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ON IRREVERSIBLE PHENOMENA IN FLUID MIXTURES

by
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ON POSSIBLE INTERACTIONS AMONG DIELECTRIC RELAXATION, MAGNETIC RELAXATION, HEAT CONDUCTION, ELECTRIC CONDUCTION, DIFFUSION PHENOMENA, VISCOUS FLOW AND CHEMICAL REACTIONS IN FLUID MIXTURES (*)

by

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Synopsis

A thermodynamic theory for dielectric and magnetic relaxation phenomena in polarizable and magnetizable fluid mixtures consisting of \( n \) chemical components among which \( r \) chemical reactions are possible is developed. Using the general methods of non-equilibrium thermodynamics a polar and an axial vector field are introduced as internal thermodynamic degrees of freedom in the entropy in order to investigate the possibility of cross effects among dielectric and magnetic relaxation and heat conduction, electric conduction, diffusion flow, viscous flow and chemical reactions. The phenomenological equations for these irreversible processes are formulated. The symmetry relations and the Onsager-Casimir reciprocity relations for the phenomenological coefficients are derived. The Curie principle is stated and among other things it is seen that, if the fluid mixture under consideration is isotropic with respect to all rotations and to reflections of the frame of axes (isotropy under all orthogonal transformations), there are no contributions in the expression for the entropy production due to the cross effects among magnetic relaxation phenomena and the other irreversible phenomena.

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Sommario

Utilizzando i principi ed i metodi generali della termodinamica dei processi irreversibili si sviluppa una teoria termodinamica per i fenomeni di rilassamento dielettrico e magnetico che avvengono in miscele fluide polarizzabili e magnetizzabili, costituite da \( n \) componenti chimici fra cui sono possibili \( r \) reazioni chimiche. Introducendo un campo vettoriale polare ed uno assiale, come gradi interni termodinamici di libertà, nell’espressione della entropia si studia la possibilità di interazione fra fenomeni di rilassamento dielettrico e magnetico e conduzione del calore, conduzione elettrica, flusso diffusivo della materia, flusso viscoso e reazioni chimiche. Si formulano le equazioni fenomenologiche per questi fenomeni irreversibili. Si derivano le relazioni di simmetria e le relazioni di reciprocità di Onsager-Casimir per i coefficienti fenomenologici. Si formula il principio di Curie e tra l’altro si osserva che, se il sistema fluido considerato presenta proprietà di simmetria invarianti rispetto a tutte le rotazioni e le riflessioni del sistema di riferimento (isotropia sotto tutte le trasformazioni ortogonali), nell’espressione della produzione di entropia non sono presenti contributi dovuti alla interazione fra i fenomeni di rilassamento magnetico e gli altri fenomeni irreversibili.
1. Introduction

Studies on dielectric and magnetic phenomena have been developed in $^{16}$ with the help of the thermodynamics of irreversible processes (see references $^1$, $^6$-$^9$). Furthermore, in $^{10}$ a thermodynamic theory for some types of dielectric and magnetic relaxation phenomena in polarizable and magnetizable media is formulated by assuming that a polar and an axial vector field occur as internal thermodynamic degrees of freedom and that these fields influence the polarization and the magnetization, respectively. Snoek’s equation for magnetic after-effects is derived and Debye’s theory for dielectric relaxation phenomena in polar fluids is obtained as a special case of the developed theory.

In reference $^{11}$ it is shown that if $Z$ is a vectorial internal degree of freedom which influences the polarization, a new internal degree of freedom $p^{(\text{int})}$ may be defined, which may replace $Z$ as internal variable, which is a function of $Z$ only and which is introduced in such a way that it is a part of the total polarization $p$. The remaining part $p^{(\text{el})}$ is given by

$$p^{(\text{el})} = p - p^{(\text{int})}. \tag{1.1}$$

The vector $p^{(\text{el})}$ has the property that it vanishes for all values of $p^{(\text{int})}$ if the medium is in states where the temperature equals some reference temperature and the mechanical elastic stress and the electric field vanish. Furthermore, $p^{(\text{el})}$ is proportional to the electric field $E$ and it is called the elastic part of the polarization because a sudden change in the electric field $E$ leads to a sudden change in $p^{(\text{el})}$. Sudden changes in $p^{(\text{int})}$ are impossible and for this reason $p^{(\text{int})}$ may be called the inelastic part of the polarization. Furthermore, from (1.1) $p^{(\text{int})}$ is a measurable quantity in contradistinction to an arbitrary "hidden" vectorial internal degree of freedom. If $p^{(\text{int})}$ is chosen as internal variable, in the linear approximation and in the isotropic case, the Debye equation is obtained.

Analogous results are obtained for magnetic relaxation phenomena.

A different formulation of the theory developed in references $^{10}$ and $^{11}$ is given in reference $^{12}$, where it is assumed that all changes in the polarization and magnetization are irreversible phenomena since they are connected with the motion of any kind of microscopic particles, which cannot be infinitely fast (see also reference $^{13}$).

In this paper, using the general methods of non-equilibrium thermodynamics, we study dielectric and magnetic relaxation phenomena in fluid mixtures.

By introducing a polar and an axial vector field, which play the role of thermodynamic internal degrees of freedom, we investigate the possibility of cross effects among dielectric and magnetic relaxation, heat conduction, electric conduction, diffusion, viscous flow and chemical reactions.

Some phenomena of the type "cross effects" have already been studied. In particular the cross effects between heat conduction and electric conduction have been discussed (see for instance chapter XIII of reference $^1$). The relativistic theory of heat conduction and electric conduction has been studied in references $^3$-$^6$. The relativistic theory of polarizable and magnetizable
media has been formulated in references 14-16. Furthermore one of us investigated the influence of tensorial internal degrees of freedom on the mechanical behaviour of materials and the possibility of cross effects among the mechanical phenomena connected with these tensor fields and heat conduction, electric conduction, viscous flow, dielectric and magnetic relaxation.

In this paper, in section 2 we consider a polarizable and magnetizable fluid mixture consisting of \( n \) chemical components among which \( r \) chemical reactions are possible and we give the first law of thermodynamics.

In section 3 the physical assumption is introduced that the entropy depends not only on the internal energy, the specific volume, the polarization vector, the magnetization vector and the concentrations of the \( n \) components but also on two internal variables: a polar and an axial vector field. The entropy balance is obtained and it is seen that the entropy production is composed of a sum of terms, where each term is the inner product of two factors of which one is a flux and the other is the thermodynamic force, or affinity, conjugate to the flux.

In section 4 the phenomenological equations for the irreversible processes of heat conduction, diffusion of matter, viscous flow, changes in the vectorial internal degrees of freedom and chemical reactions are formulated and the possible cross effects among these irreversible processes are explicitly obtained. Some symmetry relations and the Onsager-Casimir reciprocity relations for the phenomenological coefficients are derived.

In section 5 it is seen that symmetry properties of the fluid mixture under consideration may have the effect that the Cartesian components of the fluxes do not depend on all Cartesian components of the thermodynamic forces (Curie principle) and in the case of isotropy with respect to all rotations of the frame of axes the phenomenological equations and the expression of the entropy production are derived.

