: $\boldsymbol{\mathcal{H}} = \text{constant}$ (during the process).

On the basis of the previous results we can separate the contribution of the magnetic work on the magnetic medium ($\eth\mathcal{L}_{\mathrm{m}}$) from those on the auxiliary non-magnetic system ($\delta W'_{\mathcal{H}}$):

$$\eth\mathcal{L}_{\mathrm{m}}^{(\tau)} = \eth\mathcal{L}_{\mathrm{m}} + \delta W'_{\mathcal{H}}\,, \tag{80a}$$
$$\delta\mathcal{L}_{\mathrm{m}} = \eth\mathcal{L}_{\mathrm{M}} + \delta W_{\mathcal{H}}\,. \tag{80b}$$

For the magnetic work on the magnetic medium (the subsystem $\mathfrak{S}$) we observe two interpretations in the case when $\mathfrak{S}$ is homogeneous[23]:

1. we take into account only the magnetization work $\eth\mathcal{L}_{\mathrm{M}}$ and we neglect systematically the energy of the magnetic field inside the magnetic medium $\delta W_{\mathcal{H}}$; then the magnetization work in the uniform magnetic field can be expressed with the dipolar magnetic moment

$$\eth\mathcal{L}_{\mathrm{M}} = \overline{\mu}_0\, \boldsymbol{\mathcal{H}}\cdot\delta\int_V \mathrm{d}^3\mathbf{r}\, \boldsymbol{M} = \overline{\mu}_0\, \boldsymbol{\mathcal{H}}\cdot\delta\boldsymbol{\mathcal{M}}\,; \tag{81}$$

2. we estimate the contributions of the both terms from Eq. (80b), taking into account the implications due to the homogeneity of the system:

$$\eth\mathcal{L}_{\mathrm{M}} = \overline{\mu}_0\, \mathcal{H}\, \mathrm{d}\mathcal{M} = \overline{\mu}_0\, \mathcal{H}\, \mathrm{d}(VM)\,,$$
$$\mathrm{d}W_{\mathcal{H}} = \mathrm{d}\Big(\frac{\overline{\mu}_0\mathcal{H}^2}{2}\, V\Big) = -\,\frac{\overline{\mu}_0\mathcal{H}^2}{2}\,\mathrm{d}V + \mathcal{H}\,\mathrm{d}(V\overline{\mu}_0\mathcal{H})\,.$$

   so that we obtain the total magnetic work performed by the magnetic system

$$\eth\mathcal{L}_{\mathrm{m}} = \eth\mathcal{L}_{\mathrm{M}} + \mathrm{d}W_{\mathcal{H}} = -\,\frac{\overline{\mu}_0\mathcal{H}^2}{2}\,\mathrm{d}V + \mathcal{H}\,\mathrm{d}(V\mathcal{B})\,, \tag{82}$$

[23] The condition of homogeneity implies an uniform magnetic field $\boldsymbol{\mathcal{H}}(\mathbf{r}) = \text{constant}$ in the subsystem $\mathfrak{S}$, and this property is realized only when the magnetic medium is an ellipsoid in an uniform external field.

and the last expression can be interpreted as an work performed on two degrees of freedom (volumic and magnetic).

We observe that for isotropic magnetic media the vectors $\boldsymbol{\mathcal{H}}$, $\boldsymbol{\mathcal{B}}$ and $\boldsymbol{M}$ are colinear; therefore, we shall omit the vector notation, for simplicity.

3.2 Thermodynamic potentials

We shall discuss, for simplicity, only the case when the magnetic system is homogeneous and of fluid type, being surrounded by a non-magnetic environment. Then, the fundamental thermodynamic differential form is:

$$\mathrm{d}\mathcal{U} = đ\,\mathcal{Q} + đ\,\mathcal{L}_V + đ\,\mathcal{L}_{\mathrm{m}} + đ\,\mathcal{L}_N \,. \tag{83}$$

For the thermodynamic study of the magnetic system there are many methods, depending the choice of the fundamental variables (corresponding to the choice of the concrete expression for the magnetic work $đ\mathcal{L}_{\mathrm{m}}$).

3.2.1 Pseudo-potentials method

We replace the expression (80b) – (81) for the magnetic work, and also the expression for the other forms of work and for the heat; then, the fundamental thermodynamic differential form has the explicit expression:

$$\mathrm{d}\mathcal{U} = T\,\mathrm{d}\mathcal{S} - \mathfrak{P}\,\mathrm{d}V + \overline{\mu}_0\mathcal{H}\,\mathrm{d}\mathcal{M} + \mathrm{d}W_{\mathcal{H}} + \mu\,\mathrm{d}N \,. \tag{84}$$

We observe that the preceding differential form contains a term $\mathrm{d}W_{\mathcal{H}}$ which is a exact total differential (from the mathematical point of view) and it represents the variation of the energy of the magnetic field located in the space occupied by the magnetic medium; we put this quantity in the left side of the above equality we obtain:

$$\mathrm{d}\widetilde{\mathcal{U}} = T\,\mathrm{d}\mathcal{S} - \mathfrak{P}\,\mathrm{d}V + \overline{\mu}_0\mathcal{H}\,\mathrm{d}\mathcal{M} + \mu\,\mathrm{d}N \,, \tag{85}$$

where $\widetilde{\mathcal{U}} \equiv \mathcal{U} - W_{\mathcal{H}}$ is the *internal pseudo-energy* of the magnetic medium[24].

We present some observations concerning the differential form (85):

• $\widetilde{\mathcal{U}}(\mathcal{S}, V, \mathcal{M}, N)$ is equivalent to the fundamental thermodynamic equation of the system, since it contains the whole thermodynamic information about the system (that is, its derivatives are the state equations); and on the other side, the pseudo-energy has no specified convexity properties (because it was obtained by subtracting a part of the energy from the total internal energy of the system);

• $\widetilde{\mathcal{U}}(\mathcal{S}, V, \mathcal{M}, N)$ is a homogeneous function of degree 1 (because it is obtained as a difference of two homogeneous functions of degree 1);

[24] Because we consider in the expression $W_{\mathcal{H}} = V\overline{\mu}_0\mathcal{H}^2/2$ the intensity of the magnetic field in the presence of the magnetic medium, this energy is due both to the vacuum and to the magnetic medium; thus, $\widetilde{\mathcal{U}}$ *is not the internal energy of the magnetic medium* (without the energy of the magnetic field in vacuum), but it is an artificial quantity.

• by considering the differential form (85) as similar to the fundamental thermodynamic differential form, it follows that the magnetic state parameters are

$$\begin{cases} \widetilde{X}_m = \mathcal{M} \ = \ M\,V \ , \\ \widetilde{P}_m = \overline{\mu}_0\,\mathcal{H} \ ; \end{cases}$$

• if we perform the Legendre transformations of the function $\widetilde{\mathcal{U}}(\mathcal{S}, V, \mathcal{M}, N)$, then we obtain objects of the thermodynamic potential types (that is, the derivatives of these quantities give the state equations of the magnetic medium); however, these objects are not true thermodynamic potentials (firstly since they have not the needed properties of convexity-concavity), so that they are usually called *thermodynamic pseudo-potentials*.

