



MARTINA COSTA REIS

**CONSTITUTIVE MODELING OF ELECTROCHEMICAL SYSTEMS VIA THE
MÜLLER-LIU ENTROPY PRINCIPLE**

***MODELAGEM CONSTITUTIVA DE SISTEMAS ELETROQUÍMICOS ATRAVÉS DO
PRINCÍPIO DE ENTROPIA MÜLLER-LIU***

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Orientador/Supervisor: Prof. Dr. Adalberto Bono Maurizio Sacchi Bassi

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PRINCÍPIO DE ENTROPIA MÜLLER-LIU***

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SACCHI BASSI.**

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5. Reis, M.C., Bassi, A.B.M.S.; Reactive continuum mixtures under the influence of electromagnetic fields in *Progress in Turbulence V*. Eds.: Talamelli, A., Oberlack, M., Peinke, J., Springer: Berlin, 2013.
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Abstract

CONSTITUTIVE MODELING OF ELECTROCHEMICAL SYSTEMS VIA THE MÜLLER-LIU ENTROPY PRINCIPLE- This work concerns the thermodynamics of electrochemical systems. Exploiting the principles of constitutive theory, few expedient assumptions, and, in special, the Müller-Liu entropy principle, a thermo-electrochemical continuum model is proposed for electrolyte solutions as well as for the bulk and double layer regions of an electrochemical system. The influence of ion-ion and ion-solvent interactions on the mixture dynamics is taken into account through the thermodynamics of polar materials and balance laws for an electrochemical system are accordingly stated. In addition, phenomenological equations are schemed for a dilute and isotropic electrolyte solution, and the conditions for local thermodynamic equilibrium of bulk and double layer regions are investigated. Comparing the residual entropy inequalities obtained for each region of an electrochemical system, it is shown that some mechanisms develop only in the double layer, such as the thermal diffusion, thermoelectricity and electrophoresis phenomena. As a consequence, the local thermodynamic equilibrium state in the double layer requires stricter conditions than in the bulk. Although the constitutive equations are the simplest possible, the constitutive models proposed for the double layer and bulk regions are physically consistent and more comprehensive than the usual models since the emerging equations do not constrain themselves to equilibrium neither limiting conditions. Therefore, the thermodynamic description provided in this work may stimulate chemists and chemical engineers to take advantage of it to study the flow of ions and other chemical species across cell membranes, ionic mobility in bio and geological media, and processes whose heat and mass transfers are enhanced by electromagnetic fields.

KEYWORDS: Thermodynamic modeling, Electrochemistry, Müller-Liu entropy, diffusion-mathematical models, mechanics of continuous media.

RESUMO

MODELAGEM CONSTITUTIVA DE SISTEMAS ELETROQUÍMICOS ATRAVÉS DO PRINCÍPIO DE ENTROPIA MÜLLER-LIU- Este trabalho descreve a termodinâmica de sistemas eletroquímicos. Explorando os princípios da teoria constitutiva, algumas hipóteses *ad hoc* e, em especial, o princípio de entropia Müller-Liu, modelos termo-eletroquímicos são propostos para soluções eletrolíticas e para as regiões de *bulk* e dupla camada de um sistema eletroquímico. A influência das interações íon-íon e íon-solvente sobre a dinâmica da mistura é considerada através da termodinâmica de contínuos polares e as equações de balanço são apropriadamente postuladas. Além disso, equações fenomenológicas são apresentadas para uma solução eletrolítica diluída e isotrópica e as condições para o equilíbrio termodinâmico local do *bulk* e da dupla camada são investigadas. Comparando-se as desigualdades residuais de entropia obtidas para cada região, foi demonstrado que alguns processos, tais como os fenômenos de difusão térmica, termoeletricidade e eletroforese, desenvolvem-se somente na dupla camada. Consequentemente, o estado de equilíbrio termodinâmico local na dupla camada requer condições termodinâmicas mais severas do que no *bulk*. Apesar das equações constitutivas serem as mais simples possíveis, os modelos constitutivos propostos para as regiões de dupla camada e *bulk* são fisicamente consistentes e mais abrangentes do que os modelos eletroquímicos usuais, visto que as equações e relações termodinâmicas obtidas não se limitam às condições limites e nem de equilíbrio. Portanto, a descrição termodinâmica mostrada neste trabalho pode estimular químicos e engenheiros químicos a usar a abordagem contínua no estudo da mobilidade iônica em meios bio e geológicos, fluxos de íons e de outras espécies químicas através de membranas e processos cujas transferências de calor e massa são intensificadas por campos eletromagnéticos.

PALAVRAS-CHAVE: Modelagem termodinâmica, eletroquímica, entropia Müller-Liu, difusão- modelos matemáticos, mecânica dos meios contínuos.

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List of Symbols

$\bar{\kappa}$	Undistorted configuration
$\bar{\mu}_a$	Chemical potential of a
\bar{D}	Traceless part of D
Λ^ω	Lagrange multiplier of spin
Λ^ν	Lagrange multiplier of velocity
ν_a	Rotational diffusion velocity of a
ω_a	Local angular velocity of a
ϕ	Extra entropy flux
Φ^γ	Local flux of γ
Φ_a	Entropy flux of a
τ_a	Angular momentum production density of a
ϖ_a	Angular velocity of a relative to vorticity
C_a	Total coupling stress tensor of a
D	Stretching tensor
I_a	Inertia momentum tensor of a
T_a	Total stress tensor of a
χ	Motion of a material body
δ_{ij}	Kronecker delta
ϵ_a	Energy production density of a

ϵ_o	Permittivity of free space
η_a	Entropy density of a
γ	Local arbitrary physical quantity
γ^m	m -th electric susceptibility
γ_t	History function of a quantity γ
$\hat{\mathbf{t}}$	Dual vector associated to the skew-symmetric part of the total stress tensor
κ_t	Current configuration
Λ^ρ	Lagrange multiplier of mass
Λ^ε	Lagrange multiplier of energy
Λ^{ξ_a}	Lagrange multiplier of mass concentration
Λ^G	Lagrange multiplier of Gauss
$[[\gamma]]$	Jump of γ across the discontinuity surface
\mathbb{R}	One-dimensional space of real numbers
\mathbf{a}_a	Acceleration of a
\mathbf{B}	Magnetic flux vector
\mathbf{b}_a	Mechanical body force density of a
\mathbf{D}	Electric displacement vector
\mathbf{E}^{ef}	Effective electric field
\mathbf{E}_a	Electric field acting on a
\mathbf{H}	Magnetic field
\mathbf{h}_a	Heat flux of a
\mathbf{i}_a	Electric current density of a due to the diffusive motion
\mathbf{j}_a	Diffusive flux of a
\mathbf{l}_a	Mechanical coupling body force density of a

\mathbf{M}	Magnetization field
\mathbf{m}_a	Linear momentum production density of a
\mathbf{n}	Unit normal vector
\mathbf{n}_m	Unit vector in the direction m
\mathbf{o}_o	Position vector of an arbitrary fixed point
\mathbf{P}_a	Electric polarization field acting on a
\mathbf{s}_a	Spin density of a
\mathbf{t}_a	Total stress vector of a
\mathbf{u}_a	Translational diffusion velocity of a
\mathbf{v}	Barycentric velocity
\mathbf{v}_a	Velocity of a
\mathbf{w}	Vorticity
\mathbf{X}_a	Material coordinate of a
\mathbf{x}_a	Spatial coordinate of a
κ	Configuration
\mathcal{B}	Material body
\mathcal{B}_a	a -th constituent of the mixture
\mathcal{C}	Arbitrary constitutive quantity
\mathcal{E}	Three-dimensional Euclidean space
$\mathcal{F}_{\mathcal{G}}$	Global flux of \mathcal{G}
\mathcal{G}	Global arbitrary physical quantity
$\mathcal{L}(V)$	General linear transformation
$\mathcal{M}_{\kappa}(V)$	Material symmetry group
$\mathcal{M}_{\kappa}^1(V)$	Material symmetry group of transversely isotropic bodies

$\mathcal{M}_\kappa^2(V)$	Material symmetry group of orthotropic bodies
$\mathcal{O}(V)$	Orthogonal group
$\mathcal{O}^+(V)$	Proper orthogonal group
\mathcal{P}	Finite part of a continuous body
$\mathcal{P}_\mathcal{G}$	Global production of \mathcal{G}
\mathcal{Q}	Orthogonal transformation
\mathcal{R}	Response functional
$\mathcal{SL}(V)$	Special linear group
$\mathcal{S}_\mathcal{G}$	Global supply of \mathcal{G}
\mathcal{T}	Arbitrary linear transformation
$\mathcal{U}(V)$	Unimodular group
\mathcal{V}	Volume of a part \mathcal{P}
\mathcal{W}	Newtonian space-time
1	Unit tensor
skw	Skew-symmetric part of a second-order tensor
sym	Symmetric part of a second-order tensor
\mathfrak{U}_r	Symmetrical of chemical affinity of a chemical reaction r
μ_a	Electrodynamic potential of a
μ_o	Permeability of free space
$\nabla\bar{\omega}$	Traceless part of $\nabla\omega$
Π	Residual entropy production
π^γ	Local production of γ
π_a	Entropy production density of a
ρ_a	Mass density of a

σ^γ	Local supply of γ
σ_a	Entropy supply density of a
\triangleleft	Frame of reference
\star	Change of reference frame
θ	Empirical temperature
Υ_r	Rate of conversion of a chemical reaction r
ε_a	Internal energy density of a
φ	Electric potential
ξ_a	Mass concentration of constituent a
c_{aj}	Velocity of mass conversion from a to j
c_a	Mass production density of a
da	Area element
dv	Volume element
f^{emf}	Electromotive force
m	Mass distribution of a finite part
$O(2)$	Terms of order bigger than one
p	Hydrostatic pressure
q_a	Charge density of a
r_a	Mechanical energy supply density of a
t	Time
u_n	Propagation speed of the singular surface
V	Vector space
X_a	Particle of a
z_a	Charge <i>per</i> unit mass of a

1 Introduction

Since the mid-19th century, when the first electrochemical experiments were done, the study of the dynamic behavior of ions in electric-conducting solutions has been one of the major fields of study in Physical Chemistry. In 1887, van't Hoff [69] published a work, reporting deviations in the values of freezing points, boiling points, osmotic pressure, and vapor pressures for electrolyte solutions. Few months later, Arrhenius [1] suggested that charged chemical species should be present in electric-conducting solutions, even in the absence of external electric fields.

From van't Hoff and Arrhenius' works, several studies [76] showed that the interionic forces should play an important role in the physico-chemical properties of electrolyte solutions. This became more evident when the results obtained from conductometric and amperometric experiments indicated that the nature and concentration of ions change the conductivity, viscosity, and mass transport of solutions. Since then, many attempts [3] have been made to derive theories of interionic interaction, being most of them based on statistical mechanics whose focus relies on the time-averaged spatial distribution of ions. According to these models, a volume element of the solution is completely filled with a dielectric continuum, where discrete point charges, regarded as hard spheres, are immersed. Evidently, these approximations are shortcomings because real ions are not hard spheres, and the solvent is not a dielectric continuum. However, in the limit of very dilute solutions, these approximations are acceptable, as Debye and Hückel demonstrated in reference [18].

In the Debye-Hückel model, thermodynamic properties of the solution are calculated from the electrostatic interaction energy between an ion, chosen as a reference one, and all other ions in solution. In order to determine this interaction energy, one considers that the averaged distribution of ions around the reference ion follows the Boltzmann distribution law, whereas the relation between the charge density of each ion and the electrostatic potential is given by the Poisson's equation. The combination of these two equations leads to the so-called Poisson-Boltzmann equation, which, in general, is solved by numerical or series methods. To make further progress, Debye and Hückel focused on systems where the average electrostatic potential energy is much smaller than the ther-

mal one, allowing the Poisson-Boltzmann equation to be linearized and solved analytically. However, despite the great contribution of the Debye-Hückel model to the development of a coherent interionic theory, it provides theoretical results that are in good agreement with experimental data for only very dilute solutions.

In view of the limitations of the Debye-Hückel model, other theoretical models based on more realistic assumptions have been developed. Some of these models, for instance, are founded on the use of the unlinearized Poisson-Boltzmann equation [25, 27, 51], the virial expansion of the excess Gibbs energy (Pitzer equation) [52, 53], and the intermolecular potential theory (McMillan-Mayer theory) [38]. Nevertheless, despite the impressive success reached by these models, the lack of data about ionic and molecular *radii*, dielectric saturation, and electrostriction effects has hindered their application in more complex systems. Even with the advances in computational molecular dynamics, the determination of thermodynamic properties of simple electrolyte solutions is frequently a long and tedious process as it requires several computer cycles *per* chemical species. As a result, continuum models for mixtures have become an alternative approach, especially with the progresses obtained in electrorheological fluids and continuum mixtures models during the last decades. For instance, Maugin and co-authors [42, 43] developed various continuum models to study the behavior of polyelectrolytes in non-homogeneous velocity gradient flows, either in the presence or absence of electric fields. Moreover, several continuum models have been developed in order to associate the material properties of electrorheological fluids to measurable macroscopic quantities.

The literature provides numerous works about constitutive modeling of polyelectrolytes, ionic polymer-metal composites, and electrorheological fluids with practical applications in automotive industries, polishing solutions, biomedical devices *etc.* In references [55, 77], phenomenological models of ion transport were given with basis in linear irreversible thermodynamics. In reference [50], Placidi and co-authors provided a continuum model for polymer-metal composites, where chemically induced deformations are described through a distortion field induced by solvated ions. However, although several continuum models are available for electrolyte mixtures, the most fundamental aspects of electrolyte dynamics have not been sufficiently explored. Hence, the aim of this work is to propose a general thermo-electrochemical theory to investigate the diffusive, reactive, and advective structures of dilute electrolyte solutions. These solutions present close connection with the fields of surface chemistry (the stability of many colloids depends on the interionic interactions in solution), biochemistry (blood is an ion carrier and changes in the ions concentrations affect the blood flow), metallurgy (successful electroplating processes require the control of ions transport in solutions), and geology (soils with high concen-

tration of ions flow faster), and differ from the polyelectrolyte ones because they do not contain ionic or polarizable macromolecules, but only monoatomic or molecular ions of low molecular weight.

Chapter 2 is devoted to the presentation of the foundations of continuum thermodynamics. Particularly, attention is focused on the continuum concept, basic laws of Physics, and principles of the constitutive theory. Here, the concept of continuum particle is also differentiated from the classical concept of particles in Chemistry and Physics. In Chapter 3, the dynamics of reacting ionic mixtures is outlined by emphasizing the relation between inner structure of the mixture and interionic interactions. In turn, the next two chapters are dedicated to exploitation of the Müller-Liu entropy principle for electrochemical systems. In Chapter 4, thermodynamic restrictions on constitutive functions and their consequences for dilute electrolyte solutions whose constituents present the same temperature field are shown. In order to assess the implications of this constitutive theory for electrolyte solutions, some results are compared with those of classical thermostatics. Finally, in Chapter 5, some comments are addressed to the structure of electrochemical systems, and continuum models for the double layer and bulk regions are developed. From these models, transport phenomena in the bulk and double layer are investigated and compared, and the implications of material equations on the properties of each region are discussed.

Despite the continuum models proposed are limited to electrochemical systems, the results presented can be extended to study the flow of ions and other chemical species across cell membranes, ionic mobility in bio and geological media, and processes whose heat and mass transfers are enhanced by electromagnetic fields.

2 Foundations of Continuum Thermodynamics

Continuum thermodynamics is a branch of physical science concerned with deformations and motions of continuous material media under the influence of mechanical, electromagnetic, thermal, and chemical sources. Since mid-1960, the continuum approach for material bodies has been an important theoretical tool for engineers and applied mathematicians because it provides a very useful and reliable representation for macroscopic bodies whose characteristic dimensions are much bigger than the molecular ones. On the other hand, most of the chemists are still not aware of the methods of continuum thermodynamics as an alternative to traditional thermodynamic theories.

The subsequent sections are destined to present the basic concepts of continuum thermodynamics whose phenomenology is restricted to the Newtonian space-time,

$$\triangleleft : \mathcal{W} \rightarrow \mathcal{E} \times \mathbb{R}, \quad (2.0.1)$$

where \triangleleft is a frame of reference or observer, \mathcal{E} is the three-dimensional Euclidean space, and \mathbb{R} is the one-dimensional space of real numbers. For a complete overview of the foundations of continuum thermodynamics, the readers are advised to consult the references [29, 35, 47, 68].

2.1 The continuum concept

On a small scale, an aluminum sheet is a collection of discrete aluminum atoms stacked on one another in a repetitive lattice. On an even smaller scale, the aluminum atoms consist of a core of protons and neutrons around which electrons move. Thus, clearly, matter is not continuous. However, if the continuum concept of matter is accepted, one ignores the discrete composition of material bodies and assumes that the mass of such bodies is distributed throughout, so filling the whole space that it occupies. In keeping with this continuum model, matter may be divided indefinitely into smaller and smaller portions,

each of which retains all the physical properties of the original body. Accordingly, physical quantities, such as energy and velocity, are ascribed to every single point of the region of space that the body occupies as continuous functions or piecewise continuous functions of space and time.

In continuum thermodynamics, the mass of a body is a fundamental physical property, and it is *a priori* assigned as a part of the specification of a continuous body. Hence, consider a finite part \mathcal{P} of a body. For all points inside \mathcal{P} , the mass density ρ is defined by the limit

$$\rho(\cdot) = \lim_{\mathcal{V} \rightarrow 0} \frac{m}{\mathcal{V}} > 0, \quad (2.1.1)$$

where m is a non-negative scalar measure, named the mass distribution of \mathcal{P} , \mathcal{V} is the volume of \mathcal{P} , and ρ is independent of the size of \mathcal{P} , but depends on position and time.

Moreover, classical continuum thermodynamic theories, also known as local continuum theories, are based on the fundamental hypothesis that the state of a body at any material point is influenced only by the infinitesimal neighborhood of that point. This assumption eliminates the long-range effect of loads on the motion and on the evolution of the state of the body, as well as ignores the effect of long-range interactions among physical particles. In fact, this premise is valid for a class of materials where experimental probes measure the average outcome on some spatial and/or temporal domains over which non-local variations of fields are small and external applied loads are often very smooth. But, for another class of materials, such as blood, polymeric substances, solids with micro-cracks, fluids in a state of turbulence, liquid crystals *etc.* classical continuum theories do not give reliable predictions since the individual response of the constituents of the body becomes important, so that the hypothesis of locality fails.

The departure from local theories begins with polar theories, initially proposed by the Cosserat brothers in 1909 [15]. According to them, the material points are considered geometrical points that possess properties similar to rigid particles (micropolar media) or deformable particles (micromorphic media). These properties are then introduced through independent degrees of freedom provided by a set of vectors or even by tensors of order bigger than two, resulting in higher-order polar theories. Nevertheless, this process soon ceases to be useful because the consequent field equations become increasingly complicated. Conversely, polar theories of the first order (micropolar and micromorphic theories) are simple enough and have found important applications in a variety of materials as previously mentioned, although they are not expected to bridge the gap between macroscopic and atomic physics. For this purpose, it is necessary to construct non-local theories in which a finite neighborhood of a material point influences the response at that point or

even mesoscopic theories, where macroscopic quantities are obtained from a statistical distribution function.

2.2 Motion of a body

The starting point of continuum thermodynamics is a material body \mathcal{B} , which consists of infinite material points or particles X , considered primitive elements. In order to describe the presence of a continuum body \mathcal{B} in the space, one maps \mathcal{B} on a region of the three-dimensional Euclidean space \mathcal{E} ,

$$\kappa : \mathcal{B} \rightarrow \mathcal{E}, \quad (2.2.1)$$

for some configuration κ . Usually, κ is some particular configuration of \mathcal{B} referred to as the reference configuration, while κ_t is the current configuration at time t .

Once the presence of \mathcal{B} in the space has been defined, the motion of a material body may be investigated. In the reference configuration, a referential or material coordinate \mathbf{X} is assigned to the particle X . Nonetheless, when a continuum body moves or deforms with time, the body particles found at positions \mathbf{X} in the reference configuration κ occupy new positions \mathbf{x} after certain time t . These new positions occupied by the body particles in the current configuration κ_t are denominated spatial coordinates. Then, the motion χ of a particle can be mathematically described as

$$\begin{aligned} \chi : \mathcal{B}_\kappa \times \mathbb{R}^+ &\rightarrow \mathcal{B}_t, \\ (\mathbf{X}, t) &\mapsto \mathbf{x} = \chi(\mathbf{X}, t), \end{aligned} \quad (2.2.2)$$

such that χ is invertible,

$$\mathbf{X} = \chi^{-1}(\mathbf{x}, t), \quad (2.2.3)$$

and \mathcal{B}_κ and \mathcal{B}_t represent the body \mathcal{B} in the configuration κ and κ_t , respectively. In other terms, Equation (2.2.3) implies that, if all positions \mathbf{x} in \mathcal{B}_t and the motion $\chi(\mathbf{X}, t)$ are known, the positions of the particles in the reference configuration can be determined.

Evidently, different observers may measure space-time events in different ways. However, as this work only deals with the framework of Newtonian mechanics, the distance and time intervals between events must have the same values in two reference frames whose relative motion is rigid. That is, let a change of reference frame, \star , from a non-

starred observer to a starred observer

$$\begin{aligned} \star : \mathcal{E} \times \mathbb{R}^+ &\rightarrow \mathcal{E} \times \mathbb{R}^+ , \\ \star : (\mathbf{x}, t) &\mapsto (\mathbf{x}^*, t^*) , \end{aligned} \tag{2.2.4}$$

such that the observers follow an event in terms of position and time with proper measuring devices. Of course, they may use different measuring instruments and obtain distinct results for the same event. But, if one imposes that these observers must use measuring devices with the same units of measure, they should obtain the same distance and time lapse between two events under consideration, although the values of the parameters measured may be different. Mathematically, this is expressed as

$$\begin{aligned} \mathbf{x}^* &= \mathcal{Q}(t) (\mathbf{x} - \mathbf{x}_o) + \mathbf{c}(t) , \\ t^* &= t + a , \end{aligned} \tag{2.2.5}$$

where $a \in \mathbb{R}^+$, $\mathbf{x}_o \in \mathcal{E}$, $\mathbf{c}(t)$ is an arbitrary time-dependent vector, and $\mathcal{Q}(t) \in \mathcal{O}(V)$, such that $\mathcal{Q}(t)$ is a time-dependent orthogonal transformation and $\mathcal{O}(V)$ is the orthogonal group on a vector space V .

A change of reference frame defined by Equation (2.2.5) is referred to as a Euclidean transformation, the most general form of a time-dependent rigid transformation between two reference systems moving relative to each other. Then, in the Newtonian space-time one says that a physical quantity is objective or form-invariant under a change of observers given by Equation (2.2.5) if ¹

$$\begin{aligned} f^*(t^*) &= f(t) , \\ \mathbf{f}^*(t^*) &= \mathcal{Q}(t) \mathbf{f}(t) , \\ \mathbf{F}^*(t^*) &= \mathcal{Q}(t) \mathbf{F}(t) \mathcal{Q}(t)^T , \end{aligned} \tag{2.2.6}$$

¹ The definition of objectivity of an observable quantity is more general. An observable quantity f is said to be form-invariant or objective with respect to some class of change of frame, if

$$f(\cdot^*) = \mathcal{Q}^\dagger f(\cdot) ,$$

where \mathcal{Q}^\dagger is an induced linear transformation on the m -th order tensor space of f . If the class of change of frame is given by Equation (2.2.5), then f is form-invariant or objective in relation to Euclidean transformations and $\mathcal{Q}^\dagger = \mathcal{Q}(t)$.

where $f(t)$, $\mathbf{f}(t)$, and $\mathbf{F}(t)$ are arbitrary scalar, vector, and second-order tensor physical quantities dependent on time. In other terms, if the physical quantities noted by two different observers for the same event are interrelated through the transformation rules (2.2.6), then they are objective or form-invariant.²

Besides, one may further restrict the generality of Equation (2.2.5) by imposing that $Q(t)$ is constant in time and $\mathbf{c}(t)$ is linear in time. Then, Equation (2.2.5) is rewritten as

$$\begin{aligned}\mathbf{x}^* &= Q(\mathbf{x} - \mathbf{x}_o) + \mathbf{y}t + \mathbf{c}_o, \\ t^* &= t + a,\end{aligned}\tag{2.2.7}$$

where \mathbf{y} and \mathbf{c}_o are arbitrary constant vectors in the three-dimensional Euclidean space \mathcal{E} . Equation (2.2.7) is called a Galilean transformation, a subclass of Euclidean transformations. Accordingly, every movement can be written in a unique way as a composition of rotation, translation, and uniform motion.

2.3 General balance statements

As a result of the continuum hypothesis, a physical property \mathcal{G} assigned to a finite part \mathcal{P}_t of a continuum body \mathcal{B}_t , such as energy, linear momentum or entropy, is defined by some equation analogous to Equation (2.1.1), *i.e.*, as a density *per* unit mass or area at every point inside \mathcal{P}_t . In addition, any physical property may change with time through three kinds of mechanisms: the first one, named supply $\mathcal{S}_{\mathcal{G}}$, whose actions are transmitted at a distance from outside of the body, so that the whole volume of \mathcal{B} is directly influenced; the second mechanism, named flux $\mathcal{F}_{\mathcal{G}}$, whose actions are transmitted from outside into the body through its surface; and the last one, named production $\mathcal{P}_{\mathcal{G}}$, whose actions occur inside the body itself. While the first and the last mechanisms are expressed by mass densities, the second one is given by surface densities. Hence, the time rate of change for a physical variable \mathcal{G} of the body is written as

$$\frac{d\mathcal{G}}{dt} = \mathcal{S}_{\mathcal{G}} + \mathcal{F}_{\mathcal{G}} + \mathcal{P}_{\mathcal{G}},\tag{2.3.1}$$

or, by the transport theorem [35],

² Hereafter, the adjectives *objective* and *form-invariant* will be always used to express objective quantities with respect to Euclidean transformations.

$$\frac{\partial \gamma}{\partial t} + \operatorname{div}(\gamma \otimes \mathbf{v} - \Phi^\gamma) - \sigma^\gamma - \pi^\gamma = 0, \quad (2.3.2)$$

where $\mathcal{G} = \int_{\mathcal{P}_t} \gamma(\mathbf{x}, t) dv$, $\mathcal{S}_\mathcal{G} = \int_{\mathcal{P}_t} \sigma^\gamma(\mathbf{x}, t) dv$, $\mathcal{F}_\mathcal{G} = \int_{\partial \mathcal{P}_t} \Phi^\gamma(\mathbf{x}, t) \mathbf{n} da$, and $\mathcal{P}_\mathcal{G} = \int_{\mathcal{P}_t} \pi^\gamma(\mathbf{x}, t) dv$ are equivalent to the sum of individual contributions of all particles contained in a part \mathcal{P}_t of \mathcal{B}_t , dv and da are volume and area elements, respectively, \mathbf{v} is the barycentric velocity, and \mathbf{n} is the outward unit normal vector to the boundary of the region \mathcal{B}_t . Furthermore, the quantities γ , σ^γ , and π^γ are tensor fields of order m , while Φ^γ is a tensor field of order $m + 1$. Of course, if γ is a tensor field of order $m = 0$, the tensor product $\gamma \otimes \mathbf{v}$ should be understood as $\gamma \mathbf{v}$.