Finally, in section 6 it is shown that if the fluid mixture has symmetry properties invariant with respect to all rotations and to reflections of the frame of axes, fluxes and thermodynamic forces of different tensorial character (polar or axial) do not couple. Therefore, there are no contributions due to the cross effects among magnetic relaxation phenomena and the other irreversible phenomena in the expression for the entropy production.

2. The law of conservation of mass, Maxwell’s equations and the first law of thermodynamics

Let us consider a fluid mixture consisting of \( n \) chemical components, among which \( r \) chemical reactions are possible (see reference 1). Let this mixture be influenced by an electromagnetic field.

The conservation of mass is expressed by the relation

\[
\frac{\partial \rho}{\partial t} = -\text{div} \rho \mathbf{v},
\]

(2.1)

where \( \rho \) is the total mass density
\[ \rho = \sum_{k=1}^{n} \rho^{(k)}, \]  
(2.2)

where \( \rho^{(k)} \) is the mass density of chemical component \( k \) and \( v \) is the barycentric velocity given by

\[ v = \rho^{-1} \sum_{k=1}^{n} \rho^{(k)} v^{(k)}. \]  
(2.3)

In the preceding relation \( v^{(k)} \) is the velocity of component \( k \).

Using the equation (2.2), the relation (2.1) can also be written in the form

\[ \frac{\partial \rho}{\partial t} = - \text{div} (\sum_{k=1}^{n} \rho^{(k)} v^{(k)}). \]  
(2.4)

We define the specific volume \( v \) by

\[ v = \rho^{-1}. \]  
(2.5)

The substantial (material) derivative with respect to time is the linear operator defined by

\[ \frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{\gamma=1}^{3} v_{\gamma} \frac{\partial}{\partial x_{\gamma}}, \]  
(2.6)

where \( \frac{\partial}{\partial t} \) is the local derivative with respect to time, which appears on the left-hand side of equation (2.1), \( x_1, x_2 \) and \( x_3 \) are the coordinates of a point in space with respect to an orthogonal Cartesian frame of axes fixed in space and \( v_1, v_2 \) and \( v_3 \) are the components of the velocity field with respect to this frame.

With the aid of the equations (2.5) and (2.6), the conservation law (2.1) may also be written as

\[ \rho \frac{dv}{dt} = \text{div} v. \]  
(2.7)

The mass fractions \( c^{(k)} \) are defined by

\[ c^{(k)} = \rho^{(k)} / \rho \quad (k = 1, 2, \cdots, n). \]  
(2.8)

From this definition and (2.2) we obtain

\[ \sum_{k=1}^{n} c^{(k)} = 1. \]  
(2.9)

The diffusion flow of substance \( k \) with respect to the barycentric motion is defined by

\[ J_{(k)}^{(diff)} = \rho^{(k)} (v^{(k)} - v) \quad (k = 1, 2, \cdots, n). \]  
(2.10)

Using (2.2) and (2.3) we obtain from this definition
\[
\sum_{k=1}^{n} J_{(\text{diff})}^{(k)} = 0 \quad (2.11)
\]

(which means that only \( n - 1 \) of the \( n \) diffusion flows are independent).

The following balance equations hold for the \( c^{(k)} \) (see reference 1)
\[
\rho \frac{dc^{(k)}}{dt} = -\text{div} \, J_{(\text{diff})}^{(k)} + \sum_{h=1}^{r} v^{(kh)} J_{(\text{chem})}^{(h)} \quad (k = 1, 2, \ldots, n), \quad (2.12)
\]

where \( v^{(kh)} J_{(\text{chem})}^{(h)} \) is the production of component \( k \) per unit volume and per unit time by the \( h \)-th chemical reaction, the quantity \( v^{(kh)} \) divided by the molecular mass \( M^{(k)} \) of component \( k \) is proportional to the stoichiometric coefficient with which the component \( k \) appears in the chemical reaction \( h \) and \( J_{(\text{chem})}^{(h)} \) is the chemical reaction rate of reaction \( h \).

Maxwell's equations for the electric and magnetic fields read (in the rationalized Gauss system)
\[
\begin{align*}
\text{rot} \, H - \frac{1}{c} \frac{\partial D}{\partial t} &= \frac{1}{c} \mathbf{I} , \quad (2.13) \\
\text{div} \, D &= \rho^{(el)} , \quad (2.14) \\
\text{rot} \, E + \frac{1}{c} \frac{\partial B}{\partial t} &= 0 , \quad (2.15) \\
\text{div} \, B &= 0 , \quad (2.16)
\end{align*}
\]

where \( \rho^{(el)} \) is the electric charge per unit volume (electric charge density), \( \mathbf{I} \) is the density of the total electric current, \( c \) is the velocity of light, \( E \) and \( B \) are the electric and magnetic field strengths respectively, \( D \) and \( H \) are the electric and magnetic displacement vectors.

We indicate by \( e^{(k)} \) the charge per unit of mass of component \( k \), the total charge \( e \) per unit of mass of the system is given by
\[
e = \rho^{-1} \sum_{k=1}^{n} \rho^{(k)} e^{(k)} = \sum_{k=1}^{n} c^{(k)} e^{(k)} , \quad (2.17)
\]

where we have used the equation (2.8).

In the equation (2.13) \( \mathbf{I} \) is defined by
\[
\mathbf{I} = \sum_{k=1}^{n} \rho^{(k)} e^{(k)} v^{(k)} . \quad (2.18)
\]

In the equation (2.14) \( \rho^{(el)} \) is given by
\[
\rho^{(el)} = \sum_{k=1}^{n} \rho^{(k)} e^{(k)} \quad (2.19)
\]

and satisfies the law of conservation of charge (see for example reference 1).
\[
\frac{\partial \rho^{(e)}}{\partial t} = -\text{div} \, I. \quad (2.20)
\]

By applying the definition (2.10) and the equation (2.19), (2.18) can be written in the form

\[
I = \rho^{(e)} \, v + \sum_{k=1}^{n} \varepsilon^{(k)} J^{(k)}_{(diff)}. \quad (2.21)
\]

where on the right-hand side the first term \( \rho^{(e)} \, v \) is the electric current due to convection, the second term is the electric current due to the relative motion of the various components, which is called the conduction current \( j^{(i)} \), i.e.

\[
j^{(e)} = \sum_{k=1}^{n} \varepsilon^{(k)} J^{(k)}_{(diff)}. \quad (2.22)
\]

Finally, we define the polarization vector \( P \) and the magnetization vector \( M \) by

\[
P = D - E, \quad (2.23)
\]

\[
M = B - H, \quad (2.24)
\]

and the vectors of the specific polarization \( p \) and the specific magnetization \( m \) by

\[
p = v \, P, \quad (2.25)
\]

\[
m = v \, M \quad (2.26)
\]

(with \( v \) given by (2.5)).