In the following we shall present briefly only the most used pseudo-potentials: the *magnetic pseudo-free energy* and the *magnetic Gibbs pseudo-potential*.

a.1. The magnetic pseudo-free energy is the Legendre transformation on the thermal and magnetic degrees of freedom[25]

$$\widetilde{\mathcal{F}}^* \equiv \widetilde{\mathcal{U}} - T\,\mathcal{S} - \overline{\mu}_0 \mathcal{H}\,\mathcal{M} \ , \tag{86}$$

having the differential form[26]:

$$\mathrm{d}\widetilde{\mathcal{F}}^* = -\,\mathcal{S}\ \mathrm{d}T - \mathfrak{P}\ \mathrm{d}V - \mathcal{M}\ \mathrm{d}(\overline{\mu}_0\mathcal{H}) + \mu\ \mathrm{d}N \ , \tag{87}$$

so that it allows the deduction of the state equations in the representation $(T, V, \mathcal{H}, N)$.
We consider the simplest case, when the magnetic medium behaves as a neutral fluid, having the free energy $\mathcal{F}_0(T, V, N)$, in the absence of the magnetic field and when the magnetic susceptibility is $\chi_m(T, V/N)$; then, we can consider as known the magnetic state equation (the expression of the dipolar magnetic moment):

$$\left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial\,\mathcal{H}}\right)_{T,V,N} = -\,\overline{\mu}_0\,\mathcal{M}(T, V, \mathcal{H}, N) = -\,\overline{\mu}_0\,\chi_m(T, V/N)\ \mathcal{H}\,V \ .$$

By partial integration, with respect to the magnetic field, and taking into account that at vanishing magnetic field the magnetic pseudo-free energy reduces to the proper free energy (the Helmholtz potential):

$$\widetilde{\mathcal{F}}^*\Big|_{\mathcal{H}=0} = \mathcal{U}_0 - T\,\mathcal{S}_0 = \mathcal{F}_0(T, V, N) \ ,$$

we obtain:

$$\widetilde{\mathcal{F}}^*(T, V, \mathcal{H}, N) = \mathcal{F}_0(T, V, N) + \mathcal{F}^*_{\mathrm{mag}}(T, V, \mathcal{H}, N) \ , \tag{88a}$$

$$\mathcal{F}^*_{\mathrm{mag}}(T, V, \mathcal{H}, N) \equiv -\,\frac{\overline{\mu}_0 \mathcal{H}^2}{2}\ \chi_m(T, V/N)\ V \ , \tag{88b}$$

[25] Because the absence of the correct properties of the convexity, we shall use only the classic definition of the Legendre transformation.

[26] In the strictly sense, $\widetilde{\mathcal{F}}^*$ is a simple Gibbs potential, so that the common terminology is criticizable.

that is, the magnetic pseudo-free energy of the magnetic medium is the sum of the free energy at null magnetic field and the magnetic part $\mathcal{F}^*_{\text{mag}}$.

The factorization property of the magnetic pseudo-free energy is transmitted to the non-magnetic state equations: the entropy, the pressure and the chemical potential (these are sums of the non-magnetic part, corresponding to null magnetic field, and the magnetic part):

$$\mathcal{S}(T,V,\mathcal{H},N) = -\left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial\,T}\right)_{V,\mathcal{H},N} = \mathcal{S}_0(T,V,N) + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,\chi_m}{\partial\,T}\right)_{V,N} V\,, \tag{89a}$$

$$\mathfrak{P}(T,V,\mathcal{H},N) = -\left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial\,V}\right)_{T,\mathcal{H},N} = \mathfrak{P}_0(T,V,N) + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,(\chi_m V)}{\partial\,V}\right)_{T,N}\,, \tag{89b}$$

$$\mu(T,V,\mathcal{H},N) = \left(\frac{\partial\,\widetilde{\mathcal{F}}^*}{\partial N}\right)_{T,V,\mathcal{H}} = \mu_0(T,V,N) - \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,\chi_m}{\partial N}\right)_{T,V} V\,. \tag{89c}$$

a.2. The magnetic Gibbs pseudo-potential is defined, analogously to the previous case, as the Legendre transformation on the thermal, volumic and magnetic degrees of freedom[27]

$$\widetilde{\mathcal{G}}^* \equiv \widetilde{\mathcal{U}} - T\,\mathcal{S} + \mathfrak{P}\,V - \overline{\mu}_0\mathcal{H}\,\mathcal{M}\,, \tag{90}$$

having the differential form

$$\mathrm{d}\widetilde{\mathcal{G}}^* = -\,\mathcal{S}\,\mathrm{d}T + V\,\mathrm{d}\mathfrak{P} - \mathcal{M}\,\mathrm{d}(\overline{\mu}_0\mathcal{H}) + \mu\,\mathrm{d}N\,, \tag{91}$$

so that it allows the deduction of the state equations in the representation $(T,\mathfrak{P},\mathcal{H},N)$.
We consider the simplest case (analogously in the former case), when the magnetic medium behaves as a neutral fluid, having the proper Gibbs potential (the free enthalpy) $\mathcal{G}_0(T,\mathfrak{P},N)$ in the absence of the magnetic field and when the magnetic susceptibility is $\overline{\chi}_m(T,\mathfrak{P})$; then, we can consider as known the magnetic state equation (the expression of the dipolar magnetic moment):

$$\left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,\mathcal{H}}\right)_{T,\mathfrak{P},N} = -\,\overline{\mu}_0\,\mathcal{M}(T,\mathfrak{P},\mathcal{H},N) = -\,\overline{\mu}_0\,\overline{\chi}_m(T,\mathfrak{P})\;\mathcal{H}\,N\,.$$

By partial integration, with respect to the magnetic field, and because at null magnetic field the magnetic Gibbs pseudo-potential reduces to the proper Gibbs potential:

$$\widetilde{\mathcal{G}}^*\Big|_{\mathcal{H}=0} = \mathcal{U}_0 - T\,\mathcal{S}_0 + \mathfrak{P}\,V_0 = \mathcal{G}_0(T,\mathfrak{P},N)\,,$$

we obtain:

$$\widetilde{\mathcal{G}}^*(T,\mathfrak{P},\mathcal{H},N) = \mathcal{G}_0(T,\mathfrak{P},N) + \mathcal{G}^*_{\text{mag}}(T,\mathfrak{P},\mathcal{H},N)\,, \tag{92a}$$

$$\mathcal{G}^*_{\text{mag}}(T,\mathfrak{P},\mathcal{H},N) \equiv -\,\frac{\overline{\mu}_0\mathcal{H}^2}{2}\,\overline{\chi}_m(T,\mathfrak{P})\;N\,, \tag{92b}$$

that is, the magnetic Gibbs pseudo-potential of the magnetic medium is the sum of the Gibbs potential at null magnetic field and the magnetic part $\mathcal{G}^*_{\text{mag}}$.