Equation (2.3.1) is the general balance equation of a field \mathcal{G} in its integral form, whereas Equation (2.3.2) is the general balance equation valid at a regular point \mathbf{x} . Both equations can be interpreted as asserting that the variation rate of the quantity \mathcal{G} in a part of \mathcal{B}_t is affected by the supply and production of \mathcal{G} , as well as by the flux $\mathcal{F}_\mathcal{G}$ through the boundary region $\partial \mathcal{P}_t$. Then, if the body is isolated, $\mathcal{S}_\mathcal{G} = 0$, $\mathcal{F}_\mathcal{G} = 0$, and $\mathcal{P}_\mathcal{G} = 0$, such that \mathcal{G} is constant in time and it is said to be conserved.

One can extend the observations above to a surface in a material body, where the physical quantity experiences a discontinuity. Across this surface, called singular surface, the general balance equation is

$$[[\rho \gamma (\mathbf{v} \cdot \mathbf{n} - u_n)]] - [[\Phi^\gamma]] \cdot \mathbf{n} = 0, \quad (2.3.3)$$

where $[[\gamma]] = \gamma^+ - \gamma^-$ stands for the jump of γ across the discontinuity surface, u_n is the normal velocity or propagation speed of the singular surface, and, for the sake of convention, \mathbf{n} points into the positive-side of the surface. Nonetheless, if $u_n = \mathbf{v} \cdot \mathbf{n}$, then the surface is termed material surface and Equation (2.3.3) becomes

$$[[\Phi^\gamma]] \cdot \mathbf{n} = 0. \quad (2.3.4)$$

Physically, material surfaces differ from singular ones because the former are constituted by the same particles of the material body at all times, whereas singular surfaces do not consist of the same particles of \mathcal{B} at all instants t . Some examples of singular surfaces are the interface between two immiscible liquids, the phase equilibrium between two fluids, the shock front in supersonic flows, among others.

2.4 Principles of constitutive theory

In continuum mechanics, material characterization is made by the establishment of some functional relations, called constitutive equations, among the constitutive variables. The selection of these variables and the restrictions on these equations are based on the principles of constitution as well as on the basic laws of mechanics [29, 35, 37, 68]. Therewith, one can restrict the generality of the constitutive functions and, if possible, to reduce them to a small number of coefficients whose values can be experimentally measured.

The principles of constitutive theory are:

PRINCIPLE OF CAUSALITY

The principle of causality is intended for the selection of the independent constitutive variables of a material subjected to certain actions. In a material subjected to mechanical, thermal, electromagnetic and chemical sources, some observable changes may occur. At the outset, one can select a set of independent observable changes as the effects produced inside the body by such sources. Then, this is the set of independent constitutive variables for a limited class of physical and chemical phenomena in the material. Once the independent constitutive variables are selected, all other material properties included in the balance equations are considered dependent constitutive variables, defined from the set of independent ones. Note that the balance equations also include external supplies, which are considered known actions. Usually, it is assumed that dependent constitutive variables are not explicitly dependent on external supplies.

Of course, the decision about including a constitutive variable into the dependent or independent set is taken in agreement with the physical effects that one intends to evaluate. If a given variable at (\mathbf{x}, t) can be solved in terms of other variables of the problem, an explicit functional mapping from the set of independent variables to the dependent one can be settled. In general, this mapping is not one-to-one, but, for a large class of materials, the relation cause-and-effect is well-established within the domain of the experiment. Consequently, such relation can be used to distinguish the set of independent constitutive variables from the set of dependent ones.

For instance, in a material body, thermomechanical effects are produced by motion and thermal changes. Thus, the thermomechanical independent variables are usually the temperature, velocity and its gradient, acceleration, and mass density. If the body responds to electromagnetic *stimuli*, it may be polarized and/or magnetized, and it even may conduct electricity. These effects result from redistribution and motion of bound and free charges and, therefore, it seems reasonable to consider the electric polarization vector,

the electric current vector, and the density of free charges as independent variables. Here, it is worthwhile to point out that different constitutive models can arise for a given material since the choice of independent and dependent variables is not unique.

PRINCIPLE OF DETERMINISM

The principle of determinism only considers the dependence of the material behavior at a particle X on particles $Y \in \mathcal{B}$, and past and current events. Accordingly, the future phenomena concerning the behavior of the body are fully determined and observable once all past motions of the body are known. As a direct result, quantum mechanical phenomena are excluded. Complying with this principle, constitutive equations may be written as

$$\mathcal{C}(X, t) = \mathcal{R}(\gamma_t(Y, t - s), X), \quad (2.4.1)$$

where \mathcal{C} denotes an arbitrary constitutive quantity, \mathcal{R} is the response functional or constitutive functional of \mathcal{C} , γ_t is the history of γ up to time t , and $s \in [0, \infty)$ stands for the time-coordinate pointed from the present time t into the past.

Equation (2.4.1) allows the description of non-local effects as well as memory effects in \mathcal{B} . The argument γ_t runs through all instants in the past, from $t - \infty$ to the present time $t - 0$, describing the memory or remembering capacity of a material in relation to γ_t . In turn, the dependence of the response functional on every material point of the body $Y \in \mathcal{B}$ corresponds to non-local effects. Finally, the explicit dependence of \mathcal{R} on X means the inhomogeneity of the material body, that is, the response functional depends on the particle X . However, if a response functional of \mathcal{B} is the same for all X to a given reference configuration,

$$\mathcal{C}(\cdot, t) = \mathcal{R}(\gamma_t(Y, t - s)), \quad (2.4.2)$$

and \mathcal{B} is called a homogeneous body. In other terms, for an inhomogeneous body, the constitutive quantity is expressed by (2.4.1), while for a homogeneous one, the constitutive quantity is given by (2.4.2).

PRINCIPLE OF EQUIPRESENCE

This principle assigns equal rights to all response functionals to depend on all independent constitutive variables. The principle of admissibility together with various approximations may eliminate the dependence on some of these variables. But, until such is the case, one should employ the same list of independent constitutive variables in all response functionals.

PRINCIPLE OF MATERIAL OBJECTIVITY

Just as constitutive quantities depend on the material point and time, they are also dependent on the choice of the reference frame,

$$\mathcal{C}(X, t, \star) = \mathcal{R}(\gamma_t(Y, t - s), X, \star) . \quad (2.4.3)$$

Nonetheless, the principle of material objectivity imposes that the response functional of any objective constitutive quantity \mathcal{C} must be the same for any two observers related by (2.2.5),

$$\mathcal{R}^*(\cdot) = \mathcal{R}(\cdot) . \quad (2.4.4)$$

Clearly, for any non-objective quantity, such as total energy density, velocity, acceleration, the spin tensor *etc.*, Equation (2.4.4) does not need to hold. As a consequence, they need to be replaced by objective quantities in the set of constitutive variables, which can be done by adding, subtracting or associating other non-objective quantities [35].

Besides imposing that constitutive quantities are independent of the observers, the principle of material objectivity brings other immediate consequences on the response functionals. For the sake of simplicity, suppose that γ_t is a scalar function e.g. temperature or mass density. Then, one has

$$\mathcal{R}(\gamma_t^*(Y, t^* - s), X, t^*) = \mathcal{Q}(t) \mathcal{R}(\gamma_t(Y, t - s), X, t) , \quad (2.4.5)$$

or by recalling Equation (2.2.6)₁,

$$\mathcal{R}(\gamma_t(Y, t - s), X, t^*) = \mathcal{Q}(t) \mathcal{R}(\gamma_t(Y, t - s), X, t) . \quad (2.4.6)$$

Choosing $\mathcal{Q}(t) = 1$ and $c(t) = \mathbf{x}_o$, it follows from Equation (2.2.5) that

$$\mathbf{x}^* = \mathbf{x}, \quad t^* = t + a ,$$

for any $a \in \mathbb{R}^+$. Therefore, Equation (2.4.6) takes the form

$$\mathcal{R}(\gamma_t(Y, t - s), X, t + a) = \mathcal{R}(\gamma_t(Y, t - s), X, t) , \quad (2.4.7)$$

whence one concludes that the response functionals cannot depend explicitly on time. For this reason, the time dependence in (2.4.1) and (2.4.2) has been omitted since the explicit dependence of \mathcal{R} on t would imply the dependence on the choice of the reference frame.

Here, it is worthwhile to remark that the principle of material objectivity should not

to be confused with the term objectivity [20]. The term objectivity denotes transformation properties of given quantities, whereas the principle of material objectivity postulates the complete independence of the response functional of an objective constitutive quantity on the reference frame.

PRINCIPLE OF MATERIAL SYMMETRY

Crystallographic orientations of a body give rise to symmetries in material properties, which must be accounted for in the constitutive functionals. In fact, one should expect that the response functionals at two different configurations κ and κ' should not be identical, unless the material body presents a particular symmetry that makes it impossible to distinguish the configurations κ and κ' . For example, the material properties of a body with cubic symmetry must be invariant in relation to rotation of the reference configuration κ by 90 degrees about one of the crystal axes. Referring to the body configuration after this rotation to as κ' , the configurations κ and κ' are said to be materially indistinguishable, if

$$\mathcal{R}(\cdot) = \mathcal{R}'(\cdot), \quad (2.4.8)$$

and

$$\kappa(\mathcal{B}) \xrightarrow{\mathcal{M}} \kappa'(\mathcal{B}), \quad (2.4.9)$$

where both configurations are associated through a linear material symmetry transformation \mathcal{M} that preserves the volume of the body with respect to κ .³ Thus, physically, the principle of material symmetry indicates that the response functional of \mathcal{C} in relation to a configuration κ of a material body cannot be distinguished from that in a configuration κ' , provided both configurations are related through a material symmetry transformation \mathcal{M} .

Of course, there are many linear transformations for a given configuration κ that satisfy Equation (2.4.9) and imply Equation (2.4.8). One names all of these linear transformations as the material group symmetry, $\mathcal{M}_\kappa(V)$. Hence, a material is called solid if there exists an undistorted configuration $\bar{\kappa}$, such that the material group symmetry is the orthogonal group $\mathcal{O}(V)$ or is contained in it:

$$\mathcal{M}_\kappa(V) \subseteq \mathcal{O}(V). \quad (2.4.10)$$

In turn, a material is a fluid if there exists any configuration κ and $\bar{\kappa}$, where

³ See Appendix I for more information about groups of symmetry.

$$\mathcal{M}_\kappa(V) = \mathcal{U}(V) . \quad (2.4.11)$$

Therefore, unlike solids, fluids do not present a preferred configuration.

One may indeed particularize the symmetry conditions above to describe the material properties of isotropic, anisotropic, and hemitropic bodies. Hereby, one defines:

- An isotropic body is a body whose material group symmetry is either equal to the unimodular group or equal to the orthogonal group,

$$\mathcal{M}_\kappa(V) = \mathcal{O}(V) , \quad \mathcal{M}_\kappa(V) = \mathcal{U}(V) .$$

Otherwise, any other materials whose material group symmetry is not the orthogonal group neither the unimodular group are called anisotropic.

- Generally, anisotropic bodies possess material symmetries that can be represented by directions, lines or planes. In doing so, anisotropic bodies can be defined as transversely isotropic and orthotropic bodies, among other classes of symmetry. For instance, if the material symmetry group satisfies the condition

$$\mathcal{M}_\kappa^1(V) = \{ \mathcal{Q} \in \mathcal{O}(V) \mid \mathcal{Q}\mathbf{n} = \mathbf{n} \} , \quad (2.4.12)$$

$\mathcal{M}_\kappa^1(V)$ presents a preferred direction characterized by \mathbf{n} and, then, the material is said to be a transversely isotropic material. Conversely, if the material symmetry group follows the condition

$$\mathcal{M}_\kappa^2(V) = \{ \mathcal{Q} \in \mathcal{O}(V) \mid \mathcal{Q}(\mathbf{n}_m \otimes \mathbf{n}_m) \mathcal{Q}^T = \mathbf{n}_m \otimes \mathbf{n}_m \} , \quad (2.4.13)$$

where \mathbf{n}_m is a unit vector in the direction m , so $\mathcal{M}_\kappa^2(V)$ preserves the characteristic space of $\mathbf{n}_m \otimes \mathbf{n}_m$. In other terms, $\mathcal{M}_\kappa^2(V)$ maintains three mutually orthogonal lines in the directions \mathbf{n}_1 , \mathbf{n}_2 , and \mathbf{n}_3 . A body with this symmetry is named an orthotropic material.

- A hemitropic body is a body whose material group is the proper orthogonal group $\mathcal{O}^+(V)$,

$$\mathcal{M}_\kappa(V) = \mathcal{O}^+(V) .$$

A body may possess various types of material symmetries for its different properties. For example, an isotropic material with respect to stress and strain may not be isotropic with

respect to another property e.g. electric polarization and displacement vectors. In addition, materials may also be subject to other geometrical and internal constraints, such as rubbery materials, which are incompressible. This is expressed in the constitutive equations by the additional condition that the local volume remains unchanged.

PRINCIPLE OF LOCALITY

According to this principle, the values of the response functional at X are not affected appreciably by the values of the independent constitutive variables at distant points from X . In other words, the principle of locality implies that the greatest contributions to the constitutive response at a material point are due to its neighborhoods. Mathematically, the principle of locality may be expressed in two different ways: the first way, named the hypothesis of smooth neighborhood, describes the spatial dependence of values of γ_t through a Taylor expansion of t about X , and the second one, named the attenuating neighborhood hypothesis, describes the spatial dependence of γ_t by introducing an influence function that evaluates how much the points in a distant neighborhood influence the values of γ_t at a specific material point. As the hypothesis of smooth neighborhood is much more common in continuum thermodynamics than the attenuating neighborhood hypothesis, it is detailed below.

Suppose that the function $\gamma_t(Y, t - s)$ admits Taylor expansions about $X = Y$ for all $t - s$ with $s \in [0, \infty)$,

$$\begin{aligned} \gamma_t(Y, t - s) = & \gamma_t(X, t - s) + \sum_{i_1=1}^3 (Y_{i_1} - X_{i_1}) \gamma_t^{(i_1)}(X, t - s) + & (2.4.14) \\ & \frac{1}{2!} \sum_{i_1=1}^3 \sum_{i_2=1}^3 (Y_{i_1} - X_{i_1}) (Y_{i_2} - X_{i_2}) \gamma_t^{(i_1 i_2)}(X, t - s) + \dots + \\ & \frac{1}{m!} \sum_{i_1=1}^3 \dots \sum_{i_m=1}^3 (Y_{i_1} - X_{i_1}) \dots (Y_{i_m} - X_{i_m}) \gamma_t^{(i_1 \dots i_m)}(X, t - s) + \dots, \end{aligned}$$

where $\gamma_t^{(i_1 \dots i_m)}(X, t - s)$ is the m -th order partial derivative of γ_t relative to the vector components Y_{i_1}, \dots, Y_{i_m} evaluated on X at time $t - s$. If the material point Y is confined in a small enough neighborhood of X , $\gamma_t(Y, t - s)$ can be approximated by truncating Equation (2.4.14) at its first-order directional derivative on X in the direction of Y , viz.

$$\gamma_t(Y, t - s) \approx \gamma_t(X, t - s) + \sum_{i_1=1}^3 (Y_{i_1} - X_{i_1}) \gamma_t^{(i_1)}(X, t - s). \quad (2.4.15)$$

In this case, one says that the material at X for all $t - s$ satisfies the smooth neighborhood hypothesis.

In general, it suffices to assume that the response functional depends only on the history of γ and its first-order gradient. Thus, Equation (2.4.1) becomes

$$\mathcal{C}(X, t) = \mathcal{R} \left(\gamma_t(X, t - s), \gamma_t^{(i_1)}(X, t - s), X \right) \quad (i_1 = 1, 2, 3) . \quad (2.4.16)$$

Of course, for non-local materials, where the effect of long-range intermolecular forces cannot be negligible, Equation (2.4.16) does not hold. In this case, one should introduce higher-order gradients of γ_t . Theories in which the principle of locality is not obeyed are referred to as non-local continuum theories.

PRINCIPLE OF MEMORY

This principle is considered the counterpart of the principle of locality in the time domain. For some materials, physical processes that affected them in a distant past are mostly erased. In other words, these materials possess weak memory, so that the constitutive variables at a distant past do not appreciably affect the values of the response functional at present.

In practical terms, it is extremely rare that a material can remember its whole history whereby was affected since its memory is bounded. Then, instead of using $t - s$ with $s \in [0, \infty)$ as an argument of γ_t , one can proceed analogously to the principle of locality and use a Taylor series to write $\gamma_t(Y, t - s)$ as

$$\begin{aligned} \gamma_t(Y, t - s) = & \gamma_t(Y, t) - s\gamma_t^{(1)}(Y, t) + \frac{1}{2!}s^2\gamma_t^{(2)}(Y, t) - \\ & \frac{1}{3!}s^3\gamma_t^{(3)}(Y, t) + \dots + \frac{1}{m!}(-s)^m\gamma_t^{(m)}(Y, t) + \dots , \end{aligned} \quad (2.4.17)$$

where $\gamma_t^{(m)}(Y, t)$ denotes the m -th partial time derivative of γ_t evaluated at point Y and time t . The use of a Taylor series to express the memory effect of a material body is known as the hypothesis of smooth memory. If the constitutive functionals are sufficiently smooth, so that the dependence on $\gamma_t(Y, t - s)$ can be replaced by

$$\gamma_t(Y, t - s) \approx \gamma_t(Y, t) - s\gamma_t^{(1)}(Y, t) + \frac{1}{2!}s^2\gamma_t^{(2)}(Y, t) - \dots + \frac{1}{m!}(-s)^m\gamma_t^{(m)}(Y, t) , \quad (2.4.18)$$

one says that the material presents smooth memory, and Equation (2.4.1) becomes

$$\mathcal{C}(X, t) = \mathcal{R} \left(\gamma(Y, t), \gamma_t^{(1)}(Y, t), \dots, \gamma_t^{(m)}(Y, t), X \right). \quad (2.4.19)$$

In this case, the material is called a rate dependent material of degree m with respect to the variable γ , so that the far past histories of any physical quantity at Y do not affect the material behavior at X for time t .

Frequently, materials may not present so a smooth memory as to admit a Taylor expansion of the form (2.4.17). Then, analogously to the attenuating neighborhood hypothesis, one needs to introduce an influence function which takes into account the time dependence of the functionals in the far past. Such materials are said to present a fading memory.

PRINCIPLE OF ADMISSIBILITY

This principle states that constitutive equations must be consistent with the second law of thermodynamics. In fact, since the second law of thermodynamics must be not violated for all realizable physical processes, one finds that the thermodynamic admissibility imposed by the entropy inequality severely restricts the form of constitutive equations.

In practical terms, the principle of admissibility helps to eliminate the dependence on certain constitutive variables. One can reduce the generality of the constitutive relations relying upon either different formulations of the entropy principle or even variational methods. For example, in reference [24] the principle of virtual work is employed to deduce the proper constitutive equations for an elastic dielectric medium under equilibrium conditions. In turn, in references [61, 62] Sieniutycz proposed a variational approach based on Onsager's principle for an electrochemical system under a non-stationary quasi-linear regime. Even though, despite the impressive results obtained in these works, application of variational methods is not well-posed for non-isolated systems under the influence of external forces and also for systems where there exists the possibility of several coupling phenomena, such as in chemical systems [60]. As a matter of fact, it seems that reacting chemical systems do not obey the same phenomenological formalism of non-chemical ones. In electrochemical systems, for instance, coupling between chemical reactions and non-chemical processes are very common, and one should certainly take them into account. This is a critical point in the development of a constitutive theory for a reacting ionic mixture, which requires a more comprehensive approach. Under these circumstances, the use of entropy principles, in particular the Müller-Liu entropy principle, is more convenient to restrict the material equations of electrolyte solutions.

2.5 Second law of thermodynamics

The second law of thermodynamics or entropy principle has been one of the main discussion topics in Thermodynamics. Since the publication of Carnot and Clausius' works [8, 9, 10, 11], different enunciations for the entropy principle have been proposed, with most of them based on the physical notion of temperature [28].

Following the thermodynamics of homogeneous processes approach [56, 57], the second law of thermodynamics is formally expressed as:

If at a certain instant, a system absorbs heat Q in a thermally homogeneous way, at that instant, its entropy S will increase at a rate at least equal to the ratio between the thermal power absorbed and the empirical temperature $\theta \in \mathbb{R}^+$. Conversely, if at a moment the entropy S of the system is decreasing in a thermally homogeneous way, at that moment heat Q will be liberated and the ratio between the modulus of the thermal power emitted, and the empirical temperature is at least equal to the rate of the entropy S decrease, viz.

$$\frac{dQ}{dt} \leq \theta \frac{dS}{dt}.$$

The statement above is known as the Clausius-Planck inequality and it was proposed by Planck [54] from his observations about Clausius' work. Clearly, the extension of this principle to a continuous body \mathcal{B} is not straightforward as the temperature, heat, and entropy depend not only on time, but also on the point \mathbf{x} . In addition, a deeper insight into the Clausius-Planck inequality indicates that this assumption has serious shortcomings since it cannot explain many phenomena occurring inside the system [67]. For this reason, one needs a more general formulation of the entropy principle, such as the Clausius-Duhem inequality.

The origins of the Clausius-Duhem inequality go back to the works of Eckart [21, 22] and Meixner [39] who were responsible for the development of the first consistent non-equilibrium theory. In non-equilibrium thermodynamics, the so-called entropy balance equation

$$\rho\pi = \rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho\sigma \geq 0 \quad (2.5.1)$$

plays a central role as it relates the entropy production density, π , to various irreversible processes that occur in a system through macroscopic balance laws. In this equation, η is the entropy density, Φ is the entropy flux vector, and σ is the entropy supply density. Moreover, from Equation (2.3.3), one may also write the entropy jump condition at a singular surface as

$$\llbracket \rho \eta (\mathbf{v} \cdot \mathbf{n} - u_n) \rrbracket - \llbracket \Phi \rrbracket \cdot \mathbf{n} \geq 0. \quad (2.5.2)$$

Within the theoretical framework of thermodynamics of irreversible processes [17], the entropy production density may be calculated if one makes use of the Gibbs' relation that connects, for instance, the rates of change of entropy in each regular point to the rates of change of energy and composition in an isotropic multi-component fluid. Complying with this approach, Φ is given by the ratio between the heat flux vector \mathbf{h} and the empirical temperature θ , whereas σ is given by the ratio between the energy supply density r and θ ,

$$\rho \pi = \rho \frac{d\eta}{dt} + \operatorname{div} \left(\frac{\mathbf{h}}{\theta} \right) - \rho \frac{r}{\theta} \geq 0. \quad (2.5.3)$$

Inequality (2.5.3) is frequently called of Clausius-Duhem inequality because it represents Duhem's extrapolation for the Clausius's formulation of the second law for non-homogeneous temperature fields.

For a long period, the inequality (2.5.3), whose exploitation method is based on the works of Coleman and Noll [13, 67, 68], was extensively used in the development of modern continuum thermodynamics to impose thermodynamic restrictions on the constitutive responses of a material body. For simple materials, that is, material bodies whose values of the constitutive quantities at \mathbf{x} depend only on the histories of the deformation gradient, and temperature and its gradient, linear irreversible thermodynamics and modern continuum thermodynamics with the Clausius-Duhem inequality lead to the same practical results. This is the reason why linear irreversible thermodynamics and the Clausius-Duhem inequality are still widely employed. Nevertheless, with the development of continuum theories for mixtures, porous media, and other non-simple material bodies, it was realized that the two main constitutive assumptions adopted by Coleman and Noll,

$$\Phi = \frac{\mathbf{h}}{\theta}, \quad \sigma = \frac{r}{\theta},$$

are not very satisfactory [73]. Moreover, large deviations from linear behavior are observed for chemical reactions, restricting the application of linear irreversible thermodynamics to reacting systems. Since then, other formulations to the entropy principle have been proposed, among which the one most employed was proposed by Müller [44, 47].

According to Müller's proposition, the behavior of a continuum body must obey the general entropy balance stated in (2.5.1), where Φ and σ are not *a priori* given constitutive quantities, such as in the Coleman-Noll exploitation method, but rather constitutive functions on which thermodynamic restrictions must be placed. Even though this approach of the entropy principle is less restrictive than that proposed by Coleman and

Noll, its practical application was still very laborious, even for simple and free of external supplies bodies. Then, Liu [33] suggested to incorporate new auxiliary quantities, termed of Lagrange multipliers, in the entropy inequality in order to take into account all balance equations in the exploitation of the entropy inequality. Thanks to its comprehensive scope, nowadays the Müller-Liu approach to the entropy principle is widely employed to deduce restrictions on constitutive equations and thermodynamically consistent constitutive laws in many research fields. Some examples can be found in references [29, 75].

2.6 Quasistatic approximation of electromagnetism

In addition to the basic laws of motion, electrically polarizable material bodies must obey Maxwell's laws of electromagnetism. However, while the former are Galilean invariant, *i.e.*, the dynamic laws have the same expressions in any frame related to an inertial frame by a Galilean transformation, the latter are invariant with relation to the Lorentz transformation. Consequently, in order to obtain a coherent theory for charged/magnetized continuum bodies, it is necessary to propose either a relativistic formulation for the laws of dynamics or employ an approximation in which both the basic laws of motion and Maxwell's laws are form-invariant in relation to the same transformation.