The first law of thermodynamics for polarizable and magnetizable fluid mixtures in an electromagnetic field reads (see reference 1)

\[
\rho \frac{du}{dt} = -\text{div} \, J^{(q)} + \sum_{\alpha, \beta = 1}^{3} \tau_{\alpha \beta} \frac{d \varepsilon_{\alpha \beta}}{dt} + j^{(e)} \cdot E + \rho \, E \cdot \frac{dp}{dt} + \rho \, B \cdot \frac{dm}{dt}. \quad (2.27)
\]

In (2.27) \( u \) is the specific internal energy of the system, \( J^{(q)} \) is the heat flow, \( \tau_{\alpha \beta} \) is the mechanical stress tensor and \( \varepsilon_{\alpha \beta} \) is the strain tensor defined by

\[
\varepsilon_{\alpha \beta} = \frac{1}{2} \left( \frac{\partial u_{\alpha}}{\partial x_{\beta}} + \frac{\partial u_{\beta}}{\partial x_{\alpha}} \right) \quad (\alpha, \beta = 1, 2, 3). \quad (2.28)
\]

if we suppose that the deformations and the rotations of the medium are small from a kinematical point of view. In (2.28) \( u \) is the displacement field of the medium. In a first approximation \( \frac{d}{dt} \varepsilon_{\alpha \beta} \) is given by

\[
\frac{d}{dt} \varepsilon_{\alpha \beta} = \frac{1}{2} \left( \frac{\partial v_{\alpha}}{\partial x_{\beta}} + \frac{\partial v_{\beta}}{\partial x_{\alpha}} \right) \quad (\alpha, \beta = 1, 2, 3). \quad (2.29)
\]

as may be shown from (2.28).

In the equation (2.27) all the quantities are per unit of volume and per unit of time. On the right-
hand side the first term is the heat supply, the second term is the work done by mechanical stress
the third term is the Joule heat, $\rho E \cdot \frac{d \mathbf{p}}{dt}$ is the work done by the electric field to change the
polarization, $\rho B \cdot \frac{d \mathbf{m}}{dt}$ is the work done by the magnetic field to change the magnetization.

Now, let $A_{\alpha \beta}$ be an arbitrary tensor field of order two. The deviator $\mathbf{A}_{\alpha \beta}$ and the scalar part
$A$ of $A_{\alpha \beta}$ are defined by

$$\mathbf{A}_{\alpha \beta} = A_{\alpha \beta} - \frac{1}{3} \left( \sum_{\gamma=1}^{3} A_{\gamma \gamma} \right) \delta_{\alpha \beta}$$

(2.30)

and

$$A = \frac{1}{3} \sum_{\gamma=1}^{3} A_{\gamma \gamma}.$$  

(2.31)

Hence,

$$A_{\alpha \beta} = \mathbf{A}_{\alpha \beta} + A \delta_{\alpha \beta}$$

(2.32)

and

$$\sum_{\gamma=1}^{3} \mathbf{A}_{\gamma \gamma} = 0.$$  

(2.33)

Moreover, if $A_{\alpha \beta}$ is symmetric also $\mathbf{A}_{\alpha \beta}$ is symmetric and reversely.

From the definition (2.28), it is obvious that $\mathbf{e}_{\alpha \beta}$ is a symmetric tensor field.

Furthermore, from the equations (2.28), (2.30) and (2.31) it follows that the scalar part $\mathbf{e}$ and
the deviator $\mathbf{e}_{\alpha \beta}$ of $\mathbf{e}_{\alpha \beta}$ are given by

$$\mathbf{e} = \frac{1}{3} \text{div} \mathbf{u}$$

(2.34)

and

$$\mathbf{e}_{\alpha \beta} = \frac{1}{2} \left[ \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha \beta} \text{div} \mathbf{u} \right].$$

(2.35)

With the aid of (2.34) the equation (2.7) may also be written as

$$\rho \frac{dv}{dt} = 3 \frac{d \mathbf{e}}{dt}.$$  

(2.36)

In a first approximation, if we replace in (2.36) $\rho$ by $1/\nu_0$, with $\nu_0$ the specific volume in the
reference state (i.e. the state of the medium with respect to which the displacements of the medium
are measured), we obtain

$$\nu = \nu_0(1 + 3 \mathbf{e}).$$

(2.37)
3. The balance equation for the entropy

Let us introduce the physical assumption that the specific entropy $s$ (i.e. the entropy per unit of mass) for polarizable and magnetizable fluid mixtures is a function of the specific internal energy $u$, the specific volume $v$, the specific polarization $p$, the specific magnetization $m$, the concentrations $c^{(k)}$ of $n$ components ($k = 1, 2, \ldots, n$) and a polar vector field $p^{(\text{int})}$ and an axial vector field $m^{(\text{int})}$ which represent thermodynamic internal degrees of freedom and which give rise to dielectric and magnetic relaxation phenomena, respectively

$$s = s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}).$$  \hfill (3.1)

We shall define the temperature $T$, the scalar field $P^{(eq)}$, the vector fields $E^{(eq)}$, $B^{(eq)}$, $E^{(\text{int})}$, $B^{(\text{int})}$ and the scalar fields $u^{(k)}$ ($k = 1, 2, \ldots, n$) by

$$T^{-1} = \frac{\partial}{\partial u} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.2)

$$P^{(eq)} = T \frac{\partial}{\partial v} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.3)

$$E^{(eq)} = -T \frac{\partial}{\partial p} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.4)

$$B^{(eq)} = -T \frac{\partial}{\partial m} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.5)

$$E^{(\text{int})} = T \frac{\partial}{\partial p^{(\text{int})}} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.6)

$$B^{(\text{int})} = T \frac{\partial}{\partial m^{(\text{int})}} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.7)

$$\mu^{(k)} = -T \frac{\partial}{\partial c^{(k)}} s(u, v, p, m, p^{(\text{int})}, m^{(\text{int})}, c^{(1)}, c^{(2)}, \ldots, c^{(n)}),$$  \hfill (3.8)

$k = 1, 2, \ldots, n$.

From (3.1) we obtain for the differential of $s$

$$T \, ds = d\, u + P^{(eq)} \, dv - E^{(eq)} \cdot d\, p - B^{(eq)} \cdot d\, m +$$

$$+ E^{(\text{int})} \cdot d\, p^{(\text{int})} + B^{(\text{int})} \cdot d\, m^{(\text{int})} - \sum_{k=1}^{n} \mu^{(k)} \, d\, c^{(k)},$$  \hfill (3.9)

where we used the equations (3.2) - (3.8).

An expression of the type (3.9) for $ds$ is called Gibbs relation. In (3.3) - (3.7) $P^{(eq)}$ is the equilibrium pressure, $E^{(eq)}$ is the equilibrium electric field, $B^{(eq)}$ is the equilibrium magnetic field, $E^{(\text{int})}$ and $B^{(\text{int})}$ are the vectorial thermodynamic affinities conjugate to the internal variables $p^{(\text{int})}$ and $m^{(\text{int})}$, respectively. $E^{(\text{int})}$ is a polar vector field, $B^{(\text{int})}$ is an axial vector field. In (3.8) $\mu^{(k)}$ is the thermodynamic or chemical potential of component $k$. 
If we neglect in (3.9) the terms \( E^{(in)} \cdot dp^{(in)} \) and \( B^{(in)} \cdot dm^{(in)} \) the equation reduces to equation (5.5) on pag. 386 of reference 1.