[27] Because the absence of the correct properties of the convexity, we shall use only the classic definition of the Legendre transformation (like in the preceding case).

The additivity (factorization) property of the magnetic Gibbs pseudo-potential is transmitted to the non-magnetic state equations: the entropy, the volume and the chemical potential (these are sums of the non-magnetic part, corresponding to vanishing magnetic field, and the magnetic part):

$$\mathcal{S}(T,\mathfrak{P},\mathcal{H},N) = -\left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,T}\right)_{\mathfrak{P},\mathcal{H},N} = \mathcal{S}_0(T,\mathfrak{P},N) + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,\overline{\chi}_m}{\partial\,T}\right)_{\mathfrak{P}} N\,, \tag{93a}$$

$$V(T,\mathfrak{P},\mathcal{H},N) = \left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,\mathfrak{P}}\right)_{T,\mathcal{H},N} = V_0(T,\mathfrak{P},N) - \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,\overline{\chi}_m}{\partial\,\mathfrak{P}}\right)_{T} N\,, \tag{93b}$$

$$\mu(T,\mathfrak{P},\mathcal{H},N) = \left(\frac{\partial\,\widetilde{\mathcal{G}}^*}{\partial\,N}\right)_{T,\mathfrak{P},\mathcal{H}} = \mu_0(T,\mathfrak{P}) - \frac{\overline{\mu}_0\mathcal{H}^2}{2}\,\overline{\chi}_m(T,\mathfrak{P})\,. \tag{93c}$$

We observe, in addition, that the magnetic Gibbs pseudo-potential is a maximal Legendre transformation, so that with the Euler relation we obtain

$$\widetilde{\mathcal{G}}^*(T,\mathfrak{P},\mathcal{H},N) = \mu(T,\mathfrak{P},\mathcal{H})\;N\,. \tag{94}$$

3.2.2 The method of modified potentials

We use the expression (82) for the magnetic work, without to extract terms of the total exact differential type from the internal energy of the magnetic medium; then, the differential form (83) can be written in the following explicit manner:

$$\begin{aligned}\mathrm{d}\,\mathcal{U} &= T\;\mathrm{d}\mathcal{S} - \left(\mathfrak{P} + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\right)\;\mathrm{d}V + \mathcal{H}\;\mathrm{d}(\mathcal{B}\,V) + \mu\;\mathrm{d}N \\ &= T\;\mathrm{d}\mathcal{S} - \pi\;\mathrm{d}V + \mathcal{H}\;\mathrm{d}\mathfrak{B} + \mu\;\mathrm{d}N\,.\end{aligned} \tag{95}$$

We observe that in this case the magnetic work has contributions on two thermodynamic degrees of freedom, so that we must redefine the magnetic and volumic state parameters:

$$X_V = V\,, \qquad P'_V = -\pi \equiv -\left(\mathfrak{P} + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\right)\,, \tag{96a}$$

$$X'_{\mathcal{H}} = \mathfrak{B} \equiv \mathcal{B}\;V\,, \qquad P_{\mathcal{H}} = \mathcal{H}\,. \tag{96b}$$

In this last case it appears the following peculiarities:

– V and $\mathfrak{B} \equiv \mathcal{B}\;V$ must be considered as independent variables,

– the effective pressure has an supplementary magnetic contribution $\overline{\mu}_0\,\mathcal{H}^2/2$.

Although the modified potential method implies the employment of some unusual state parameters, however it has the major advantage that $\mathcal{U}(\mathcal{S},V,\mathfrak{B},N)$ is the true fundamental energetic thermodynamic equation, and it is a *convex* and *homogeneous of degree* 1 function; thus, it is valid the Euler equation:

$$\mathcal{U} = T\,\mathcal{S} - \pi\,V + \mathcal{H}\,\mathfrak{B} + \mu\,N \tag{97}$$

and it is possible to define true thermodynamic potential with Legendre transformations. From the Euler relation (97) and passing to the common variables, it results

$$\mathcal{U} = T\,\mathcal{S} - \mathfrak{P}\,V + \overline{\mu}_0 \mathcal{H}\; M\,V + \frac{\overline{\mu}_0 \mathcal{H}^2}{2}\; V + \mu\, N\;,$$

so that it is ensured that $\widetilde{\mathcal{U}} \equiv \mathcal{U} - W_{\mathcal{H}}$ is a homogeneous function of degree 1 with respect to the variables $(\mathcal{S}, V, \mathcal{M}, N)$.

In order to compare the results of the method of modified potentials with those of the method of the pseudo-potentials we shall present only *the magnetic free energy* and *the magnetic Gibbs potential* as energetic thermodynamic potentials.

b.1. The magnetic free energy is the Legendre transformation on the thermal and magnetic degrees of freedom

$$\mathcal{F}^*(T, V, \mathcal{H}, N) \equiv \inf_{\mathcal{S},\mathfrak{B}} \left\{ \mathcal{U}(\mathcal{S}, V, \mathfrak{B}, N) - T\,\mathcal{S} - \mathcal{H}\,\mathfrak{B} \right\}\;, \tag{98}$$

and it has the following differential form[28]:

$$\mathrm{d}\mathcal{F}^* = -\,\mathcal{S}\;\mathrm{d}T - \pi\;\mathrm{d}V - \mathfrak{B}\;\mathrm{d}\mathcal{H} + \mu\;\mathrm{d}N\;. \tag{99}$$

We shall emphasize some important properties of the magnetic free energy $\mathcal{F}^*(T, V, \mathcal{H}, N)$.

1. When the magnetic field vanishes it becomes the proper free energy (Helmholtz potential)

$$\mathcal{F}^*(T, V, 0, N) = \mathcal{U}_0(T, V, N) - T\,\mathcal{S}_0(T, V, N) = \mathcal{F}_0(T, V, N)\;.$$

2. The magnetic state equation is

$$\left(\frac{\partial\,\mathcal{F}^*}{\partial\,\mathcal{H}}\right)_{T,V,N} = -\,\mathfrak{B}(T, V, \mathcal{H}, N) = -\,\overline{\mu}_0\,\left[\,1 + \chi_m(T, V/N)\,\right]\,\mathcal{H}\,V\;.$$

3. By partial integration with respect to the magnetic field and the use of the condition of null field, we obtain the general expression of the magnetic free energy (for a linear and homogeneous magnetic medium)

$$\mathcal{F}^*(T, V, \mathcal{H}, N) = \mathcal{F}_0(T, V, N) - \frac{\overline{\mu}_0 \mathcal{H}^2}{2}\,\left[\,1 + \chi_m(T, V/N)\,\right]\,V\;. \tag{100}$$

4. $\mathcal{F}^*(T, V, \mathcal{H}, N)$ is a function *concave* in respect to the variables T and $\mathcal{H}$; as a result we get the relation

$$\left(\frac{\partial^2\,\mathcal{F}^*}{\partial\,\mathcal{H}^2}\right)_{T,V,N} = -\,\overline{\mu}_0\,\left[\,1 + \chi_m\,\right]\,V < 0\;,$$

and it follows "the stability condition" $\chi_m > -1$. We observe that the thermodynamics allows the existence of negative values of the magnetic susceptibility, that is the diamagnetism; the minimum value $\chi_m = -1$ corresponds to the *perfect diamagnetism*.