With a quasistatic approximation, temporal change rates of electromagnetic quantities are so small that only low acoustic frequencies and non-relativistic velocities are considered [40, 41]. In this case, Maxwell's equations are form-invariant with respect to Galilean transformations, and they are given by

FARADAY'S LAW

$$\text{curl}(\mathbf{E}) = \mathbf{0}, \quad (2.6.1)$$

AMPÈRE'S LAW

$$\text{curl}(\mathbf{H}) = \mathbf{I} + \frac{\partial \mathbf{D}}{\partial t} + \text{curl}(\mathbf{P} \times \mathbf{v}), \quad (2.6.2)$$

GAUSS'S LAW

$$\text{div}(\mathbf{D}) = q, \quad (2.6.3)$$

MAGNETIC FLUX LAW

$$\operatorname{div}(\mathbf{B}) = 0, \quad (2.6.4)$$

where \mathbf{E} is the electric field, \mathbf{H} is the magnetic field, \mathbf{I} is the electric current, \mathbf{D} is the electric displacement vector, \mathbf{P} is the electric polarization vector, q is the charge density, and \mathbf{B} is the magnetic flux vector. Following Chu's formulation [26] of electromagnetism, the electric field and the magnetic field are regarded as fundamental quantities, whereas \mathbf{D} and \mathbf{B} are auxiliary quantities. These quantities are interrelated by

$$\mathbf{D} = \epsilon_o \mathbf{E} + \mathbf{P}, \quad \mathbf{B} = \mu_o (\mathbf{H} + \mathbf{M}), \quad (2.6.5)$$

where ϵ_o and μ_o are respectively the permittivity and the permeability of free space, and \mathbf{M} is the magnetization field.

Equations (2.6.1)–(2.6.4) are analogous to Maxwell's laws of electrostatics, but by no means do the above equations result in a static model. In fact, the temporal dependence of quasi-electrostatic fields can be regarded as a secondary effect because once given the sources of electromagnetic fields at a particular instant, the fields at that same instant are determined without knowing what their sources were in earlier times. Therefore, the mathematical problem of finding a quasistatic electric field for a charge distribution dependent on time is equivalent to the evaluation of a succession of static fields, each one with a different charge distribution at various instants t .

Furthermore, according to the quasi-electrostatic approximation, \mathbf{E} is an irrotational field, and dynamic currents are so small that the magnetic induction is ignorable. Thus, from Equation (2.6.3), if the charge density is given, both the curl and divergence of the electric field are specified.

2.7 Theory of continuum mixtures

The first systematic study of non-equilibrium behavior of continuum mixtures was given by Truesdell [66, 67] in 1957, and later was extended by Kelly [31] by incorporating electromagnetic fields. According to Truesdell's view, a continuum mixture is formed by superposing constituents, so that each spatial point is simultaneously occupied by particles of all constituents. Incidentally, particles in continuum theories do not represent atoms, molecules, ions or other classical particles, which can be easily labeled, but rather mathematical points endowed with physical properties, such as mass density, velocity, electric

field, internal energy density *etc.* Then, in admitting this hypothesis, only mixtures whose constituents are not macroscopically distinguishable can be accounted for. Examples of such mixtures, usually termed classical continuum mixtures, are gas and aqueous solutions and other monophasic systems consisting of two or more chemical species.

A further hypothesis assumed by Truesdell refers to the individual character of each constituent. Accordingly, each constituent behaves as a single fluid and by analogy one may assign balance laws for the constituents with single pure materials. Here, the only difference that appears between these balance laws, and those for single fluids is the fact that the balance laws of mass, linear and angular momenta, and energy are not conserved, but only their sums as a whole are formally the same as for a single material. Hence, it is taken for granted that the motion of a mixture is governed by the same equations as for a single body. In other words, by this principle, properties of constituents are taken as primitives and the properties and balances of the mixture are formulated with basis in the characteristics of pure chemical substances.

There is indeed another kind of continuum mixtures, where constituent particles are macroscopically identifiable. This kind of mixture, often referred to as multicomponent mixtures, does not obey all the assumptions made above since constituents are intimately intermixed only at the microscopic level. For example, soils, porous rock, suspensions of coal particles in water, packed powders, granular propellants *etc.* consist of macroscopic identifiable solid particles surrounded by one or more continuous media or an identifiable porous matrix through the continua are dispersed. In this work, multicomponent mixtures will not be considered.

3 Dynamics of Electrochemical Systems

A number of the fundamental laws of continuum mechanics are expressions of the conservation of some physical quantity. These balance laws are applicable to all continua and result in equations, either in their integral or local forms, that must always be satisfied. On the other hand, phenomenological aspects of material bodies are brought through constitutive equations that, unlike balance laws, are specific for each body because they reflect the internal constitution of a material. However, it is impossible to write down one constitutive equation, which is capable of representing a given material over its entire range of application since many materials behave quite differently under changing levels of loading. Then, perhaps it is better to think of constitutive equations as being representative of a particular behavior rather than of a particular material. In fact, the usefulness of the constitutive equations is to describe the relationships among the kinematic, mechanical, and thermal field equations and to permit the formulation of well-posed problems in continuum thermodynamics. This will be the subject in the next two chapters.

Hereafter, the motion of the mixture and its constituents are given with relation to an orthonormal frame of reference, and all quantities are given in terms of the current configuration, that is, physical properties are expressed in terms of the spatial coordinates \mathbf{x} and time t . Moreover, $\mathbf{1}$ denotes the unit tensor, δ_{ij} is the Kronecker delta, and brackets and parentheses are used to represent the antisymmetry and the symmetry of second-order tensors, respectively.

3.1 Kinematics of electrolyte solutions

Let \mathcal{B} be a mixture of n constituents \mathcal{B}_a , such that a particle of \mathcal{B}_a is represented by X_a with $a = 1, \dots, n$, being the index n reserved for solvent. In addition, let a region of the Euclidean space \mathcal{E} in the current configuration be simultaneously occupied by different constituent particles. Thus, if \mathbf{X}_a is the material coordinate in some reference configuration

κ , the motion $\mathbf{x} = \mathbf{x}_a(\mathbf{X}_a, t)$ of a constituent a is a smooth function of space and time, which relates a particle X_a to a place \mathbf{X}_a at the time t in the reference configuration κ .

Each constituent has its own kinematics. The velocity and acceleration of the constituent a at time t are, respectively,

$$\mathbf{v}_a \equiv \frac{\partial \mathbf{x}_a(\mathbf{X}_a, t)}{\partial t}, \quad \mathbf{a}_a \equiv \frac{\partial^2 \mathbf{x}_a(\mathbf{X}_a, t)}{\partial t^2}. \quad (3.1.1)$$

Likewise, each \mathcal{B}_a has its own mass and, consequently, its positive mass density $\rho_a(\mathbf{x}, t)$ at each point \mathbf{x} and time t . The mass density of the whole mixture $\rho(\mathbf{x}, t)$ is related to $\rho_a(\mathbf{x}, t)$ by

$$\rho \equiv \sum_{a=1}^n \rho_a. \quad (3.1.2)$$

At every (\mathbf{x}, t) , one also defines the mass concentration of \mathcal{B}_a as

$$\xi_a \equiv \frac{\rho_a}{\rho}, \quad (3.1.3)$$

whence Equations (3.1.2) and (3.1.3) imply $\sum_{a=1}^n \xi_a = 1$.

The mean velocity of \mathcal{B} is defined by

$$\rho \mathbf{v} \equiv \sum_{a=1}^n \rho_a \mathbf{v}_a, \quad (3.1.4)$$

and the translational diffusion velocity of \mathcal{B}_a is

$$\mathbf{u}_a = \mathbf{v}_a - \mathbf{v}. \quad (3.1.5)$$

Thus, it follows from Equations (3.1.2), (3.1.4), and (3.1.5) that $\sum_{a=1}^n \rho_a \mathbf{u}_a = \mathbf{0}$.

Until now, the kinematics of reacting ionic mixtures obeys the general framework of classical mixtures set up by Truesdell [67]. However, in contrast with the classical theories of mixtures, it has long been accepted that the dynamics of electrolyte solutions depends on the short-range and long-range interactions among the constituent particles [76]. Following Eringen and Toupin's ideas [19, 23, 24, 63, 64, 65], the interactions among the constituent particles are accounted for by considering the electrolyte solution as a polar elastic dielectric medium. Then, under an applied electric field, which may be due to an external source and/or generated by dissociated ions in solution, constituent particles will interact with the electric field, producing extrinsic body couples and extrinsic surface

couples. Consequently, to describe accurately the material behavior of such solutions, it is necessary to use the theoretical framework of polar theories, where the action of extrinsic body couples and surface body couples caused by electromagnetic fields on the constituent particles is properly considered.

Thus, polar theories encompass not only the short-range interactions among the constituent particles as do the classical local ones, but also the long-range interaction forces. In this sense, electrolyte solutions differ from the classical mixtures because the behavior of their material points is influenced by all points of the solution independently of ions concentrations. Then, in order to include the microscopic structure of electrolyte solutions into the continuum model, new kinematic variables are associated to each point (\mathbf{x}, t) of the mixture [58].

In contrast with the local theories, where the only kinematic vector field is the velocity $\mathbf{v}(\mathbf{x}, t)$, polar materials present two independent kinematic vector fields to describe the translational and rotational motions of the fluid particles. If the mechanics of rigid bodies is assumed, each constituent particle possesses a spin field $\mathbf{s}_a(\mathbf{x}, t)$ and a local angular velocity $\boldsymbol{\omega}_a(\mathbf{x}, t)$, which are interrelated by

$$\mathbf{s}_a \equiv \mathbf{I}_a \boldsymbol{\omega}_a, \quad (3.1.6)$$

where \mathbf{I}_a is the inertia momentum tensor.

In polar media, the angular velocity of the particle does not coincide with the angular velocity of the mixture, *viz.*, vorticity $\boldsymbol{\omega}$. The angular velocity of a particle in relation to the fluid vorticity is given by

$$\boldsymbol{\varpi}_a \equiv \boldsymbol{\omega}_a - \boldsymbol{\omega}, \quad (3.1.7)$$

where $\boldsymbol{\varpi}_a$ represents the angular velocity of the constituent particle relative to the angular velocity of the region in which it is embedded. Clearly, all definitions extend to the mixture particle, so one may equally assign to the mixture particles a spin field \mathbf{s} , an angular velocity $\boldsymbol{\omega}$, and an inertia tensor \mathbf{I} , which are related to those of the constituents by

$$\rho \mathbf{s} \equiv \sum_{a=1}^n \rho_a \mathbf{s}_a, \quad \rho \boldsymbol{\omega} \equiv \sum_{a=1}^n \rho_a \boldsymbol{\omega}_a, \quad \rho \mathbf{I} \equiv \sum_{a=1}^n \rho_a \mathbf{I}_a. \quad (3.1.8)$$

Likewise the translational motion, one also defines a rotational diffusion velocity of the constituent a as

$$\boldsymbol{\nu}_a \equiv \boldsymbol{\omega}_a - \boldsymbol{\omega}, \quad (3.1.9)$$

such that $\sum_{a=1}^n \rho_a \mathbf{v}_a = \mathbf{0}$.

3.2 Balance laws for continuum mixtures and their constituents

It is the main purpose of Electrochemistry to investigate the properties of ionic conductors and of electric circuits containing ionic conductors, as well as the phenomena that occur during the passage of an electric current through such circuits. These phenomena include chemical reactions, structural deformations, mass transport, dissipation of energy to name only a few. Then, modeling the behavior of electrochemical systems in its simplest form demands the coupling of balance equations of continuum mixture theory and Maxwell's equations. Coupling these equations, one can describe the essential phenomena which occur in electrochemical systems. However, since interactions among the constituent particles play an important role in the physico-chemical behavior of these systems, one should use the conceptual basis of the thermodynamics of polar continua to represent these interactions.

In order to derive the local balance equations, one starts from the general balance law for the constituents of the mixture,

$$\frac{\partial \gamma_a}{\partial t} + \text{div} (\gamma_a \otimes \mathbf{v}_a - \Phi_a^\gamma) - \sigma_a^\gamma - \pi_a^\gamma = 0, \quad (3.2.1)$$

which holds at all points of the body except on the singular surfaces. Once defined Equation (3.2.1), one relates each variable in Equation (3.2.1) to the physical quantities which must be present in the mass, linear and angular momenta, energy, and entropy balance equations. The identifications of the variables for each balance are given in Table 2.1, where ε_a is the internal energy density, η_a is the entropy density, \mathbf{t}_a is the total stress vector related to the total stress tensor \mathbf{T}_a by $\mathbf{t}_a(\mathbf{x}, \mathbf{n}, t) = \mathbf{T}_a(\mathbf{x}, t) \mathbf{n}$, \mathbf{C}_a is the total coupling stress tensor, \mathbf{h}_a is the heat flux, Φ_a is the entropy flux let as an unspecified quantity, \mathbf{b}_a is the mechanical body force density, q_a is the charge density defined by $\rho_a z_a$, being z_a the charge *per* unit mass, \mathbf{E}_a and \mathbf{P}_a are the electric field and the electric polarization field acting on the constituent a , respectively, \mathbf{l}_a is the mechanical coupling body force density, r_a is the mechanical energy supply density, \mathbf{i}_a is the electric current density due to the diffusive motion, σ_a is the entropy supply density let as an unspecified quantity, c_a , \mathbf{m}_a , $\boldsymbol{\tau}_a$, ϵ_a and π_a are the mass, linear and angular momenta, energy and entropy productions, and \mathbf{o}_o is the position vector of an arbitrary fixed point.

3.2.1 Mass balance

Analogously to a single constituent body, flux and supply vanish in the mass balance of \mathcal{B}_a . Nonetheless, as constituents can take part in chemical reactions, a term of mass production, c_a , should be accounted for. For a regular point \mathbf{x} , the mass balance for the a -th constituent of the mixture is

$$\frac{\partial \rho_a}{\partial t} + \operatorname{div}(\rho_a \mathbf{v}_a) - c_a = 0, \quad (3.2.2)$$

where the mass production term is related to the velocities of mass conversion, c_{aj} and c_{ja} , by [7]

$$c_a = \sum_{j=1}^n (c_{ja} - c_{aj}). \quad (3.2.3)$$

If the constituent a is converted into the constituent j at a spatial point \mathbf{x} , but the species j is not converted into the constituent a , then $c_{aj} > 0$ and $c_{ja} = 0$. Inversely, if the constituent j is converted into the species a and the latter is not converted into the former, then $c_{ja} > 0$ and $c_{aj} = 0$. However, since in chemical systems, chemical reactions can proceed in both directions, c_{aj} and c_{ja} can be simultaneously positive at \mathbf{x} . Thus, while c_{aj} and c_{ja} are non-negative quantities because they correspond to the forward and inverse chemical reactions velocities, respectively, c_a may be positive, negative or null.

The introduction of terms relative to the mass conversion rate of a constituent a into a constituent j is fundamental to associate the nature of electrolytes to ion-ion interactions, which determine the properties of electrolyte solutions. The degree with which these interactions affect the properties of the solution depends on the density of the distribution of ions in solution that, in turn, depends on the nature of the electrolyte, *i.e.*, it depends on the electrolyte to be a real or potential one.

Potential electrolytes are those, which through chemical reactions with the solvent molecules, dissociate into ions. Many of the solutions of potential electrolytes contain only a small concentration of ions and, therefore, the effects of ion-ion interactions are often overlooked. The behavior of these solutions is predominantly governed by the equilibrium position of the reaction between the potential electrolyte and the solvent molecules. Thus, c_{aj} and c_{ja} are different for the same point of the mixture until the kinetic equilibrium is reached.

In contrast, real electrolytes originate ions in solution through physical interactions between ions in the ionic solid and solvent molecules. Usually, real electrolytes are completely dissolved in water, so that the resulting solution consists of solvent and solvated

ions only. For these solutions, the dependence of their properties on concentration is determined by the strength of the ionic interactions.

The classification of real and potential electrolytes is a modern one [3] that aims to describe the behavior of electrolytes through their structures and not through their behaviors at some particular solvent. Historically, however, the classification was proposed with basis in a specific solvent, generally water. Weak electrolytes were then those which produced solutions with low electrical conductivity when dissolved in water, while strong electrolytes were those which originated high electric-conducting aqueous solutions. The disadvantage of the older classification consists in the fact of that as soon as a different solvent is chosen, a strong electrolyte in water can behave as a weak electrolyte in a non-aqueous solvent and *vice-versa*.

The mass balance for the mixture is obtained by considering null the sum of mass production terms over all constituents that take part in reaction, $\sum_{j=1}^n \sum_{a=1}^n (c_{ja} - c_{aj}) = 0$.

Consequently, the last equality imposes that chemical reactions do not change the mass density of the mixture at every spatial point and time. Hence, from Equations (3.1.2) and (3.2.2), there remains

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \quad (3.2.4)$$

or yet

$$\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) = 0, \quad (3.2.5)$$

where the material time derivative following the motion of the mixture, $d(\cdot)/dt = \partial(\cdot)/\partial t + \mathbf{v} \cdot \nabla(\cdot)$, was used.

Similarly, one may also employ the material time derivative following the motion of the mixture to simplify Equation (3.2.2). In this case, one recalls Equation (3.1.3), and then Equation (3.2.2) takes the form

$$\rho \frac{\partial \xi_a}{\partial t} + \xi_a \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \xi_a \mathbf{v}_a) - c_a = 0. \quad (3.2.6)$$

Thus, with help of the vector identity $\operatorname{div}(f\mathbf{u}) = \nabla f \cdot (\mathbf{u}) + f \operatorname{div}(\mathbf{u})$ and Equation (3.2.5), it follows that

$$\rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) - c_a = 0, \quad (3.2.7)$$

where $\mathbf{j}_a \equiv \rho_a (\mathbf{v}_a - \mathbf{v})$ is the diffusive flux of the constituent a .

3.2.2 Linear momentum balance

In electrochemical systems, the movement of ions is responsible for the electric-conducting properties exhibited by the electrolyte solution. This phenomenon implies the existence of some force whose character is not exclusively electrostatic since ions experience mechanical and chemical forces. If the total electric field is called the effective electric field \mathbf{E}^{ef} , then \mathbf{E}^{ef} will not necessarily be a solenoidal vector field [59]. In fact, for an electric-conducting medium, one has $\text{div}(\mathbf{E}^{ef}) = f^{emf}$, where f^{emf} is the electromotive force and it represents the ratio between the energy applied by a power supply and the charge carried by a particle in an electric circuit [30]. For electrochemical cells, the electromotive force is the electric potential difference between the electrodes when the current through the cell is null (zero current potential).

If all forces acting on an electric-conducting body, with exception of the Lorentz force, $\mathbf{F}^L = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$, which represents the total electromagnetic force on a charged species, are combined into a single term, \mathbf{F}^W , one has

$$\begin{aligned} q\mathbf{E}^{ef} &= q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \mathbf{F}^W \\ &= q\mathbf{E} + \mathbf{I} \times \mathbf{B} + \mathbf{F}^W, \end{aligned} \quad (3.2.8)$$

where the definition of electric current, $\mathbf{I} = \sum_{a=1}^n \rho_a z_a \mathbf{v}_a$, was used.¹ Besides, for any system considered under the quasi-electrostatic approximation [40], $q\mathbf{E} \gg \mathbf{I} \times \mathbf{B}$ and, therefore, the magnetic contribution to the Lorentz force can be neglected. Thus, it follows that the effective electric field is given only by $q\mathbf{E}^{ef} = q\mathbf{E} + \mathbf{F}^W$.

¹ The electric current density \mathbf{I} can be written as follows,

$$\begin{aligned} \mathbf{I} &= \sum_{a=1}^n \rho_a z_a \mathbf{v}_a \\ &= \sum_{a=1}^n \rho_a z_a \mathbf{v} + \sum_{a=1}^n z_a \mathbf{j}_a, \end{aligned}$$

where the definition of diffusive flux has been used. The second term of the right-hand side of the expression above is the electric current due to the relative motion of the various components. Defining

$\mathbf{i} = \sum_{a=1}^n z_a \mathbf{j}_a$ and $\mathbf{i}_a = z_a \mathbf{j}_a$, the expression for \mathbf{I} becomes

$$\mathbf{I} = \sum_{a=1}^n \rho_a z_a \mathbf{v} + \mathbf{i}.$$

Evidently, the ion-ion interactions are different from ion-solvent interactions. If the charge carrier constituents were the only ones responsible for the forces that per chance exist in a mixture, it would not be possible to explain the real behavior of electrolyte solutions. While coulombic forces are responsible for the ion-ion interactions, the Kelvin polarization force, $\mathbf{P} \cdot (\nabla \mathbf{E})$, is the result of the action of the electric field on the dipoles of water molecules that make up the solvent. In addition, because the medium is continuous, one can assume a continuous distribution of dipoles given by

$$\Gamma = -\text{div}(\mathbf{P}) . \quad (3.2.9)$$

Hence, on the basis of the quantities given in Table 2.1, the linear momentum balance equations for the a -th constituent of the mixture and for the mixture as a whole are, respectively,

$$\frac{\partial \rho_a \mathbf{v}_a}{\partial t} + \text{div}(\rho_a \mathbf{v}_a \otimes \mathbf{v}_a - \mathbf{T}_a) - \rho_a \mathbf{b}_a - q_a \mathbf{E}_a - \mathbf{P}_a \cdot (\nabla \mathbf{E}_a) - \mathbf{m}_a = \mathbf{0} , \quad (3.2.10)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \text{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{T}) - \rho \mathbf{b} - q \mathbf{E} - \mathbf{P} \cdot (\nabla \mathbf{E}) = \mathbf{0} , \quad (3.2.11)$$

or

$$\rho \frac{d\mathbf{v}}{dt} - \text{div}(\mathbf{T}) - \rho \mathbf{b} - q \mathbf{E} - \mathbf{P} \cdot (\nabla \mathbf{E}) = \mathbf{0} , \quad (3.2.12)$$

where $\rho \mathbf{b} = \sum_{a=1}^n \rho_a \mathbf{b}_a$, $q \mathbf{E} = \sum_{a=1}^n q_a \mathbf{E}_a$, $\mathbf{P} = \sum_{a=1}^n \mathbf{P}_a$, $\sum_{a=1}^n \mathbf{m}_a = \mathbf{0}$, such that \mathbf{m}_a represents the force *per* unit volume exerted by all other chemical species of the mixture on the constituent a , and the total stress tensor should be interpreted as the sum of the mechanical and electromagnetic stress tensors.

Moreover, $\sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{v}_a - \mathbf{T}_a) = \sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{v}_a) - \sum_{a=1}^n \mathbf{T}_a$, which with the use of Equation (3.1.5), becomes $\sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{v}_a - \mathbf{T}_a) = \sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{v}) + \sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{u}_a) - \sum_{a=1}^n \mathbf{T}_a$. Thus, since $\rho \mathbf{v} = \sum_{a=1}^n \rho_a \mathbf{v}_a$ and $\mathbf{T}^I = \sum_{a=1}^n \mathbf{T}_a$, it follows that $\sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{v}_a - \mathbf{T}_a) = \rho \mathbf{v} \otimes \mathbf{v} - \mathbf{T}^I + \sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{u}_a)$, whence one concludes that the total stress tensor of the mixture is

given by $\mathbf{T} = \mathbf{T}^I - \sum_{a=1}^n (\rho_a \mathbf{v}_a \otimes \mathbf{u}_a)$, being \mathbf{T}^I the constitutive part of the stress tensor of the mixture.

Equation (3.2.12) also offers the opportunity of introducing an important tensor of electrodynamics theory. For this purpose, all mechanical contributions of Equation (3.2.12) are neglected. In addition, the velocity is supposed to be constant, so that its time derivative is zero. Thus, from Equation (3.2.12), there remains

$$-\text{div}(\mathbf{T}) = q\mathbf{E} + \mathbf{P} \cdot (\nabla\mathbf{E}) . \quad (3.2.13)$$

Besides, writing down the coulombic force as $q\mathbf{E} = \mathbf{E}\text{div}(\mathbf{D})$, Equation (3.2.13) becomes

$$-\text{div}(\mathbf{T}) = \mathbf{E}\text{div}(\mathbf{D}) + \mathbf{P} \cdot (\nabla\mathbf{E}) . \quad (3.2.14)$$

This expression may be further simplified by making use of the vector identities $\text{div}(\mathbf{u} \otimes \mathbf{y}) = \nabla\mathbf{u}(\mathbf{y}) + \mathbf{u}\text{div}(\mathbf{y})$, $1/2\nabla(\mathbf{u} \cdot \mathbf{y}) = \mathbf{y} \times \text{rot}(\mathbf{u}) + \nabla\mathbf{u}(\mathbf{y})$, $\nabla(\mathbf{u} \cdot \mathbf{y}) = \text{div}[(\mathbf{u} \cdot \mathbf{y}) \mathbf{1}]$, Equation (2.6.5)₁, and recalling that, according to the quasi-electrostatic approximation, the electric field is irrotational. Hence,

$$\text{div}(\mathbf{T}) = \text{div} \left(\frac{1}{2} \epsilon_o E^2 \mathbf{1} - \mathbf{P} \otimes \mathbf{E} - \mathbf{E} \otimes \mathbf{E} \right) , \quad (3.2.15)$$

whence one obtains that the electromagnetic contribution for the total stress tensor is given by $\mathbf{P} \otimes \mathbf{E} + \mathbf{E} \otimes \mathbf{E} - 1/2\epsilon_o E^2 \mathbf{1}$, being the non-symmetric part given by $T_{ij} = \mathbf{P}_i \mathbf{E}_j$, and the symmetric part, also known as Maxwell stress tensor, given by $T_{(ij)} = E_i E_j - 1/2\epsilon_o E^2 \delta_{ij}$.

3.2.3 Angular momentum balance

Since the electrolyte is composed of continuous polar bodies in each point of the mixture, the angular momentum of each constituent is given by the sum of two parts: the angular momentum at the center of mass with respect to an arbitrary fixed point, $\mathbf{o}_o \times \rho_a \mathbf{v}_a$, and the angular momentum of the constituent relative to its center of mass (spin), $\rho_a \mathbf{s}_a$. Similarly, the supply of angular momentum is the sum of the electromagnetic coupling, $\mathbf{P}_a \times \mathbf{E}_a$, the coupling of mechanical forces, $\rho_a \mathbf{l}_a$, and the angular momentum with respect to an arbitrary fixed point of the forces acting on the center of mass, $\mathbf{o}_o \times [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla\mathbf{E}_a)]$. In turn, the flux of angular momentum is given by the coupling stress tensor, \mathbf{C}_a , and the cross product between the position vector and the total stress tensor, $\mathbf{o}_o \times \mathbf{T}_a$.² Finally,

² See Appendix II for more information about properties of skew-symmetric tensors.

the production of angular momentum, τ_a , is given by the spin production and the angular momentum production at the mass center.

Then, having defined these quantities, the angular momentum balance equations for the a -th constituent and for the whole mixture are, respectively,

$$\begin{aligned} & \frac{\partial (\mathbf{o}_o \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a)}{\partial t} + \text{div} [(\mathbf{o}_o \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a) \otimes \mathbf{v}_a - \mathbf{C}_a - \mathbf{o}_o \times \mathbf{T}_a] - \\ & \mathbf{o}_o \times [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)] - \mathbf{P}_a \times \mathbf{E}_a - \rho_a \mathbf{l}_a - \tau_a = \mathbf{0}, \end{aligned} \quad (3.2.16)$$

$$\begin{aligned} & \frac{\partial (\mathbf{o}_o \times \rho \mathbf{v} + \rho \mathbf{s})}{\partial t} + \text{div} [(\mathbf{o}_o \times \rho \mathbf{v} + \rho \mathbf{s}) \otimes \mathbf{v} - \mathbf{C} - \mathbf{o}_o \times \mathbf{T}] - \\ & \mathbf{o}_o \times [\rho \mathbf{b} + q \mathbf{E} + \mathbf{P} \cdot (\nabla \mathbf{E})] - \mathbf{P} \times \mathbf{E} - \rho \mathbf{l} = \mathbf{0}, \end{aligned} \quad (3.2.17)$$

where $\mathbf{C} = \sum_{a=1}^n \mathbf{C}_a - \sum_{a=1}^n (\rho_a \mathbf{s}_a \otimes \mathbf{u}_a)$, such that the first term of the right-hand side corresponds to the constitutive part of the coupling stress tensor and $\sum_{a=1}^n \tau_a = \mathbf{0}$.

Equation (3.2.17) may be further simplified to give the balance of spin. Then, with the definition of the material time derivative following the motion of the mixture, and $\text{div} (\mathbf{o}_o \times \mathbf{T}) = \mathbf{o}_o \times \text{div} (\mathbf{T}) + 2\hat{\mathbf{t}}$, one obtains

$$\rho \frac{ds}{dt} - \text{div} (\mathbf{C}) + 2\hat{\mathbf{t}} - \mathbf{P} \times \mathbf{E} - \rho \mathbf{l} = \mathbf{0}, \quad (3.2.18)$$

where $\hat{\mathbf{t}}$ is the dual vector associated to the skew-symmetric part of the stress tensor.

Hence, from Equation (3.2.18), the total stress tensor \mathbf{T} will be symmetric only if simultaneously, the time derivative of spin is zero, \mathbf{C} is a solenoidal field, the electric field is strong enough to keep aligned \mathbf{P} and \mathbf{E} , and mechanical coupling stresses are absent. Consequently, as usual for polar material bodies, the conservation law of angular momentum cannot be mutually obtained from the conservation law of linear momentum since not all torques and forces arise from macroscopic body forces.

The antisymmetry of the stress tensor has been closely related to the microscopic structure of the mixture, in particular, to the torques that act on the electric dipoles of ions. When an electric field is imposed on an electrolyte solution, either by an external source or due to the presence of dissociated ions in solution, the polarization equilibrium of the electric dipoles of the water molecules is affected. Then, the solvent dipoles are rotated by a torque given by $\mathbf{P} \times \mathbf{E}$ in order to align them to the electric field. The release of this

process to a new position of equilibrium dissipates energy, causing a greater friction on the ion than that expected if the solvent was an unpolarizable viscous fluid. Therefore, the ionic mobility and conductivity of the solution are changed as a result of the effects of electrophoresis and relaxation caused, respectively, by the ion-ion interactions and the viscous drag force on the ion due to the solvent.

3.2.4 Energy balance

For polar continua subject to the influence of mechanical and electromagnetic fields, the total energy density is composed of the kinetic energy of rotation, $^{1/2}\rho_a \mathbf{s}_a \cdot \boldsymbol{\omega}_a$, kinetic energy of translation, $^{1/2}\rho_a v_a^2$, as well the density of internal energy, $\rho_a \varepsilon_a$. Likewise, the heat flux vector encompasses contributions from mechanical and electromagnetic sources, with the latter being given by the Poynting vector, $\mathbf{E}_a \times \mathbf{H}_a$, that represents the directional energy flux density of an electromagnetic field. Accordingly, the energy supply and the energy production are also given by both mechanical and electromagnetic contributions, namely:

- The rate of electrical work *per* unit volume, $\mathbf{i}_a \cdot \mathbf{E}_a$;
- The rate of energy supplied *per* unit volume due to the polarization process of the medium, $\dot{\mathbf{P}}_a \cdot \mathbf{E}_a$;
- The mechanical power due to the translational motion, $\mathbf{v}_a \cdot [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)]$, and the rotational motion, $\boldsymbol{\omega}_a \cdot (\mathbf{P}_a \times \mathbf{E}_a + \rho_a \mathbf{l}_a)$;
- The energy supply, $\rho_a r_a$, due to external sources, such as radiation;
- The energy production, ϵ_a , which accounts for the production of energy due to chemical reactions, and translational and rotational motions.

Thus, the local forms of the energy balances for each constituent of the mixture and for the mixture as a whole are, respectively,

$$\frac{\partial \left[\rho_a \varepsilon_a + \frac{1}{2} (\rho_a v_a^2 + \rho_a \mathbf{s}_a \cdot \boldsymbol{\omega}_a) \right]}{\partial t} + \text{div} \left\{ \left[\rho_a \varepsilon_a + \frac{1}{2} (\rho_a v_a^2 + \rho_a \mathbf{s}_a \cdot \boldsymbol{\omega}_a) \right] \mathbf{v}_a \right\} + \quad (3.2.19)$$

$$\text{div} (\mathbf{h}_a - \mathbf{T}_a \mathbf{v}_a - \mathbf{C}_a \boldsymbol{\omega}_a) - \mathbf{v}_a \cdot [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)] -$$

$$\boldsymbol{\omega}_a \cdot (\mathbf{P}_a \times \mathbf{E}_a + \rho_a \mathbf{l}_a) - \rho_a r_a - \mathbf{i}_a \cdot \mathbf{E}_a - \dot{\mathbf{P}}_a \cdot \mathbf{E}_a - \epsilon_a = 0,$$

$$\begin{aligned}
& \frac{\partial \left[\rho\varepsilon + \frac{1}{2}(\rho v^2 + \rho \mathbf{s} \cdot \boldsymbol{\omega}) \right]}{\partial t} + \operatorname{div} \left\{ \left[\rho\varepsilon + \frac{1}{2}(\rho v^2 + \rho \mathbf{s} \cdot \boldsymbol{\omega}) \right] \mathbf{v} \right\} + \\
& \operatorname{div}(\mathbf{h} - \mathbf{T}\mathbf{v} - \mathbf{C}\boldsymbol{\omega}) - \mathbf{v} \cdot [\rho\mathbf{b} + q\mathbf{E} + \mathbf{P} \cdot (\nabla\mathbf{E})] - \\
& \boldsymbol{\omega} \cdot (\mathbf{P} \times \mathbf{E} + \rho\mathbf{l}) - \rho r - \mathbf{i} \cdot \mathbf{E} - \dot{\mathbf{P}} \cdot \mathbf{E} = 0,
\end{aligned} \tag{3.2.20}$$

where the quantities of the mixture are related to those of the constituents by

$$\begin{aligned}
\mathbf{i} &= \sum_{a=1}^n \mathbf{i}_a, \quad \sum_{a=1}^n \varepsilon_a = 0, \\
\rho\varepsilon &= \sum_{a=1}^n \left(\rho_a \varepsilon_a + \frac{1}{2} \rho_a u_a^2 + \frac{1}{2} \rho_a \nu_a^2 \right), \\
\rho r &= \sum_{a=1}^n \left\{ \rho_a r_a + \frac{1}{2} [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)] \cdot \mathbf{u}_a + \frac{1}{2} (\mathbf{P}_a \times \mathbf{E}_a + \rho_a \mathbf{l}_a) \cdot \boldsymbol{\nu}_a \right\}, \\
\mathbf{h} &= \sum_{a=1}^n \left[\mathbf{h}_a - \mathbf{T}_a \mathbf{u}_a - \mathbf{C}_a \boldsymbol{\nu}_a + \left(\rho_a \varepsilon_a + \frac{1}{2} \rho_a u_a^2 + \frac{1}{2} \rho_a \mathbf{s}_a \cdot \boldsymbol{\omega}_a \right) \mathbf{u}_a \right].
\end{aligned}$$

Here, note that the heat flux vector and the internal energy density of the mixture contain terms due to the translational and rotational motions that cannot be mutually eliminated, indicating that the translational and rotational motions contribute differently to \mathbf{h} and ε . Similarly, the energy supply density presents contributions from mechanical and electromagnetic sources as well as from the macroscopic and microscopic structures of the solution that cannot be canceled too. Thus, mechanical and electromagnetic sources and macroscopic and microscopic structures of the mixture have different effects on r .

Equation (3.2.20) may be written in an alternative form, if the material time derivative following the motion of the mixture, and Equations (3.2.5), (3.2.12) and (3.2.18) are used. Then, Equation (3.2.20) takes the form

$$\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla \mathbf{v} - \mathbf{C} \cdot \nabla \boldsymbol{\omega} - 2\boldsymbol{\omega} \cdot \hat{\mathbf{t}} - \rho r - \mathbf{i} \cdot \mathbf{E} - \dot{\mathbf{P}} \cdot \mathbf{E} = 0, \tag{3.2.21}$$

which is known as the balance of internal energy of the mixture.

3.2.5 Entropy balance

The entropy balance reflects the fact that observable thermodynamic processes are irreversible. With this in mind, it is postulated that [49] **(i)** there exists an additive objective scalar quantity, named entropy density, for each constituent and the mixture as one, **(ii)** the entropy density and the entropy flux are constitutive quantities, and **(iii)** the entropy production of the whole mixture is a non-negative quantity for all realizable physical processes. With these assumptions, the entropy balance for each constituent of the mixture is given by

$$\frac{\partial \rho_a \eta_a}{\partial t} + \operatorname{div} (\rho_a \eta_a \mathbf{v}_a + \mathbf{\Phi}_a) - \rho_a \sigma_a - \rho_a \pi_a = 0, \quad (3.2.22)$$

whereas the entropy balance for the mixture is

$$\rho \pi = \frac{\partial \rho \eta}{\partial t} + \operatorname{div} (\rho \eta \mathbf{v} + \mathbf{\Phi}) - \rho \sigma \geq 0, \quad (3.2.23)$$

or yet by Equation (2.5.1),

$$\rho \pi = \rho \frac{d\eta}{dt} + \operatorname{div} (\mathbf{\Phi}) - \rho \sigma \geq 0,$$

where $\rho \eta = \sum_{a=1}^n \rho_a \eta_a$, $\mathbf{\Phi} = \sum_{a=1}^n (\mathbf{\Phi}_a - \rho_a \eta_a \mathbf{u}_a)$, $\rho \sigma = \sum_{a=1}^n \rho_a \sigma_a$, and $\rho \pi = \sum_{a=1}^n \rho_a \pi_a \geq 0$.

Observe that the entropy production for each constituent, π_a , may take any value, provided the entropy production of the whole mixture, π , is a non-negative quantity. This assumption results in a weak limitation of the entropy principle that is termed Truesdell's axiom of dissipation [67].

Table 2.1. Physical quantities of a constituent of the mixture.

Quantity	Mass	Linear Momentum	Angular Momentum	Energy	Entropy
γ_a	ρ_a	$\rho_a \mathbf{v}_a$	$\mathbf{o}_o \times \rho_a \mathbf{v}_a + \rho_a \mathbf{s}_a$	$\rho_a \varepsilon_a + 1/2 (\rho_a v_a^2 + \rho_a \mathbf{s}_a \cdot \boldsymbol{\omega}_a)$	$\rho_a \eta_a$
Φ_a^γ	0	\mathbf{T}_a	$\mathbf{o}_o \times \mathbf{T}_a + \mathbf{C}_a$	$-\mathbf{h}_a + \mathbf{T}_a \mathbf{v}_a + \mathbf{C}_a \boldsymbol{\omega}_a$	$-\Phi_a$
σ_a^γ	0	$\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)$	$\mathbf{o}_o \times [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)] +$ $\mathbf{P}_a \times \mathbf{E}_a + \rho_a \mathbf{l}_a$	$\rho_a r_a + \mathbf{i}_a \cdot \mathbf{E}_a + \dot{\mathbf{P}}_a \cdot \mathbf{E}_a +$ $\mathbf{v}_a \cdot [\rho_a \mathbf{b}_a + q_a \mathbf{E}_a + \mathbf{P}_a \cdot (\nabla \mathbf{E}_a)] +$ $\boldsymbol{\omega}_a \cdot (\mathbf{P}_a \times \mathbf{E}_a + \rho_a \mathbf{l}_a)$	$\rho_a \sigma_a$
π_a^γ	c_a	\mathbf{m}_a	$\boldsymbol{\tau}_a$	ϵ_a	π_a

4 Electrochemical Systems: Interionic Interactions

The balance equations previously shown are fundamental physical laws that are valid for all bodies irrespective of their constitution and unalterable within the domain of classical mechanics. On the other hand, the responses of different material bodies of same geometry subject to identical loads are, in general, different. To take into account the nature of different materials, a set of constitutive equations must be constructed. These equations depend on the nature and the range of physical effects desired, and they are based on certain basic principles and thermodynamic restrictions deduced from the entropy inequality. Together with the balance field equations, constitutive equations form a system of differential equations whose every solution is a thermodynamic process. These solutions, in turn, are particularized through initial and boundary conditions for certain experimental conditions. Once this is done, the constitutive theory proposed is ready to be exploited in several practical applications.

4.1 Interactions among the constituent particles in electrolyte solutions

The dependence of many properties of electrolyte solutions on concentration is determined by interionic interactions and ultimately by the mean distance among the ions in solution. A requirement for studying in detail ion-ion and ion-solvent interactions is to compute the chemical potential change due to the interactions of the ionic species a with other ions in solution and the solvent. The latter can be determined by considering the transfer of an ion from medium 1 of relative permittivity ϵ_1 to medium 2 of relative permittivity ϵ_2 . If medium 1 is set up as vacuum, the energy required in this process is the energy of solvation and it provides a notion about whether ionic species in solution interact with the solvent molecules (Born solvation model). Conversely, analysis of interaction forces among the ions in solution comes from the calculation of the electrostatic potential

produced at a reference ion by the rest of ions in solution (Debye-Hückel model). If one knows the time-averaged spatial distribution of the ions, one can determine how the other charges are distributed as a function of distance from the reference ion. Hereby, one of the fundamental laws of electrostatics, namely, the law of the superposition of potentials, may be used to set the potential at a point as being the sum of the potentials due to each of the charges in the assembly [3, 51].

Of course, as any theoretical model, the ideas above present shortcomings, but both models represented a great advance in the understanding of the behavior of ionic mixtures. Particularly, the study of interionic interactions allows to understand the departure from ideality in electrolyte solutions, which was shown to be mainly due to the changes in the nature of interactions among the particles. As the solution becomes more concentrated, chemical species are closer and long-range as well as short-range interactions become important. In short, coulombic interactions among ions are not sufficient to describe the dynamics of concentrated solutions, and other types of interactions must be included e.g. repulsion among the chemical species, ion-dipole interactions, and dipole-dipole interactions.

As a matter of fact, when the Debye-Hückel model is tested against experimental results, it is very successful in accounting for the behavior at low concentrations. However, at moderate and higher concentrations deviations from ideal behavior become more apparent because other assumptions made by Debye and Hückel also fail, *viz.* [25]:

- Because interionic forces are treated only in terms of short-range coulombic forces, the random motion of ions is neglected;
- All electrolytes behave as real electrolytes;
- Ions are considered spherically symmetrical and unpolarisable. This hypothesis is not valid even for simple ions, such as $NO_3^-(aq)$ and $SO_4^{2-}(aq)$, which are not spherically symmetrical. Other large ions, such as ethylenediaminetetraacetate and many of those encountered in bio and geological media, certainly are non-spherically symmetrical. Likewise, many ions are not unpolarisable and simple ions such as $I^-(aq)$ are indeed highly polarisable;
- The solvent is a structureless dielectric, so that its molecular structure is assumed not to interfere in the way ions interact with the solvent;
- Electrostriction of ions is ignored. But, because of the intense electric fields near the ions, they may be deformed;

- Ions are spherically distributed around the central ion. This is a crucial part of the Debye-Hückel model, and even though it has been dealt with by statistical mechanical averaging procedures [27], only spherical symmetry has been assumed. Any distribution of ions around a spherically symmetrical central ion does not necessarily need to be spherically symmetrical, but on average, all possible arrangements will correspond to spherical symmetry. Because a charge density corresponds to an average distribution of ions, so conversion of the Poisson-Boltzmann equation to spherical symmetry is purely formal. However, as was stated above, there is one important limitation to this when considering large ions. Here, the central ion is non-spherical and, therefore, a spherically symmetrical distribution of charge around it may not be possible. Briefly, the Debye-Hückel model is applicable only for a spherical central ion.

An interionic theory under these conditions is obviously limited and other attempts to overcome these constraints are desirable. One way of coping with these limitations is to employ the continuum thermodynamics approach by coupling elements of polar theory with classical continuum mixture theory. With this approach, one shows that it is possible to account for microscopic interactions with the fluid flow through a skew-symmetric stress tensor and body couplings.

4.2 Proposed continuum model

It is the purpose of this chapter to discuss the dynamics of aqueous electrolyte solutions. Such solutions are assumed to be diluted, so the main fluid (water) is much more dominant than all other constituents. As a result, the thermodynamics of the mixture can be described as that of the main fluid. Under these conditions, one temperature field is required and the linear and angular momenta of the mixture coincide with those of solvent. Consequently, only the balances of energy and linear and angular momenta for the whole mixture are employed.

Moreover, in determining the behavior of electrochemical systems by evaluating the fields $\rho(\mathbf{x}, t)$, $\xi_a(\mathbf{x}, t)$, $\mathbf{v}(\mathbf{x}, t)$, $\boldsymbol{\varpi}(\mathbf{x}, t)$, $\theta(\mathbf{x}, t)$, and $\mathbf{E}(\mathbf{x}, t)$, one presumes that most of the effects revealed by electrochemical systems are accounted for by the dependence on the mass density and its gradient, concentration and its gradient, velocity and its gradient, relative local angular velocity, gradient of local angular velocity, temperature and its gradient, and electric field. In other words, the set of the independent constitutive variables y is

$$y \in \{\rho, \nabla\rho, \xi_a, \nabla\xi_b, \mathbf{v}, \nabla\mathbf{v}, \boldsymbol{\varpi}, \nabla\boldsymbol{\omega}, \theta, \nabla\theta, \mathbf{E}\} \quad (\forall a, b = 1, \dots, n-1) . \quad (4.2.1)$$

Nonetheless, as the principle of material objectivity requires that constitutive functions must be independent of the observers, constitutive functions do not depend on the velocity, and they depend on the velocity gradient only through its symmetric part, called the stretching tensor, \mathbf{D} . Furthermore, $\boldsymbol{\varpi}$ is also a non-objective quantity, but by using a linear map (duality map) one can establish a one-to-one correspondence between a skew-symmetric objective tensor and a non-objective vector. That is, the dependence of the constitutive functions on $\boldsymbol{\varpi}$ occurs by a skew-symmetric tensor of type $W_{ij} = e_{ijk}\varpi_k$.

One may also exploit the irrotational nature of the quasistatic electric field and define it in terms of a scalar function. Recalling the Helmholtz theorem, one writes

$$\mathbf{E} \equiv -\nabla\varphi, \quad (4.2.2)$$

where φ is the electric potential. In other words, the electric field in quasi-electrostatic approximation is completely specified only by its scalar source (Gauss law).

With these assumptions, (4.2.1) becomes

$$y \in \{\rho, \nabla\rho, \xi_a, \nabla\xi_b, \theta, \nabla\theta, \mathbf{E}, \mathbf{D}, \mathbf{W}, \nabla\boldsymbol{\omega}\} \quad (\forall a, b = 1, \dots, n-1) , \quad (4.2.3)$$

where \mathbf{E} transforms as an objective quantity in the quasi-electrostatic approximation. Incidentally, constitutive relations must be formulated for

$$\mathcal{C} \in \{\mathbf{j}_a, c_a, \mathbf{T}, \mathbf{C}, \mathbf{P}, \varepsilon, \mathbf{h}, \mathbf{i}, \eta, \Phi\} \quad (\forall a = 1, \dots, n-1) , \quad (4.2.4)$$

which are dependent on the variables (4.2.3). Through the dependence of (4.2.4) on (4.2.3), one proposes a constitutive class capable of describing the chemical changes caused by the passage of electric current, and the transport phenomena caused by electrochemical reactions in a viscous fluid. This constitutive class will characterize the material response of a mixture of viscous polar fluids with diffusion, chemical reactions, and conduction of heat and electric current.

Once all relevant constitutive assumptions and balance equations have been established, the entropy principle can be exploited. For a physically realizable process of the mixture investigated, the entropy inequality (2.5.1) must be satisfied subject to the simultaneous satisfaction of the balance laws (2.6.3), (3.2.5), (3.2.7), (3.2.12), (3.2.18),

and (3.2.21). Instead of fulfilling the entropy inequality for independent fields that are constrained by the balance laws, one employs the method of Lagrange multipliers proposed by Liu [33]. According to this approach, the entropy inequality is subtracted from the products of each balance equation with its corresponding Lagrange multiplier, so that it can be satisfied for unrestricted independent fields. For the mixture investigated, the extended entropy inequality

$$\begin{aligned}
\Pi = & \rho \frac{d\eta}{dt} + \text{div}(\Phi) - \rho\sigma - \Lambda^\rho \left(\frac{d\rho}{dt} + \rho \text{div}(\mathbf{v}) \right) - \\
& \Lambda^{\mathbf{v}} \cdot \left(\rho \frac{d\mathbf{v}}{dt} - \text{div}(\mathbf{T}) - q\mathbf{E} - \rho\mathbf{b} - \mathbf{P} \cdot \nabla \mathbf{E} \right) - \\
& \sum_{a=1}^{n-1} \Lambda^{\xi_a} \left(\rho \frac{d\xi_a}{dt} + \text{div}(\mathbf{j}_a) - c_a \right) - \Lambda^\omega \cdot \left(\rho \mathbf{I} \frac{d\omega}{dt} - \text{div}(\mathbf{C}) + 2\hat{\mathbf{t}} - \rho \mathbf{l} - \mathbf{P} \times \mathbf{E} \right) - \\
& \Lambda^\varepsilon \left(\rho \frac{d\varepsilon}{dt} + \text{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla \mathbf{v} - \mathbf{C} \cdot \nabla \omega - 2\omega \cdot \hat{\mathbf{t}} - \rho r - \dot{\mathbf{P}} \cdot \mathbf{E} - \mathbf{i} \cdot \mathbf{E} \right) - \\
& \Lambda^G (\text{div}(\mathbf{P}) - \epsilon_o \text{div}(\mathbf{E}) - q) \geq 0
\end{aligned} \tag{4.2.5}$$

holds for any solution $\{\rho(\mathbf{x}, t), \xi_a(\mathbf{x}, t), \mathbf{v}(\mathbf{x}, t), \omega(\mathbf{x}, t), \theta(\mathbf{x}, t), \mathbf{E}(\mathbf{x}, t)\}$ of the field equations, where ϵ_o is homogeneous. Here, the quantities Λ^ρ , $\Lambda^{\mathbf{v}}$, Λ^{ξ_a} , Λ^ω , Λ^ε , and Λ^G represent the Lagrange multipliers associated with the constraints placed on the entropy inequality by the balance equations. These Lagrange multipliers may be given by constitutive relations too.

In addition to previous constitutive assumptions, some further premises must be taken into account, most of which are plausible. They are:

- Even though the solvent mass is much bigger than the masses of the other constituents of the mixture (this hypothesis is feasible up to $1.0 \times 10^{-1} \text{ mol L}^{-1}$), the electrolyte solution may not behave as an ideal dilute solution. If so, interactions among the constituent particles of the mixture have a great influence on the thermodynamic behavior of the solution and, thus, they must be accounted for. In this chapter, such interactions are considered by assembling concepts of polar and continuum mixture theories. Consequently, new phenomenological coefficients should appear in the constitutive model proposed;
- For many materials whose constitutive class does not encompass the time derivative of temperature, $d\theta/dt$, in the set of independent constitutive variables, and the heat flux is collinear to the entropy flux, then the Lagrange multiplier of energy is the

reciprocal of the empirical temperature, $\Lambda^\varepsilon = 1/\theta$, also referred to as coldness [73]. This definition was obtained by Müller [45, 46, 47, 48] by assuming the existence of a special kind of material singular surface, the so-called ideal surface, across which the entropy jump condition is

$$\llbracket \Phi \rrbracket \cdot \mathbf{n} = \llbracket \Lambda^\varepsilon \mathbf{h} \rrbracket \cdot \mathbf{n} = 0 \Leftrightarrow \llbracket \theta \rrbracket = 0. \quad (4.2.6)$$

Whenever an ideal wall separates two bodies, the jump condition above is the requirement that the normal component of the entropy flux is continuous. In practical terms, Müller took for granted that Equation (4.2.6) is necessary to make the temperature measurable through a thermometer. Moreover, as a direct consequence of the existence of such ideal surfaces between any material body brought into contact with a single body, Equation (4.2.6) always will imply that $\Lambda^\varepsilon = 1/\theta$. However, for many material classes e.g. granular and porous media and multiphase mixtures exhibiting a single temperature, ideal material surfaces do not exist. In reference [74], Wilmanski found conditions for which the temperature is continuous across a material singular surface in a fluid-solid mixture. The first of these conditions allows no entropy production on the singular surface, and the second one requires either impermeability of the surface or continuity of the Gibbs energy across the surface. Indeed, for theories with multiple temperatures, this situation is even worse since the problem does not have a solution yet. Hence, in view of these considerations, in this work it is assumed that under sufficiently general conditions, there exists an ideal surface across which the temperature, and the tangential velocity are continuous, such that the behavior of the electrochemical system is not affected;

- The definition of Λ^{ξ_a} can be obtained by taking into account a semipermeable membrane, which separates the reacting ionic mixture and one of its constituents a [36]. Excluding the possibility of tangential velocities at the wall and by assuming that the temperature is continuous at the membrane, one obtains the following jump expression,

$$\llbracket -\frac{\Lambda^{\xi_a}}{\Lambda^\varepsilon} + \frac{1}{2} (\mathbf{v}_a - u_n \mathbf{n})^2 \rrbracket = 0.$$

The first term on the left-hand side of the expression is named chemical potential, $\bar{\mu}_a$, whereas the second one is the kinetic energy of the motion of the constituent a in relation to the semipermeable wall. Clearly, only the chemical potential is a constitutive quantity, and it is easily related to the Lagrange multiplier of concentration by $\bar{\mu}_a = -\Lambda^{\xi_a}/\Lambda^\varepsilon$;

- The definition of Λ^ρ comes from the evaluation of equilibrium conditions for a viscous heat-conducting fluid, *i.e.*, $p = -\rho\Lambda^\rho/\Lambda^\varepsilon$ [29, 74]. Then, because of the great excess of solvent mass in relation to the masses of other constituents, the dynamics of a reacting ionic mixture is nearly the same as for a viscous heat-conducting fluid. Consequently, one may use the previous definition without loss of generality;
- Since the constitutive properties of a reacting ionic mixture should not depend on external supplies, it suffices to consider supply-free mixtures. In other terms, the entropy supply vanishes as long as the linear momentum, spin, and energy sources are null,

$$\rho\mathbf{b} = \mathbf{0}, \rho\mathbf{l} = \mathbf{0}, \rho r = 0 \Rightarrow \rho\sigma = 0.$$

- The mixture is an isotropic medium. However, exceptionally, the degree of polarization of the electrolyte solution and its constituents is completely determined by a non-linear anisotropic function of type $P_i = \gamma_{ij}^1 E_j + \gamma_{ijk}^2 E_j E_k + \dots$, where γ^m is the m -th order electric susceptibility. In general, for weak electric fields, γ^m is a constant characteristic of the dielectric medium, and it depends on the temperature since thermal agitation tends to oppose the order of electric dipoles induced by \mathbf{E} [59]. Thus, owing to the great excess of solvent mass in relation to the masses of the other constituents, the dielectric properties of the whole solution are due almost exclusively to the electric dipoles of water molecules.

Substituting the constitutive relations (4.2.3) and (4.2.4) into inequality (4.2.5) and by performing all required differentiations according to the chain-rule, one obtains

$$\begin{aligned} \Pi = & \frac{d\rho}{dt} \left(\rho \frac{\partial\eta}{\partial\rho} - \Lambda^\rho - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\rho} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial\mathbf{P}}{\partial\rho} \right) + \\ & \frac{d\nabla\rho}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\rho} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\rho} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\rho} \right) + \\ & \sum_{a=1}^{n-1} \frac{d\xi_a}{dt} \left(\rho \frac{\partial\eta}{\partial\xi_a} - \rho\Lambda^{\xi_a} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\xi_a} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial\mathbf{P}}{\partial\xi_a} \right) + \\ & \sum_{b=1}^{n-1} \frac{d\nabla\xi_b}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\xi_b} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\xi_b} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\xi_b} \right) + \\ & \frac{d\mathbf{W}}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\mathbf{W}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{W}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\mathbf{W}} \right) + \frac{d\boldsymbol{\omega}}{dt} \cdot (-\rho\mathbf{I}\Lambda^\omega) + \\ & \frac{d\nabla\boldsymbol{\omega}}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\boldsymbol{\omega}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\boldsymbol{\omega}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\boldsymbol{\omega}} \right) + \end{aligned} \quad (4.2.7)$$

$$\begin{aligned}
& \frac{d\theta}{dt} \left(\rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \theta} \right) + \\
& \frac{d\nabla\theta}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \nabla\theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla\theta} + \Lambda^\varepsilon \mathbf{E} \frac{\partial \mathbf{P}}{\partial \nabla\theta} \right) + \\
& \frac{d\mathbf{E}}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \mathbf{E}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{E}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial \mathbf{P}}{\partial \mathbf{E}} \right) + \\
& \frac{d\mathbf{D}}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial \mathbf{P}}{\partial \mathbf{D}} \right) + \frac{d\mathbf{v}}{dt} \cdot (-\rho \Lambda^\nu) + \\
& \nabla \rho \cdot \left(\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \rho} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) + \\
& \nabla (\nabla \rho) \cdot \left(\frac{\partial \Phi}{\partial \nabla \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \rho} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \rho} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \nabla \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \rho} \right) + \\
& \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \xi_b} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) + \\
& \sum_{b=1}^{n-1} \nabla (\nabla \xi_b) \cdot \left(\frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} \Big|_{a \neq b} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \xi_b} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \nabla \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) + \\
& \nabla \mathbf{W} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{W}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{W}} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{W}} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \mathbf{W}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{W}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{W}} \right) + \\
& \nabla (\nabla \omega) \cdot \left(\frac{\partial \Phi}{\partial \nabla \omega} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \omega} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \omega} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \nabla \omega} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \omega} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \omega} \right) + \\
& \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \theta} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) + \\
& \nabla (\nabla \theta) \cdot \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \theta} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) + \\
& \nabla \mathbf{E} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{E}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{E}} + \Lambda^\nu \cdot \mathbf{P} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{E}} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \mathbf{E}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{E}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{E}} \right) + \\
& \nabla \mathbf{D} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{D}} + \Lambda^\omega \frac{\partial \mathbf{C}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} \right) - \\
& 2\Lambda^\omega \cdot \hat{\mathbf{t}} + \Lambda^\omega \cdot (\mathbf{P} \times \mathbf{E}) + \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} + 2\Lambda^\varepsilon \hat{\mathbf{t}} \cdot \boldsymbol{\omega} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} + \\
& \Lambda^G \epsilon_o \operatorname{div}(\mathbf{E}) + \Lambda^G q + \Lambda^\varepsilon \mathbf{C} \cdot \nabla \boldsymbol{\omega} + \sum_{a=1}^{n-1} \Lambda^{\xi_a} c_a + \Lambda^\varepsilon \mathbf{i} \cdot \mathbf{E} \geq 0.
\end{aligned}$$

Alternatively, inequality (4.2.7) can be expressed as

$$\Pi = \mathbf{A}(y) \cdot \mathbf{Z} + B(y) \geq 0, \quad (4.2.8)$$

where $\mathbf{A}(y)$ and $B(y)$ are respectively vector and scalar functions of the variables y listed in (4.2.3), but not of \mathbf{Z} ,

$$\mathbf{Z} \in \left\{ \frac{d\rho}{dt}, \frac{d\nabla\rho}{dt}, \frac{d\xi_b}{dt}, \frac{d\nabla\xi_b}{dt}, \frac{d\theta}{dt}, \frac{d\nabla\theta}{dt}, \frac{d\mathbf{W}}{dt}, \frac{d\boldsymbol{\omega}}{dt}, \frac{d\nabla\boldsymbol{\omega}}{dt}, \frac{d\mathbf{E}}{dt}, \frac{d\mathbf{D}}{dt}, \frac{d\mathbf{v}}{dt}, \nabla(\nabla\rho), \nabla(\nabla\xi_b), \nabla(\nabla\theta), \nabla\mathbf{E}, \nabla\mathbf{D}, \nabla\mathbf{W}, \nabla(\nabla\boldsymbol{\omega}), \text{div}(\mathbf{E}) \right\}. \quad (4.2.9)$$

Hence, by the principle of local solvability [33, 35] Liu demonstrated that the inequality (4.2.8) must hold for arbitrary values of y and \mathbf{Z} . The necessary and sufficient condition for this is

$$\mathbf{A}(y) = \mathbf{0}, \quad B(y) \geq 0. \quad (4.2.10)$$

In other words, (4.2.10) indicates that the coefficients of \mathbf{Z} must vanish, otherwise expression (4.2.8) could be violated. These arguments lead to the following Liu identities

$$\begin{aligned} \rho \frac{\partial\eta}{\partial\rho} - \Lambda^\rho - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\rho} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial\mathbf{P}}{\partial\rho} &= 0, \\ \rho \frac{\partial\eta}{\partial\nabla\rho} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\rho} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\rho} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\xi_a} - \rho\Lambda^{\xi_a} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\xi_a} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial\mathbf{P}}{\partial\xi_a} &= 0 \quad (\forall a = 1, \dots, n-1), \\ \rho \frac{\partial\eta}{\partial\nabla\xi_b} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\xi_b} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\xi_b} &= \mathbf{0} \quad (\forall b = 1, \dots, n-1), \\ \rho \frac{\partial\eta}{\partial\mathbf{W}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{W}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\mathbf{W}} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\nabla\boldsymbol{\omega}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\boldsymbol{\omega}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\boldsymbol{\omega}} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\theta} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\theta} + \Lambda^\varepsilon \mathbf{E} \cdot \frac{\partial\mathbf{P}}{\partial\theta} &= 0, \\ \rho \frac{\partial\eta}{\partial\nabla\theta} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\theta} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\nabla\theta} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\mathbf{E}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{E}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\mathbf{E}} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\mathbf{D}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{D}} + \Lambda^\varepsilon \mathbf{E} \frac{\partial\mathbf{P}}{\partial\mathbf{D}} &= \mathbf{0}, \\ -\rho I \Lambda^\omega &= \mathbf{0}, \quad -\rho \Lambda^\nu = \mathbf{0}, \quad \Lambda^G = 0, \end{aligned} \quad (4.2.11)$$

$$\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \rho} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \rho} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \nabla \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \rho} \right) = \mathbf{0}, \quad (4.2.12)$$

$$\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \xi_b} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \nabla \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) = \mathbf{0} \quad (\forall b = 1, \dots, n-1),$$

$$\frac{\partial \Phi}{\partial \mathbf{W}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{W}} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{W}} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \mathbf{W}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{W}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{W}} = \mathbf{0},$$

$$\frac{\partial \Phi}{\partial \nabla \omega} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \omega} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \omega} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \nabla \omega} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \omega} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \omega} = \mathbf{0},$$

$$\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \theta} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) = \mathbf{0},$$

$$\frac{\partial \Phi}{\partial \mathbf{E}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{E}} + \Lambda^{\mathbf{v}} \cdot \mathbf{P} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{E}} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \mathbf{E}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{E}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{E}} = \mathbf{0},$$

$$\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{D}} + \Lambda^{\omega} \frac{\partial \mathbf{C}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} = \mathbf{0},$$

whence certain thermodynamic relations are expected to be maintained, namely:

1. The thermodynamic potential, $\psi = \varepsilon - \theta\eta - 1/\rho \mathbf{P} \cdot \mathbf{E}$, is function of ρ , ξ_a , θ , and \mathbf{E} ;
2. The Lagrange multipliers of the balance equations of linear momentum, spin, and Gauss law are zero:

$$\Lambda^{\omega} = \mathbf{0}, \quad \Lambda^{\mathbf{v}} = \mathbf{0}, \quad \Lambda^G = 0;$$

3. The extra entropy flux vector, $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$, which takes into account all deviations of the entropy flux vector in relation to the heat and diffusive flux vectors, does not amount to a restriction.

The first statement follows from identities (4.2.11)_{2,4,5,6,8,10} which demonstrate a reduced independence on the list (4.2.3) for the thermodynamic potential ψ . Then, with the aid of the thermodynamic potential ψ and the definitions of hydrostatic pressure, $p = -\rho\Lambda^\rho/\Lambda^\varepsilon$, chemical potential, $\bar{\mu}_a = -\Lambda^{\xi_a}/\Lambda^\varepsilon$, and coldness, $\Lambda^\varepsilon = 1/\theta$, the identities (4.2.11)_{1,3,7,9} produce

$$d\psi = \frac{p}{\rho^2}d\rho + \sum_{a=1}^{n-1} \bar{\mu}_a d\xi_a - \eta d\theta - \mathbf{P} \cdot d\left(\frac{\mathbf{E}}{\rho}\right), \quad (4.2.13)$$

whence $\partial\psi/\partial\rho = p/\rho^2 + \mathbf{P} \cdot \mathbf{E}/\rho^2$, $\partial\psi/\partial\xi_a = \bar{\mu}_a$, $\partial\psi/\partial\theta = -\eta$, and $\partial\psi/\partial\mathbf{E} = -\mathbf{P}/\rho$. If electromagnetic fields are absent, relation (4.2.13) coincides with the Helmholtz relation of the classical thermostatics. However, the former is more comprehensive than that of classical thermostatics because it holds for any point of the material body and it is valid under equilibrium and non-equilibrium conditions.

Moreover, in view of previous constitutive assumptions presented, one demonstrates by cross differentiation of the Liu identities (4.2.11)_{1,3,7,9} that $\eta = \hat{\eta}(\rho, \theta, \xi_a)$, $\varepsilon = \hat{\varepsilon}(\rho, \theta, \xi_a)$, $\Lambda^\rho = \hat{\Lambda}^\rho(\rho, \theta, \xi_a)$, and $\Lambda^{\xi_a} = \hat{\Lambda}^{\xi_a}(\rho, \theta, \xi_a)$. One also shows from relation (4.2.13) and the reduced dependencies above that the integrability conditions for $d\psi$ are

$$\frac{\partial \bar{\mu}_a}{\partial \rho} = \frac{\partial (p/\rho^2)}{\partial \xi_a}, \quad \frac{\partial (p/\rho^2)}{\partial \theta} = -\frac{\partial \eta}{\partial \rho}, \quad \frac{\partial \bar{\mu}_a}{\partial \theta} = -\frac{\partial \eta}{\partial \xi_a}, \quad (4.2.14)$$

where \mathbf{P} is function only of \mathbf{E} , as previously stated.

The second statement is a direct result of identity (4.2.11)₁₁ and it does not deserve additional comments. On the other hand, the third statement results from identity (4.2.12), which suggests the introduction of an extra entropy flux defined by $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$. Here, it is worthwhile remembering that in obtaining the identities (4.2.12)_{1,2,5}, the theorem of Cartesian decomposition of tensors was used in order to impose that only the symmetric parts of $\nabla(\nabla\rho)$, $\nabla(\nabla\xi_b)$, and $\nabla(\nabla\theta)$ need to vanish. The proof of this statement can be easily found in reference [35].

Substituting the definition of extra entropy flux into identity (4.2.12), results in

$$\begin{aligned} \text{sym} \left(\frac{\partial \phi}{\partial \nabla \rho} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \nabla \rho} \mathbf{j}_a \right), \quad \text{sym} \left(\frac{\partial \phi}{\partial \nabla \xi_b} \right) = \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \nabla \xi_b} \mathbf{j}_a \Big|_{a \neq b} \right) \quad (\forall b = 1, \dots, n-1), \\ \frac{\partial \phi}{\partial \mathbf{W}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \mathbf{W}} \mathbf{j}_a, \quad \frac{\partial \phi}{\partial \nabla \boldsymbol{\omega}} = \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \nabla \boldsymbol{\omega}} \mathbf{j}_a, \\ \text{sym} \left(\frac{\partial \phi}{\partial \nabla \theta} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \nabla \theta} \mathbf{j}_a \right), \quad \frac{\partial \phi}{\partial \mathbf{E}} = \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \mathbf{E}} \mathbf{j}_a, \\ \frac{\partial \phi}{\partial \mathbf{D}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \bar{\mu}_a}{\partial \mathbf{D}} \mathbf{j}_a. \end{aligned} \quad (4.2.15)$$

With the definition $\bar{\mu}_a = -\Lambda^{\xi_a}/\Lambda^\varepsilon$, the reduced dependence of Λ^{ξ_a} should be reflected in $\bar{\mu}_a$ and, then, $\bar{\mu}_a = \hat{\mu}_a(\rho, \theta, \xi_a)$. Consequently, since the derivatives above must vanish, $\text{sym}(\partial\phi/\partial\nabla\rho) = \mathbf{0}$, $\text{sym}(\partial\phi/\partial\nabla\xi_b) = \mathbf{0}$, $\partial\phi/\partial\mathbf{W} = \mathbf{0}$, $\partial\phi/\partial\nabla\boldsymbol{\omega} = \mathbf{0}$, $\text{sym}(\partial\phi/\partial\nabla\theta) = \mathbf{0}$, $\partial\phi/\partial\mathbf{E} = \mathbf{0}$, and $\partial\phi/\partial\mathbf{D} = \mathbf{0}$, the extra entropy flux vector is zero, and Φ can be rewritten as $\Phi = \Lambda^\varepsilon\mathbf{h} - \Lambda^\varepsilon\sum_{a=1}^{n-1}\bar{\mu}_a\mathbf{j}_a$.

After elimination of the linear terms, one uses $\nabla\bar{\mu}_a = (\partial\bar{\mu}_a/\partial\rho)\nabla\rho + \sum_{b=1}^{n-1}(\partial\bar{\mu}_a/\partial\xi_b)\nabla\xi_b|_{a\neq b} + (\partial\bar{\mu}_a/\partial\theta)\nabla\theta$ and $\Phi = \Lambda^\varepsilon\mathbf{h} - \Lambda^\varepsilon\sum_{a=1}^{n-1}\bar{\mu}_a\mathbf{j}_a$ to rewrite inequality (4.2.7) as

$$\begin{aligned} \Pi = & -\sum_{a=1}^{n-1}\mathbf{j}_a \cdot \nabla\bar{\mu}_a + \left(\sum_{a=1}^{n-1}\bar{\mu}_a\mathbf{j}_a - \mathbf{h}\right) \cdot \frac{\nabla\theta}{\theta} + \mathbf{C} \cdot \nabla\boldsymbol{\omega} + \\ & \mathbf{T} \cdot \mathbf{D} + p\mathbf{1} \cdot \mathbf{D} - \sum_{a=1}^{n-1}\bar{\mu}_a c_a + \mathbf{i} \cdot \mathbf{E} \geq 0, \end{aligned} \quad (4.2.16)$$

whence one may obtain other important thermodynamic restrictions on the constitutive relations.

Nevertheless, before discussing the consequences of inequality (4.2.16) on the constitutive quantities listed in (4.2.4), an important concept of chemical thermodynamics deserves to be presented. The symmetrical of the chemical affinity of a reaction r is

$$\mathcal{U}_r = \sum_{a=1}^{n-1}\nu_{ar}\bar{\mu}_a, \quad (4.2.17)$$

where ν_{ar} divided by the molecular mass of constituent a is proportional to the corresponding stoichiometric coefficient in the chemical reaction r , and the solvent is regarded as inert because of its great excess in the mixture. For the sake of convention, ν_{ar} is taken as positive for the products of a reaction, and negative for the reagents. In addition, in agreement with Bedford and Bowen's ideas [2, 5, 7], the mass production of a is the net rate of mass supply to constituent a resulting from chemical reactions. Mathematically, the mass production of constituent a is expressed by

$$c_a = \sum_{r=1}^R \nu_{ar}\Upsilon_r, \quad (4.2.18)$$

where Υ_r is the rate of conversion of r , supposing R independent chemical reactions.

Combining Equations (4.2.17) and (4.2.18), one writes $\sum_{a=1}^{n-1} c_a \bar{\mu}_a = \sum_{r=1}^R \Upsilon_r \Upsilon_r$, and inequality (4.2.16) reduces to

$$\begin{aligned} \Pi = & - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \bar{\mu}_a + \left(\sum_{a=1}^{n-1} \bar{\mu}_a \mathbf{j}_a - \mathbf{h} \right) \cdot \frac{\nabla \theta}{\theta} + \mathbf{C} \cdot \nabla \boldsymbol{\omega} + \mathbf{T} \cdot \mathbf{D} + \\ & p1 \cdot \mathbf{D} - \sum_{r=1}^R \Upsilon_r \Upsilon_r + \mathbf{i} \cdot \mathbf{E} \geq 0. \end{aligned} \quad (4.2.19)$$

Inequality (4.2.19) is the residual entropy production and comprises a necessary condition to inequality (4.2.5) to be maintained for any solution $\{\rho(\mathbf{x}, t), \xi_a(\mathbf{x}, t), \mathbf{v}(\mathbf{x}, t), \boldsymbol{\omega}(\mathbf{x}, t), \theta(\mathbf{x}, t), \mathbf{E}(\mathbf{x}, t)\}$ of the field equations.

4.2.1 Thermodynamic restrictions

The thermodynamic equilibrium state at (\mathbf{x}, t) of a reacting ionic mixture is defined as that thermodynamic state in which the residual entropy production attains the minimum value, expressly zero. This definition of local thermodynamic equilibrium state does not require that the quantities $\zeta \in \{\Upsilon_r, \nabla \theta, \nabla \bar{\mu}_a, \mathbf{E}, \nabla \boldsymbol{\omega}, \mathbf{D}\}$ are time independent neither spatially homogeneous nor null. In other words, this condition asserts that, at a material point, any local thermo-electromechanical state can be an equilibrium state provided the ζ quantities have appropriate values. As a consequence, Π must satisfy

$$\begin{aligned} \Pi : \zeta \rightarrow Y \mid \zeta \in \{\Upsilon_r, \nabla \theta, \nabla \bar{\mu}_a, \mathbf{E}, \nabla \boldsymbol{\omega}, \mathbf{D}\} \\ \left(\frac{\partial \Pi}{\partial \zeta} \right) \Big|_E = 0, \quad \left(\frac{\partial^2 \Pi}{\partial \zeta \partial \zeta} \right) \Big|_E \geq 0, \end{aligned} \quad (4.2.20)$$

where the index E stands for local equilibrium state.

From inequality (4.2.19) and relation (4.2.20), the first-order derivatives of the residual entropy production in relation to $\nabla \bar{\mu}_a$, $\nabla \theta$, and $\nabla \boldsymbol{\omega}$ result in

$$\left(\frac{\partial \Pi}{\partial \nabla \bar{\mu}_a} \right) \Big|_E = -\mathbf{j}_a = \mathbf{0} \quad (\forall a = 1, \dots, n-1), \quad (4.2.21)$$

$$\left(\frac{\partial \Pi}{\partial \nabla \theta} \right) \Big|_E = \frac{1}{\theta} \left(\sum_{a=1}^{n-1} \bar{\mu}_a \mathbf{j}_a - \mathbf{h} \right) = \mathbf{0}, \quad (4.2.22)$$

or yet

$$\left(\frac{\partial \Pi}{\partial \nabla \theta} \right) \Big|_E = -\frac{1}{\theta} \mathbf{h} = \mathbf{0},$$

and

$$\left(\frac{\partial \Pi}{\partial \nabla \boldsymbol{\omega}} \right) \Big|_E = \mathbf{C} = \mathbf{0}. \quad (4.2.23)$$

Hence, at local equilibrium, there are no diffusive fluxes of species neither flux of heat, nor coupling stresses. Moreover, for Υ_r , inequality (4.2.19) and relation (4.2.20) lead to

$$\left(\frac{\partial \Pi}{\partial \Upsilon_r} \right) \Big|_E = -\mathcal{U}_r = 0 \quad (\forall r = 1, \dots, R), \quad (4.2.24)$$

where the result above is the known local chemical equilibrium condition. Note that the local chemical equilibrium does not require local kinetic equilibrium, that is, the mass concentrations time derivative of the constituents of the mixture may not be null. In fact, since for non-homogeneous electrochemical systems Equation (2.2.7) holds, one easily obtains from relations (4.2.17) and (4.2.18),

$$-\sum_{a=1}^{n-1} \rho \bar{\mu}_a \frac{d\xi_a}{dt} - \sum_{a=1}^{n-1} \bar{\mu}_a \operatorname{div}(\mathbf{j}_a) = -\sum_{r=1}^R \mathcal{U}_r \Upsilon_r, \quad (4.2.25)$$

whence one concludes that if and only if $-\mathcal{U}_r = 0$ for all r and $\operatorname{div}(\mathbf{j}_a) = 0$ for all a , $d\xi_a/dt$ is zero.

Other conditions to ensure $\Pi = 0$ at (\mathbf{x}, t) are

$$\left(\frac{\partial \Pi}{\partial \mathbf{D}} \right) \Big|_E = \mathbf{T} + p \mathbf{1} = \mathbf{0} \quad (4.2.26)$$

that produces

$$\mathbf{T} = -p \mathbf{1},$$

and

$$\left(\frac{\partial \Pi}{\partial \mathbf{E}} \right) \Big|_E = \mathbf{i} = \mathbf{0}. \quad (4.2.27)$$

In addition, observe that the necessary conditions to obtain local thermodynamic equilibrium are different that characterize macroscopic thermodynamic equilibrium, *viz.* a state in which all constituents are at rest in relation to one frame of reference and thermo-

dynamic quantities, such as temperature gradient, velocity gradient, rate of conversion of a reaction *etc.* are time-independent and uniform [47]. On the other hand, one can obtain these conditions from the local thermodynamic equilibrium conditions by constructing appropriate Lyapunov functions through the definition of the entropy flux vector and the balance equations, as shown in [12].

The constitutive modeling of reacting ionic mixtures proceeds by analyzing the second restriction invoked by the entropy principle on (4.2.4) to find restrictions on phenomenological parameters. For the sake of simplicity, it is imposed that the microscopic structure of the system does not influence diffusive fluxes as well as the current flow. Thus, the influence of local angular motion was considered only on the total stress tensor, coupling stress tensor, and the heat flux, such as in references [14, 16, 32].

Furthermore, unlike common electrolyte models, the fluxes of heat, mass and electric current are not given exclusively by their usual sources, but also by the cross phenomena of thermo-electricity, thermal diffusion, and electrophoresis. Therefore, considering the representation of isotropic constitutive functions [70, 71, 72], it follows that

$$\begin{aligned}
T_{ij} &= -p\delta_{ij} + \left(\alpha + \frac{2}{3}\beta \right) D_{mm}\delta_{ij} + 2\beta\bar{D}_{ij} + 2\vartheta e_{ijk}\varpi_k + O(2) , \\
C_{ij} &= \left(\lambda + \frac{2}{3}\tau \right) \omega_{k,k}\delta_{ij} + 2\tau\bar{\omega}_{i,j} + \delta\omega_{j,i} + \varsigma e_{ijk}\theta_{,k} + O(2) , \\
h_i &= k_1\theta_{,i} + k_2E_i + k_3\bar{\mu}_{,i}^a + k_4e_{ijk}\omega_{k,j} + O(2) , \\
i_i &= \iota_1\theta_{,i} + \iota_2E_i + \iota_3\bar{\mu}_{,i}^a , \\
j_i^a &= C_1^a\theta_{,i} + C_2^aE_i + C_3^a\bar{\mu}_{,i}^a ,
\end{aligned} \tag{4.2.28}$$

where \bar{D}_{ij} and $\bar{\omega}_{i,j}$ are respectively the traceless part of \mathbf{D} and $\nabla\boldsymbol{\omega}$, $O(2)$ denotes the terms whose order is bigger than one in each constitutive function, and all phenomenological coefficients are functions of ρ , θ , ξ_a , $\nabla\xi_a \cdot \nabla\xi_a$, $\nabla\theta \cdot \nabla\theta$, $\mathbf{E} \cdot \mathbf{E}$, $\nabla\xi_a \cdot \nabla\theta$, $\nabla\xi_a \cdot \mathbf{E}$, $\nabla\theta \cdot \mathbf{E}$, and $\text{tr}\mathbf{D}$. Note that if the microscopic structure of the mixture had been included in the conduction current and the diffusive flux, new phenomenological coefficients should appear in Equations (4.2.28)_{4,5} whose physical meaning has not been clarified yet.

Despite its inherent simplicity, Equation (4.2.28) is suitable to describe the diffusive and advective structures of electrolyte solutions far from the equilibrium. Nonetheless, as de Groot and Mazur [17] pointed out, the linear approximation for chemical reactions is not justifiable, except near an equilibrium state when the chemical affinity holds a reciprocal relation with the rate of conversion. Indeed, far from the equilibrium, chemical affinity is essentially a non-linear function of Υ_r , and its form varies according to the complexity of

the reaction. Actually, the task of determining a phenomenological equation for \mathcal{U}_r is quite complicated and unusual in Chemistry. Then, on account of these arguments, chemical affinity is treated only in general terms without specifying its constitutive nature.

Inserting Equation (4.2.28) into inequality (4.2.19), the residual entropy inequality becomes

$$\begin{aligned} \Pi = & - \sum_{a=1}^{n-1} (C_1^a \theta_{,i} + C_2^a E_i + C_3^a \bar{\mu}_{,i}^a) \mu_{,i}^a + \sum_{a=1}^{n-1} (C_1^a \theta_{,i} + C_2^a E_i + C_3^a \bar{\mu}_{,i}^a) \mu^a \frac{\theta_{,i}}{\theta} - \\ & (k_1 \theta_{,i} + k_2 E_i + k_3 \bar{\mu}_{,i}^a + k_4 e_{ijk} \omega_{k,j}) \frac{\theta_{,i}}{\theta} + \left(\alpha + \frac{2}{3} \beta \right) D_{mm}^2 + 2\beta \bar{D}_{ik} \bar{D}_{ik} + 2\vartheta e_{ijk} \omega_k D_{ij} + \\ & \left(\lambda + \frac{2}{3} \tau \right) \omega_{k,k}^2 + 2\tau \bar{\omega}_{i,j} \bar{\omega}_{i,j} + \delta \omega_{j,i} \omega_{j,i} + \varsigma e_{ijk} \theta_{,k} \omega_{i,j} - \sum_{r=1}^R \mathcal{U}_r \Upsilon_r - (\iota_1 \theta_{,i} - \iota_2 E_i + \iota_3 \bar{\mu}_{,i}^a) E_i \geq 0, \end{aligned} \quad (4.2.29)$$

and by performing the second-order derivatives of Π with respect to the variables listed in the set ζ , results in

$$\begin{aligned} \sum_{a=1}^{n-1} C_3^a & \leq 0, \quad \sum_{a=1}^{n-1} \frac{C_1^a \bar{\mu}^a}{\theta} + \frac{k_1}{\theta} \leq 0, \quad \iota_2 \leq 0, \\ -\sum_{a=1}^{n-1} C_1^a + \sum_{a=1}^{n-1} \frac{C_3^a \bar{\mu}^a}{\theta} - \frac{k_3}{\theta} & \geq 0, \quad \sum_{a=1}^{n-1} \frac{C_2^a \bar{\mu}^a}{\theta} - \frac{k_2}{\theta} - \iota_1 \geq 0, \\ \sum_{a=1}^{n-1} C_2^a + \iota_3 & \leq 0, \quad -k_4 + \varsigma \geq 0, \quad \vartheta \geq 0, \\ \lambda + \frac{2}{3} \tau & \geq 0, \quad \tau \geq 0, \quad \alpha + \frac{2}{3} \beta \geq 0, \\ \beta & \geq 0, \quad \delta \geq 0, \quad \varsigma \geq 0. \end{aligned} \quad (4.2.30)$$

C_3^a , k_1 , and ι_2 stand for diffusion, thermal conductivity, and resistivity coefficients, respectively. In turn, phenomenological coefficients C_1^a and k_3 are characteristic for the phenomenon of thermal diffusion, k_2 and ι_1 for the thermoelectric phenomenon, and C_2^a and ι_3 for the electrophoretic phenomenon. All these effects mentioned are known as cross phenomena and they present reciprocal nature in contrast to Fick's law, Fourier's law, and Ohm's law. Viscous properties of the electrolyte solution are accounted for by $\alpha + 2/3\beta$, β , ϑ , $\lambda + 2/3\tau$, τ , δ , and ς , where $\alpha + 2/3\beta$ and β denote respectively the bulk and shear viscosities of Newtonian fluids, while $\lambda + 2/3\tau$, τ , δ , and ς are the rotational viscosities that arise due to the inner structure of the mixture. An electrolyte solution which presents

rotational viscosities constrained by (4.2.30)_{9,10,13,14} exhibits a resistance to motion bigger than or equal to that of the viscous fluids under usual flow conditions.

Moreover, if one neglects all phenomena with exception of the chemical reactions in inequality (4.2.29), one writes

$$\Pi = -\sum_{r=1}^R \dot{U}_r \Upsilon_r \geq 0, \quad (4.2.31)$$

which is the criterion for spontaneity of chemical reactions.

5 Electrochemical Systems: Transport Phenomena

The study of ion-ion and ion-solvent interactions aims to know whether ions interact dynamically with the solvent molecules and other ions in solution. In turn, the study of mass transport in electrolyte mixtures covers diffusion and conductance of ions, where much of the basis is phenomenological. As a matter of fact, one may study the mass transport in electrolyte solutions by focusing on the individual motion of ions, that is, by following ions trajectories in the electrolyte and the speeds with which they stream around. Nonetheless, because these ionic movements are of random nature with relation to direction and speed, it is quite hard to trace individual ions trajectories in the mixture, unless some radioactive tracer is used.

Conversely, one may investigate the mass transport in electrochemical systems by tracking the movement of a group of ions in a certain direction, producing a drift or flux. This point of view is much more interesting than the first one since ionic drift results in matter transport and flow of charge. Moreover, there is another aspect that justifies the analysis of ionic drift, instead of the individual motion of ions: if a directional ionic flow did not occur, the interfaces between the electrodes and electrolyte of an electrochemical system would be out of ions to maintain the charge-transfer reactions that happen at these interfaces. Therefore, the drift of ions is of fundamental significance to the dynamics of an electrochemical system.

Electrochemistry literature [3, 4] supposes that a flux of ions can arise from three mechanisms. If there is a difference in the concentration of ions in different regions of the electrolyte, the resulting concentration gradient produces a flow of ions, and the phenomenon is termed diffusion. If there is a difference in electric potential at various points in the electrolyte, then the resulting electric field produces a flow of charge in its direction, and the phenomenon is termed migration or conduction. Finally, if a difference in pressure, density or even temperature exists in various parts of the electrolyte, then there exists a fluid flow caused by natural or forced convection whose flow regime may be characterized by stagnant regions, laminar flow, turbulent flow, among others.

Obviously, the relative contributions of diffusion and migration to the flux of a species differ at a certain instant for different locations in the electrochemical system. Near the electrode, an electroactive substance is, in general, transported by both processes. Differently, far from the electrodic surface, an electroactive substance is carried by the migrational mechanism, and the diffusion plays a secondary role because the concentration gradient is generally small in the bulk phase.

For many electrochemical systems, the mathematical treatments are simplified if the migrational and convective components to the flux of the electroactive substance are made negligible. This may be reached if an excess of supporting electrolyte— an electrolyte solution whose constituents are not electroactive in the range of applied potentials and whose ionic strength is usually much larger than that of the electroactive substance under consideration— is added into the solution, and the electrochemical system is kept at rest. Even so, one needs more physical restrictions on the electrochemical system in order to obtain a simplified mathematical treatment.

In a more realistic description of electrochemical systems, where the temperature is not spatially uniform, it seems that the definitions above are not very convenient. In this case, the theoretical framework provided by the classical electrochemistry literature may not be comprehensive enough, and a new approach should be used. Such an approach is provided next.

5.1 Proposed continuum model

The electrochemical system is regarded as an apolar material body formed by two regions: a region of ionic conduction (bulk) and another that corresponds to an electrically charged interface (double layer). The former is an isotropic medium whose concentration and electric potential gradients of species are not significant. Consequently, the concentration of any species is virtually constant and the basic phenomena involve ion-solvent and ion-ion interactions. On the other hand, the double layer is an inhomogeneous and anisotropic medium in relation to the mass, heat and current fluxes, and it comprises the region where the transfer of electrons between the electrode and the ionic solution takes place. For the sake of simplicity, the anisotropy of the double layer is treated as a special case of transverse isotropy, *i.e.*, there is an isotropic plane such that all directions in this plane are equivalent and all constitutive relations remain unchanged under arbitrary rotations of a coordinate system in relation to a major axis. Under these conditions, the fluxes of mass, heat and electric current present a preferred direction that is orthogonal to the isotropic plane.

Furthermore, the separation between the double layer and the bulk is marked by abrupt changes of the electric potential and species concentrations. Mathematically, these changes are accounted for through a singular surface that separates the bulk and double layer. At the singular surface, corresponding jump conditions for balance equations must be formulated. Nevertheless, the properties of the singular surface are not examined in this work.

5.1.1 Bulk region

In order to investigate the occurring physical phenomena in the bulk region, the basic fields— mass density of the mixture, $\rho(\mathbf{x}, t)$, mass concentration, $\xi_a(\mathbf{x}, t)$, empirical temperature, $\theta(\mathbf{x}, t)$, electric potential, $\varphi(\mathbf{x}, t)$, and velocity of the mixture, $\mathbf{v}(\mathbf{x}, t)$ — are evaluated by regarding the bulk as a heat and electric conducting viscous mixture. Thus, most of its properties are taken into account through the set of independent constitutive variables

$$y \in \{\rho, \nabla\rho, \xi_a, \theta, \nabla\theta, \varphi, \mathbf{v}, \nabla\mathbf{v}\} \quad (a = 1, \dots, n-1) . \quad (5.1.1)$$

However, as the principle of material objectivity requires that constitutive quantities must not depend on the observer, constitutive functions are independent of velocity, and they only depend on the gradient of velocity through its symmetric part, represented by the stretching tensor \mathbf{D} . Thus,

$$\mathcal{C} = \hat{\mathcal{C}}(\rho, \nabla\rho, \xi_a, \theta, \nabla\theta, \varphi, \mathbf{D}) , \quad (5.1.2)$$

where $\mathcal{C} \in \{\eta, \Phi, \mathbf{T}, \mathbf{P}, \varepsilon, \mathbf{h}, \mathbf{i}\}$.

The determination of the basic fields proceeds by evaluating the inequality,

$$\begin{aligned} \Pi = & \rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho\sigma - \Lambda^\rho \left(\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) \right) - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \left(\rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) \right) - \\ & \Lambda^{\mathbf{v}} \cdot \left(\rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}) + q \nabla\varphi - \rho \mathbf{b} + \mathbf{P} \cdot \nabla(\nabla\varphi) \right) - \\ & \Lambda^\varepsilon \left(\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla\mathbf{v} - \rho r + \dot{\mathbf{P}} \cdot \nabla\varphi + \mathbf{i} \cdot \nabla\varphi \right) - \\ & \Lambda^G (\operatorname{div}(\mathbf{P}) + \epsilon_o \nabla^2\varphi - q) \geq 0 \end{aligned} \quad (5.1.3)$$

which does not need to hold for arbitrary fields $\rho(\mathbf{x}, t)$, $\xi_a(\mathbf{x}, t)$, $\theta(\mathbf{x}, t)$, $\varphi(\mathbf{x}, t)$, and $\mathbf{v}(\mathbf{x}, t)$, but rather for those that are solutions of the balance equations considered. Thus, one

may take the balance equations as representing constraints on the fields that satisfy the entropy inequality [33].

In addition to the constitutive assumptions presented in the previous section, further hypotheses are necessary to guarantee the adequacy of the constitutive model. These auxiliary hypotheses are valid for both bulk and double layer regions. They are:

- The influence of interactions among the constituent particles on the system dynamics is neglected. In fact, there are many reasons to consider the bulk and double layer as apolar media and, consequently, overlook these interactions. The first motive is associated with the experimental difficulties in dealing with some phenomenological coefficients that appear in the diffusive and electric current fluxes, which have not been experimentally well-established yet. The second reason concerns the experimental limitations of electrochemical devices in operating with concentrated or moderately concentrated mixtures. In this case, the approximation of ideal dilute solution is not valid, resulting in the lack of reliable data in the electrochemical literature for these solutions. Finally, even if the influence of interactions among the constituents particles on concentrations was taken into account through the activity of ions, the Debye-Hückel model can no longer be used to relate the activity to the concentration of ions in non-dilute electrolyte solutions. Hence, if one desires to test the continuum model here proposed and compare the theoretical values obtained with the experimental ones, one should start with dilute solutions of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ – $1.0 \times 10^{-3} \text{ mol L}^{-1}$, where the contribution of interactions among species particles on mixture dynamics can be neglected;
- The Lagrange multiplier for the energy equation is inversely proportional to the temperature,

$$\Lambda^\varepsilon = \frac{1}{\theta}.$$

This assumption is valid, provided one assumes the existence of an impermeable ideal wall in electrochemical systems, where the entropy production vanishes, and the entropy flux and the temperature are continuous;

- Extending the definition of Λ^{ξ_a} provided in the last chapter to a medium under influence of quasi-electrostatic fields, Λ^{ξ_a} may be decomposed into an intrinsic constitutive part, a kinetic part, and an electric potential contribution, *viz.*

$$\llbracket -\frac{\Lambda^{\xi_a}}{\Lambda^\varepsilon} + \frac{1}{2} (\mathbf{v}_a - u_n \mathbf{n})^2 - z_a \varphi \rrbracket = 0.$$

The intrinsic part of Λ^{ξ_a} is the chemical potential of a , $\bar{\mu}_a = -\Lambda^{\xi_a}/\Lambda^\varepsilon$. On the other

hand, $\mu_a = \bar{\mu}_a - z_a \varphi$ is the electrodynamic potential since the energy state of a constituent carrier of charge in any location of the electrolyte solution clearly depends on the chemical environment and its own electric nature. Of course, if the chemical species is not a charge carrier, $\mu_a = \bar{\mu}_a$;

- The term c_a only deals with mass production due to electrodic reactions, *i.e.*, reactions that take place at the electrode surface. Thus, $c_a = 0$ for the bulk, and $c_a \neq 0$ for the double layer;
- As the medium is apolar, angular momentum balance indicates that the stress tensor is symmetric,

$$\mathbf{T} = \mathbf{T}^T,$$

and $\mathbf{P} \times \mathbf{E}$ and all coupling terms in the balance equations may be neglected. Consequently, the degree of polarization of each region of an electrochemical system is completely determined by an isotropic function of type $\mathbf{P} = -\epsilon_o \gamma^1 \nabla \varphi$. Thus, thanks to the great excess of solvent mass in relation to the masses of other constituents, the dielectric properties of each region of an electrochemical system are almost exclusively due to the solvent (water).

If the constitutive functions considered in (5.1.2) are introduced into inequality (5.1.3), and all differentiations are carried out according to the chain rule, the inequality (5.1.3) can be rewritten as

$$\begin{aligned} \Pi = & \frac{d\rho}{dt} \left(\rho \frac{\partial \eta}{\partial \rho} - \Lambda^\rho - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \rho} - \Lambda^\epsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \rho} \right) + \\ & \frac{d\nabla \rho}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \nabla \rho} - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \nabla \rho} - \Lambda^\epsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \nabla \rho} \right) + \\ & \sum_{a=1}^{n-1} \frac{d\xi_a}{dt} \left(\rho \frac{\partial \eta}{\partial \xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \xi_a} - \Lambda^\epsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \xi_a} \right) + \\ & \frac{d\theta}{dt} \left(\rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \theta} - \Lambda^\epsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \theta} \right) + \\ & \frac{d\nabla \theta}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \nabla \theta} - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \nabla \theta} - \Lambda^\epsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \nabla \theta} \right) + \\ & \frac{d\varphi}{dt} \left(\rho \frac{\partial \eta}{\partial \varphi} - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \varphi} - \Lambda^\epsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \varphi} \right) + \\ & \frac{d\mathbf{D}}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\epsilon \frac{\partial \epsilon}{\partial \mathbf{D}} - \Lambda^\epsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} \right) + \frac{d\mathbf{v}}{dt} \cdot (-\rho \Lambda^\nu) + \end{aligned} \quad (5.1.4)$$

$$\begin{aligned}
& \nabla \rho \cdot \left(\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) + \\
& \nabla (\nabla \rho) \cdot \left(\frac{\partial \Phi}{\partial \nabla \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \rho} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \rho} \right) + \\
& \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) + \\
& \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) + \\
& \nabla (\nabla \theta) \cdot \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) + \\
& \nabla \varphi \cdot \left(\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \varphi} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} \right) + \\
& \nabla \mathbf{D} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} \right) - \\
& \Lambda^{\mathbf{v}} \cdot [\mathbf{P} \cdot \nabla (\nabla \varphi)] + \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} - \Lambda^G \varepsilon_o \nabla^2 \varphi + \Lambda^G q \geq 0,
\end{aligned}$$

where ε_o is homogeneous. Inequality (5.1.4) is alternatively expressed as

$$\Pi = \mathbf{A}(y) \cdot \mathbf{Z} + B(y) \geq 0, \quad (5.1.5)$$

where $\mathbf{A}(y)$ and $B(y)$ respectively are vector and scalar functions of y , and \mathbf{Z} is a constitutive variable not listed in (5.1.1). Since the inequality above is linear in

$$\begin{aligned}
\mathbf{Z} \in \left\{ \frac{d\rho}{dt}, \frac{d\nabla \rho}{dt}, \frac{d\xi_a}{dt}, \frac{d\theta}{dt}, \frac{d\nabla \theta}{dt}, \frac{d\varphi}{dt}, \frac{d\mathbf{D}}{dt}, \frac{d\mathbf{v}}{dt}, \nabla (\nabla \rho), \right. \\
\left. \nabla \xi_b, \nabla (\nabla \theta), \nabla \varphi, \nabla (\nabla \varphi), \nabla \mathbf{D}, \nabla^2 \varphi \right\}, \quad (5.1.6)
\end{aligned}$$

it must hold for arbitrary values of y and \mathbf{Z} . The necessary and sufficient condition for this is

$$\mathbf{A}(y) = 0, \quad B(y) \geq 0. \quad (5.1.7)$$

In other terms, (5.1.7) indicates that the coefficients of \mathbf{Z} must vanish, otherwise inequality (5.1.5) could be violated. These arguments lead to the following Liu identities

$$\begin{aligned}
\rho \frac{\partial \eta}{\partial \rho} - \Lambda^\rho - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \rho} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \rho} &= 0, \\
\rho \frac{\partial \eta}{\partial \nabla \rho} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \rho} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \nabla \rho} &= \mathbf{0}, \\
\rho \frac{\partial \eta}{\partial \xi_a} - \rho \Lambda^{\xi_a} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \xi_a} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \xi_a} &= 0 \quad (a = 1, \dots, n-1), \\
\rho \frac{\partial \eta}{\partial \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \theta} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \theta} &= 0, \\
\rho \frac{\partial \eta}{\partial \nabla \theta} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \theta} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \nabla \theta} &= \mathbf{0}, \\
\rho \frac{\partial \eta}{\partial \varphi} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varphi} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \varphi} &= 0, \\
\rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{D}} &= \mathbf{0}, \\
-\rho \Lambda^\nu &= \mathbf{0}, \quad \Lambda^G = 0,
\end{aligned} \tag{5.1.8}$$

$$\begin{aligned}
\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \rho} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \rho} \right) &= \mathbf{0}, \\
\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} &= \mathbf{0} \quad (b = 1, \dots, n-1), \\
\text{sym} \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) &= \mathbf{0}, \\
\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \varphi} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} &= \mathbf{0}, \\
\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^\nu \frac{\partial \mathbf{T}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} &= \mathbf{0},
\end{aligned} \tag{5.1.9}$$

as well as the residual inequality

$$\begin{aligned}
\Pi = & \nabla \rho \cdot \left(\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) + \\
& \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) + \\
& \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} \geq 0.
\end{aligned} \tag{5.1.10}$$

In obtaining the Equations (5.1.9)_{1,3}, the theorem of Cartesian decomposition of tensors was employed to impose that only the symmetric parts of $\nabla(\nabla\rho)$ and $\nabla(\nabla\theta)$ need to vanish. Furthermore, in view of the constitutive assumptions previously established, one shows by cross differentiation of identity (5.1.8) that $\eta = \hat{\eta}(\rho, \xi_a, \theta)$, $\varepsilon = \hat{\varepsilon}(\rho, \xi_a, \theta)$, $\Lambda^\rho = \hat{\Lambda}^\rho(\rho, \xi_a, \theta)$, and $\Lambda^{\xi_a} = \hat{\Lambda}^{\xi_a}(\rho, \xi_a, \theta, \varphi)$. From Liu identity (5.1.8) and $\psi = \varepsilon - \theta\eta + \nabla\varphi \cdot \mathbf{P}/\rho$, one also demonstrates that the thermodynamic relation

$$d\psi = \frac{p}{\rho^2} d\rho + \sum_{a=1}^{n-1} \mu_a d\xi_a - \eta d\theta + \mathbf{P} \cdot d\left(\frac{\nabla\varphi}{\rho}\right) \tag{5.1.11}$$

holds at every point of the bulk, whether at equilibrium or not. Moreover, from identity (5.1.8) and relation (5.1.11), one obtains the integrability conditions,

$$\frac{\partial(p/\rho^2)}{\partial\theta} = -\frac{\partial\eta}{\partial\rho}, \quad \frac{\partial(p/\rho^2)}{\partial\xi_a} = \frac{\partial\mu_a}{\partial\rho}, \quad \frac{\partial\mu_a}{\partial\theta} = -\frac{\partial\eta}{\partial\xi_a}, \tag{5.1.12}$$

as well as the reduced dependence $\psi = \hat{\psi}(\rho, \xi_a, \theta, \nabla\varphi)$, where \mathbf{P} is a function of $\nabla\varphi$ only.

Using the definitions of Lagrange multipliers $\Lambda^{\mathbf{v}}$ and Λ^G , the extra entropy flux $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$ is introduced. Then, the Liu identity (5.1.9) become

$$\text{sym} \left(\frac{\partial \phi}{\partial \nabla \rho} \right) = \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \rho} \mathbf{j}_a \right), \quad \frac{\partial \phi}{\partial \xi_b} = \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \xi_b} \mathbf{j}_a \Big|_{a \neq b} \quad (\forall b = 1, \dots, n-1), \tag{5.1.13}$$

$$\text{sym} \left(\frac{\partial \phi}{\partial \nabla \theta} \right) = \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \theta} \mathbf{j}_a \right), \quad \frac{\partial \phi}{\partial \varphi} = \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \varphi} \mathbf{j}_a + \Lambda^\varepsilon \mathbf{i},$$

$$\frac{\partial \phi}{\partial \mathbf{D}} = \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{D}} \mathbf{j}_a,$$

where the definition of Λ^{ξ_a} was employed. However, as the reduced dependence of Λ^{ξ_a}

reflects on μ_a , one has $\mu_a = \hat{\mu}_a(\rho, \xi_a, \theta, \varphi)$, and from Equation (5.1.13), it follows that $\text{sym}(\partial\phi/\partial\nabla\rho) = \mathbf{0}$, $\partial\phi/\partial\xi_b = \mathbf{0}$, $\text{sym}(\partial\phi/\partial\nabla\theta) = \mathbf{0}$, and $\partial\phi/\partial\mathbf{D} = \mathbf{0}$, though $\partial\phi/\partial\varphi$ is not a null vector. Then, if one imposes that the extra entropy flux is an isotropic vector, ϕ is null because there are no scalar generators for an isotropic vector function [70, 71, 72].

Consequently, Equation (5.1.13)₄ becomes $\mathbf{i} = -\sum_{a=1}^{n-1} (\partial\mu_a/\partial\varphi) \mathbf{j}_a$. Applying the electrody-

namic potential definition, the latter can be simplified to the following expression $\mathbf{i} = \sum_{a=1}^{n-1} \mathbf{i}_a$,

which implies that the total current in the bulk is given by the algebraic sum of all flows of charge carrier constituents, also known as faradaic currents.

Recalling $\phi = \mathbf{0}$, the definition of the mass Lagrange multiplier, and $\nabla\mu_a = (\partial\mu_a/\partial\rho)\nabla\rho + (\partial\mu_a/\partial\theta)\nabla\theta$, the entropy flux takes the form $\Phi = \Lambda^\varepsilon \mathbf{h} + \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a$, and inequality (5.1.10) is rewritten as

$$\Pi = -\frac{\nabla\theta}{\theta} \cdot \mathbf{h} - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla\mu_a + \mathbf{T} \cdot \mathbf{D} + p\mathbf{l} \cdot \mathbf{D} \geq 0. \quad (5.1.14)$$

The left-hand side of expression (5.1.14) is the residual entropy production, a non-negative quantity for arbitrary values of $\{\rho, \xi_a, \nabla\mu_a, \theta, \nabla\theta, \varphi, \mathbf{D}\}$. Whenever Π takes the zero value, there is no entropy production, and one says that the point (\mathbf{x}, t) is at a thermodynamic equilibrium state. Necessary conditions for $\Pi = 0$ at (\mathbf{x}, t) are

$$\left(\frac{\partial\Pi}{\partial y_B}\right)\Big|_E = 0, \quad \left(\frac{\partial^2\Pi}{\partial y_B \partial y_B}\right)\Big|_E \geq 0, \quad (5.1.15)$$

where $y_B \in \{\nabla\theta, \nabla\mu_a, \mathbf{D}\}$, and the index E stands for the equilibrium state. Expressly, the heat conduction, the mass transport, and the deformations that occur in the electrolyte bulk are mechanisms that contribute to the production of residual entropy density.

In exploiting the first-order derivatives of Π with relation to y_B , constraints are imposed on the constitutive quantities. Thus, immediate consequences of (5.1.15)₁ are

$$\left(\frac{\partial\Pi}{\partial\nabla\theta}\right)\Big|_E = -\frac{1}{\theta} \mathbf{h} = \mathbf{0}, \quad (5.1.16)$$

$$\left(\frac{\partial\Pi}{\partial\nabla\mu_a}\right)\Big|_E = -\mathbf{j}_a = \mathbf{0} \quad (\forall a = 1, \dots, n-1), \quad (5.1.17)$$

and

$$\left. \left(\frac{\partial \Pi}{\partial \mathbf{D}} \right) \right|_E = \mathbf{T} + p\mathbf{1} = 0, \quad (5.1.18)$$

$$\mathbf{T} = -p\mathbf{1}.$$

Restrictions on constitutive functions also come from the second-order derivatives of Π with relation to y_B . Supposing an isotropic Newtonian fluid and following the theorem of representation of isotropic functions [70, 71, 72], one writes in component form

$$T_{ij} = -p\delta_{ij} + \left(\alpha + \frac{2}{3}\beta \right) D_{nn}\delta_{ij} + 2\beta\bar{D}_{ij} + O(2), \quad (5.1.19)$$

$$h_i = k_1\theta_{,i} + k_2\mu_{,i}^a + O(2),$$

$$j_i^a = C_1^a\mu_{,i}^a + C_2^a\theta_{,i} + O(2),$$

where all phenomenological coefficients are material functions \mathcal{P}_B of type

$$\mathcal{P}_B = \hat{\mathcal{P}}_B(\rho, \xi_a, \theta, \varphi, \nabla\theta \cdot \nabla\theta, \text{tr}\mathbf{D}). \quad (5.1.20)$$

Here, one points out that the definition of diffusive flux employed in continuum thermodynamics does not correspond to that of the classical electrochemistry literature [3, 4, 25] presented in the beginnings of this chapter. In continuum thermodynamics, the diffusive motion is the relative motion of the particles of constituents in relation to the barycentric motion and it is not exclusively due to the concentration gradient, unlike that found by the classical electrochemistry approach. In fact, only if $\nabla\mu_a = (\partial\mu_a/\partial\xi_a)\nabla\xi_a$ and $j_i^a = C_1^a\mu_{,i}^a$, the physical meanings of the diffusive flux in the classical electrochemistry and continuum thermodynamics approaches would be the same.

Then, considering (5.1.19), the residual entropy inequality becomes

$$\Pi = -k_1\frac{\theta_{,i}}{\theta}\theta_{,i} - \sum_{a=1}^{n-1} C_1^a\mu_{,i}^a\mu_{,i}^a - \left(\frac{k_2}{\theta} + \sum_{a=1}^{n-1} C_2^a \right) \theta_{,i}\mu_{,i}^a + \quad (5.1.21)$$

$$\left(\alpha + \frac{2}{3}\beta \right) D_{nn}^2 + 2\beta\bar{D}_{ij}\bar{D}_{ij} \geq 0,$$

which implies the following restrictions on the phenomenological parameters

$$\begin{aligned} \frac{k_1}{\theta} \leq 0, \quad \sum_{a=1}^{n-1} C_2^a - \frac{k_2}{\theta} \leq 0, \quad \sum_{a=1}^{n-1} C_1^a \leq 0, \\ \alpha + \frac{2}{3}\beta \geq 0, \quad \beta \leq 0, \end{aligned} \quad (5.1.22)$$

where k_1 is the thermal conductivity coefficient, C_1^a is the mass transport coefficient, C_2^a and k_2 are phenomenological coefficients related to thermophoresis, and β and $\alpha + 2/3\beta$ are the shear and bulk viscosities, respectively. Physically, the inequalities above evidence that the heat flux vector opposes the temperature gradient (Fourier's law) as well as the diffusive flux vector being opposed to the gradient of electrodynamic potential. Moreover, the transport of matter through bulk is also caused by the coupling of heat and mass flows, and the particles of the electrolyte bulk flow in the direction of the shearing forces.

5.1.2 Double-layer region

It has been long recognized that the introduction of an electrode under potential control into an electrolyte solution disrupts the bulk solution structure, modifying the interactions that occur between the ions/molecules in solution and the electrode surface. As a result, different physical and chemical phenomena arise in the electrochemical system, and a new constitutive class should be formulated.

In the double layer, one is interested in determining the same basic fields accounted for in the bulk region, but, unlike there, one assumes that the double layer is a viscous heat and electric conducting mixture with chemical reactions and mass transport caused by sources different than those in the bulk. Thus, the constitutive response of double layer depends on

$$w \in \{\rho, \nabla\rho, \theta, \nabla\theta, \xi_a, \nabla\xi_b, \varphi, \nabla\varphi, \mathbf{v}, \nabla\mathbf{v}\} \quad (\forall a, b = 1, \dots, n-1). \quad (5.1.23)$$

where $\mathcal{C} \in \{\mathbf{j}_a, c_a, \mathbf{T}, \varepsilon, \mathbf{h}, \mathbf{P}, \mathbf{i}, \eta, \Phi\}$.

Principles of constitutive theory require that all variables listed in (5.1.23) are objective scalars, vectors, and tensors. In addition, all constitutive equations must obey the principle of material objectivity. Then, \mathcal{C} does not depend explicitly on \mathbf{v} , and it depends on $\nabla\mathbf{v}$ only through its symmetric part \mathbf{D} , that is,

$$w \in \{\rho, \nabla\rho, \theta, \nabla\theta, \xi_a, \nabla\xi_b, \varphi, \nabla\varphi, \mathbf{D}\} \quad (\forall a, b = 1, \dots, n-1). \quad (5.1.24)$$

According to the method of Lagrange multipliers for exploitation of entropy inequality [33], there exist Lagrange multipliers Λ^ρ , Λ^{ξ_a} , $\Lambda^{\mathbf{v}}$, Λ^ε , and Λ^G that, whenever multiplied by their corresponding balance laws, they produce an inequality

$$\begin{aligned} \Pi = & \rho \frac{d\eta}{dt} + \operatorname{div}(\Phi) - \rho\sigma - \Lambda^\rho \left(\frac{d\rho}{dt} + \rho \operatorname{div}(\mathbf{v}) \right) - \\ & \sum_{a=1}^{n-1} \Lambda^{\xi_a} \left(\rho \frac{d\xi_a}{dt} + \operatorname{div}(\mathbf{j}_a) - c_a \right) - \\ & \Lambda^{\mathbf{v}} \cdot \left(\rho \frac{d\mathbf{v}}{dt} - \operatorname{div}(\mathbf{T}) + q\nabla\varphi - \rho\mathbf{b} + \mathbf{P} \cdot \nabla(\nabla\varphi) \right) - \\ & \Lambda^\varepsilon \left(\rho \frac{d\varepsilon}{dt} + \operatorname{div}(\mathbf{h}) - \mathbf{T} \cdot \nabla\mathbf{v} - \rho r + \dot{\mathbf{P}} \cdot \nabla\varphi + \mathbf{i} \cdot \nabla\varphi \right) - \\ & \Lambda^G (\operatorname{div}(\mathbf{P}) + \epsilon_o \nabla^2\varphi - q) \geq 0, \end{aligned} \quad (5.1.25)$$

which is valid for any solution $\{\rho(\mathbf{x}, t), \xi_a(\mathbf{x}, t), \theta(\mathbf{x}, t), \varphi(\mathbf{x}, t), \mathbf{v}(\mathbf{x}, t)\}$ of field equations. After introducing constitutive equations into inequality (5.1.25) and all differentiations are performed according to the chain rule, the entropy inequality becomes

$$\begin{aligned} \Pi = & \frac{d\rho}{dt} \left(\rho \frac{\partial\eta}{\partial\rho} - \Lambda^\rho - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\rho} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\rho} \right) + \\ & \frac{d\nabla\rho}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\rho} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\rho} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\rho} \right) + \\ & \sum_{a=1}^{n-1} \frac{d\xi_a}{dt} \left(\rho \frac{\partial\eta}{\partial\xi_a} - \rho\Lambda^{\xi_a} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\xi_a} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\xi_a} \right) + \\ & \sum_{b=1}^{n-1} \frac{d\nabla\xi_b}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\xi_b} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\xi_b} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\xi_b} \right) + \\ & \frac{d\theta}{dt} \left(\rho \frac{\partial\eta}{\partial\theta} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\theta} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\theta} \right) + \\ & \frac{d\nabla\theta}{dt} \cdot \left(\rho \frac{\partial\eta}{\partial\nabla\theta} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\theta} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\theta} \right) + \end{aligned} \quad (5.1.26)$$

$$\begin{aligned}
& \frac{d\varphi}{dt} \left(\rho \frac{\partial \eta}{\partial \varphi} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \varphi} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \varphi} \right) + \\
& \frac{d\nabla \varphi}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \nabla \varphi} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \nabla \varphi} - \Lambda^\varepsilon \nabla \varphi \cdot \frac{\partial \mathbf{P}}{\partial \nabla \varphi} \right) + \\
& \frac{d\mathbf{D}}{dt} \cdot \left(\rho \frac{\partial \eta}{\partial \mathbf{D}} - \rho \Lambda^\varepsilon \frac{\partial \varepsilon}{\partial \mathbf{D}} - \Lambda^\varepsilon \nabla \varphi \frac{\partial \mathbf{P}}{\partial \mathbf{D}} \right) + \frac{d\mathbf{v}}{dt} \cdot (-\rho \Lambda^\mathbf{v}) + \\
& \nabla \rho \cdot \left(\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) + \\
& \nabla (\nabla \rho) \cdot \left(\frac{\partial \Phi}{\partial \nabla \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \rho} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \nabla \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \rho} \right) + \\
& \sum_{b=1}^{n-1} \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) + \\
& \sum_{b=1}^{n-1} \nabla (\nabla \xi_b) \cdot \left(\frac{\partial \Phi}{\partial \nabla \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \xi_b} \Big|_{a \neq b} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \nabla \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \xi_b} \right) + \\
& \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) + \\
& \nabla (\nabla \theta) \cdot \left(\frac{\partial \Phi}{\partial \nabla \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \theta} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \nabla \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \theta} \right) + \\
& \nabla \varphi \cdot \left(\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \varphi} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} \right) + \\
& \nabla (\nabla \varphi) \cdot \left(\frac{\partial \Phi}{\partial \nabla \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \varphi} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \nabla \varphi} - \Lambda^\mathbf{v} \cdot \mathbf{P} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \varphi} \right) + \\
& \nabla \mathbf{D} \cdot \left(\frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^\mathbf{v} \frac{\partial \mathbf{T}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} \right) + \\
& \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho 1 \cdot \mathbf{D} - \Lambda^G \varepsilon_o \nabla^2 \varphi + \Lambda^G q + \sum_{a=1}^{n-1} \Lambda^{\xi_a} c_a \geq 0,
\end{aligned}$$

where ε_o is homogeneous.

Analogously to inequality (5.1.5), inequality (5.1.26) can be expressed as

$$\Pi = \mathbf{A}(w) \cdot \mathbf{Z} + B(w) \geq 0,$$

which is linear in

$$\mathbf{Z} \in \left\{ \frac{d\rho}{dt}, \frac{d\nabla\rho}{dt}, \frac{d\xi_a}{dt}, \frac{d\nabla\xi_b}{dt}, \frac{d\theta}{dt}, \frac{d\nabla\theta}{dt}, \frac{d\varphi}{dt}, \frac{d\nabla\varphi}{dt}, \frac{d\mathbf{D}}{dt}, \frac{d\mathbf{v}}{dt}, \nabla(\nabla\rho), \nabla(\nabla\xi_b), \nabla(\nabla\theta), \nabla(\nabla\varphi), \nabla\mathbf{D}, \nabla^2\varphi \right\}. \quad (5.1.27)$$

Hence, the coefficients of \mathbf{Z} must vanish, otherwise the entropy inequality could be violated. These arguments lead to the Liu identities

$$\begin{aligned} \rho \frac{\partial\eta}{\partial\rho} - \Lambda^\rho - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\rho} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\rho} &= 0, \\ \rho \frac{\partial\eta}{\partial\nabla\rho} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\rho} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\rho} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\xi_a} - \rho\Lambda^{\xi_a} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\xi_a} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\xi_a} &= 0 \quad (a = 1, \dots, n-1), \\ \rho \frac{\partial\eta}{\partial\nabla\xi_b} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\xi_b} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\xi_b} &= \mathbf{0} \quad (b = 1, \dots, n-1), \\ \rho \frac{\partial\eta}{\partial\theta} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\theta} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\theta} &= 0, \\ \rho \frac{\partial\eta}{\partial\nabla\theta} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\theta} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\nabla\theta} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\varphi} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\varphi} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\varphi} &= 0, \\ \rho \frac{\partial\eta}{\partial\nabla\varphi} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\nabla\varphi} - \Lambda^\varepsilon \nabla\varphi \cdot \frac{\partial\mathbf{P}}{\partial\nabla\varphi} &= \mathbf{0}, \\ \rho \frac{\partial\eta}{\partial\mathbf{D}} - \rho\Lambda^\varepsilon \frac{\partial\varepsilon}{\partial\mathbf{D}} - \Lambda^\varepsilon \nabla\varphi \frac{\partial\mathbf{P}}{\partial\mathbf{D}} &= \mathbf{0}, \\ -\rho\Lambda^\mathbf{v} &= \mathbf{0}, \quad \Lambda^G = 0, \end{aligned} \quad (5.1.28)$$

$$\begin{aligned} \text{sym} \left(\frac{\partial\Phi}{\partial\nabla\rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial\mathbf{j}_a}{\partial\nabla\rho} + \Lambda^\mathbf{v} \frac{\partial\mathbf{T}}{\partial\nabla\rho} - \Lambda^G \frac{\partial\mathbf{P}}{\partial\nabla\rho} - \Lambda^\varepsilon \frac{\partial\mathbf{h}}{\partial\nabla\rho} \right) &= \mathbf{0}, \\ \text{sym} \left(\frac{\partial\Phi}{\partial\nabla\xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial\mathbf{j}_a}{\partial\nabla\xi_b} \Big|_{a \neq b} + \Lambda^\mathbf{v} \frac{\partial\mathbf{T}}{\partial\nabla\xi_b} - \Lambda^G \frac{\partial\mathbf{P}}{\partial\xi_b} - \Lambda^\varepsilon \frac{\partial\mathbf{h}}{\partial\nabla\xi_b} \right) &= \mathbf{0} \quad (b = 1, \dots, n-1), \\ \text{sym} \left(\frac{\partial\Phi}{\partial\nabla\theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial\mathbf{j}_a}{\partial\nabla\theta} + \Lambda^\mathbf{v} \frac{\partial\mathbf{T}}{\partial\nabla\theta} - \Lambda^G \frac{\partial\mathbf{P}}{\partial\nabla\theta} - \Lambda^\varepsilon \frac{\partial\mathbf{h}}{\partial\nabla\theta} \right) &= \mathbf{0}, \end{aligned} \quad (5.1.29)$$

$$\begin{aligned} \text{sym} \left(\frac{\partial \Phi}{\partial \nabla \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \nabla \varphi} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \nabla \varphi} - \Lambda^{\mathbf{v}} \cdot \mathbf{P} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \nabla \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \nabla \varphi} \right) &= \mathbf{0}, \\ \frac{\partial \Phi}{\partial \mathbf{D}} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \mathbf{D}} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \mathbf{D}} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \mathbf{D}} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \mathbf{D}} &= \mathbf{0}, \end{aligned}$$

as well as the residual entropy inequality

$$\begin{aligned} \Pi = & \nabla \rho \cdot \left(\frac{\partial \Phi}{\partial \rho} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \rho} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \rho} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \rho} \right) + \\ & \nabla \xi_b \cdot \left(\frac{\partial \Phi}{\partial \xi_b} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \xi_b} \Big|_{a \neq b} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \xi_b} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \xi_b} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \xi_b} \right) + \\ & \nabla \theta \cdot \left(\frac{\partial \Phi}{\partial \theta} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \theta} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \theta} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \theta} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \theta} \right) + \\ & \nabla \varphi \cdot \left(\frac{\partial \Phi}{\partial \varphi} - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \frac{\partial \mathbf{j}_a}{\partial \varphi} + \Lambda^{\mathbf{v}} \frac{\partial \mathbf{T}}{\partial \varphi} - \Lambda^G \frac{\partial \mathbf{P}}{\partial \varphi} - \Lambda^\varepsilon \frac{\partial \mathbf{h}}{\partial \varphi} - \Lambda^\varepsilon \mathbf{i} \right) - \\ & \Lambda^\varepsilon \mathbf{i} \cdot \nabla \varphi + \Lambda^\varepsilon \mathbf{T} \cdot \mathbf{D} - \rho \Lambda^\rho \mathbf{1} \cdot \mathbf{D} + \sum_{a=1}^{n-1} \Lambda^{\xi_a} c_a \geq 0. \end{aligned} \quad (5.1.30)$$

Further conclusions can be drawn from the Liu identities above. Since \mathbf{P} is a function of $\nabla \varphi$ and Λ^ε depends exclusively on θ , by the cross differentiation of identity (5.1.28), one proves that $\eta = \hat{\eta}(\rho, \theta, \xi_a)$, $\varepsilon = \hat{\varepsilon}(\rho, \theta, \xi_a)$, $\Lambda^\rho = \hat{\Lambda}^\rho(\rho, \theta, \xi_a)$, $\Lambda^{\xi_a} = \hat{\Lambda}^{\xi_a}(\rho, \theta, \xi_a, \varphi)$, and

$$\frac{\partial (p/\rho^2)}{\partial \theta} = -\frac{\partial \eta}{\partial \rho}, \quad \frac{\partial (p/\rho^2)}{\partial \xi_a} = \frac{\partial \mu_a}{\partial \rho}, \quad \frac{\partial \mu_a}{\partial \theta} = -\frac{\partial \eta}{\partial \xi_a}, \quad (5.1.31)$$

where (5.1.31) is the integrability condition for the thermodynamic potential $\psi = \varepsilon - \theta \eta + \mathbf{P}/\rho \cdot \nabla \varphi$. Thus, one has the thermodynamic relation

$$d\psi = \frac{p}{\rho^2} d\rho + \sum_{a=1}^{n-1} \mu_a d\xi_a - \eta d\theta + \mathbf{P} \cdot d \left(\frac{\nabla \varphi}{\rho} \right), \quad (5.1.32)$$

whence $\psi = \hat{\psi}(\rho, \theta, \xi_a, \nabla \varphi)$.

In turn, from Liu identity (5.1.29), one introduces the extra entropy flux $\phi = \Phi - \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a - \Lambda^\varepsilon \mathbf{h}$, where $\Lambda^{\mathbf{v}} = \mathbf{0}$ and $\Lambda^G = 0$ were used. Substituting the expression for the extra entropy flux into identity (5.1.29) and making use of definition of Λ^{ξ_a} , it follows that

$$\begin{aligned}
\text{sym} \left(\frac{\partial \phi}{\partial \nabla \rho} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \rho} \mathbf{j}_a \right), & \text{sym} \left(\frac{\partial \phi}{\partial \nabla \xi_b} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \xi_b} \mathbf{j}_a \Big|_{a \neq b} \right) \quad (\forall b = 1, \dots, n-1), \\
\text{sym} \left(\frac{\partial \phi}{\partial \nabla \theta} \right) &= \text{sym} \left(\Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \theta} \mathbf{j}_a \right), & \frac{\partial \phi}{\partial \nabla \varphi} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \nabla \varphi} \mathbf{j}_a, \\
\frac{\partial \phi}{\partial \mathbf{D}} &= \Lambda^\varepsilon \sum_{a=1}^{n-1} \frac{\partial \mu_a}{\partial \mathbf{D}} \mathbf{j}_a.
\end{aligned} \tag{5.1.33}$$

Moreover, as μ_a should present the same reduced dependence of Λ^{ξ_a} , one has from identity (5.1.33) that $\text{sym}(\partial\phi/\partial\nabla\rho) = \mathbf{0}$, $\text{sym}(\partial\phi/\partial\nabla\xi_b) = \mathbf{0}$, $\text{sym}(\partial\phi/\partial\nabla\theta) = \mathbf{0}$, $\partial\phi/\partial\nabla\varphi = \mathbf{0}$, and $\partial\phi/\partial\mathbf{D} = \mathbf{0}$. Consequently, $\phi = 0$, and then the entropy flux can be rewritten as $\Phi = \Lambda^\varepsilon \mathbf{h} + \sum_{a=1}^{n-1} \Lambda^{\xi_a} \mathbf{j}_a$ or $\Phi = \Lambda^\varepsilon \mathbf{h} - \Lambda^\varepsilon \sum_{a=1}^{n-1} \mu_a \mathbf{j}_a$. Here, it is worth remembering that, unlike the total current in the bulk region, \mathbf{i} is not exclusively given by partial faradaic currents. In fact, the total current in the double layer is due to the non-faradaic currents associated with the charging of the electrical double layer at the electrode-solution interface, and the faradaic currents corresponding to the reduction or oxidation of some chemical substance.

In view of the above restrictions, one uses $\nabla \mu_a = (\partial \mu_a / \partial \rho) \nabla \rho + \sum_{b=1}^{n-1} (\partial \mu_a / \partial \xi_b) \Big|_{a \neq b} \nabla \xi_b + (\partial \mu_a / \partial \theta) \nabla \theta + (\partial \mu_a / \partial \varphi) \nabla \varphi$ and $\sum_{a=1}^{n-1} c_a \mu_a = \sum_{r=1}^R \Upsilon_r \Upsilon_r$ to write inequality (5.1.30) as

$$\Pi = - \sum_{a=1}^{n-1} \mathbf{j}_a \cdot \nabla \mu_a + \left(\sum_{a=1}^{n-1} \mu_a \mathbf{j}_a - \mathbf{h} \right) \cdot \frac{\nabla \theta}{\theta} + \mathbf{T} \cdot \mathbf{D} + p1 \cdot \mathbf{D} - \sum_{r=1}^R \Upsilon_r \Upsilon_r - \mathbf{i} \cdot \nabla \varphi \geq 0. \tag{5.1.34}$$

Inequality (5.1.34) evidences that some phenomena in an electrochemical system, e.g. electrophoresis, electrodic reactions and Joule's effect, take place only in the double layer. Moreover, observe that the gradient of electrodynamic potential is given in terms of $\nabla \rho$, $\nabla \xi_a$, $\nabla \varphi$, and $\nabla \theta$, unlike the bulk. As a consequence, the thermodynamic equilibrium state at the point (\mathbf{x}, t) in the double layer requires a more complex set of conditions than in the bulk.

In fact, one has the same necessary conditions to ensure $\Pi = 0$ at any (\mathbf{x}, t) in the double layer,

$$\left(\frac{\partial \Pi}{\partial w_{DB}} \right) \Big|_E = 0, \quad \left(\frac{\partial^2 \Pi}{\partial w_{DB} \partial w_{DB}} \right) \Big|_E \geq 0,$$

but w_{DB} is given by $w_{DB} \in \{\nabla \mu_a, \nabla \theta, \nabla \varphi, \Upsilon_r, \mathbf{D}\}$. Performing the first-order derivatives of Π in relation to w_{DB} , one obtains

$$\left(\frac{\partial \Pi}{\partial \nabla \mu_a} \right) \Big|_E = -\mathbf{j}_a = \mathbf{0} \quad (\forall a = 1, \dots, n-1), \quad (5.1.35)$$

$$\begin{aligned} \left(\frac{\partial \Pi}{\partial \nabla \theta} \right) \Big|_E &= \frac{1}{\theta} \left(\sum_{a=1}^{n-1} \mu_a \mathbf{j}_a - \mathbf{h} \right) = \mathbf{0} \\ &-\frac{1}{\theta} \mathbf{h} = \mathbf{0}, \end{aligned} \quad (5.1.36)$$

$$\left(\frac{\partial \Pi}{\partial \nabla \varphi} \right) \Big|_E = -\mathbf{i} = \mathbf{0}, \quad (5.1.37)$$

$$\left(\frac{\partial \Pi}{\partial \Upsilon_r} \right) \Big|_E = -\mathcal{U}_r = 0, \quad (5.1.38)$$

$$\begin{aligned} \left(\frac{\partial \Pi}{\partial \mathbf{D}} \right) \Big|_E &= \mathbf{T} + p\mathbf{1} = \mathbf{0} \\ \mathbf{T} &= -p\mathbf{1}, \end{aligned} \quad (5.1.39)$$

whence one concludes that, at the local thermodynamic equilibrium state, the mass flux, the heat flux and the electric current flux vanish, the reactions are at chemical equilibrium, and the stress tensor is given by the hydrostatic pressure.

In order to evaluate further constraints on the constitutive quantities listed in (5.1.24), some restrictions are imposed on the forms of the constitutive relations. If the gradients of temperature, electrodynamic potential and electric potential and the strains are not very large, constitutive equations with only first-order terms are suitable for treatment of constitutive responses of the double layer. However, once more, linear constitutive functions for chemical affinity are only suitable close to chemical equilibrium, otherwise \mathcal{U}_r presents a highly non-linear relation to the rate of conversion Υ_r . In view of these arguments, the constitutive relation for the chemical affinity of a reaction r is not discussed again.