Now, we define (see for instance reference 19) the mechanical pressure tensor \( P_{\alpha \beta} \) by

\[
P_{\alpha \beta} = -\tau_{\alpha \beta} \quad (\alpha, \beta = 1, 2, 3),
\]

(3.10)

where \( \tau_{\alpha \beta} \) is the mechanical stress tensor which occurs in the equation of motion and in the first law of thermodynamics.

The viscous stress tensor \( \tau_{\alpha \beta}^{(v)} \) is defined by

\[
\tau_{\alpha \beta}^{(v)} = \tau_{\alpha \beta} - \tau_{\alpha \beta}^{(eq)} \quad (\alpha, \beta = 1, 2, 3),
\]

(3.11)

where \( \tau_{\alpha \beta}^{(eq)} \) is the equilibrium stress tensor.

Hence,

\[
\tau_{\alpha \beta} = \tau_{\alpha \beta}^{(eq)} + \tau_{\alpha \beta}^{(v)} \quad (\alpha, \beta = 1, 2, 3).
\]

(3.12)

For a fluid we have

\[
\tau_{\alpha \beta}^{(eq)} = -P^{(eq)} \delta_{\alpha \beta} \quad \text{(fluid)} \quad (\alpha, \beta = 1, 2, 3).
\]

(3.13)

From (3.9) it follows that

\[
\frac{ds}{dt} = \frac{du}{dt} + p^{(eq)} \frac{dv}{dt} - E^{(eq)} \cdot \frac{dp}{dt} - B^{(eq)} \cdot \frac{dm}{dt} + E^{(in)} \cdot \frac{dp^{(in)}}{dt} + B^{(in)} \cdot \frac{dm^{(in)}}{dt} - \sum_{k=1}^{n} \mu^{(k)} \frac{dc^{(k)}}{dt}.
\]

(3.14)

By eliminating the internal energy \( u \) from (3.14) and (2.27) we obtain the following equation

\[
\rho \frac{ds}{dt} = T^{-1} \left( -\text{div} \ J^{(q)} + \sum_{\alpha, \beta=1}^{3} \tau_{\alpha \beta}^{(v)} \frac{d\epsilon_{\alpha \beta}}{dt} + J^{(r)} \cdot E + \right.
\]

\[
+ \rho E^{(ir)} \cdot \frac{dp}{dt} + \rho B^{(ir)} \cdot \frac{dm}{dt} + \rho E^{(in)} \cdot \frac{dp^{(in)}}{dt} + \right.
\]

\[
+ \rho B^{(in)} \cdot \frac{dm^{(in)}}{dt} - \rho \sum_{k=1}^{n} \mu^{(k)} \frac{dc^{(k)}}{dt} \}.
\]

(3.15)

In (3.15) we have introduced the definitions of the irreversible electric field \( E^{(ir)} \) and of the irreversible magnetic field \( B^{(ir)} \), given by

\[
E^{(ir)} = E - E^{(eq)}
\]

(3.16)

and
and we have used the equations (2.7), (2.34), (2.36), (3.11) and (3.13).

We multiply both sides of (2.12) by \( \frac{\mu^{(k)}}{T} \) and sum over \( k \). Introducing the so-called chemical affinity of the reaction \( h \), defined by (see reference 1)

\[
A^{(h)} = \sum_{k=1}^{n} \mu^{(k)} \nu^{(kh)} \quad (h = 1, 2, \ldots, r),
\]

we obtain

\[
\frac{\partial}{\partial t} \sum_{k=1}^{n} \mu^{(k)} \frac{dc^{(k)}}{dt} = -\text{div} \left\{ T^{-1} \sum_{k=1}^{n} \mu^{(k)} J^{(k)}_{(\text{diff})} \right\} + \\
+ \sum_{k=1}^{n} J^{(k)}_{(\text{diff})} \cdot \text{grad} \left[ \frac{\mu^{(k)}}{T} \right] + T^{-1} \sum_{k=1}^{r} A^{(h)} J^{(h)}_{(\text{chem})}.
\]

(3.19)

Moreover, we introduce the notations

\[
A^{(k)} = -A^{(h)} \quad (h = 1, 2, \ldots, r),
\]

we define the thermodynamic force \( \chi^{(k)} \) conjugate to the diffusion flow of matter \( J^{(k)}_{(\text{diff})} \), by

\[
\chi^{(k)} = -\left( T \text{grad} \left[ \frac{\mu^{(k)}}{T} \right] - e^{(k)} \mathbb{E} \right) \quad (k = 1, 2, \ldots, n)
\]

(3.21)

and we write the following equality (obtained with the aid of the equation (2.11))

\[
\sum_{k=1}^{n} J^{(k)}_{(\text{diff})} \cdot \chi^{(k)} = \sum_{k=1}^{n-1} J^{(k)}_{(\text{diff})} \cdot (\chi^{(k)} - \chi^{(\alpha)}).
\]

(3.22)

If we define the vector \( X^{(k)} \) by

\[
X^{(k)} = \chi^{(k)} - \chi^{(\alpha)}, \quad (k = 1, 2, \ldots, n - 1),
\]

(3.23)

the equation (3.22) becomes

\[
\sum_{k=1}^{n} J^{(k)}_{(\text{diff})} \cdot X^{(k)} = \sum_{k=1}^{n-1} J^{(k)}_{(\text{diff})} \cdot X^{(k)}.
\]

(3.24)

Using in (3.15) the definition (2.22) of \( j^{(\alpha)} \) and the equations (3.19) - (3.24), it is easy to write the equation (3.15) in the form of a balance equation, i.e.

\[
\rho \frac{dx}{dt} = -\text{div} \ J^{(\alpha)} + \sigma^{(\alpha)},
\]

(3.25)

where \( J^{(\alpha)} \) is defined by
\[ J^{(s)} = T^{-1} \left\{ J^{(s)} - \sum_{k=1}^{n} \mu^{(k)} J^{(\text{diff})}_{(k)} \right\} \]  
(3.26)

and \( \sigma^{(s)} \) is the entropy production per unit volume and per unit time, given by

\[
\sigma^{(s)} = T^{-1} \left\{ -T^{-1} J^{(s)} \cdot \text{grad} T + \sum_{k=1}^{n-1} J^{(k)}_{(\text{diff})} \cdot X^{(k)} + \right. \\
+ \sum_{\alpha, \beta=1}^{3} \tau^{(\alpha)}_{\beta} \frac{d\epsilon_{\alpha\beta}}{dt} + \rho E^{(\epsilon)} \cdot \frac{dp}{dt} + \rho B^{(\epsilon)} \cdot \frac{dm}{dt} + \\
\left. + \rho E^{(\text{int})} \cdot \frac{dp^{(\text{int})}}{dt} + \rho B^{(\text{int})} \cdot \frac{dm^{(\text{int})}}{dt} + \sum_{k=1}^{r} A^{(k)} J^{(k)}_{(\text{chem})} \right\}.
\]  
(3.27)

In (3.26) \( J^{(s)} \) is the entropy flow which is additively composed of two parts: the "reduced" heat flow \( J^{(q)} / T \) and the part connected with the diffusion flows of matter \( J^{(\text{diff})}_{(k)} \) \((k = 1, 2, \cdots, n)\).

In (3.27) the entropy source strength \( \sigma^{(s)} \) (a non-negative quantity) is zero if the system is in thermodynamic equilibrium.

From (3.27) it is seen that the entropy production is additively composed of eight different contributions: the first term arises from heat conduction, the second from diffusion of matter, the third is connected with the gradient of the velocity field giving rise to viscous effects, the terms with \( \frac{dp}{dt} \) and \( \frac{dp^{(\text{int})}}{dt} \) are connected with entropy production due to dielectric relaxation, the terms with \( \frac{dm}{dt} \) and \( \frac{dm^{(\text{int})}}{dt} \) are connected with entropy production due to magnetic relaxation, the last term is due to chemical reactions.

4. Phenomenological equations, symmetry relations and Onsager-Casimir reciprocity relations

It is seen from (3.27) that the expression of \( \sigma^{(s)} \) is a bilinear form composed of a sum of terms, where each term is the inner product of two factors of which one is a flux and the other is the thermodynamic force or "affinity" conjugate to the flux.

According to the usual procedure of non-equilibrium thermodynamics (see references 1 and 19) we have for polarizable and magnetizable fluid mixtures the following phenomenological equations in which the irreversible flows are linear functions of the thermodynamic forces:

\[
E^{(\epsilon)}_{\alpha} = \rho \sum_{\beta=1}^{3} L^{(\epsilon)(\beta)}_{\alpha\beta} \frac{dp_{\beta}}{dt} + \rho \sum_{\beta=1}^{3} L^{(\text{int})(\beta)}_{\alpha\beta} \frac{dm_{\beta}}{dt} + 
\]
\[ + \sum_{\beta=1}^{3} L_{(PP)X_{\beta}}^{(0)} E_{\beta}^{(0)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} B_{\beta}^{(0)} - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{(PP)X_{\beta}}^{(1)} \frac{\partial T}{\partial X_{\beta}} + \sum_{\beta=1}^{3} \sum_{k=1}^{n-1} L_{(PM)X_{\beta}}^{(1)} X_{\beta}^{(k)} + \]
\[ + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} A^{(k)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} \frac{d E_{\beta}}{d t} , \]

(4.1)

\[ B_{a}^{(i)} = \rho \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} \frac{d p_{\ast}}{d t} + \rho \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} \frac{d m_{\ast}}{d t} + \]
\[ + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} E_{\beta}^{(i0)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} B_{\beta}^{(i0)} - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} \frac{\partial T}{\partial X_{\beta}} + \sum_{\beta=1}^{n-1} \sum_{k=1}^{N} L_{(PM)X_{\beta}}^{(1)} X_{\beta}^{(k)} + \]
\[ + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} A^{(k)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} \frac{d E_{\beta}}{d t} , \]

(4.2)

\[ \rho \frac{d p_{a}^{(i0)}}{d t} = \rho \sum_{\beta=1}^{3} L_{(PP)X_{\beta}}^{(0)} \frac{d p_{\ast}}{d t} + \rho \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} \frac{d m_{\ast}}{d t} + \]
\[ + \sum_{\beta=1}^{3} L_{(PP)X_{\beta}}^{(0)} E_{\beta}^{(i0)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} B_{\beta}^{(i0)} - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{(PP)X_{\beta}}^{(1)} \frac{\partial T}{\partial X_{\beta}} + \sum_{\beta=1}^{n-1} \sum_{k=1}^{N} L_{(PM)X_{\beta}}^{(1)} X_{\beta}^{(k)} + \]
\[ + \sum_{\beta=1}^{3} L_{(PP)X_{\beta}}^{(0)} A^{(k)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} \frac{d E_{\beta}}{d t} , \]

(4.3)

\[ \rho \frac{d m_{a}^{(i0)}}{d t} = \rho \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} \frac{d p_{\ast}}{d t} + \rho \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} \frac{d m_{\ast}}{d t} + \]
\[ + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(0)} E_{\beta}^{(i0)} + \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} B_{\beta}^{(i0)} - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{(PM)X_{\beta}}^{(1)} \frac{\partial T}{\partial X_{\beta}} + \sum_{\beta=1}^{n-1} \sum_{k=1}^{N} L_{(PM)X_{\beta}}^{(1)} X_{\beta}^{(k)} + \]
\[ J^{(a)}_\alpha = \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dp_B}{dt} + \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dm_B}{dt} + \]
\[ + \sum_{k=1}^{3} L_{ij(\alpha)\beta} E^{(out)}_B - \sum_{k=1}^{3} L_{ij(\alpha)\beta} B^{(out)}_B - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{ij(\alpha)} \frac{\partial T}{\partial x_B} + \sum_{k=1}^{n-1} \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} X^{(k)}_B + \]
\[ + \sum_{k=1}^{r} L_{ij(\alpha)\beta} A^{(k)} + \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{de_{PT}}{dt} \text{ (4.4)} \]

\[ J^{(diff)}_{\alpha} = \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dp_B}{dt} + \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dm_B}{dt} + \]
\[ + \sum_{k=1}^{3} L_{ij(\alpha)\beta} E^{(out)}_B + \sum_{k=1}^{3} L_{ij(\alpha)\beta} B^{(out)}_B - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{ij(\alpha)} \frac{\partial T}{\partial x_B} + \sum_{k=1}^{n-1} \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} X^{(k)}_B + \]
\[ + \sum_{k=1}^{r} L_{ij(\alpha)\beta} A^{(k)} + \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{de_{PT}}{dt} \text{ (4.5)} \]

\[ J^{(chem)}_{\alpha} = \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dp_B}{dt} + \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dm_B}{dt} + \]
\[ + \sum_{k=1}^{3} L_{ij(\alpha)\beta} E^{(out)}_B + \sum_{k=1}^{3} L_{ij(\alpha)\beta} B^{(out)}_B - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{ij(\alpha)} \frac{\partial T}{\partial x_B} + \sum_{k=1}^{n-1} \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} X^{(k)}_B + \]
\[ + \sum_{k=1}^{r} L_{ij(\alpha)\beta} A^{(k)} + \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{de_{PT}}{dt} \text{ (4.6)} \]

\[ J^{(l)}_{\alpha} = \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dp_B}{dt} + \rho \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{dm_B}{dt} + \]
\[ + \sum_{k=1}^{3} L_{ij(\alpha)\beta} E^{(out)}_B + \sum_{k=1}^{3} L_{ij(\alpha)\beta} B^{(out)}_B - \]
\[ - T^{-1} \sum_{\beta=1}^{3} L_{ij(\alpha)} \frac{\partial T}{\partial x_B} + \sum_{k=1}^{n-1} \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} X^{(k)}_B + \]
\[ + \sum_{k=1}^{r} L_{ij(\alpha)\beta} A^{(k)} + \sum_{\beta=1}^{3} L_{ij(\alpha)\beta} \frac{de_{PT}}{dt} \text{ (4.7)} \]

\[ r^{(i)}_{\alpha} = \rho \sum_{\tau=1}^{3} L_{ij(\alpha)\beta} \frac{dp_T}{dt} + \rho \sum_{\tau=1}^{3} L_{ij(\alpha)\beta} \frac{dm_T}{dt} + \]
\[ + \sum_{\tau=1}^{3} L_{ij(\alpha)\beta} E^{(out)}_T + \sum_{\tau=1}^{3} L_{ij(\alpha)\beta} B^{(out)}_T - \]
The equations (4.1) and (4.3) are connected with irreversible changes in the polarization and (4.2) and (4.4) with irreversible changes in the magnetization. Moreover, the phenomenological equations (4.5) - (4.7) are connected with the irreversible processes of heat flow, diffusion and chemical reactions, respectively. The equation (4.8) is a generalization of Newton's law for viscous fluid flow.

The quantities $L^{(vi)}$, $L^{(vi)}$, etc. which occur in (4.1) - (4.8) are called phenomenological tensors. For instance, $L^{(vi)}$ is the viscosity tensor of order four, $L^{(h)}$ is a polar tensor of order two connected with the diffusion flow of substance $k$, $L^{(l)}$ is a scalar connected with the chemical affinity of the reaction $h(l, h = 1, 2, \ldots, r)$, $L^{(p)}$ is a pseudo tensor of order three connected with the influence of the viscous flow on the magnetic relaxation. In principle, all irreversible phenomena described by (4.1) - (4.8) can influence each other. For instance, the second, fourth, fifth, sixth, seventh and eighth term on the right-hand sides of (4.1) and (4.3) describe the influences of magnetic relaxation, heat flow, diffusion flow, chemical reactions and viscous flow on dielectric relaxation. Phenomena of this type are called cross effects (see references 1 and 19).

By virtue of (2.28) the strain tensor $e_{\alpha\beta}$ is symmetric and from (3.13) and (3.3) the equilibrium stress tensor $\tau^{(vi)}$ is also symmetric. Furthermore, we suppose that the mechanical stress tensor, which occurs in the first law (2.27) and in the equations of motion, is symmetric. Hence, it follows from (3.11) that the viscous stress $\tau^{(vi)}$ is also a symmetric tensor.

Because of the symmetry of $e_{\alpha\beta}$ and $\tau^{(vi)}$ we can choose the phenomenological tensors

$$L^{(vi)}$, $L^{(vi)}$, $L^{(vi)}$, $L^{(vi)}$, $L^{(vi)}$,

$$L^{(h)}$, $L^{(l)}$, $L^{(p)}$, $L^{(p)}$,

$$L^{(p)}$, $L^{(p)}$, $L^{(p)}$,

$$L^{(p)}$, $L^{(p)}$, $L^{(p)}$,

so that they satisfy the following symmetry relations

$$L^{(vi)} = L^{(vi)}$$

$$L^{(vi)} = L^{(vi)}$$

$$L^{(vi)} = L^{(vi)}$$

$$L^{(vi)} = L^{(vi)}$$
\[
L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad (4.12)
\]
\[
L^{(\nu_1, \nu_2)} = L^{(\nu_1, \nu_2)}, \quad L^{(\nu_1, \nu_2)} = L^{(\nu_1, \nu_2)}, \quad (4.13)
\]
\[
L^{(\nu_1, \nu_2)}_{(L)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(L)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(L)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(L)\rho \sigma} (j = 1, 2, \ldots, n - 1), \quad (4.14)
\]
\[
L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} (l = 1, 2, \ldots, r), \quad (4.15)
\]
\[
L^{(\nu_1, \nu_2)}_{(P)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(P)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(P)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(P)\rho \sigma}, \quad (4.16)
\]

\[E^{(\nu_1)}, E^{(\nu_2)}, \rho \frac{dm^{(\nu_1)}}{dt}, \rho \frac{dm^{(\nu_2)}}{dt}, A^{(h)} (h = 1, 2, \ldots, r), T^{-1} \text{grad} T,\]

X^{(k)} (k = 1, 2, \ldots, n - 1) and \(\tau^{(\nu)}_{\rho \sigma}\) are even functions of the microscopic particle velocities while \(\rho \frac{dP^{(\nu_1)}}{dt}, \rho \frac{dP^{(\nu_2)}}{dt}, B^{(\nu_1)}, B^{(\nu_2)}, J^{(\nu)}, J^{(\nu)}_{(\text{diff})} (k = 1, 2, \ldots, n - 1),\)

\[J^{(\nu)}_{(\text{chem})} (l = 1, 2, \ldots, r), \frac{dJ^{(\nu)}}{dt}, \text{are odd functions of these velocities, (see references 1 and 19).}\]

Hence, according to the usual procedure of non-equilibrium thermodynamics, we have for the cross effects, which occur in (4.1) - (4.8), the following Onsager-Casimir reciprocity relations

\[
L^{(\nu_1, \nu_2)}_{(FF)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(FF)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad (4.17)
\]
\[
L^{(\nu_1, \nu_2)}_{(P)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(P)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad (4.18)
\]
\[
L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} (j = 1, 2, \ldots, n - 1), \quad (4.19)
\]
\[
L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} (j, k = 1, 2, \ldots, n - 1), \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} (l, h = 1, 2, \ldots, r), \quad (4.20)
\]
\[
L^{(\nu_1, \nu_2)}_{(P)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(P)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad (4.21)
\]
\[
L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad (4.22)
\]
\[
L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(F)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(F)\rho \sigma}, \quad (4.23)
\]
\[
L^{(\nu_1, \nu_2)}_{(P)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(P)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} (k = 1, 2, \ldots, n - 1), \quad (4.24)
\]
\[
L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} (h = 1, 2, \ldots, r), \quad (4.25)
\]
\[
L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(F)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(F)\rho \sigma}, \quad (4.26)
\]
\[
L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad (4.27)
\]
\[
L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} (j = 1, 2, \ldots, n - 1; h = 1, 2, \ldots, r), \quad (4.28)
\]
\[
L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(F)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(F)\rho \sigma} (k = 1, 2, \ldots, n - 1), \quad (4.29)
\]
\[
L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(M)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(M)\rho \sigma} (k = 1, 2, \ldots, n - 1), \quad (4.30)
\]
\[
L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = -L^{(\nu_1, \nu_2)}_{(C)\rho \sigma}, \quad L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} = L^{(\nu_1, \nu_2)}_{(C)\rho \sigma} (h = 1, 2, \ldots, r), \quad (4.31)
\]
The relations (4.9) - (4.34) reduce the number of independent components of the phenomenological coefficients.

5. Phenomenological equations and entropy production for media which are isotropic (with respect to all rotations of the frame of axes)

The existence of spatial symmetry properties in a system may simplify the form of the phenomenological equations in such a way that the Cartesian components of the fluxes do not depend on all the Cartesian components of the thermodynamic forces. This statement is called the Curie symmetry principle (see chapter VI of reference 1).

First, we shall suppose that the considered fluid system has symmetry properties such that it is isotropic with respect to all rotations of the frame of axes. In this case (see for instance references 1 and 20) the phenomenological tensor $L_{ij}$ of order four must have the following form

$$L_{ij} = \frac{1}{2} \eta_s (\delta_{ij} \delta_{lk} + \delta_{ik} \delta_{lj}) + \frac{1}{3} (\eta_v - \eta_s) \delta_{ij} \delta_{lk} ,$$

where the scalars $\eta_s$ and $\eta_v$ are the shear viscosity and the volume viscosity, respectively.

A polar or pseudo tensor of order three $L_{ijk}$ must have the form

$$L_{ijk} = \epsilon_{ijk} \cdot$$

where $\epsilon_{ijk}$ is the Levi-Civita tensor.

If a tensor $L_{ij}$ has zero trace one has from (5.4)

$$L_{ij} = 0 \quad \text{(if the trace is zero)} .$$

If $L_{ij}$ is a polar or axial vector, it has the form
Using the symmetry relations (4.9) - (4.16), the Onsager-Casimir relations (4.17) - (4.34), the properties of isotropy (5.1), (5.3) - (5.6) and the equations (2.30) - (2.33), the phenomenological equations (4.1) - (4.8) read in the case of media which are isotropic with respect to all rotations of the frame of axes

\[ E_{a}^{(ir)} = \rho \left( L_{PP}^{(0)} \frac{dp_{a}}{dt} + \rho \left( L_{MM}^{(1)} \frac{dm_{a}}{dt} + L_{PP}^{(0, int)} E_{a}^{(int)} \right) + \right. \]

\[ + L_{PP}^{(0, int)} B_{a}^{(int)} - T^{-1} L_{P}^{(q)} \frac{dT}{dx_{a}} + \sum_{k=1}^{n-1} L_{P}^{(k)} X_{a}^{(k)} , \]  

(5.7)

\[ B_{a}^{(ir)} = -\rho \left( L_{PP}^{(0)} \frac{dp_{a}}{dt} + \rho \left( L_{MM}^{(1)} \frac{dm_{a}}{dt} + L_{PP}^{(0, int)} E_{a}^{(int)} \right) + \right. \]

\[ + L_{MM}^{(1, int)} B_{a}^{(int)} - T^{-1} L_{P}^{(k)} \frac{dT}{dx_{a}} + \sum_{k=1}^{n-1} L_{M}^{(k)} X_{a}^{(k)} , \]  

(5.8)

\[ \rho \frac{dp_{a}^{(int)}}{dt} = \rho \left( -L_{PP}^{(0, int)} \frac{dp_{a}}{dt} + L_{MM}^{(1, int)} \frac{dm_{a}}{dt} \right) + L_{PP}^{(0, int)} E_{a}^{(int)} + \right. \]

\[ + L_{PP}^{(0, int)} B_{a}^{(int)} - T^{-1} L_{P}^{(q, int)} \frac{dT}{dx_{a}} + \sum_{k=1}^{n-1} L_{P}^{(k, int)} X_{a}^{(k)} , \]  

(5.9)

\[ \rho \frac{dm_{a}^{(int)}}{dt} = \rho \left( L_{PP}^{(0, int)} \frac{dp_{a}}{dt} - L_{MM}^{(1, int)} \frac{dm_{a}}{dt} \right) - L_{PP}^{(0, int)} E_{a}^{(int)} + \right. \]

\[ + L_{MM}^{(1, int)} B_{a}^{(int)} - T^{-1} L_{P}^{(q, int)} \frac{dT}{dx_{a}} + \sum_{k=1}^{n-1} L_{M}^{(k, int)} X_{a}^{(k)} , \]  

(5.10)

\[ J_{a}^{(s)} = \rho \left( -L_{P}^{(0, q)} \frac{dp_{a}}{dt} + L_{M}^{(q, q)} \frac{dm_{a}}{dt} \right) + L_{P}^{(q, int)} E_{a}^{(int)} + \right. \]

\[ \left. - L_{M}^{(q, q)} B_{a}^{(int)} - T^{-1} L_{P}^{(q, q)} \frac{dT}{dx_{a}} + \sum_{k=1}^{n-1} L_{D}^{(q, k)} X_{a}^{(k)} , \right) \]  

(5.11)

\[ J_{\text{diff}, a}^{(j)} = \rho \left( -L_{P}^{(0, j)} \frac{dp_{a}}{dt} + L_{M}^{(j, j)} \frac{dm_{a}}{dt} \right) + L_{P}^{(j, int)} E_{a}^{(int)} + \right. \]

\[ \left. - L_{M}^{(j, j)} B_{a}^{(int)} - T^{-1} L_{P}^{(j, j)} \frac{dT}{dx_{a}} + \sum_{k=1}^{n-1} L_{D}^{(j, k)} X_{a}^{(k)} \right) \]  

(5.12)
\[ J_{\text{chem}}^{(i)} = \sum_{k=1}^{r} L_{[CC]}^{(l,h)} A^{(k)} + 3 L_{[C]}^{(vi)} \frac{de}{dt}, \quad (5.13) \]

\[ \tau_{\text{ib}}^{(b)} = - \sum_{k=1}^{r} L_{[C]}^{(vi)} A^{(k)} \delta_{a\beta} + \eta_{a} \frac{d\varepsilon_{ab}}{dt} + \eta_{v} \frac{de}{dt} \delta_{ab}. \quad (5.14) \]

If one substitutes the phenomenological laws (5.7) - (5.14) in the expression (3.27) for the entropy production one obtains

\[
\sigma^{(s)} = T^{-1} \left\{ \rho^{2} L_{[PF]}^{(0,0)} \left[ \frac{dp}{dt} \right]^{2} + \rho^{2} L_{[MD]}^{(0)} \left[ \frac{dm}{dt} \right]^{2} - 2 T^{-1} L_{[PF]}^{(int, int)} (E^{(int)})^{2} + L_{[MD]}^{(int, int)} (B^{(int)})^{2} + T^{-2} L^{(t,t)} (\text{grad} T)^{2} + \right. \\
+ \frac{\sum_{j,k=1}^{n-1} L_{[PD]}^{(j,k)} X^{(k)} \cdot X^{(j)} + \sum_{l,h=1}^{r} L_{[CC]}^{(l,h)} A^{(k)} A^{(l)} + \right. \\
+ \eta_{a} \left[ d\varepsilon_{ab} \right]^{2} + 3 \eta_{v} \left[ \frac{de}{dt} \right]^{2} - 2 T^{-1} \sum_{k=1}^{n-1} L_{[B]}^{(k)} X^{(k)} \cdot \text{grad} T + \right. \\
+ 2 \rho L_{[PF]}^{(int, int)} B^{(int)} \cdot \frac{dp}{dt} + 2 \rho L_{[MD]}^{(int, int)} E^{(int)} \cdot \frac{dm}{dt} - \right. \\
- 2 \rho T^{-1} L_{[MD]}^{(0)} \frac{dm}{dt} \cdot \text{grad} T + 2 \rho \sum_{k=1}^{n-1} L_{[MD]}^{(l,k)} \frac{dm}{dt} \cdot X^{(k)} \right\}, \quad (5.15) 
\]

where we have used the equations (2.30) - (2.33).

From (5.15) it is seen that the entropy production is a nonnegative bilinear quadratic form in the components of the time derivative of the specific total polarization vector, the components of the time derivative of the specific total magnetization vector, the components of the thermodynamic forces conjugate to the vectorial internal degrees of freedom, the components of the gradient of the temperature, the components of the thermodynamic forces conjugate to the diffusion flows of matter, the chemical affinities, the components of the time derivative of the deviator of the strain tensor and the time derivative of the scalar part of this tensor.

Because of the nonnegative character of the entropy production, it follows from (5.15) that the phenomenological coefficients satisfy inequalities as

\[ L_{[PF]}^{(0,0)} \geq 0, \quad L_{[PF]}^{(int, int)} \geq 0, \quad L_{[MD]}^{(0)} \geq 0, \quad (5.16) \]

\[ L_{[MD]}^{(int, int)} \geq 0, \quad L^{(t,t)} \geq 0, \quad \eta_{a} \geq 0, \quad \eta_{v} \geq 0, \quad (5.17) \]
6. Phenomenological equations and entropy production for perfect isotropic systems

In this section we consider perfect isotropic systems for which the symmetry properties are invariant with respect to all rotations and to inversion of the frame of axes (under orthogonal transformations). In this case it can be shown that fluxes and thermodynamic forces of different tensorial character (polar or axial) do not couple (see references 1 and 20).

The phenomenological polar tensor $L_{\alpha\beta\gamma\delta \, \nu \rho}$ of order four has the form (5.1).

The polar tensors of order three vanish, i.e.

$$L_{\alpha\beta\gamma \, \nu \rho} = 0.$$  \hspace{1cm} (6.1)

The pseudo tensors of order three keep the form

$$L_{\alpha\beta\gamma \, \nu \rho} = \epsilon_{\alpha\beta\gamma},$$  \hspace{1cm} (6.2)

but, because of the symmetry properties of $L_{\alpha\beta\gamma}$ (see (4.9)-(4.16)), one has

$$L_{\alpha\beta\gamma} = 0.$$ \hspace{1cm} (6.3)

The polar tensors of order two keep the form

$$L_{\alpha\beta} = \delta_{\alpha\beta},$$ \hspace{1cm} (6.4)

which reduces to

$$L_{\alpha\beta} = 0 \quad \text{(with zero trace)},$$ \hspace{1cm} (6.5)

if $L_{\alpha\beta}$ has zero trace.

The axial tensors of order two must have the form

$$L_{\alpha\beta} = 0.$$ \hspace{1cm} (6.6)

The polar and axial vectors $L_{\alpha}$ vanish, i.e.

$$L_{\alpha} = 0.$$ \hspace{1cm} (6.7)

With the aid of (5.1), (6.1), (6.3) - (6.7), the phenomenological equations (4.1) - (4.8) become (see also the equations (4.9)-(4.16) and (4.17)-(4.34))

$$E_{\alpha}^{(p)} = \rho \, L_{(\nu \nu \rho)} \frac{dp_{\alpha}}{dt} + L_{(\nu \nu \rho \mu \nu)} \, E_{\alpha}^{(\mu \nu)} - T^{-1} \, L_{(\nu \rho \sigma)} \, \frac{\partial T}{\partial \xi_{\sigma}} +$$
Introducing the phenomenological equations (6.8) - (6.15) in the expression (3.27) we obtain for the entropy production the form

\[
\sigma^{(\epsilon)} = T^{-1} \left\{ \rho^2 L(p_{pp}) \left[ \frac{dp}{dt} \right]^2 + L(p_{pp}) \left[ (E^{(int)})^2 - 2 T^{-1} L(p_{\alpha\beta}) \frac{\partial T}{\partial x_{\alpha}} \right]^2 \right. \\
+ \rho^2 L(H_{MM}) \left[ \frac{dm}{dt} \right]^2 + L(H_{MM}) \left[ (B^{(int)})^2 + T^{-2} L(q_{\alpha\beta}) \left( \frac{\partial T}{\partial x_{\alpha}} \right)^2 \right] \\
+ \sum_{j,k=1}^{n-1} L_{(p)_{ij}} X^{(k)} \cdot X^{(j)} + \sum_{l,k=1}^{r} L_{(C)_{jk}} A^{(l)} A^{(k)} + \sum_{k=1}^{n-1} L_{(E)_{ik}} X^{(k)} \cdot \left( \frac{d\xi}{dt} \right)^2 + 3 \eta_v \left[ \frac{d\xi}{dt} \right]^2 - 2 T^{-1} \sum_{k=1}^{n-1} L_{(p_{\alpha\beta})} X^{(k)} \cdot \frac{\partial T}{\partial x_{\alpha}} \right. \\
+ \sum_{j=1}^{n-1} L_{(p_{ij})} \left( \frac{dp}{dt} \right) \left. \left[ \frac{dm}{dt} + \frac{\partial T}{\partial x_{\alpha}} \right] \right\}.
\]
\[ + 2 \sum_{k=1}^{n-1} L^{(int)^k}_{(PD)} \mathbf{X}^{(k)} \cdot \mathbf{E}^{(int)} \].

(6.16)

From (6.16) it is seen that there are no contributions due to the cross effects among magnetic relaxation phenomena and the other irreversible phenomena, because fluxes and thermodynamic forces of different tensorial character (polar or axial) do not couple and from (6.6) the phenomenological coefficients \( L^{(int)}_{(PV)}, L^{(int)^{me}}_{(MV)}, L^{(int)^{e}}_{(MV)}, L^{(int)^{k}}_{(MV)} (k = 1, 2, \ldots, n - 1) \) vanish.

In (6.16) the terms with \( \left( \frac{dp}{dt} \right)^2 \) and \( (\mathbf{E}^{(int)})^2 \) are connected with entropy production due to dielectric relaxation, the term with \( \mathbf{E}^{(int)} \cdot \text{grad} \mathbf{T} \) arises from the cross effects among dielectric relaxation and heat conduction, the terms with \( \left( \frac{dm}{dt} \right)^2 \) and \( (\mathbf{B}^{(int)})^2 \) are connected with entropy production due to magnetic relaxation, the terms with \( (\text{grad} \mathbf{T})^2, \mathbf{X}^{(k)} \cdot \mathbf{X}^{(j)} (k, j = 1, 2, \ldots, n - 1), A^{(l)} A^{(h)} (l, h = 1, 2, \ldots, r) \) and \( \left( \frac{d \delta_{ab}}{dt} \right)^2, \left( \frac{d \delta}{dt} \right)^2 \) are due to the affinities conjugate to heat conduction, diffusion flows of matter, chemical reaction rates and viscous flow, respectively. Finally, the terms with \( \mathbf{X}^{(k)} \cdot \text{grad} \mathbf{T} \) and \( \mathbf{X}^{(k)} \cdot \mathbf{E}^{(int)} (k = 1, 2, \ldots, n - 1) \) arise from the cross effects among diffusion of matter and heat conduction and among diffusion of matter and dielectric relaxation.

Because of the nonnegative character of the entropy production it is seen from (6.16) that the phenomenological coefficients satisfy inequalities as (5.16) - (5.18).
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