[28] In the strictly sense, $\mathcal{F}^*$ is a simple Gibbs potential, so that the common terminology is criticizable.

5. The state equations, deduced from Eq. (100) are:

$$\mathcal{S}(T,V,\mathcal{H},N) = -\left(\frac{\partial\,\mathcal{F}^*}{\partial\,T}\right)_{V,\mathcal{H},N} = \mathcal{S}_0(T,V,N) + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,\chi_m}{\partial\,T}\right)_{V,N} V\,, \tag{101a}$$

$$\pi(T,V,\mathcal{H},N) = -\left(\frac{\partial\,\mathcal{F}^*}{\partial\,V}\right)_{T,\mathcal{H},N} = \mathfrak{P}_0(T,V,N) + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left[1+\left(\frac{\partial\,(\chi_m V)}{\partial\,V}\right)_{T,N}\right] \tag{101b}$$

$$\mu(T,V,\mathcal{H},N) = \left(\frac{\partial\,\mathcal{F}^*}{\partial\,N}\right)_{T,V,\mathcal{H}} = \mu_0(T,V,N) - \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\,\chi_m}{\partial N}\right)_{T,V} V\,. \tag{101c}$$

Because $\pi = \mathfrak{P} + \overline{\mu}_0\mathcal{H}^2/2$, it results that the state equations (101) are identical with Eqs. (89), and this shows that $\widetilde{\mathcal{F}}^*$ (the correspondent pseudo-potential to $\mathcal{F}^*$) gives correct state equations.

From Eq. (100) it result that the free energy (Helmholtz potential) is

$$\mathcal{F} = \mathcal{F}^* + \mathcal{H}\,\mathfrak{B} = \mathcal{F}_0 + \frac{\mathcal{H}\,\mathcal{B}}{2}\,V\,,$$

so that the electric part of the volumic density of free energy is:

$$\mathfrak{f}_{\rm mag} \equiv \frac{\mathcal{F}-\mathcal{F}_0}{V} = \frac{\mathcal{H}\,\mathcal{B}}{2}\,.$$

We emphasize that in many books the previous expression for the magnetic part of the free energy density is erroneously considered as magnetic part of the internal energy density.

Correctly, the internal energy has the expression

$$\mathcal{U} = \mathcal{F}^* + T\,\mathcal{S} + \mathcal{H}\,\mathfrak{B} = \left(\mathcal{F}_0 + T\,\mathcal{S}_0\right) + \left(\frac{\mathcal{H}\,\mathcal{B}}{2} + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\,T\,\frac{\partial\,\chi_m}{\partial\,T}\right) V\,,$$

so that the magnetic part of the volumic density of internal energy is

$$\mathfrak{u}_{\rm mag} = \frac{\mathcal{U}-\mathcal{U}_0}{V} = \frac{\mathcal{H}\,\mathcal{B}}{2} + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\,T\,\frac{\partial\,\chi_m}{\partial\,T} \neq \frac{\mathcal{H}\,\mathcal{B}}{2}\,.$$

b.2. The magnetic Gibbs potential is defined analogously, as the Legendre transformation on the thermal, volumic and magnetic degrees of freedom

$$\mathcal{G}^*(T,\pi,\mathcal{H},N) \equiv \inf_{\mathcal{S},V,\mathfrak{B}}\left\{\mathcal{U}(\mathcal{S},V,\mathfrak{B},N) - T\,\mathcal{S} + \pi\,V - \mathcal{H}\,\mathfrak{B}\right\}, \tag{102}$$

and it has the differential form

$$\mathrm{d}\mathcal{G}^* = -\,\mathcal{S}\,\mathrm{d}T + V\,\mathrm{d}\pi - \mathfrak{B}\,\mathrm{d}\mathcal{H} + \mu\,\mathrm{d}N\,. \tag{103}$$

According to the definition, $\mathcal{G}^*$ is a maximal Legendre transform, so that the Euler relation leads to:

$$\mathcal{G}^* = \mu\,N\,. \tag{104}$$

On the other side, by replacing the variables π and $\mathfrak{B}$, accordingly to the definitions (96), we obtain the *the magnetic Gibbs potential is equal to the magnetic Gibbs pseudo-potential*[29] (but they have different variables):

$$\mathcal{G}^*(T,\pi,\mathcal{H},N) = \widetilde{\mathcal{G}}^*(T,\mathfrak{P},\mathcal{H},N)$$
$$\pi = \mathfrak{P} + \frac{\overline{\mu}_0\mathcal{H}^2}{2} .$$

From the preceding properties it follows that the equations deduced from the potential $\mathcal{G}^*$ are identical with Eqs. (93); we observe, however, that it is more convenient to use the pseudo-potential $\widetilde{\mathcal{G}}^*$, because this has more natural variables than the corresponding potential $\mathcal{G}^*$.

3.2.3 Thermodynamic potentials for open systems

Previously we have shown that the magnetic work implies two methods for treating the magnetic media: either as a closed subsystem of a compound system (this situation was discussed above), or as an open system located in a fixed volume (and the magnetic field is different from zero only inside the domain with fixed volume).

If we use the second method, then the magnetic work has the expression (78) and the magnetic medium system has only 3 thermodynamic degrees of freedom: thermal, magnetic and chemical (the volumic degree of freedom is frozen); then, the fundamental differential form is

$$\mathrm{d}\,\mathcal{U} = T\,\mathrm{d}\mathcal{S} + \mathcal{H}\,\mathrm{d}(V_0\,\mathcal{B}) + \mu\,\mathrm{d}N\,. \tag{105}$$

Among the thermodynamic potentials, obtained by Legendre transformations of the energetic fundamental thermodynamic equation, denoted as $\mathcal{U}(\mathcal{S},V_0\,\mathcal{B},N) \equiv \mathcal{U}(\mathcal{S},\mathfrak{B},N;V_0)$, we shall present only the magnetic free energy:

$$\mathcal{F}^*(T,\mathcal{H},N;V_0) \equiv \inf_{\mathcal{S},\mathfrak{B}} \left\{ \mathcal{U}(\mathcal{S},\mathfrak{B},N;V_0) - T\,\mathcal{S} - \mathcal{H}\,\mathfrak{B} \right\} , \tag{106}$$

which has the following properties:

1. the differential form:
$$\mathrm{d}\mathcal{F}^* = -\,\mathcal{S}\,\mathrm{d}T - V_0\,\mathcal{B}\,\mathrm{d}\mathcal{H} + \mu\,\mathrm{d}N\,; \tag{107}$$
2. it reduces to the free energy (the Helmholtz potential) at vanishing magnetic field
$$\mathcal{F}^*(T,0,N;V_0) = \mathcal{U}_0(T,N;V_0) - T\,\mathcal{S}_0(T,N;V_0) = \mathcal{F}_0(T,N;V_0)\,;$$
3. by integrating the magnetic state equation, that is written in the form $V_0\,\mathcal{B}(T,\mathcal{H},N) = V_0\,[1+\chi_m]\,\overline{\mu}_0\mathcal{H}$, we obtain
$$\mathcal{F}^*(T,\mathcal{H},N;V_0) = \mathcal{F}_0(T,N;V_0) - \,V_0\,\frac{\overline{\mu}_0\mathcal{H}^2}{2}\,\left[1+\chi_m(T,V/N)\right] . \tag{108}$$

We note that the results are equivalent to those obtained by the previous method, but the situation is simpler because the volumic degree of freedom is frozen.