Under these conditions, one considers the symmetry group $\mathcal{M}_{\kappa}^1(V)$, which characterizes transversely isotropic material bodies and next uses the theorem of representa-

tion of constitutive functions [34] to set

$$\begin{aligned}
T_{ij} &= -p\delta_{ij} + \left(\alpha + \frac{2}{3}\beta\right) D_{mm}\delta_{ij} + 2\beta\bar{D}_{ij} + O(2), \\
h_i &= k_1\theta_{,i} + k_2\varphi_{,i} + k_3\mu_{,i}^a + k_4n_i + O(2), \\
i_i &= \iota_1\theta_{,i} + \iota_2\varphi_{,i} + \iota_3\mu_{,i}^a + \iota_4n_i + O(2), \\
j_i^a &= C_1^a\theta_{,i} + C_2^a\varphi_{,i} - C_3^a\mu_{,i}^a + C_4^an_i + O(2),
\end{aligned} \tag{5.1.40}$$

where all phenomenological coefficients are material functions \mathcal{P}_{DB} of the type

$$\mathcal{P}_{DB} = \hat{\mathcal{P}}_{DB}(\rho, \theta, \varphi, \xi_a, \nabla\theta \cdot \nabla\theta, \nabla\xi_a \cdot \nabla\xi_a, \nabla\varphi \cdot \nabla\varphi, \text{tr}\mathbf{D}), \tag{5.1.41}$$

and the scalar product $\mathbf{n} \cdot \mathbf{n}$ has been eliminated because it is equal to a unity. Moreover, observe that the same phenomenological coefficients may be numerically different in the bulk and double layer (compare Equations (5.1.20) and (5.1.41)) since they are not constants that depend only on the chemical species or medium under question, but constitutive functions that suffer the influence of temperature, electric potential, viscosity among others. Finally, note that the current in the double layer region cannot be split up into the migrational and diffusive components as usual because the physical meaning of diffusive and migrational fluxes given in the electrochemistry literature does not coincide with those of continuum thermodynamics.

Inserting Equation (5.1.40) into inequality (5.1.34), one obtains

$$\Pi = - \sum_{a=1}^{n-1} (C_1^a\theta_{,i} + C_2^a\varphi_{,i} + C_3^a\mu_{,i}^a + C_4^an_i) \mu_{,i}^a + \sum_{a=1}^{n-1} (C_1^a\theta_{,i} + C_2^a\varphi_{,i} + C_3^a\mu_{,i}^a + C_4^an_i) \mu^a \frac{\theta_{,i}}{\theta} - \tag{5.1.42}$$

$$\begin{aligned}
&(k_1\theta_{,i} + k_2\varphi_{,i} + k_3\mu_{,i}^a + k_4n_i) \frac{\theta_{,i}}{\theta} + \left(\alpha + \frac{2}{3}\beta\right) D_{mm}^2 + 2\beta\bar{D}_{ik}\bar{D}_{ik} - \sum_{r=1}^R \Upsilon_r \Upsilon_r - \\
&(\iota_1\theta_{,i} + \iota_2\varphi_{,i} + \iota_3\mu_{,i}^a + \iota_4n_i) \varphi_{,i} \geq 0,
\end{aligned}$$

and by carrying out the second-order derivatives of Π with relation to w_{DB} , it results in

$$\begin{aligned}
\sum_{a=1}^{n-1} C_3^a &\leq 0, & \sum_{a=1}^{n-1} \frac{C_1^a \mu^a}{\theta} - \frac{k_1}{\theta} &\geq 0, & \iota_2 &\leq 0, & (5.1.43) \\
\alpha + \frac{2}{3}\beta &\geq 0, & \beta &\geq 0, & \sum_{a=1}^{n-1} C_4^a &\leq 0, \\
\sum_{a=1}^{n-1} \frac{C_4^a \mu^a}{\theta} - \frac{k_4}{\theta} &\geq 0, & \iota_4 &\leq 0, & \sum_{a=1}^{n-1} C_2^a + \iota_3 &\leq 0, \\
\sum_{a=1}^{n-1} \frac{C_2^a \mu^a}{\theta} - \frac{k_2}{\theta} - \iota_1 &\geq 0, & \sum_{a=1}^{n-1} C_1^a + \sum_{a=1}^{n-1} \frac{\mu^a C_3^a}{\theta} + \frac{k_3}{\theta} &\leq 0.
\end{aligned}$$

The phenomenological equations proposed in (5.1.40) incorporate many cross phenomena that are impossible to occur in the bulk region, such as thermoelectric and electrophoretic effects, and thermal diffusion. These effects are due to the coupling of fields, which interfere in a reciprocal way in the heat, mass and electric current flows. For example, $C_2^a \neq 0$ and $\iota_3 \neq 0$, both constrained by the condition (5.1.43)₉, evidence that the gradient of electric potential opposes the electrodynamic potential gradients of all ions. This thermodynamic condition recalls an important non-equilibrium phenomenon observed in electrolyte solutions: the development of a diffusion potential. Whenever an electrolyte is brought into contact with water, a gradient of electrodynamic potential arises for both the positive and negative ions and, therefore, they start flowing away. Then, because of the difference of ionic mobilities, there appears to be a tendency for segregation of cations and anions, so that a gradient of electric potential develops across the interface that marks the local separation of ions. It is precisely this gradient of electric potential that inhibits the charge segregation as the accelerated cations face resistance to their motion, whereas the slower anions are pushed up by the gradient of electric potential. Similar conclusions can be obtained for the remaining phenomenological coefficients, where $C_1^a \neq 0$ and $k_1 \neq 0$ are related to the thermal diffusion, $C_2^a \neq 0$ and $k_2 \neq 0$ to the thermoelectric phenomenon, and $C_3^a \neq 0$ and $k_3 \neq 0$ to the electrophoretic effects.

Although the constitutive nature of the chemical affinity will not be discussed because of the reasons already presented, one can obtain the spontaneity criterion for electrodic reactions from inequality (5.1.34), as in the expression (4.2.31).

6 Final remarks

A continuum model for electrochemical systems was developed with basis in the principles of constitutive theory and the Müller-Liu entropy principle. The mathematical formulation of the thermodynamics of electrochemical systems was based on the balance laws of polar continuum mixtures and the Maxwell's laws under the quasi-electrostatic approximation. Some phenomena, such as diffusion, conduction of heat and electricity, deformation, polarization, and chemical reactions, including their coupling effects, were emphasized during the constitutive modeling. In particular, a thermodynamic model for a dilute electrolyte solution was introduced. It was shown that contrary to the Debye-Hückel model, where ions are regarded as non-polarizable hard spheres and deviations from ideality are exclusively due to the ion-ion interactions, the constitutive model here formulated can properly take into account the effect of electrostriction, the coupling effect in the electrodiffusion processes, and the ion-solvent interactions.

Constitutive models were also proposed for the bulk and double layer regions of an electrochemical system. While the material response of both regions was considered in the simplest way because the intensities of thermo-electromechanical fields are not so strong, the bulk and double layer were modeled as isotropic and anisotropic media, respectively. In considering the transport phenomena in each region, it was demonstrated that the concepts of diffusion and conduction flows in the classical electrochemistry literature do not coincide with those of modern continuum thermodynamics. In fact, according to continuum thermodynamics approach, one finds that diffusive fluxes are not directly related to the concentration gradients, but rather they are associated to the motion of a constituent a relative to the barycentric motion. Moreover, comparison of residual entropy productions of the bulk and double layer regions showed that some processes occur only in the double layer, thus resulting in stricter conditions for the local thermodynamic equilibrium.

In addition, the results presented in this work offered the possibility of discussing certain fundamental concepts of modern continuum thermodynamics, in special, continuum mixtures theories. The concept of a continuum particle was clearly differentiated from the classical particles, such as ions, atoms, molecules *etc.* Basic equations were

still modified in order to account properly for interactions among constituents particles, and physical quantities were analyzed in view of the characteristics of electrochemical systems. Then, the Kelvin polarization force was assumed to represent ion-solvent interactions, ion-ion interactions were given by coulombic forces, and $\mathbf{P} \times \mathbf{E}$ was related to the torques that electric dipoles of water molecules suffer due to the action of the electric field. As a consequence of these intermolecular phenomena, the stress tensor is not symmetric, affecting linear and angular momenta conservation.

A few comments were indeed addressed to the physical meaning of the Lagrange multipliers, especially to the energy Lagrange multiplier. Even though, many thermodynamicists claim that in a good application of the Müller-Liu entropy principle, the constitutive dependence of any Lagrange multiplier must be reached as a final result of the entropy inequality, in this work coldness was assumed to be a universal function. While this hypothesis is subject to criticism, by now, it seems quite hard to provide a constitutive model for continuum mixtures without accepting that $\Lambda^\varepsilon = 1/\theta$ as the problem of non-ideal material surfaces in continuum mixtures does not have a solution yet. Thus, the reliability of the constitutive model provided here deserves to be investigated as well as whether the definition $\Lambda^\varepsilon = 1/\theta$ is appropriate for non-equilibrium systems.

Therefore, with the results obtained in this work, one intends that the Müller-Liu entropy principle is not viewed as a mathematical method whence one obtains thermodynamic relations without inquiring whether the results make physical sense or not. On the condition that concepts of modern continuum thermodynamics are correctly applied, and a proper formulation for the second law is employed, one can obtain a more comprehensive thermodynamic theory for non-equilibrium systems without using the Onsager reciprocal relations.

7 Appendix I

Let U and V be two vector spaces with inner product. A mapping

$$\mathcal{L}(U, V) = \{\mathcal{T} : U \rightarrow V\}$$

is called a linear transformation \mathcal{T} , if for any $\mathbf{u}, \mathbf{y} \in U$, and $a \in \mathbb{R}$,

$$\mathcal{T}(\mathbf{u} + a\mathbf{y}) = \mathcal{T}(\mathbf{u}) + a\mathcal{T}(\mathbf{y}) .$$

If the mapping $\mathcal{L}(U, V)$ is specified by

$$\mathcal{L}(V, V) = \{\mathcal{T} : V \rightarrow V\} ,$$

where $\mathcal{L}(V, V) = \mathcal{L}(V) = V \otimes V$, then the linear transformations \mathcal{T} in $\mathcal{L}(V)$ are second-order tensors.

Hence, $\mathcal{Q} \in \mathcal{L}(V)$ is an orthogonal transformation, if the inner product of V for all vectors $\mathbf{u}, \mathbf{y} \in V$ is preserved:

$$\mathcal{Q}\mathbf{u} \cdot \mathcal{Q}\mathbf{y} = \mathbf{u} \cdot \mathbf{y} .$$

If \mathcal{Q} is an orthogonal transformation, thus

1. $\mathcal{Q}^T = \mathcal{Q}^{-1}$,
2. $\det \mathcal{Q} = \pm 1$,
3. $|\mathcal{Q}\mathbf{v}| = |\mathbf{v}|$,
4. $\ell(\mathcal{Q}\mathbf{v}, \mathcal{Q}\mathbf{u}) = \ell(\mathbf{v}, \mathbf{u}) \in [0, 90^\circ]$,

and it forms an orthogonal group $\mathcal{O}(V)$. Furthermore, if $\det \mathcal{Q} = 1$, so the orthogonal group is a proper orthogonal group or a rotation group $\mathcal{O}^+(V)$ because its elements represent rotations.

Now, let a linear transformation $\mathcal{T} \in \mathcal{L}(V)$ be, such that

1. $|\det \mathcal{T}| = 1$,

2. $\det \mathcal{T} = 1$.

The set of linear transformations \mathcal{T} , which satisfies the first condition above, forms the unimodular group $\mathcal{U}(V)$ of the vector space, whereas the set of linear transformations \mathcal{T} , which satisfies the second condition, constitutes the special linear group $\mathcal{SL}(V)$. Evidently, $\mathcal{O}(V) \subset \mathcal{U}(V)$ and $\mathcal{O}^+(V) \subset \mathcal{SL}(V)$.

8 Appendix II

Let an arbitrary tensor $O = A + B$, such that $A \in \mathcal{SYM}(V)$ and $B \in \mathcal{SKW}(V)$. The cross product of a vector $\mathbf{y} \in V$ with A [6, 29] is defined as

$$\mathbf{y} \times \mathbf{A} = e_{ijk} y_i A_{(jl)} \mathbf{c}_k \otimes \mathbf{c}_l,$$

whereas $\mathbf{y} \times B$ is given by

$$\mathbf{y} \times \mathbf{B} = e_{ijk} y_i B_{[jl]} \mathbf{c}_k \otimes \mathbf{c}_l,$$

where $\epsilon_{ijk} = e_{ijk}$ is the permutation symbol when the basis \mathbf{c}_i is orthonormal.

Now, let the divergent of $\mathbf{y} \times \mathbf{A}$, which is defined in component form as

$$\begin{aligned} \operatorname{div}(\mathbf{y} \times \mathbf{A}) &= (e_{ijk} y_i A_{(jl)})_{,l} \\ &= e_{ijk} y_i A_{(jl),l} + e_{ijk} y_{i,l} A_{(jl)}. \end{aligned}$$

Since one has $y_{i,l} = \delta_{il}$, it follows that

$$\operatorname{div}(\mathbf{y} \times \mathbf{A}) = e_{ijk} A_{ji} + e_{ijk} y_i A_{(jl),l},$$

which is reduced to

$$\begin{aligned} \operatorname{div}(\mathbf{y} \times \mathbf{A}) &= \mathbf{y} \times \operatorname{div}(\mathbf{A}) \\ &= e_{ijk} y_i A_{(jl),l}, \end{aligned}$$

because $e_{ijk} A_{ji} = 0$.

In addition, the divergent of $\mathbf{y} \times B$ is also defined in component form as

$$\begin{aligned}\operatorname{div}(\mathbf{y} \times \mathbf{B}) &= (e_{ijk}y_i B_{[jl]})_{,l} \\ &= e_{ijk}y_i B_{[jl],l} + e_{ijk}y_{i,l} B_{[jl]}.\end{aligned}$$

But, if the identity $y_{i,l} = \delta_{il}$ is used, the vector identity above reduces to

$$\begin{aligned}\operatorname{div}(\mathbf{y} \times \mathbf{B}) &= \mathbf{y} \times \operatorname{div}(\mathbf{B}) + 2\hat{\mathbf{b}} \\ &= e_{ijk}y_i B_{[jl],l} + e_{ijk}B_{[ji]},\end{aligned}$$

where $\hat{b}_k = 1/2 e_{ijk} B_{[ji]}$ is the dual or axial vector associated with the skew-symmetric tensor \mathbf{B} .

Bibliography

- [1] ARRHENIUS, S. Über die Dissociation der in Wasser gelösten Stoffe. *Zeitschrift für physikalische Chemie* 01 (1887), 631–648.
- [2] BEDFORD, A. On the balance equations for chemically reacting mixtures. *Acta Mechanica* 30 (1978), 275–282.
- [3] BOCKRIS, J., AND REDDY, A. *Modern Electrochemistry. Ionics*. Kluwer, New York, 2002.
- [4] BOCKRIS, J., REDDY, A., AND GAMBOA-ALDECO, M. *Modern Electrochemistry. Electrodeics*. Kluwer, New York, 2002.
- [5] BOWEN, R. The thermochemistry of a reacting mixture of elastic materials with diffusion. *Archive for Rational Mechanics and Analysis* 34 (1969), 97–127.
- [6] BOWEN, R. *Introduction to Continuum Mechanics for Engineers*. Plenum Press, New York, 1989.
- [7] BOWEN, R., AND WIESE, J. Diffusion in mixtures of elastic materials. *International Journal of Engineering Science* 07 (1969), 689–722.
- [8] CARNOT, N. *Réflexions sur la Puissance Motrice du Feu et sur les Machines Propres à Développer Cette Puissance*. Dover, New York, 1945.
- [9] CLAUDIUS, R. Über die bewegende Kraft der Wärmer. Part I. *Annalen der Physik* 79 (1850), 368–397.
- [10] CLAUDIUS, R. Über die bewegende Kraft der Wärmer. Part II. *Annalen der Physik* 79 (1850), 500–524.
- [11] CLAUDIUS, R. *The Mechanical Theory of Heat: With Its Applications to the Steam-engine and to the Physical Properties of Bodies*. J. van Voorst, London, 1867.
- [12] COLEMAN, B., AND NOLL, W. On the thermostatics of continuous media. *Archive for Rational Mechanics and Analysis* 04 (1960), 97–128.
- [13] COLEMAN, B., AND NOLL, W. The thermodynamics of elastic materials with heat conduction and viscosity. *Archive for Rational Mechanics and Analysis* 13 (1963), 167–178.
- [14] CONDIFF, D., AND DAHLER, J. Fluid mechanical aspects of antisymmetric stress. *The Physics of Fluids* 07 (1964), 842–854.

- [15] COSSERAT, E., AND COSSERAT, F. *Théorie des Corps Deformables*. Librairie Scientifique A. Hermann et Fils, Paris, 1909.
- [16] COWIN, S. Polar fluids. *The Physics of Fluids* 11 (1968), 1919–1927.
- [17] DE GROOT, S., AND MAZUR, P. *Non-equilibrium Thermodynamics*. Dover, New York, 1984.
- [18] DEBYE, P., AND HÜCKEL, E. Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen. *Physikalische Zeitschrift* 24 (1923), 185–206.
- [19] DIXON, R., AND ERINGEN, A. A dynamical theory of polar elastic dielectrics. Part I. *International Journal of Engineering Science* 03 (1965), 359–377.
- [20] DUTTA, M. Principle of objectivity and classical physics. *International Journal of Mathematics and Mathematical Science* 02 (1979), 127–141.
- [21] ECKART, C. The thermodynamics of irreversible processes. I. The simple fluid. *Physical Review* 58 (1940), 267–269.
- [22] ECKART, C. The thermodynamics of irreversible processes. II. Fluid mixtures. *Physical Review* 58 (1940), 269–275.
- [23] ERINGEN, A. Foundations of electroelastostatics. *International Journal of Engineering Science* 01 (1963), 127–153.
- [24] ERINGEN, A. Nonlocal polar elastic continua. *International Journal of Engineering Science* 10 (1972), 01–16.
- [25] HARNED, H., AND OWEN, B. *The Physical Chemistry of Electrolytic Solutions*. Reinhold, Amsterdam, 1958.
- [26] HAUS, H. Electrodynamics of moving media and the force on a current loop. *Applied Physics A: Solids and Surfaces* 27 (1982), 99–105.
- [27] HILL, T. *An Introduction to Statistical Thermodynamics*. Dover, Mineola, 1987.
- [28] HUTTER, K. The foundations of thermodynamics, its basic postulates and implications. A review of modern thermodynamics. *Acta Mechanica* 21 (1977), 01–54.
- [29] HUTTER, K., AND JÖHNK, K. *Continuum Methods of Physical Modeling. Continuum Mechanics, Dimensional Analysis and Turbulence*. Springer, Berlin, 2004.
- [30] INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY- IUPAC. *Compendium of Chemical Terminology- The gold book*. Blackwell Scientific Publications, Oxford, 1997.
- [31] KELLY, P. A reacting continuum. *International Journal of Engineering Science* 02 (1964), 129–153.

- [32] LESLIE, F. On the thermodynamics of polar fluids. *Archive for Rational Mechanics and Analysis* 70 (1979), 189–202.
- [33] LIU, I.-S. The method of Lagrange multipliers for exploitation of the entropy principle. *Archive for Rational Mechanics and Analysis* 46 (1972), 131–148.
- [34] LIU, I.-S. On representations of anisotropic invariants. *International Journal of Engineering Science* 20 (1982), 1099–1109.
- [35] LIU, I.-S. *Continuum Mechanics*. Springer, Berlin, 2002.
- [36] LIU, I.-S., AND MÜLLER, I. Thermodynamics of mixtures of fluids. In *Rational Thermodynamics* (Berlin, 1984), C. Truesdell, Ed., Springer, pp. 264–285.
- [37] MAUGIN, G., AND ERINGEN, A. *Electrodynamics of Continua. Part I. Foundations and Solid Media*. Springer, London, 1990.
- [38] MCMILLAN, W., AND MAYER, J. The statistical thermodynamics of multicomponent systems. *Journal of Chemical Physics* 13 (1945), 276–306.
- [39] MEIXNER, J. Zur Thermodynamik der irreversiblen Prozesse in Gasen mit chemisch reagierenden, dissozierenden and anregbaren Komponenten. *Annalen der Physik* 43 (1943), 245–270.
- [40] MELCHER, J. *Continuum Electromechanics*. MIT Press, Cambridge, 1981.
- [41] MELCHER, J., AND TAYLOR, G. Electrohydrodynamics: A review of the role of interfacial shear stresses. *Annual Reviews of Fluid Dynamics* 01 (1969), 111–146.
- [42] MORRO, A., DROUOT, R., AND MAUGIN, G. Thermodynamics of polyelectrolyte solutions in an electric field. *Journal of Non-Equilibrium Thermodynamics* 10 (1985), 131–144.
- [43] MORRO, A., MAUGIN, G., AND DROUOT, R. Diffusion in polyelectrolyte solutions. *Rheologica Acta* 29 (1990), 215–222.
- [44] MÜLLER, I. A thermodynamic theory of mixtures of fluids. *Archive for Rational Mechanics and Analysis* 28 (1967), 01–39.
- [45] MÜLLER, I. The coldness, a universal function in thermoelastic bodies. *Archive for Rational Mechanics and Analysis* 41 (1971), 319–332.
- [46] MÜLLER, I. Die Kältenfunktion, eine universelle Funktion in der Thermodynamik viskoser wärmeleitender Flüssigkeiten. *Archive for Rational Mechanics and Analysis* 40 (1971), 01–36.
- [47] MÜLLER, I. *Thermodynamics*. Pitman, Boston, 1985.
- [48] MÜLLER, I. Thermodynamics of diffusive and reacting mixtures of fluids. *Physica* 20D 01 (1986), 35–66.

- [49] MUSCHIK, W., PAPPENFUSS, C., AND EHRENTRAUT, H. A sketch of continuum thermodynamics. *Journal of Non-Newtonian Fluid Mechanics* 96 (2001), 255–290.
- [50] NARDINOCCHI, P., PEZZULLA, M., AND PLACIDI, L. Thermodynamically based multiphysic modeling of ionic polymer-metal composites. *Journal of Intelligent Material Systems and Structures* 16 (2011), 1887–1897.
- [51] PETRUCCI, S. *Ionic Interactions: From Dilute Solution to Fused salts*. Elsevier Science, Amsterdam, 2012.
- [52] PITZER, K. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *Journal Physical Chemistry* 77 (1973), 268–277.
- [53] PITZER, K., AND CURL, R. The volumetric and thermodynamic properties of fluids. III. Empirical equation for the second virial coefficient. *Journal of American Chemical Society* 79 (1957), 2369–2370.
- [54] PLANCK, M. *Treatise on Thermodynamics*. Dover, New York, 1945.
- [55] RATKJE, S. Irreversible thermodynamics applied to electrolyte transport. *Journal of Non-Equilibrium Thermodynamics* 04 (1979), 75–92.
- [56] REIS, M., AND BASSI, A. On the two main laws of Thermodynamics. In *Thermodynamics* (Vienna, 2011), M. Tadashi, Ed., Intech, pp. 99–120.
- [57] REIS, M., AND BASSI, A. A segunda lei da termodinâmica. *Química Nova* 35 (2012), 1057–1061.
- [58] REIS, M., AND BASSI, A. Reacting ionic mixtures under the influence of electromagnetic fields. In *Interdisciplinary Turbulence Initiative V* (Berlin, 2013), A. Talamelli, M. Oberlack, and J. Peinke, Eds., Springer, pp. 195–200.
- [59] REITZ, J., AND MILFORD, F. *Foundations of Electromagnetic Theory*. Addison-Wesley, Reading, 1960.
- [60] SHINER, J., AND SIENIUTYCZ, S. The chemical dynamics of biological systems: Variational and extremal formulations. *Progress in Biophysics and Molecular Biology* 62 (1994), 203–221.
- [61] SIENIUTYCZ, S., AND RATKJE, S. Perturbational thermodynamics of coupled electrochemical heat and mass transfer. *International Journal of Heat and Mass Transfer* 39 (1996), 3293–3303.
- [62] SIENIUTYCZ, S., AND RATKJE, S. Variational principle for entropy in electrochemical transport phenomena. *International Journal of Engineering Science* 34 (1996), 549–560.
- [63] TOUPIN, R. The elastic dielectric. *Journal of Rational Mechanics and Analysis* 05 (1956), 849–915.

- [64] TOUPIN, R. Stress tensors in elastic dielectrics. *Archive for Rational Mechanics and Analysis* 05 (1960), 440–452.
- [65] TOUPIN, R. A dynamical theory of elastic dielectrics. *International Journal of Engineering Science* 01 (1963), 101–126.
- [66] TRUESDELL, C. Sulle basi della termomeccanica. *Rendiconti Accademia dei Lincei* 22 (1957), 33–88.
- [67] TRUESDELL, C. *Rational Thermodynamics*. Springer, Berlin, 1984.
- [68] TRUESDELL, C., AND NOLL, W. The non-linear field theories of mechanics. S. Antman, Ed., Springer.
- [69] VAN'T HOFF, J. Die Rolle des osmotischen Druckes in Analogie zwischen Lösungen und Gasen. *Zeitschrift für physikalische Chemie* 01 (1887), 481–508.
- [70] WANG, C.-C. On representations for isotropic functions. Part 1. Isotropic functions of symmetric tensors and vectors. *Archive for Rational Mechanics and Analysis* 33 (1969), 249–267.
- [71] WANG, C.-C. On representations for isotropic functions. Part 2. Isotropic functions of skew-symmetric tensors, symmetric tensors, and vectors. *Archive for Rational Mechanics and Analysis* 33 (1969), 268–287.
- [72] WANG, C.-C. A new representation theorem for isotropic functions: An answer to professor G.F. Smith's criticism of my papers on representations for isotropic functions. Part 1. Scalar-valued isotropic functions. *Archive for Rational Mechanics and Analysis* 36 (1970), 166–197.
- [73] WANG, Y., AND HUTTER, K. Phenomenological thermodynamics and entropy principles. In *Entropy* (Princeton, 2003), A. Greven, G. Keller, and G. Warnecke, Eds., Princeton University Press, pp. 57–77.
- [74] WILMANSKI, K. Lagrangean model of two-phase porous material. *Journal of Non-Equilibrium Thermodynamics* 20 (1995), 50–77.
- [75] WILMANSKI, K. *Continuum Thermodynamics. Part I. Foundations*. World Scientific Publishing Company, New Jersey, 2008.
- [76] WOLYNES, P. Dynamics of electrolyte solutions. *Annual Reviews of Physical Chemistry* 31 (1980), 345–376.
- [77] ZHOU, S.-A., AND UESAKA, M. Modeling of transport phenomena of ions and polarizable molecules: A generalized Poisson–Nernst–Planck theory. *International Journal of Engineering Science* 44 (2006), 938–948.