[29] The equality $\mathcal{G}^* = \widetilde{\mathcal{G}}^*$ (as quantities, but not as functions) can be obtained directly by comparing the consequences of the Euler equation (94) and (104).

3.3 Thermodynamic coefficients and processes

3.3.1 Definitions for the principal thermodynamic coefficients

Because the magnetic media has 4 thermodynamic degrees of freedom (in the simplest case, when it is fluid), there are a great number of simple thermodynamic coefficients; taking into account this complexity, we shall present only the common coefficients, corresponding to closed magnetic media systems (N = constant).

a.1. The sensible specific heats are defined for non-isothermal processes "φ":

$$c_{\varphi} = \frac{1}{N}\, T \left(\frac{\partial \mathcal{S}}{\partial T}\right)_{\varphi} = T \left(\frac{\partial s}{\partial T}\right)_{\varphi} . \tag{109}$$

In the case, when the process φ is simple, we obtain the following specific isobaric/isochoric and iso-magnetization/iso-field heats: $c_{V,\mathfrak{m}}$, $c_{V,\mathcal{H}}$, $c_{P,\mathfrak{m}}$, $c_{P,\mathcal{H}}$.

a.2. The latent specific heats are defined for isothermal processes "ψ":

$$\lambda_{\psi}^{(a)} = \frac{1}{N}\, T \left(\frac{\partial \mathcal{S}}{\partial a}\right)_{\psi} = T \left(\frac{\partial s}{\partial a}\right)_{\psi} . \tag{110}$$

The most important cases (for "ψ" and a) are the isothermal-isobaric process with $a = \mathcal{H}$ when we have *the isobaric magnetic-caloric coefficient* λ and the conjugated isothermal-isofield process with $a = \mathfrak{P}$, when we have *the iso-field piezo-caloric coefficient* $\lambda_{\mathcal{H}}^{(P)}$:

$$\lambda = T \left(\frac{\partial s}{\partial \mathcal{H}}\right)_{T,\mathfrak{P}} , \qquad \lambda_{\mathcal{H}}^{(P)} = T \left(\frac{\partial s}{\partial \mathfrak{P}}\right)_{T,\mathcal{H}} . \tag{111}$$

a.3. The thermodynamic susceptibilities are of two types: for the volumic degree of freedom (in this case they are called *compressibility coefficients*) and for the magnetic degree of freedom (these are called *magnetic susceptibilities*):

$$\varkappa_{\varphi} = \frac{-1}{V}\left(\frac{\partial V}{\partial \mathfrak{P}}\right)_{\varphi} = \frac{-1}{v}\left(\frac{\partial v}{\partial \mathfrak{P}}\right)_{\varphi} , \tag{112}$$

$$\chi_{\psi}^{(\mathrm{m})} = \frac{1}{V}\left(\frac{\partial \mathcal{M}}{\partial\,(\overline{\mu}_0 \mathcal{H})}\right)_{\psi} = \frac{1}{\overline{\mu}_0}\left(\frac{\partial M}{\partial \mathcal{H}}\right)_{\psi} . \tag{113}$$

In the simple cases "φ" is an isothermal/adiabatic and iso-magnetization/iso-field processes; it results the following simple compressibility coefficients: $\varkappa_{T,M}$, $\varkappa_{T,\mathcal{H}}$, $\varkappa_{s,M}$ and $\varkappa_{s,\mathcal{H}}$. Analogously "$\psi$" as simple process can be isothermal/adiabatic and isobaric/isochoric, resulting the following simple magnetic susceptibilities: $\chi_{T,v}^{(\mathrm{m})}$, $\chi_{T,\mathfrak{P}}^{(\mathrm{m})}$, $\chi_{s,v}^{(\mathrm{m})}$ and $\chi_{s,\mathfrak{P}}^{(\mathrm{m})}$.

From Eq. (71b) we observe that the isothermal magnetic susceptibility is proportional to the susceptibility used in the electrodynamics:

$$\chi_{T,v}^{(\mathrm{m})} = \left(\frac{\partial M}{\partial \mathcal{H}}\right)_{T,v} = \frac{1}{\overline{\mu}_0}\, \chi_m(T,v) .$$

a.4. The thermal coefficients are of two types, corresponding to the two non-thermal and non-chemical degrees of freedom (the volumic and the magnetic ones). If we consider only thermal coefficients for extensive parameters, then we can define the following types of simple coefficients:

- the *isobaric thermal expansion coefficients* (also iso-magnetization/iso-field)

$$\alpha_y = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathfrak{P},y,N} = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_{\mathfrak{P},y} , \tag{114}$$

  where the index y is $\mathcal{M}$ or $\mathcal{H}$;

- the *pyro-magnetic coefficients* (also isochoric/isobaric)

$$\pi_a = \frac{1}{N}\left(\frac{\partial \mathcal{M}}{\partial T}\right)_{\mathcal{H},a,N} = \left(\frac{\partial \mathfrak{m}}{\partial T}\right)_{\mathcal{H},a} , \tag{115}$$

  where the index a is V (for the volume V) or P (for the pressure $\mathfrak{P}$).

a.5. The mixed coefficients express correlations between the volumic and the magnetic degrees of freedom; we mention the following simple coefficients:

- the *magnetic-strictive coefficient*

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial \mathcal{H}}\right)_{T,\mathfrak{P},N} = \frac{1}{v}\left(\frac{\partial v}{\partial \mathcal{H}}\right)_{T,\mathfrak{P}} ; \tag{116}$$

- the *piezo-magnetic coefficient*

$$\varrho = \frac{1}{N}\left(\frac{\partial \mathcal{M}}{\partial \mathfrak{P}}\right)_{T,\mathcal{H},N} = \left(\frac{\partial \mathfrak{m}}{\partial \mathfrak{P}}\right)_{T,\mathcal{H}} . \tag{117}$$

3.3.2 Relations between simple coefficients

Because the great number of thermodynamic coefficients, corresponding to the magnetic media, we must select among all possible relations between the simple coefficients; therefore, we shall present only the most important relations: the symmetry relations (consequences of some Maxwell relations) and special relations (of the type Reech or Mayer).

In order to emphasize symmetry relations expressed by the temperature, the pressure and the magnetic field intensity $(T, \mathfrak{P}, \mathcal{H})$, as variables, for an closed system (N = constant), we use the differential form of the reduced Gibbs pseudo-potential $\widetilde{g}^*(T, \mathfrak{P}, \mathcal{H})$, which is obtained with the general reduction formulae from Eqs. (90) – (91):

$$\mathrm{d}\widetilde{g}^* = -s\,\mathrm{d}T + v\,\mathrm{d}\mathfrak{P} - \mathfrak{m}\,\mathrm{d}(\overline{\mu}_0\mathcal{H}) . \tag{118}$$

From the above differential form it results 3 Maxwell relations, which can be expressed by simple coefficients, resulting symmetry relations between these coefficients:

$$\left(\frac{\partial s}{\partial \mathfrak{P}}\right)_{T,\mathcal{H}} = -\left(\frac{\partial v}{\partial T}\right)_{\mathfrak{P},\mathcal{H}} \qquad \Longrightarrow \qquad \lambda_{\mathcal{H}}^{(P)} = -T\,v\,\alpha_{\mathcal{H}} , \tag{119a}$$

(the relation between the iso-field piezo-caloric coefficient and the isobaric-isofield thermal expansion coefficient);

$$\left(\frac{\partial s}{\partial(\overline{\mu}_0\mathcal{H})}\right)_{T,\mathfrak{P}} = \left(\frac{\partial \mathfrak{m}}{\partial T}\right)_{\mathfrak{P},\mathcal{H}} \qquad \Longrightarrow \qquad \lambda = \overline{\mu}_0\,T\,\pi_P , \tag{119b}$$

(the relation between the isobaric magneto-caloric coefficient and the isobaric pyro-magnetic coefficient);

$$\left(\frac{\partial v}{\partial\left(\overline{\mu}_0\mathcal{H}\right)}\right)_{T,\mathfrak{P}} = -\left(\frac{\partial \mathfrak{m}}{\partial \mathfrak{P}}\right)_{T,\mathcal{H}} \qquad \Longrightarrow \qquad \frac{v}{\overline{\mu}_0}\,\gamma = -\varrho\,. \tag{119c}$$

(the relation between the magnetic-strictive coefficient and the piezo-magnetic coefficient).

Relations of Reech type can be obtained from the general relation (see [16] Eq. (3.25)), resulting the equality between the ratios of the isobaric specific heats, of the compressibility coefficients, and of the magnetic susceptibilities (isothermal, and respectively adiabatic):

$$\frac{c_{P,\mathfrak{m}}}{c_{P,\mathcal{H}}} = \frac{\varkappa_{s,\mathcal{H}}}{\varkappa_{T,\mathcal{H}}} = \frac{\chi^{(\mathrm{m})}_{s,\mathfrak{P}}}{\chi^{(\mathrm{m})}_{T,\mathfrak{P}}}\,. \tag{120}$$

Analogously, from the general Mayer relation for the specific heats (see [16] Eq. (3.28)) we obtain in this case

$$c_{P,\mathcal{H}} - c_{P,\mathfrak{m}} = T\,v\,\frac{\alpha^2_{\mathcal{H}}}{\chi^{(\mathrm{m})}_{T,\mathfrak{P}}}\,. \tag{121}$$

Similar relations with Eqs. (120) – (121) can be obtained for the coefficients associated to another sets of simple processes (*e.g.* isochoric, iso-magnetization processes).

3.3.3 The factorization of some simple coefficients

An important characteristics of some thermodynamic coefficients is *the factorization property*: the expression of the considered coefficient is the sum of the part corresponding to the absence of the magnetic field (like for the neutral fluid) and the "magnetic part", and this result comes from the factorization of the state equations.

We shall present the factorization of some coefficients using the variables of the magnetic Gibbs representation[30] $(T, \mathfrak{P}, \mathcal{H}, N)$; in this case the state equations are Eqs. (93).

The entropy is given by Eq. (93a), and here we write it without the variables, for simplicity and for using later the convenient variables

$$\mathcal{S} = \mathcal{S}_0 + \mathcal{S}_{\mathrm{mag}}\,, \tag{122}$$

where $\mathcal{S}_0$ is the entropy of the magnetic medium as a neutral fluid, in the absence of the magnetic field, and $\mathcal{S}_{\mathrm{mag}}$ is the magnetic part of the entropy:

$$\mathcal{S}_{\mathrm{mag}} = \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial \overline{\chi}_m}{\partial T}\right)_{\mathfrak{P}} N = \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial \chi_m}{\partial T}\right)_{v} V\,. \tag{123}$$

Accordingly to the general definition (109), we obtain a factorization of the specific heats:

$$c_\varphi = c^{(0)}_\varphi + c^{(\mathrm{mag})}_\varphi\,, \tag{124}$$

[30] We remark that some coefficients need the use of other thermodynamic representations.

where $c_{\varphi}^{(0)} = T(\partial s^{(0)}/\partial T)_{\varphi}$ is the specific heat of the magnetic medium in the absence of the magnetic field, and $c_{\varphi}^{(\mathrm{mag})} = T(\partial s^{(\mathrm{mag})}/\partial T)_{\varphi}$ is the magnetic part of the specific heat.

For the isobaric processes there are the specific heat at constant magnetic field or at constant magnetization. From Eq. (123) it results

$$c_{P,\mathcal{H}}^{(\mathrm{mag})} = T\left(\frac{\partial \overline{\chi}_m}{\partial T}\right)_{\mathfrak{P}} \frac{\overline{\mu}_0 \mathcal{H}^2}{2} \,, \tag{125}$$

To obtain $c_{P,\mathfrak{m}}^{(\mathrm{mag})}$ we express the magnetic entropy $\mathcal{S}_{\mathrm{mag}}$ in terms of the dipolar magnetic moment (instead the magnetic field), using Eq. (71b):

$$\mathcal{S}_{\mathrm{mag}} = \frac{\mathfrak{m}^2}{2\,\overline{\mu}_0\,\overline{\chi}_m^2}\left(\frac{\partial \overline{\chi}_m}{\partial T}\right)_{\mathfrak{P}} N = \frac{-\mathfrak{m}^2}{2\,\overline{\mu}_0}\left(\frac{\partial\,(\overline{\chi}_m)^{-1}}{\partial T}\right)_{\mathfrak{P}} N \,;$$

then it results for the magnetic part of the isobaric-isomagnetization specific heat the expression:

$$c_{P,\mathfrak{m}}^{(\mathrm{mag})} = \frac{-\mathfrak{m}^2}{2\,\overline{\mu}_0}\; T\left(\frac{\partial^2\,(\overline{\chi}_m)^{-1}}{\partial T^2}\right)_{\mathfrak{P}} \,; \tag{126}$$

We observe that for an ideal paramagnet $(\overline{\chi}_m)^{-1} \sim T$, so that we obtain $c_{P,\mathfrak{m}}^{(\mathrm{mag})} = 0$, that is $c_{P,\mathfrak{m}} = c_P^{(0)}$ (the iso-magnetization specific heat is independent of the magnetic field)[31].
It is interesting to emphasize that for the ideal para magnets the internal energy has also particular properties. The magnetic part of the volumic density of internal energy for an arbitrary magnetic medium has the expression

$$\mathfrak{u}^{(\mathrm{mag})} = \frac{\overline{\mu}_0 \mathcal{H}^2}{2}\left(1 + \chi_m + T\,\frac{\partial \chi_m}{\partial T}\right) \,.$$

For an ideal paramagnet we obtain that this energy density is equal to the energy density of the magnetic field $\mathfrak{u}^{(\mathrm{mag})} = \overline{\mu}_0 \mathcal{H}^2/2 = w_{\mathrm{mag}}$, that is the whole magnetic energy is given only by the magnetic field, without any contribution from the processes of the magnetization. The behavior of the iso-magnetization specific heats and of the internal energy are similar to the neutral fluids which satisfy the Clapeyron - Mendeleev equations, so that it is justified the terminology "ideal" for the para-magnets which have Curie susceptibility.

We observe, in addition, that the diamagnetic systems, having a constant magnetic susceptibility (approximatively), have null magnetic entropy $\mathcal{S}_{\mathrm{mag}}$, accordingly to Eq. (123); therefore, the diamagnetic systems have caloric properties independent of the magnetic field (or of the magnetization).

In contrast with the specific heats, the isobaric magneto-caloric coefficient has contribution only from the magnetic part of the entropy:

$$\lambda = \overline{\mu}_0\; \mathcal{H}\; T\left(\frac{\partial \overline{\chi}_m}{\partial T}\right)_{\mathfrak{P}} \,.$$

[31] For the corresponding isochoric specific heat we obtain the same result $c_{V,\mathfrak{P}}^{(\mathrm{mag})} = c_V^{(0)}$.

The volume is given by Eq. (93b), that is it can be expressed in the form:

$$V = V_0 + V_{\text{mag}} \ ,$$

where V is the volume of the magnetic medium as neutral fluid, in the absence of the magnetic field, and V_{mag} is the magnetic part of the volume:

$$V_{\text{mag}} = -\frac{\overline{\mu}_0 \mathcal{H}^2}{2} \left(\frac{\partial \overline{\chi}_m}{\partial \mathfrak{P}} \right)_T N \ . \tag{127}$$

Accordingly to the general definitions (112) and respectively (114), the isothermal compressibility coefficients $\varkappa_{T,\mathcal{H}}$ and the isobaric thermal expansion coefficient $\alpha_{\mathcal{H}}$ (both of them at constant field) factorize in non-magnetic part (corresponding to null magnetic field, when the magnetic medium behaves as a neutral fluid) and magnetic part:

$$\varkappa_{T,\mathcal{H}} = \varkappa_T^{(0)} + \varkappa_{T,\mathcal{H}}^{(\text{mag})} \ , \tag{128a}$$

$$\alpha_{\mathcal{H}} = \alpha^{(0)} + \alpha_{\mathcal{H}}^{(\text{mag})} \ , \tag{128b}$$

where[32]

$$\varkappa_{T,\mathcal{H}}^{(\text{mag})} = \frac{\overline{\mu}_0 \, \mathcal{H}^2}{2 \, v_0} \left(\frac{\partial^2 \overline{\chi}_m}{\partial \mathfrak{P}^2} \right)_T \ , \tag{129a}$$

$$\alpha_{\mathcal{H}}^{(\text{mag})} = -\frac{\overline{\mu}_0 \, \mathcal{H}^2}{2 \, v_0} \, \frac{\partial^2 \overline{\chi}_m}{\partial \, T \, \partial \mathfrak{P}} \ . \tag{129b}$$

In contrast with the previous coefficients, the magneto-strictive coefficient is obtained only from the magnetic part of the volumic state equation[33]

$$\gamma \approx -\frac{\overline{\mu}_0 \mathcal{H}}{v_0} \left(\frac{\partial \overline{\chi}_m}{\partial \mathfrak{P}} \right)_T \ . \tag{130}$$

3.3.4 Thermodynamic process

Using the previous results we shall present the most significant thermodynamic processes for the magnetic media as closed system (we shall choose the variable set T, $\mathfrak{P}$, $\mathcal{H}$, $N =$ constant).

d.1. The isothermal magnetization: we consider that initially the magnetic medium in null magnetic field $(T, \mathfrak{P}, \mathcal{H}_i = 0, N)$ and we apply the magnetic field with an isothermal-isobaric process, so that the final state has the parameters: $(T, \mathfrak{P}, \mathcal{H}_f = \mathcal{H}, N)$.

Using Eq. (93a) for the entropy, the heat transfered in this process is

$$\begin{aligned} \mathcal{Q}_{if} = T \, \Delta \, \mathcal{S}_{if} &= T \, \{ \, \mathcal{S}(T, \mathfrak{P}, \mathcal{H}, N) - \mathcal{S}(T, \mathfrak{P}, 0, N) \, \} \\ &= \frac{\overline{\mu}_0 \, \mathcal{H}^2}{2} \, T \left(\frac{\partial \overline{\chi}_m}{\partial \, T} \right)_{\mathfrak{P}} N \ . \end{aligned} \tag{131}$$

[32] In fact, the factorization is obtained only if we consider small magnetic effects, so that we could approximate $v \approx v_0$ at the denominators.

[33] We consider that the magneto-strictive effects are small, so that we can use the approximation $v \approx v_0$, at the denominator.

Since $\overline{\chi}_m(T,\mathfrak{P})$ is in general a decreasing function with respect to the temperature, it results that in the magnetization process the magnetic medium yields heat: $\mathcal{Q}_{if} < 0$.

d.2. The adiabatic-isobaric demagnetization: we consider that initially the magnetic medium is in the presence of the magnetic field $\mathcal{H}$ and it has the temperature T_i ; then, by a quasi-static adiabatic-isobaric process the magnetic field is decreasing to vanishing value.

Because the equation of this process is $\mathcal{S}(T,\mathfrak{P},\mathcal{H},N) = \text{constant}$, with the supplementary conditions $\mathfrak{P} = \text{constant}$ and $N = \text{constant}$, then by using Eq. (93a), we obtain the equation of the temperature:

$$\mathcal{S}(T_i,\mathfrak{P},\mathcal{H},N) = \mathcal{S}(T_f,\mathfrak{P},0,N) \ ;$$

that is, after simple algebraical operations, we get:

$$s^0(T_i,\mathfrak{P}) + \frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\overline{\chi}_m}{\partial T}\right)_{\mathfrak{P}} = s^0(T_f,\mathfrak{P}) \ . \tag{132}$$

Because the magnetic susceptibility is in general an decreasing function in respect to the temperature $(\partial\,\overline{\chi}_m/\,\partial T)_{\mathfrak{P}} < 0$ and the entropy $s^0(T,\mathfrak{P})$ is an increasing function of temperature, it results $s_i < s_f$, that is the paramagnet gets cool during the adiabatic demagnetization: $T_f < T_i$.

d.3. The magneto-strictive and piezo-magnetic effects

The *magneto-strictive effect* means the variation of the volume (of the magnetic medium) due to the variation of the magnetic field, in conditions isothermal-isobaric (also the magnetic medium is a closed system)[34]; and the magneto-strictive coefficient is defined by Eq. (116).

The *piezo-magnetic effect* means the variation of the dipolar magnetic moment (of the magnetic medium), due to the variation of the pressure, in conditions isothermal and at constant magnetic field (also the magnetic medium is a closed system)[35] and the piezo-magnetic effect coefficient is defined by Eq. (117).

Between the coefficients of the two effects it is the symmetry relation (53), and the corresponding expressions can be put in explicit forms using the magnetic susceptibility:

$$\gamma = -\frac{1}{v}\,\varrho = \frac{-\overline{\mu}_0\mathcal{H}}{v}\left(\frac{\partial\overline{\chi}_m}{\partial\mathfrak{P}}\right)_T \ . \tag{133}$$

We observe that the necessary condition to have an magneto-strictive effect and an piezo-magnetic effect is that $\overline{\chi}_m$ depends on the pressure; accordingly to Eqs. (76), it results that only the non-ideal para-magnets can have these effects.

Using the volumic equation of state (93b), we can evaluate the global magneto strictive effect, that is the variation of the volume (of the paramagnet) at the isothermal-isobaric magnetization:

$$\Delta\, V_{if}(\mathcal{H}) = V(T,\mathfrak{P},\mathcal{H},N) - V(T,\mathfrak{P},0,N) = -\frac{\overline{\mu}_0\mathcal{H}^2}{2}\left(\frac{\partial\overline{\chi}_m}{\partial\mathfrak{P}}\right)_T N \ . \tag{134}$$

From the previous expression it results that when the magnetic susceptibility is a decreasing function of the pressure $(\partial\overline{\chi}_m/\partial\mathfrak{P})_T < 0$, then it follows a contraction (a reduction of the volume) at the magnetization of the diamagnet.

[34] In other words, the magneto-strictive effect can be considered as the volumic response of the magnetic medium to an magnetic perturbation.

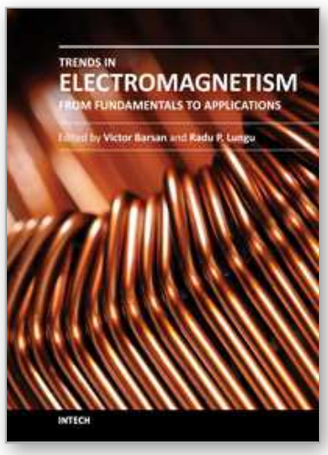
[35] We observe that the piezo-magnetic effect can be considered as the magnetic response of the magnetic medium to a volumic perturbation, being conjugated to the magneto-strictive effect.

4. Acknowledgment

The financial support of the JINR Dubna - IFIN-HH Magurele-Bucharest project no. 01-3-1072-2009/2013 is kindly acknowledged.

5. References

A. Sommerfeld, *Thermodynamics and Statistical Mechanics*, (Academic Press, New York 1956).
M. Planck, *Treatise on Thermodynamics*, (Dover Publisher, New York, 1945).
E. A. Guggenheim, *Thermodynamics – An Advanced Treatment for Chemists and Physicists*, (North Holland, Amsterdam, 1967).
A. H. Wilson, *Thermodynamics and Statistical Mechanics*, (Cambridge Univ. Press, 1957).
A. B. Pippard, *Elements of Classical Thermodynamics*, (Cambridge Univ. Press, 1966).
D. ter Haar, H. Wegeland, *Elements of Thermodynamics*, (Addison-Wesley, Reading Mass. 1966).
C. J. Adkins, *Equilibrium Thermodynamics*, (Cambridge Univ. Press, 1983).
G. N. Hatsopoulos, J. H. Keenan, *Principles of General Thermodynamics*, (John Wiley & Sons, New York, 1965).
V. S. Helrich, *Modern Thermodynamics and Statistical Mechanics*, (Springer-Verlag, Berlin, 2009).
F. Schwabl, *Statistical Mechanics*, (Springer-Verlag, Berlin, 2006).
W. Greiner, W. Neise, H. Stöcker, *Thermodynamics and Statistical Mechanics*, (Springer, New York, 2095).
L. D. Landau, E. M. Lifshitz, *Statistical Physics, Part 1* (3rd ed.), (Pergamon Press, Oxford, 1980).
H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (2nd ed.), (John Wiley & Sons, New York, 1985).
L. Tisza, *Generalized Thermodynamics*, (The MIT Press, Cambridge Mass. 1966).
E. H. Lieb, J. Yngvason, *The Physics and Mathematics of the Second Law of Thermodynamics*, *Physics Reports* 310, 1-96 (1999).
R. P. Lungu, *Thermodynamics*, `http://www.unescochair-hhf.ro/index.php?page=training`.
J. D. Jackson, *Classical Electrodynamics* (3rd ed.), (John Wiley & Sons, New York, 1999).
W. Greiner, *Classical Electrodynamics*, (Springer-Verlag, Berlin, 1998).
W. H. K. Panofsky, M. Phillips, *Classical Electrodynamics*, (Addison-Wesley, Reading Mass. 1962).
L. D. Landau, E. M. Lifshitz, *Electrodynamics of Continuous Media*, (Pergamon Press, Oxford, 1984).



Trends in Electromagnetism - From Fundamentals to Applications
Edited by Dr. Victor Barsan

ISBN 978-953-51-0267-0
Hard cover, 290 pages
Publisher InTech
Published online 23, March, 2012
Published in print edition March, 2012

Among the branches of classical physics, electromagnetism is the domain which experiences the most spectacular development, both in its fundamental and practical aspects. The quantum corrections which generate non-linear terms of the standard Maxwell equations, their specific form in curved spaces, whose predictions can be confronted with the cosmic polarization rotation, or the topological model of electromagnetism, constructed with electromagnetic knots, are significant examples of recent theoretical developments. The similarities of the Sturm-Liouville problems in electromagnetism and quantum mechanics make possible deep analogies between the wave propagation in waveguides, ballistic electron movement in mesoscopic conductors and light propagation on optical fibers, facilitating a better understanding of these topics and fostering the transfer of techniques and results from one domain to another. Industrial applications, like magnetic refrigeration at room temperature or use of metamaterials for antenna couplers and covers, are of utmost practical interest. So, this book offers an interesting and useful reading for a broad category of specialists.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

Radu Paul Lungu (2012). Thermodynamics of Electric and Magnetic Systems, Trends in Electromagnetism - From Fundamentals to Applications, Dr. Victor Barsan (Ed.), ISBN: 978-953-51-0267-0, InTech, Available from: http://www.intechopen.com/books/trends-in-electromagnetism-from-fundamentals-to-applications/thermodynamics-of-electric-and-magnetic-systems

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the Creative Commons Attribution 3.0 License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen