Pergamon

Int. J. Heat Mass Transfer. Vol. 40, No. 14, pp. 3467–3485, 1997
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Printed in Great Britain
0017–9310/97 $17.00+0.00

PII: S0017–9310(96)00235–9

Variational thermomechanical processes and chemical reactions in distributed systems

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(*Received* 10 *January* 1996)

Abstract—In this synthesizing work several interrelated variational principles are constructed for various field representations of dynamics of simultaneous transfer of heat, mass and electric charge, in chemically reacting systems at mechanical equilibrium or not. The underlying physical principle is invariance of the entropy production or energy dissipation. The variational framework, which stems from functionals of various thermodynamic potentials, is quite vast and diverse. It includes: nonstationary extension of Onsager's variational formulation, gradient representations, vectors of thermal, chemical and mechanical displacements, potentials of thermal field, functional Hamiltonian formalism, Poissonian brackets, and a thermomechanical dissipative action. Each of these methods is supplemented by a physical assumption, which is in general not incorporated into the original variational formulation: this is the assumption of a local thermal equilibrium. The most original and valuable result is inclusion of chemical reactions in variational dynamics, with chemical nonlinearities governed by kinetics of mass action. A method was also successfully discovered, based on equivalent variational problems, which makes it possible to show the equivalence of thermodynamic potentials at nonequilibrium, and, in particular, the practical usefulness of free energy functionals. Finally, an extended action approach for thermomechanical chemical kinetics in distributed systems was worked out. This should be important for biophysical systems such as, for example, contracting muscles, whose dynamics are described by dissipative Lagrange equations containing the mechanical equation of motion and equations of chemical kinetics (the Guldberg–Waage mass action law and its nonlocal generalizations). © 1997 Elsevier Science Ltd.

1. INTRODUCTION

Recently, the introduction of the concept of a nonlinear chemical resistance [1,2] has lead to a chemical equivalent of Ohm's law, and shown that the Guldberg and Waage law [2] can be the subject of nearly routine irreversible thermodynamics. The purpose of this paper is to expose various general variational methods of derivation of nonlinear chemical kinetics and accompanying thermal diffusional kinetics at mechanical equilibrium, terminating the treatment with an example of the inclusion of mechanical motion. The chemical kinetics corresponds to the Guldberg–Waage law as the 'chemical Ohm's law', and the mechanical example to an extended Euler equation with a frictional term linear with respect to the velocity.

The concept of the chemical resistance is simple, general and crucial for our purposes. To illustrate this concept, consider an open, multicomponent system, of n components undergoing N chemical reactions:

$$\sum_{i=1}^{n} \nu^{\mathrm{f}}_{ij}[i] \leftrightarrow \sum_{i=1}^{n} \nu^{\mathrm{b}}_{ij}[i] \quad i = 1,\ldots,n \quad j = 1,\ldots,N. \tag{1}$$

The system contains species i with chemical potential μ_i; T is the local temperature, and R the gas constant. The ν^{f}_{ij} and ν^{b}_{ij} are the forward and backward stoichiometric coefficients, respectively, for species i in reaction j. The advancement of the jth reaction is denoted by ξ_j, and its rate by $\dot{\xi}_j \equiv \mathrm{d}\xi_j/\mathrm{d}t$ or r_j. Since the chemical equilibrium constant for the jth reaction K_j is given by the ratio of the forward and backward reaction rate constants, $k^{\mathrm{f}}_j/k^{\mathrm{b}}_j$, the classical chemical affinity of the jth reaction can be expressed in the form

$$A_j = \sum_{i=1}^{n} (\nu^{\mathrm{f}}_{ij} - \nu^{\mathrm{b}}_{ij})\mu_i = -\sum_{i=1}^{n} \nu_{ij}\mu_i$$
$$= \mathrm{R}T \ln\left[k^{\mathrm{f}}_j \prod_{i=1}^{n} a_i^{\nu^{\mathrm{f}}_{ij}}\right] - \ln\left[k^{\mathrm{b}}_j \prod_{i=1}^{n} a_i^{\nu^{\mathrm{b}}_{ij}}\right]. \tag{2}$$

An associated meaning is the action of a chemical reaction, or 'chemaction', which contains the molar actions of the components, ϕ_i, which are the Lagrange multipliers of mass balance constraints in the action approach (see Section 7). The chemical potentials μ_i are related to the ϕ_i and their time derivatives. When the frequency of the elastic collisions vanishes ($\omega = \tau^{-1} = 0$) on the chemical time scale, $\mathrm{d}\phi_i/\mathrm{d}t = -\mu_i$; a result known from theories of perfect fluids [3]. The operator $\mathrm{d}_i/\mathrm{d}t = \partial_i/\partial t + (\mathbf{u}_i \cdot \nabla)$ is based on the absolute velocity of the ith component in a laboratory frame. When diffusion is ignored all velocities $\mathbf{u}_i$ are equal to the common barycentric velocity $\mathbf{u}$, and the operator becomes barycentric. The net stoi-

NOMENCLATURE

$\mathbf{A}_j^{\mathrm{s}}$	column matrix of extended affinities in entropy picture, equations (34) and (35)
A_j	chemical affinity of *j*th reaction, the *j*th component of the affinity vector **A**
a_i	thermodynamic activity of *i*th component
$\mathbf{a} \equiv -\partial \mathbf{C}(\mathbf{u})/\partial \mathbf{u}$	thermostatic capacitance matrix
C	vector composed of molar concentrations of components, c_i
E	total energy as the result of the minimization of the related functional, equation (61)
e_{v}	molar energy per unit volume
F	free energy as the result of the minimization of the related functional, equation (63)
$\mathbf{H}_i$	thermal displacement vector associated with the component flux J_i
H_σ	thermodynamic Hamiltonian based on entropy dissipation functions
$h(t)$	arbitrary function of time, equation (21)
I	inertial matrix (Section 7)
i	molar flux density of electric current
J	matrix of independent fluxes of species, with molar fluxes J_i, equation (6a)
J_{e}	density of total energy flux
J_{s}	density of entropy flux
L	Onsagerian matrix of phenomenological coefficients
L_σ	dissipative (thermodynamic) Lagrangian
n	number of components in the mixture
M_i	molar mass of *i*th component
p_σ	dissipative momentum, equation (74)
R	resistance matrix composed of chemical resistances R_j, equation (29)
R	universal gas constant
r	vector of reaction rates per unit volume, the chemical flux vector
S, S^{T}	total entropy and its Legendre transform, respectively
s_{v}	entropy of unit volume
T	local equilibrium temperature
t	coordinate of physical time
u	thermodynamic vector of independent intensities, equation (4)
v	vector of linear velocity
V	volume of the physical system
W	modified matrix of conductances, a positive symmetric matrix in the second-order entropy functional, equation (16)
w	vector of Lagrangian multipliers of balance laws as independent kinetic intensities
X	vector of initial Lagrangian coordinates in thermomechanical problem
X	vector composed of independent thermodynamic forces
x	vector of spatial coordinates in physical space
X_i	concentration of *i*th component in moles per unit mass of mixture (Section 7).

Greek symbols

Λ	overall Lagrangian density of dissipative field
∇	differential operator
δ	spatial operator of variational derivatives
$\boldsymbol{\varepsilon}$	mechanical displacement vector
κ_j	modified progress variable of *j*th reaction
μ_i	molar chemical potential of *i*th component
$\tilde{\mu}_i = \mu_n M_i M_n^{-1} - \mu_i$	transfer potential of *i*th component
ν_{ij}^{f}, ν_{ij}^{b}	forward and backward stoichiometric coefficients for species *i* in reaction *j*
ν_{ij}	resulting stoichiometric coefficient for species *i* in reaction *j*
ν'	extended stoichiometric matrix defined in equation (35)
ξ_j	progress variable of *j*th reaction
ϕ	electric potential molar action of component (in Section 7)
π_σ	dissipative momentum, equation (75)
σ	production density
τ	average time between elastic collisions
χ	chemical displacement variable.

Subscripts

e	total energy
j	*j*th reaction
k	*k*th component
s	entropy
σ	dissipative property
1, 2	initial and final time.

Superscripts

s	entropy representation
T	transpose matrix, transformed quantity
′	modified representation.

chiometric coefficient ν_{ij} follows the standard convention [4]. However, the definition of the affinity, and that of the associated chemaction, follow the network convention [5]. The dissipation inequality holds in the network convention used here in the form $A_j r_j > 0$. This convention insures that the rate of an isolated reaction and its affinity always have the same sign. This in turn allows one to write a 'chemical' Ohm's relation with the positive resistance R_j of the jth reaction understood as the ratio of the chemical force A_j to the chemical flux r_j:

$$R_j = A_j/r_j = \sum_{i=1}^{n} (\nu_{ij}^{\mathrm{f}} - \nu_{ij}^{\mathrm{b}})\mu_i/r_j$$

$$= \sum_{i=1}^{n} \nu_{ij}\mu_i/r_j \quad j = 1, \ldots, N. \tag{3}$$

The expression of R_j in terms of concentrations is crucial for any treatment of nonlinear kinetics. For the Guldberg–Waage kinetics of mass action the rate formula and the affinity formula (2) lead to the logarithmic resistance [1, 2]

$$R_j(\mathbf{c}, T) = \frac{\mathbf{R}T \ln \left[\left(k_j^{\mathrm{f}} \prod_{i=1}^{n} a_i^{\nu_{ij}^{\mathrm{f}}} \right) \Big/ \left(k_j^{\mathrm{b}} \prod_{i=1}^{n} a_i^{\nu_{ij}^{\mathrm{b}}} \right) \right]}{k_j^{\mathrm{f}} \prod_{i=1}^{n} a_i^{\nu_{ij}^{\mathrm{f}}} - k_j^{\mathrm{b}} \prod_{i=1}^{n} a_i^{\nu_{ij}^{\mathrm{b}}}} \tag{4}$$

where $\mathbf{c}$ is the vector of molar concentrations. In thermodynamic approaches to chemical systems, it is the resistance formula (4) rather than the mass action kinetics which is the starting point in the majority of basic considerations. One should appreciate the versatility of the chemical resistances and the related inertances $I_j = \tau R_j$ when treating chemical steady states, transients and nonlinearities. In particular, equation (4) leads immediately to the chemical dissipation function $\phi_j = (1/2)R_j r_j^2$ with the state dependent R_j, and this dissipation function satisfies Onsager's local principle of minimum dissipation [2]. The steady states can be treated by a routine procedure leading to unknown rates of resulting reactions as ratios of overall affinities to overall resistances [6]. Guldberg–Waage kinetics follow from these formalisms *a posteriori* ($r_j = A_j/R_j$): however, their generalizations are also possible as long as the standard phenomenological laws of Ohm, Fourier, Fick and Guldberg and Waage are only asymptotic formulae [7]. For very fast transients of frequency comparable with that of elastic collisions, τ^{-1}, extended kinetics correspond to a generalization of the Guldberg and Waage kinetics; this generalization involving a term with the time derivative of the reaction rate. More importantly, in general formulations, chemical kinetics are obtained in a unified treatment along with the kinetics of various nonchemical processes, i.e. transport and exchange processes. The example in Section 4 treats isobaric reaction–diffusion fields in this methodological way.

Another example, in Section 7, shows coupling of chemical reactions with a mechanical displacement field, important in the theory of contracting muscles. In this extended physical situation, the Gibbs free energy, and, hence, chemical potentials, depend explicitly on nonmechanical displacements, and correct nonequilibrium chemical potentials are necessary in the analysis. The correct result for the chemical potential is $\mu_k = \mu_k^{\mathrm{eq}} - M_k \mathbf{u}^2/2$, regardless of the thermodynamic potential used [8–11]. This result is obtained only when a Lagrangian L used to define μ_k is modified by the constraint related term expressing the dependence of concentrations $\Omega'(1 - \Sigma M_k x_k)$. The consequence of the term is the correction equation of the thermomechanochemical motion which comprises the frictional mechanical motion and chemical kinetics, very diverse phenomena whose synthetic effect is observed in various biophysical processes [12].

Some examples dealing with nonreacting systems are considered first, because of their relative simplicity: more and more complex chemical systems are then investigated. Our analysis of reacting and nonreacting continua is based on variational principles, an evergreen problem in dissipative thermomechanics. Since Onsager's [13–16] and Prigogine's [17] extremum and variational principles for linear irreversible processes, there have been numerous approaches to generalized principles which could describe nonstationary nonlinear evolutions. Gyarmati's quasi-linear generalizations [18–20], while of considerable generality, belong to the class of the restricted principles of Rosen's type [21] or local potential type [22], where some variables and/or derivatives are subjectively 'frozen' to preserve a proper result. Essex [23] has shown the potential of minimum entropy formulations to yield nonlinear balance equations for radiative transfer. Mornev and Aliev [24] have formulated a functional extension of the local Onsager's principle. With a caloric coordinate, Grmela and Teichman [25] stated a negative-entropy-based H theorem as a proper setting for the maximum entropy in Lagrangian coordinates.

Grmela [26–29] and Grmela and Lebon [30] have worked out an important two-bracket formalism, with Poissonian brackets and dissipative brackets, the latter being the functional extension of the Rayleigh dissipation function [31]. With applications to rheology, the bracket approach has been systematically exposed in a recent book [32]. Two-bracket theorems are not associated with an extremum of a definite physical quantity, however; for that purpose, the single Poissonian bracket and a Hamiltonian system are necessary. However, another approach [33, 34] has introduced certain potentials, similar to those known in the theory of electromagnetic fields, and related integrals. Their application to nonreacting systems has proved very useful [33–36]. Yet, the inclusion of the chemical reactions has required treating chemical sources as given functions of time and position. Recent approaches to coupled transport processes, based on a functional expression for the second law, with Lagrange multipliers absorbing balance constraints, have been, so far, restricted to nonreacting systems, both parabolic [37, 38] and hyperbolic [39]. These approaches may be regarded as equality counterparts of Liu's multiplier method [40], which deals with the second law in an inequality form, and, as such, leads to qualitative rather than quantitative results. Anthony's variational method [41–45], which uses a 'field of thermal excitation', a thermal analogue of quantum wave function, and certain reaction potentials, remains, to our knowledge, the only general treatment of distributed reaction–diffusion systems via a variational principle, at the expense, however, of an undefined physical origin of these potentials and their relation to the mass action law [46].

Chemical reactions with nonlinear kinetics have long remained excluded from exact variational formulations. An important step towards their inclusion was the introduction of nonlinear chemical resistances [1, 2, 47–50]. With these quantities, which correspond to the mass action law in the works quoted, nonlinear variation and extremum formulations for *lumped* systems have become possible [49–53]. In the present work, these formulations are generalized to *distributed* reaction–diffusion systems in the field (Eulerian) representation of the accompanying transport phenomena.

The admissibility of a variational formulation calls, however, for substantiation in cases when irreversibility enters into the issue. A system of differential equations admits a variational formulation if, and only if, it is self-adjoint [54–59], i.e. when stringent conditions for partial derivatives of the related differential operator are satisfied [54–59]. It is also known that typical equations of irreversible processes are, as a rule, not self-adjoint [58, 60].

A pertinent argument is valid though: while equations of irreversible processes do not admit variational formulation in the state space spanned on their own dependent variables (this is the situation where the nonself-adjointness applies), the so-called composite variational principles in the extended space spanned on these state variables and certain new variables, called state adjoints, is always possible [54, 59]. In fact, all successful recent variational formulations for irreversible continua always involve the space expansion. This claim also refers to formulations which use higher-order functionals [33–36], which can be broken down to those based on the first-order functionals in an enlarged space, as well as some action-based approaches to irreversible continua [43, 51] and reversible continua [62–67]. Reviews and books on this subject are available [68–73]. With these results in mind, the conservation laws and the idea of minimum dissipation in the case of fields [4, 74], here we search for the extrema of thermodynamic potentials [75] of inhomogeneous diffusion–reaction systems.

In recent works on lumped systems [76] and continuous system [38, 39], the necessity of a distinction between the standard Gibbsian thermodynamic intensities $\mathbf{u}$ (the temperature reciprocal and Planck chemical potentials), which are the partial derivatives of the entropy with respect to energy and mole numbers, and their transport counterparts or the Lagrangian multipliers of balance equations in thermodynamic functionals, has been discovered. While both $\mathbf{u}$ and $\mathbf{w}$ may play a role in these functionals, the distinction is important only away from local thermal equilibrium. It is stressed that the distinction is necessary only when a dynamic behavior is taken into consideration, as only then are the instantaneous potentials of transfer at a definite point of a continuum not necessary equilibrium quantities. It is not relevant for situations and models which ignore any dynamic development, such as, for example, typical models of the maximum entropy formalism [77], in which the Lagrange multipliers refer to the final state of equilibrium rather than to the variety of intermediate states.

Due to the commonness of the local equilibrium in real physical systems, the two quantities $\mathbf{u}$ and $\mathbf{w}$ coincide for the large majority of physical situations. Therefore, the condition $\mathbf{u} = \mathbf{w}$ should *a posteriori* be imposed for most models of heat and mass transport. As is commonly known [4] in the limiting local equilibrium situations one can combine the conservation laws and phenomenological equations to yield the equations of change. The latter are therefore equation-dependent with respect to the former. On the other hand, away from local equilibrium, the equations of change follow independently of the conservation laws and phenomenological equations. However, it is just the condition $\mathbf{u} = \mathbf{w}$ that drives one back to the local equilibrium situation (more restricted from the physical viewpoint than any local disequilibrium). These effects link the equilibrium and disequilibrium descriptions of continua in a natural way. They hold in both the one component and the multicomponent case, with respect to both the temperatures and chemical potentials.

In this work, these effects are discussed by means of a few novel variational principles of nonequilibrium thermodynamics, in several new and important contexts, such as:

(1) invariant functionals and gradient representations using Biot's vector of thermal displacement [78] and the potentials of thermal field introduced recently [33, 34];
(2) inclusion in a variational or extremum principle of chemical reactions and chemical nonlinearities governed by the mass action kinetics [46]:
(3) significance of various thermodynamic potentials at nonequilibrium, and, in particular, the practical role of free energy functionals;
(4) relation between Lagrangian and Hamiltonian descriptions (the latter with a bracket formalism exposed);
(5) physical limitations on results of variational analyses.

From the practical viewpoint, item 2 is of special importance as it makes it possible to solve complex partial differential equations of reaction–diffusion processes with direct variational methods [79]. We also succeeded in discovering a method, based on equivalent variational problems, which makes it possible to show the equivalence of various thermodynamic potentials at nonequilibrium. The problem is known to be difficult, and so far remains unsolved, in an exact way. The equivalence conclusion is restricted to small deviations of thermodynamic potentials from a global equilibrium, in agreement with classical statistical mechanics [80].

The system considered is composed of components with various transport phenomena and chemical reactions in the bulk. The components are reacting but neutral [81–83], obeying the phase rule [84]. As shown by Sundheim [81], this setting leads to independent fluxes of mass, energy and electric current. For an ionic description, see ref. [85]. The macroscopic motion of the system is neglected by the choice of the vanishing barycentric frame, and an assumption about the constancy of the system density, ρ, consistent with the mechanical equilibrium assumption. This is an assumption which makes the effects considered more transparent. With this assumption, the total mass density, ρ, is a constant parameter rather than a state coordinate, and a reference frame in which the whole system rests easily follows. In short, one of the main reasons for using variational approaches (leaving aside, of course, their computational virtues) is our general research direction towards extending Callen's postulational thermodynamics to inhomogeneous thermodynamic systems.

2. CONTINUOUS SYSTEMS WITH HEAT AND MASS TRANSPORT

In the entropy representation, for a continuous fluid mixture under mechanical equilibrium, the conservation laws are

$$\frac{\partial \mathbf{C}}{\partial t} + \nabla \cdot \mathbf{J} = 0. \tag{5}$$

This is the matrix notation [4] of all conservation laws consistent when $\mathbf{J}$ is the matrix of independent fluxes:

$$\mathbf{J} = (\mathbf{J}_e, \mathbf{J}_1, \mathbf{J}_2, \ldots, \mathbf{J}_{n-1}, \mathbf{i})^{\mathrm{T}} \tag{6a}$$

(the superscript T means the transpose of the matrix), and, for the corresponding column vector of densities $\mathbf{C}$,

$$\mathbf{C} = (e_v, c_1, c_2, \ldots, c_{n-1}, 0)^{\mathrm{T}}. \tag{6b}$$

The nth mass flux J_n has been eliminated by using the condition $\Sigma J_i M_i = 0$ for $i = 1, 2, \ldots, n$. The last component of $\mathbf{C}$ vanishes because of the electroneutrality. The independent transfer potentials are

$$\mathbf{u} = (T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots, \tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1}) \tag{7}$$

with $\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$. Their gradients $X \equiv \nabla \mathbf{u} = (\nabla T^{-1}, \nabla \tilde{\mu}_1^{-1} \cdots - \nabla(\phi T^{-1}))$ are independent forces. The densities (6b) and transfer potentials (7) are the two sets of variables in the Gibbs equation for entropy density $s_v = \rho s$ of an incompressible system with mass density $\rho = \Sigma M_i c_i$. The differential of the entropy density in terms of the vector $\mathbf{C}$ is $\mathrm{d}s_v = \mathbf{u} \cdot \mathrm{d}\mathbf{C}$.

Conservation laws, equation (5), are built into the entropy functional, equation (8), with the help of the vector of the Lagrangian multipliers $\mathbf{w} = (w_0, w_1, w_2, \ldots, w_{n-1}, w_n)$. The *extremum* value of the multiplier $\mathbf{w}$ in the entropy functional, equation (8), is the vector of the *kinetic* conjugates of the extensities $\mathbf{C}$, equation (6b). On the extremal surfaces of the entropy functional (8), the vector $\mathbf{w}$ coincides with the transport potential vector $\mathbf{u}$, equation (7), in the limiting situation of the local equilibrium.

The coincidence $\mathbf{u} = \mathbf{w}$ does not occur away from any extremal nonequilibrium solution, and, therefore, $\mathbf{w}$ and $\mathbf{u}$ are generally two distinctive sorts of field variables in the entropy functional equation (8). As long as the constraint $\mathbf{w} = \mathbf{u}$ is not imposed, they constitute two fields independent of each other. They may be interpreted, respectively, as the kinetic (Onsagerian) and thermodynamic (Gibbsian) intensities, which coincide in a stable extremal process with local equilibrium. Any kinetic intensity is the Lagrangian multiplier of the related conservation law, whereas any Gibbsian intensity is the appropriate partial derivative of the entropy with respect to the adjoint extensity. On extremals $\mathbf{w} = \mathbf{u}$, meaning that the extremal Lagrangian multipliers coincide with the components of the entropy gradient in the state space of C_i. In a limiting local equilibrium situation, w_i converge to the static (equilibrium) intensities, equation (7), otherwise they converge to certain nonequilibrium intensities that are still the partials of an extended entropy although they then depend on both C_i and J_i (extended thermodynamics).

To simplify the notation the single-integral symbols are used for multiplied integrals in the physical space–time. The governing functional describes the second law between the two fixed times t_1 and a subsequent t_2:

$$S(t_2) = \min \Big\langle S(t_1) + \int_{t_1,\mathbf{A}}^{t_2} -J_s(\mathbf{J}, \mathbf{u}) \cdot \mathrm{d}\mathbf{A}\,\mathrm{d}t$$
$$+ \int_{t_1,V}^{t_2} \Big\{ \frac{1}{2} \mathbf{L}^{-1}(\mathbf{u}) : \mathbf{J}\mathbf{J} + \frac{1}{2} \mathbf{L}(\mathbf{u}) : \nabla\mathbf{u}\nabla\mathbf{u}$$
$$+ \mathbf{w} \cdot \left(\frac{\partial \mathbf{C}(\mathbf{u})}{\partial t} + \nabla \cdot \mathbf{J} \right) \Big\} \mathrm{d}V \mathrm{d}t \Big\rangle \tag{8}$$

where $J_s(\mathbf{J}, \mathbf{u})$ is simply the product $\mathbf{J} \cdot \mathbf{u}$. A simple derivation of such functional structures from an error criterion has been given in earlier works [39, 52]. By simple application of the divergence theorem to the $\mathbf{w}$ term of equation (8), it was also shown that in the steady-state case of a system satisfying $\mathbf{w} = \mathbf{u}$ the above functional can be broken down to Onsager's functional:

$$\min \int_V \left(\frac{1}{2}\mathbf{L}^{-1} : \mathbf{J}\mathbf{J} - \mathbf{J}\cdot\nabla\mathbf{u}\right) \mathrm{d}V. \tag{9}$$

At the steady state, when only $\mathbf{J}$ is varied and $\mathbf{w}$ converges to $\mathbf{u}$ on the extremal surfaces, the Onsager's functional, equation (9), and the kinetic equation

$$\mathbf{J} = \mathbf{L}\cdot\nabla\mathbf{u} \tag{10}$$

follow from equation (8) as the only steady-state formulae.

In the unsteady situation, equation (8) yields, as the Euler–Lagrange equations with respect to the variables $\mathbf{u}$, $\mathbf{J}$ and $\mathbf{w}$, a more general result. It is a quasilinear set representing (at $\mathbf{w} = \mathbf{u}$) the standard model of the unsteady transfer of heat, mass and electric charge. The Euler–Lagrange equations of the entropy functional with respect to the variables $\mathbf{w}$, $\mathbf{J}$ and $\mathbf{u}$ are, respectively:

$$\frac{\partial \mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\mathbf{J} = 0 \tag{5}$$

$$\mathbf{L}(\mathbf{u})^{-1}\cdot\mathbf{J} = \nabla\mathbf{w} \tag{11}$$

$$\mathbf{a}(\mathbf{u})\cdot\frac{\partial \mathbf{w}}{\partial t} = \nabla\cdot(\mathbf{L}\cdot\nabla\mathbf{u}) \tag{12}$$

where $\mathbf{a}(\mathbf{u}) \equiv -\partial\mathbf{C}(\mathbf{u})/\partial\mathbf{u}$ is the thermodynamic capacitance matrix or the negative of the entropy Hessian. From the viewpoint of the completeness of the physical equations as extremum conditions of S, the second law Lagrangian used, i.e. the integrand of space–time integral in equation (8), does a good job since it leads to *all* pertinent equations, the property which is essentially not obeyed for older models, as we will soon see. The conservation laws, equation (5), are recovered, the other results are the quasilinear phenomenological equations and the equations of change. The last equation is the Fourier–Kirchhoff type matrix equation of change which links the fields of temperature, chemical potentials and electrical potential. At the local equilibrium, when all states of the system are located on the Gibbs manifold, the equality $\mathbf{w} = \mathbf{u}$ holds, and equations (5), (11) and (12) become dependent. This is the well-known classical situation, in which only a subset of possible solutions is realized in practice.

3. GRADIENT INVARIANT FUNCTIONALS AND GRADIENT REPRESENTATIONS

To support the conviction that nature can use only a part of solutions offered by a mathematical theory, consider a different variational formulation for the same system which uses the so called Biot's [78] thermal displacement vector, $\mathbf{H}$, in the integrand of the entropy functional. Actually, as long as the system is multicomponent, one has to use a set of such vectors. They are associated with the energy flux, component fluxes and electric current:

$$\mathbf{H} = (H_e, H_1, H_2, \ldots, H_{n-1}, H_{el})^{\mathrm{T}} \tag{13}$$

and refer to each vector component of the matrix (6a). Since each flux and each density satisfy the gradient representations

$$\mathbf{J} = \frac{\partial \mathbf{H}}{\partial t} \tag{14}$$

and

$$\mathbf{C} = -\nabla\cdot\mathbf{H} \tag{15}$$

the conservation laws are similarly satisfied. Indeed, the addition of the gradient of equation (14) to the partial time derivative of equation (15) yields equation (5).

To derive the Euler–Lagrange equations from a functional based on the representations, equation (14) and (15), it suffices to substitute them into the production part of the entropy functional, equation (8). Restricting, for brevity, to a linear system (the case of constant coefficients) yields

$$S_\sigma = \int_{t_1,V}^{t_2} \left\{\frac{1}{2}\mathbf{L}^{-1} : \frac{\partial \mathbf{H}}{\partial t}\frac{\partial \mathbf{H}}{\partial t} + \frac{1}{2}\mathbf{W} : \nabla(\nabla\cdot\mathbf{H})\nabla(\nabla\cdot\mathbf{H})\right\} \mathrm{d}V\,\mathrm{d}t \tag{16}$$

where the positive symmetric matrix $\mathbf{W}$ has been defined as

$$\mathbf{W} \equiv \mathbf{a}^{-1\mathrm{T}}\mathbf{L}\mathbf{a}^{-1}. \tag{17}$$

The matrix Euler–Lagrange equation for the above functional is

$$\mathbf{L}^{-1}\frac{\partial^2 \mathbf{H}}{\partial t^2} - \mathbf{W}\nabla^2(\nabla^2\mathbf{H}) = 0. \tag{18}$$

After using the representations, equations (14) and (15), equation (18) can be given in the form

$$\mathbf{L}^{-1}\frac{\partial \mathbf{J}}{\partial t} + \mathbf{W}\nabla^2(\nabla\mathbf{C}) = 0. \tag{19}$$

Equation (19) holds with the conservation laws, equation (5), contained in the representations, equations (14) and (15). Thus the system is now characterised by equations (14), (15) and (19). (Note that equation (19) followed from equation (16) without any prior recursion to the condition $\mathbf{w} = \mathbf{u}$, and that it can also be obtained by eliminating of the multipliers $\mathbf{w}$ from equation (11) and (12).) However, when one wants to pass to the set of equations (5), (11) and (12) from this model, a more general set is admitted by equations (14), (15) and (19):

$$\frac{\partial \mathbf{C}(\mathbf{u})}{\partial t}+\nabla\cdot\mathbf{J}=0 \tag{5}$$

$$\mathbf{L}(\mathbf{u})^{-1}\cdot\mathbf{J}=\nabla\mathbf{w}+\mathbf{c}(\mathbf{x}) \tag{20}$$

$$\mathbf{a}(\mathbf{u})\frac{\partial \mathbf{w}}{\partial t}=\nabla\cdot(\mathbf{L}\nabla\mathbf{u})+h(t) \tag{21}$$

where $\mathbf{c}(\mathbf{x})$ and $h(t)$ are arbitrary functions. Based on the last result, a claim that the physical behavior should be described by equations (14), (15) and (18) rather than by any other sets would be not entirely appropriate from the stand-point of anyone who (preferring the traditional form of heat equations) wants to operate with all three equations (5), (11) and (12). Again, the only reasonable way to resolve the dilemma is to restrict the structure of the independent equations (5), (20) and (21) to the range implied by an experiment or microscopic transport theories. This, in turn, means that their dependence is associated with taking $\mathbf{w}=\mathbf{u}$, along with $\mathbf{c}(\mathbf{x})=0$, $h(t)=0$. Thus it is the physics of the problem which requires one to restrict to the case when $\mathbf{c}(\mathbf{x})=0$, $h(t)=0$ and $\mathbf{w}=\mathbf{u}$.

Another example illustrating this sort of problems is also in order. The origin of the integrand of equation (8) lies in phenomenological equations, which have been squared in the form $\mathbf{L}^{-1}(\mathbf{u})\mathbf{J}-\nabla\mathbf{u}=0$, to generate an error expression based on the resistance [39, 52]. For the same parabolic problem, with a concept of potentials [33, 34], in the linear case, Gambar and Màrkus [36] have applied a dissipative Lagrangian obtained via squaring the variational adjoint of the equation of change [equation (12) at $\mathbf{u}=\mathbf{w}$]. This variational adjoint, which is next identified with $\mathbf{u}$, is, in the present notation,

$$\mathbf{u}=-\mathbf{a}\frac{\partial\phi}{\partial t}-\mathbf{L}\nabla^2\phi \tag{22}$$

(their $\rho S_{ik}=-a_{ik}^{-1}$). Their Lagrangian is second order:

$$\mathbf{L}(\phi,\phi_{,t},\phi_{,xx})=\frac{1}{2}\left(\mathbf{a}\frac{\partial\phi}{\partial t}+\mathbf{L}\nabla^2\phi\right)^2\quad(=\tfrac{1}{2}\mathbf{u}^2). \tag{23}$$

This Lagrangian leads to the Euler–Lagrange equation

$$\mathbf{a}\frac{\partial}{\partial t}\left(\mathbf{a}\frac{\partial\phi}{\partial t}+\mathbf{L}\nabla^2\phi\right)-\mathbf{L}\nabla^2\left(\mathbf{a}\frac{\partial\phi}{\partial t}+\mathbf{L}\nabla^2\phi\right)=0 \tag{24}$$

which is satisfied by equation (22) in the form

$$-\mathbf{a}\frac{\partial}{\partial t}\mathbf{u}+\mathbf{L}\nabla^2\mathbf{u}=0. \tag{25}$$

This is the linear form of the Fourier–Kirchhoff equation. This approach has resulted in a number of original interpretations of nonequilibrium thermodynamic [34–36]. These ingenious analyses, and a field theory constructed on the basis of the Lagrangian equation (23), provide equations of change, and extra physical conditions (obtained from some invariance requirements) should hold to obtain the phenomenological equations or conservation laws from equation (23). This conforms with our earlier conclusion that associated physical analyses should accompany the variational results. Indeed, it is easy to see that equation (24) is satisfied in the form of equation (25) not only by equation (22), but also by the more general representations containing a function $f(\mathbf{x},t)$:

$$\mathbf{u}=-\mathbf{a}\frac{\partial\phi}{\partial t}-\mathbf{L}\nabla^2\phi-f(\mathbf{x},t) \tag{26}$$

provided that the function $f(\mathbf{x},t)$ obeys the equation

$$\frac{\partial}{\partial t}f(\mathbf{x},t)+\nabla^2 f(\mathbf{x},t)=0. \tag{27}$$

An example of such function for a one-potential process is $f=(1/6)\mathbf{x}^2-t$). In this example, the representations, equation (26), have been rejected on account of the simpler representations, equation (22), regarded as, perhaps, 'more physical' since they obey the gradient invariance. One may argue that the adjoint quantities are 'nonphysical' anyhow, so it does not matter which representation, equation (22) or equation (26), is used. However, this argument is not always true since some adjoint quantities have, without doubt, a well-defined physical meaning. One example is momenta of classical mechanics, which are adjoints of coordinates. Another example is rates of dynamic equations with inverted signs of resistances, which describe fluctuations around equilibrium. Therefore, the restrictions imposed on definitions of potentials may also have physical reasons (consider, for example, restrictions on electromagnetic potentials [86]).

4. REACTION–DIFFUSION SYSTEMS AND CHEMICAL NONLINEARITIES

Consider now a generalization of the entropy production functional with two chemical dissipation functions

$$S_\sigma=\int_{t_1,V}^{t_2}\left\langle\left\{\frac{1}{2}\mathbf{L}^{-1}(\mathbf{u}):\mathbf{J}\mathbf{J}+\frac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u}+\frac{1}{2}\mathbf{R}:\mathbf{r}\mathbf{r}+\frac{1}{2}\mathbf{R}^{-1}:(v^{\mathrm{T}}\mathbf{u})(v^{\mathrm{T}}\mathbf{u})+\mathbf{w}\cdot\left[\frac{\partial\mathbf{C}(\mathbf{u})}{\partial t}+\nabla\cdot\mathbf{J}-\mathbf{v}'\mathbf{r}\right]\right\}\mathrm{d}V\mathrm{d}t\right\rangle \tag{28}$$

where the term $v'^{\mathrm{T}}\mathbf{u}$ is an extended vector of the chemical affinities in the entropy representation, $\mathbf{A}^s$, defined below, and both $\mathbf{R}$ terms refer to chemical dissipation described by the nonlinear chemical resistances $\mathbf{R}$. The chemical resistances (of the entropy representation) obey the logarithmic formula [1, 2, 47]

$$R_j(\mathbf{C}) = \frac{\mathrm{R}\ln\left[\left(k_j^{\mathrm{f}}\prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{f}}}\right)\Big/\left(k_j^{\mathrm{b}}\prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{b}}}\right)\right]}{k_j^{\mathrm{f}}\prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{f}}} - k_j^{\mathrm{b}}\prod_{i=1}^{N} a_i^{\nu_{ij}^{\mathrm{b}}}}. \quad (29)$$

Here $a_i = a_i(\mathbf{C})$ are the activities expressed as functions of the actual state.

Now by using the standard mass conservation law for each chemical reaction

$$\sum_{i=1}^{n} \nu_{ij} M_i = 0 \quad (30)$$

along with an appropriately extended stoichiometric matrix

$$\nu'_{ij} = \begin{bmatrix} \nu_{01} & \ldots \nu_{0j} & \ldots \nu_{0N} \\ \ldots & \ldots & \ldots \\ \nu_{i1} & \ldots \nu_{ij} & \ldots \nu_{iN} \\ \ldots & \ldots & \ldots \\ \nu_{n1} & \ldots \nu_{nj} & \ldots \nu_{nN} \end{bmatrix} \quad (31)$$

and the independent transfer potentials

$$\mathbf{u} = (T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots, \tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1}) \quad (32)$$

with $\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$ $k = 1, \ldots, n$ (the tilde potential of the nth component vanishes and plays no role in the definition of $\mathbf{u}$), the classical affinity definition of the jth reaction

$$\mathbf{A}_j = -\sum_{i=1}^{n} \nu_{ij}\mu_i = -(\upsilon^{\mathrm{T}}\mu)_j \quad (33)$$

can be transformed into its entropy-representation counterpart and then extended [mark ⇒ in equation (34)] to an expression which can deal with *all* components of the vector, equation (32):

$$\mathbf{A}_j^{\mathrm{s}} = -\sum_{i=1}^{n} T^{-1}\nu_{ij}\mu_i = -\sum_{i=1}^{n} T^{-1}\nu_{ij}(\mu_n M_i M_n^{-1} - \tilde{\mu}_i)$$

$$= \sum_{i=1}^{n-1} T^{-1}\nu_{ij}\tilde{\mu}_i \quad \Rightarrow (\upsilon'^{\mathrm{T}}\mathbf{u})_j \quad (34)$$

where

$$\nu'^{\mathrm{T}}_{ij} = \begin{bmatrix} \nu_{01} & \ldots \nu_{i1} & \ldots \nu_{n1} \\ \ldots & \ldots & \ldots \\ \nu_{0j} & \ldots \nu_{ij} & \ldots \nu_{nj} \\ \ldots & \ldots & \ldots \\ \nu_{0N} & \ldots \nu_{iN} & \ldots \nu_{nN} \end{bmatrix}. \quad (35)$$

In this extended affinity the component index changes from 0 (energy), through $1, 2 \ldots n-1$ (independent components), to n (electric current). To illustrate how the extended vector $\mathbf{A}_j^{\mathrm{s}}$ works, multiply the transformed stoichiometric matrix, equation (35), by the transport potential vector, equation (7). As long as all extra stoichiometric coefficients ν_{0j} and ν_{nj} are assumed to vanish, the considered product is the vector

$$\begin{bmatrix} \nu_{01} & \ldots \nu_{i1} & \ldots \nu_{n1} \\ \ldots & \ldots & \ldots \\ \nu_{0j} & \ldots \nu_{ij} & \ldots \nu_{nj} \\ \ldots & \ldots & \ldots \\ \nu_{0N} & \ldots \nu_{iN} & \ldots \nu_{nN} \end{bmatrix} \begin{bmatrix} T^{-1} \\ \ldots \\ \tilde{\mu}_i T^{-1} \\ \ldots \\ -\phi T^{-1} \\ \ldots \end{bmatrix}$$

$$= \begin{bmatrix} \nu_{01} T^{-1} + \nu_{i1}\tilde{\mu}_i T^{-1} - \nu_{n1}\phi T^{-1} \\ \ldots \\ \nu_{0j} T^{-1} + \nu_{ij}\tilde{\mu}_i T^{-1} - \nu_{nj}\phi T^{-1} \\ \ldots \\ \nu_{0N} T^{-1} + \nu_{iN}\tilde{\mu}_i T^{-1} - \nu_{nN}\phi T^{-1} \\ \ldots \end{bmatrix} \Rightarrow$$

$$-T^{-1}\nu^{\mathrm{T}}\mu = T^{-1}\mathbf{A} \quad (36)$$

whose components are ratios of the classical affinities $\mathbf{A}_j$ and the temperature T.

Consequently, extension (34), can be used in the variational principle associated with the minimum of the integral, equation (28). A gauged form, obtained by applying the divergence theorem to the $\mathbf{w}$ term of equation (28) can also be used:

$$S_\sigma^{\mathrm{T}} = \int_{t_1, V}^{t_2} \left\{ \frac{1}{2}\mathbf{L}^{-1}(\mathbf{u}) : \mathbf{J}\mathbf{J} + \frac{1}{2}\mathbf{L}(\mathbf{u}) : \nabla\mathbf{u}\nabla\mathbf{u} \right.$$

$$+ \frac{1}{2}\mathbf{R}^{-1} : (\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u}) + \frac{1}{2}\mathbf{R} : \mathbf{r}\mathbf{r} - \mathbf{C}(\mathbf{u})\frac{\partial\mathbf{w}}{\partial t}$$

$$\left. - \mathbf{J}\cdot\nabla\mathbf{w} - \mathbf{w}\cdot\mathbf{v}'\mathbf{r} \right\} \mathrm{d}V\,\mathrm{d}t. \quad (37)$$

As shown in Section 6 this form is more suitable than the original functional, equation (28), for setting the Hamiltonian formalism.

The Euler–Lagrange equations of the functionals, equation (28) or equation (37), with respect to the variables $\mathbf{w}$, $\mathbf{J}$, $\mathbf{r}$ and $\mathbf{u}$ are, respectively,

$$\frac{\partial\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\mathbf{J} = \mathbf{v}'\mathbf{r} \quad (38)$$

$$\mathbf{L}(\mathbf{u})^{-1}\cdot\mathbf{J} = \nabla\mathbf{w} \quad (39)$$

$$\mathbf{R}(\mathbf{u})\cdot\mathbf{r} = \nu'^{\mathrm{T}}\mathbf{w} \quad (40)$$

$$\mathbf{a}(\mathbf{u})\frac{\partial\mathbf{w}}{\partial t} = \nabla\cdot(\mathbf{L}\nabla\mathbf{u}) - \nu'\mathbf{R}^{-1}\mathbf{A}^{\mathrm{s}}(\mathbf{u})$$

$$\underset{\mathbf{u}=\mathbf{w}}{\Rightarrow} \nabla\cdot(\mathbf{L}\nabla\mathbf{u}) - \upsilon'\mathbf{r} \quad (41)$$

where $\mathbf{a}(\mathbf{u}) \equiv -\partial\mathbf{C}(\mathbf{u})/\partial\mathbf{u}$ and $\mathbf{A}^{\mathrm{s}} = \mathbf{v}'^{\mathrm{T}}\mathbf{u}$. The conservation laws, equation (38), contain the production terms which are nonvanishing for $i = 1, \ldots, n$. For the energy and the electric charge ($i = 0$ and $i = n$) the production terms do not appear because these quantities are conserved. (The production terms do not influence the form of the Onsagerian transport equations, equation (39).) The chemical Ohm's law is described by equation (40). The matrix equation of change, equation (41), which links the fields of temperature, chemical potentials and electrical potential, does contain sources. Now one should note that the numerator of equation (29) is the chemical affinity $\mathbf{A}^{s} = v'^{\mathrm{T}}\mathbf{u}$ [6]. Thus, provided that the local thermal equilibrium limit takes place, i.e. $\mathbf{u} = \mathbf{w}$, and the chemical resistances satisfy equation (29), equation (40) is strictly equivalent with the mass action kinetics of Guldberg and Waage. The limiting sources in equation (38) and (41) are described by the vector

$$\boldsymbol{\sigma} = \begin{bmatrix} v_{01} & \dots v_{0j} & \dots v_{0N} \\ \dots & \dots & \dots \\ v_{i1} & \dots v_{ij} & \dots v_{iN} \\ \dots & \dots & \dots \\ v_{n1} & \dots v_{nj} & \dots v_{nN} \end{bmatrix} \begin{bmatrix} r_1 \\ \dots \\ r_j \\ \dots \\ r_N \end{bmatrix} = \begin{bmatrix} 0 \\ \dots \\ \Sigma v_i r_j \\ \dots \\ 0 \end{bmatrix}. \tag{42}$$

In the above treatment, the energy and electricity play the role of massless components. However, it is interesting to note that one might extend the mass conservation in each chemical reaction, so that certain molar masses associated with the energy and electricity could be assumed in the conservation equations:

$$\sum_{i=0}^{n+1} v_{ij} M_i = 0. \tag{30'}$$

We briefly outline changes caused by the use of equation (30′) in place of equation (30). In order not to change the indices accepted earlier (i.e. preserve the index n for the electricity), to the nth mass flux J_n the extra index $n+1$ is assigned for a while in the above expression. This mass flux is next eliminated, as before, by using the condition $\Sigma J_i M_i = 0$ applied for the whole set of entities, $i = 0, 1, 2 \dots n, n+1$. It is suitable to express each independent flux in molar units, to operate with ($J_0 = J_e/c^2 M_0$, $J_1 \dots J_{n-1}$, and $i = J_{\mathrm{el}}/M_{\mathrm{el}}$). According to the relativistic link between the energy and mass, the representation of the energy flux in terms of J_0 contains the coefficient $c^2 M_0/T$ before J_0 in the classical formula describing the entropy flux in terms of all (dependent) fluxes. The elimination of the last mass component leaves the mass transfer potentials unchanged. However, the usual temperature is no longer the exact potential of the energy transfer:

$$\mathbf{u} = (\tilde{\mu}_0 M_0^{-1} c^{-2} T^{-1}, \tilde{\mu}_1 T^{-1},$$
$$\tilde{\mu}_2 T^{-1}, \dots, \tilde{\mu}_{n-1} T^{-1}, -\tilde{\phi} T^{-1}). \tag{7'}$$

(Again, $\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$, $k = 0, 1, \dots, n$, where the last value n refers to the electric flux and, again, the tilde potential of the eliminated mass component vanishes and plays no role in the definition of $\mathbf{u}$.) For $\mu_0 \equiv -M_0 c^2$, the tilde chemical potential follows

$$\tilde{\mu}_0 = \mu_n M_0 M_n^{-1} + M_0 c^2 \tag{43}$$

as the driving potential for the mass-energy flux $J_0 = J_e/c^2 M_0$. This procedure yields in equation (7′) the following effective temperature reciprocal (associated with the energy flux J_e in the traditional units):

$$\tilde{T}^{-1} \equiv \frac{\tilde{\mu}_0}{T M_0 c^2} = T^{-1}(1 + \mu_n M_n^{-1}/c^2). \tag{44}$$

Hence, only for $c \to \infty$ can the classical temperature be an exact potential for the energy transfer. A correction can also be found for the electric potential

$$\tilde{\phi} = \phi - \mu_n M_{\mathrm{el}} M_n^{-1} \tag{45}$$

which is attributed to the finite molar mass of electrons. Only for $M_{\mathrm{el}}/M_n = 0$ (massless electrons in comparison with molecules) can the traditional electric potential be an exact potential for the electricity transfer in descriptions using an independent set of fluxes.

5. THERMODYNAMIC POTENTIALS AND VARIOUS REPRESENTATIONS OF DISSIPATION

It is the entropy function which is the potential in the governing functional, equation (8). From an equivalent expression of this functional, in the form of the vanishing integral

$$\min \int_{t_1, V}^{t_2} \Bigg\langle \Bigg\{ \frac{1}{2}\mathbf{L}^{-1}(\mathbf{u}) : \mathbf{JJ} + \frac{1}{2}\mathbf{L}(\mathbf{u}) : \nabla\mathbf{u}\nabla\mathbf{u}$$
$$+ \frac{1}{2}\mathbf{R} : \mathbf{rr} + \frac{1}{2}\mathbf{R}^{-1} : (v'^{\mathrm{T}}\mathbf{u})(v'^{\mathrm{T}}\mathbf{u})$$
$$+ \mathbf{w} \cdot \left(\frac{\partial \mathbf{C}(\mathbf{u})}{\partial t} + \nabla \cdot \mathbf{J} - v'\mathbf{r} \right)$$
$$- \left(\frac{\partial s_{\mathrm{v}}(\mathbf{u})}{\partial t} + \nabla \cdot \mathbf{J}_{\mathrm{s}}(\mathbf{J}, \mathbf{u}) \right) \Bigg\} \mathrm{d}V \mathrm{d}t \Bigg\rangle = 0 \tag{46}$$

one can pass to various thermodynamic potentials associated with appropriate constraints. For any new thermodynamic potential there is no Lagrange multiplier before the four-divergence of that thermodynamic potential in the functionals like equation (46). Hence, one can derive the multiplier-free four-divergence of a new thermodynamic potential by taking the product of the integrand of equation (46) and the reciprocal of a pertinent Lagrange multiplier. There are some practical limitations when using this rule though. The concentrations of individual components are neither typical nor really suitable to be new potentials, due to the presence of the mass-source terms in mass balances. However, the balances of energy-type quantities, such as energy, free energy etc., are convenient for this purpose.

How this approach works is illustrated by constructing the governing functionals for the thermodynamic potentials of energy or free energy. Writing the integrand of equation (46) as follows:

$$\begin{aligned}
\min \int_{t_1, V}^{t_2} T^{-1} \Big\langle \Big\{ & \frac{1}{2} T\mathbf{L}^{-1}(\mathbf{u}) : \mathbf{J}\mathbf{J} \\
& + \frac{1}{2} T\mathbf{L}(\mathbf{u}) : \nabla\mathbf{u}\nabla\mathbf{u} + \frac{1}{2} T\mathbf{R} : \mathbf{r}\mathbf{r} \\
& + \frac{1}{2} (T\mathbf{R})^{-1} : (v'^{\mathrm{T}} T\mathbf{u})(v'^{\mathrm{T}} T\mathbf{u}) \\
& + \left(\frac{\partial e_{\mathrm{v}}(\mathbf{u})}{\partial t} + \nabla \cdot \mathbf{J}_{\mathrm{e}} \right) \\
& + \sum_{i=1}^{n} T w_k \left(\frac{\partial c_k(\mathbf{u})}{\partial t} + \nabla \cdot J_k - (v'\mathbf{r})_k \right) \\
& - T \left(\frac{\partial s_{\mathrm{v}}(\mathbf{u})}{\partial t} + \nabla \cdot J_{\mathrm{s}} \right) \Big\} \mathrm{d}V \mathrm{d}t \Big\rangle = 0 \qquad (47)
\end{aligned}$$

one can pass to the energy representation of thermodynamics. This will be done soon [equation (59)] after prior discussion of some relevant expressions of the entropy production which imply suitable dynamics in various frames. Take into account that, in terms of the fluxes and forces used, the entropy production and the entropy flux take the form

$$\begin{aligned}
\sigma_{\mathrm{s}} &= J_{\mathrm{e}} \cdot \nabla T^{-1} - \sum_{i=1}^{n} J_i \cdot \nabla(\mu_i T^{-1}) \\
&\quad - i \cdot \nabla(\phi T^{-1}) + \mathbf{A}^{\mathrm{s}} \cdot \mathbf{r} \\
&= J_{\mathrm{e}} \cdot \nabla T^{-1} + \sum_{i=1}^{n-1} J_i \cdot \nabla(\tilde{\mu}_i T^{-1}) \\
&\quad + i \cdot \nabla(-\phi T^{-1}) + \mathbf{A}^{\mathrm{s}} \cdot \mathbf{r} \\
&= \mathbf{J} \cdot \nabla\mathbf{u} + \mathbf{A}^{\mathrm{s}} \cdot \mathbf{r} \qquad (48)
\end{aligned}$$

and

$$\begin{aligned}
J_{\mathrm{s}} &= T^{-1} \left(J_{\mathrm{e}} - \sum_{1}^{n} \mu_k J_k - \phi i \right) \\
&= T^{-1} \left(J_{\mathrm{e}} + \sum_{1}^{n-1} \tilde{\mu}_k J_k - \phi i \right) = J \cdot \mathbf{u}. \qquad (49)
\end{aligned}$$

In the energy representation, the entropy flux J_{s} replaces the energy flux J_{e} of the entropy representation as an independent variable, whereas the other fluxes remain the same. From the last equation written in the form

$$J_{\mathrm{e}} = TJ_{\mathrm{s}} + \sum_{1}^{n} \mu_k J_k + \phi \mathbf{i} = TJ_{\mathrm{s}} - \sum_{1}^{n-1} \tilde{\mu}_k J_k + \phi i \qquad (50)$$

($\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$) and with the help of the identities of the type

$$T\nabla(\xi_i T^{-1}) = \nabla\xi_i - \xi_i T^{-1} \nabla T \qquad (51)$$

the transport part of the entropy production σ_{s}^{t} transforms as follows:

$$\begin{aligned}
\sigma_{\mathrm{s}}^{t} = \mathbf{J} \cdot \nabla\mathbf{u} &= -T^{-1} \Big\{ J_{\mathrm{e}} \cdot T^{-1} \nabla T - \sum_{i=1}^{n-1} J_i \\
&\qquad \cdot T\nabla(\tilde{\mu}_i T^{-1}) + i \cdot T\nabla(\phi T^{-1}) \Big\} \\
&= -T^{-1} \Big\{ \Big(TJ_{\mathrm{s}} - \sum_{1}^{n-1} \tilde{\mu}_k J_k + \phi i \Big) \cdot T^{-1} \nabla T \\
&\qquad - \sum_{i=1}^{n-1} J_i \cdot T\nabla(\tilde{\mu}_i T^{-1}) + i \cdot T\nabla(\phi T^{-1}) \Big\} \qquad (52)
\end{aligned}$$

whence

$$\begin{aligned}
\sigma_{\mathrm{s}}^{t} = \mathbf{J} \cdot \nabla\mathbf{u} &= -T^{-1} \Big\{ J_{\mathrm{s}} \nabla T - \sum_{1}^{n-1} J_k \nabla\tilde{\mu}_k + i \cdot \nabla\phi \Big\} \\
&= -T^{-1} J' \cdot \nabla\mathbf{u}'. \qquad (53)
\end{aligned}$$

This result leads to the total entropy production in the two forms

$$\begin{aligned}
\sigma_{\mathrm{s}} &\equiv \mathbf{J} \cdot \nabla u + \mathbf{A}^{\mathrm{s}} \cdot \mathbf{r} \\
&= -T^{-1} \sigma_{\mathrm{e}} = T^{-1} (\mathbf{J}' \cdot \nabla\mathbf{u}' + \mathbf{A} \cdot \mathbf{r}) \qquad (54)
\end{aligned}$$

where the second line expression contains the energy dissipation

$$\sigma_{\mathrm{e}} = -\mathbf{J}' \cdot \nabla\mathbf{u}' - \mathbf{A} \cdot \mathbf{r}. \qquad (54')$$

The chemical affinities $\mathbf{A}^{\mathrm{s}}$ and $\mathbf{A} = T\mathbf{A}^{\mathrm{s}}$ in these forms are consistent with the classical definition, equation (33). The two sets of the phenomenological equations are nonprimed and primed forms of equation (10), with the positive transport conductances $\mathbf{L}$ and $\mathbf{L}'$, and chemical resistances, linked, respectively, by $\mathbf{L}' = T\mathbf{L}$ and $\mathbf{R}' = \mathbf{R}T$. With the components of the entropy four-flux $(s_{\mathrm{v}}, J_{\mathrm{s}})$ as independent variables, the matrix of independent fluxes is

$$\mathbf{J}' = (J_{\mathrm{s}}, J_1, J_2, \ldots, J_{n-1}, i)^{\mathrm{T}} \qquad (55)$$

and the corresponding column vector of new densities $\mathbf{C}'$ is

$$\mathbf{C}' = (s_{\mathrm{v}}, c_1, c_2, \ldots, c_{n-1}, 0)^{\mathrm{T}}. \qquad (56)$$

The new independent transfer potentials are

$$\mathbf{u}' = (-T, \tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, -\phi) \qquad (57)$$

($\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$). Their gradients are independent forces of the transport processes, and they are associated with the Gibbs differential for the energy density $e_{\mathrm{v}} = \rho e$, written in the form

$$\mathrm{d}e_{\mathrm{v}} = -\mathbf{u} \cdot \mathrm{d}\mathbf{C}' \qquad (58)$$

(compare this with $\mathrm{d}s = \mathbf{u} \cdot \mathrm{d}\mathbf{C}$). In order not to change the signs of the Lagrange multipliers, a new vector $\mathbf{u}'$ has been defined in equation (57) so that it appears with a minus sign in equation (58). This definition also preserves a form invariance of the two production expressions in equation (54) with the conformal factor T^{-1}.

An essential result will now be shown that, due to the transformation of the Lagrange multipliers $\mathbf{w}$ to the new frame (primed variables $\mathbf{w}'$), corresponding with new constraints, the energy density e_v becomes the new potential of the system, subject to the constraint of the sourceless entropy. In the new representation, with the state variables $\mathbf{C}'$, $\mathbf{J}'$, the governing functional, equation (47), becomes

$$\min \int_{t_1,V}^{t_2} T^{-1} \left\langle \left\{ \frac{1}{2}\mathbf{L}'^{-1}(\mathbf{u}') : \mathbf{J}'\mathbf{J}' + \frac{1}{2}\mathbf{L}'(\mathbf{u}') : \nabla\mathbf{u}'\nabla\mathbf{u}' \right.\right.$$
$$+ \frac{1}{2}\mathbf{R}' : \mathbf{rr} + \frac{1}{2}\mathbf{R}'^{-1} : (v'^{\mathrm{T}}\mathbf{u}')(v'^{\mathrm{T}}\mathbf{u}')$$
$$+ \left(\frac{\partial e_v(\mathbf{u}')}{\partial t} + \nabla \cdot J_e(\mathbf{J}', \mathbf{u}') \right)$$
$$+ \sum_{k=1}^{n} w_k \cdot \left(\frac{\partial c_k(\mathbf{u}')}{\partial t} + \nabla \cdot J'_k - (v'\mathbf{r})_k \right)$$
$$\left.\left. + w'_0 \left(\frac{\partial s_v(\mathbf{u}')}{\partial t} + \nabla \cdot \mathbf{J}'_s \right) \right\} \mathrm{d}V \mathrm{d}t \right\rangle = 0. \quad (59)$$

Here $J_e = -\mathbf{J}'\mathbf{u}'$, $w'_0 = -T$, in agreement with equation (50). The transformation of the Onsager's conductivity matrices $\mathbf{L}$ follows the established rule $\mathbf{L}' = \mathbf{P}^{-1\mathrm{T}}\mathbf{L}\mathbf{P}^{-1}$ when the transformation of fluxes is of the form $\mathbf{J}' = \mathbf{PJ}$; see, for example, ref. [4]. As in the entropy representation, the introduction of dummy stoichiometric coefficients, which vanish when $k = 0$ and $k = n$, is needed to take formally all considered entities (the entropy, components and electric charge) in the standard vector of chemical affinities, $\mathbf{A} = -v^{\mathrm{T}}\mu$. The corresponding transformation to the extended affinity, which deals with *all* independent potentials [the vector $\mathbf{u}'$, equation (62)], is

$$\mathbf{A}_j = -\sum_{i=1}^{n} v_{ij}\mu_i = -\sum_{i=1}^{n} v_{ij}(\mu_n M_i M_n^{-1} - \tilde{\mu}_i) = \sum_{i=1}^{n-1} v_{ij}\tilde{\mu}_i$$
$$\Rightarrow (v'^{\mathrm{T}}\mathbf{u}')_j. \quad (60)$$

In the extended affinity of the energy representation, $\mathbf{A}'_j \equiv (v'^{\mathrm{T}}\mathbf{u}')_j$, the component index changes from 0 (entropy) through $1, 2, \ldots, n-1$ (independent components) to n (electric current). The stoichiometric matrix coincides in the new frame with the original one, equation (31), with the same dummy coefficients, provided that the dissipation expression in the first line of equation (59) is now assigned to the total energy. It follows from equation (59) or equation (60) that such an interchange of the roles of the energy and entropy is optional for isothermal processes, but it is necessary whenever the temperature T is not constant (thermal inhomogeneity).

In view of the positivity of the temperature coefficient T^{-1} before the angular bracket $\langle\ \rangle$ of equation (59) it is clear than an analogous integral obtained by taking T^{-1} off the integral, equation (59), vanishes on its extremal surfaces as well; this procedure shows how one is led to the energy functional. Such a functional contains, as its integral, the energy dissipated plus the product of new Lagrange multiplier vector and the appropriate balance constraints:

$$-E(t_2) = \min \left\langle -E(t_1) + \int_{t_1,\mathbf{A}}^{t_2} J_e(\mathbf{J}', \mathbf{u}') \cdot \mathrm{d}\mathbf{A}\, \mathrm{d}t \right.$$
$$+ \int_{t_1,V}^{t_2} \left\{ \frac{1}{2}\mathbf{L}'^{-1}(\mathbf{u}') : \mathbf{J}'\mathbf{J}' + \frac{1}{2}\mathbf{L}'(\mathbf{u}') : \nabla\mathbf{u}'\nabla\mathbf{u}' \right.$$
$$+ \frac{1}{2}\mathbf{R}' : \mathbf{rr} + \frac{1}{2}(\mathbf{R}')^{-1} : (v'^{\mathrm{T}}u')(v'^{\mathrm{T}}u')$$
$$\left.\left. + \mathbf{w}' \cdot \left(\frac{\partial \mathbf{C}'(\mathbf{u}')}{\partial t} + \nabla \cdot \mathbf{J}' - v'\mathbf{r} \right) \right\} \mathrm{d}V \mathrm{d}t \right\rangle. \quad (61)$$

Consequently, it is the energy, not the entropy, which is the potential function for the primed set of constraints and associated variables. This result represents the extension of Callen's [75] postulational thermodynamics to nonequilibrium, spatially inhomogeneous systems. The constraints, which now comprise the balances of mass, electric charge and the sourceless entropy, are multiplied by $\mathbf{w}'$ rather than by $-\mathbf{w}'$. This assures the identification $\mathbf{w}' = \mathbf{u}'$ rather than $-\mathbf{w}' = \mathbf{u}'$ at local equilibrium. New balance laws are built into the energy functional, equation (61), with the help of the vector of the Lagrangian multipliers $\mathbf{w}' = (w'_0, w'_1, w'_2, \ldots, w'_{n-1}, w'_n)$. The *extremum* value of the multiplier $\mathbf{w}'$ in the energy function, equation (61), is the vector of the *kinetic* conjugates $\mathbf{u}'$ of the densities $\mathbf{C}'$, equation (56). On the extremal surface of the energy functional (61), the vector $\mathbf{w}'$ coincides with the transport potential vector $\mathbf{u}'$, equation (57), in the limiting situation of the local thermal equilibrium:

$$\mathbf{w}' = \mathbf{u}' = (-T, \tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, -\phi). \quad (62)$$

This may be compared with the analogous equality in the entropy representation:

$$\mathbf{w} = \mathbf{u} = (T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots,$$
$$\tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1}). \quad (7)$$

Again, away from local equilibrium $\mathbf{w}'$ and $\mathbf{u}'$ are generally two distinctive field variables in the thermodynamic functional.

It follows from equation (59) that, with the approach based on invariant dissipation intensity, the direct determination of the free-energy changes from the entropy or energy dissipation expressions is consistent only for systems with homogeneous T. This restricted availability of free-energy dissipation data from the popular entropy dissipation data by no means excludes the applications of F to nonisothermal systems. Such applications involve, however, separate methods of construction for general functionals of the free energy, which is not discussed here. A simplified free-energy representation, applicable to thermally homogeneous systems, is still quite useful. From equation (59) the thermodynamic functional of the homogeneous free energy is

$$-F(t_2) = \min \left\langle -F(t_1) + \int_{t_1,\mathbf{A}}^{t_2} J_f(\mathbf{J}', \mathbf{u}') \cdot \mathrm{d}\mathbf{A}\, \mathrm{d}t \right.$$

$$+ \int_{t_1,V}^{t_2} \left\{ \frac{1}{2} \mathbf{L}'^{-1}(\mathbf{u}') : \mathbf{J}'\mathbf{J}' + \frac{1}{2} \mathbf{L}'(\mathbf{u}') : \nabla\mathbf{u}'\nabla\mathbf{u}' \right.$$

$$+ \frac{1}{2} \mathbf{R}' : \mathbf{rr} + \frac{1}{2} (\mathbf{R}')^{-1} : (v'^{\mathrm{T}}\mathbf{u}')(v'^{\mathrm{T}}\mathbf{u}')$$

$$\left. \left. + \mathbf{w}' \cdot \left(\frac{\partial \mathbf{c}(\mathbf{u}')}{\partial t} + \nabla \cdot J_k' - v'\mathbf{r} \right) \right\} \mathrm{d}V \mathrm{d}t \right\rangle \tag{63}$$

with $J_f = J_\mathrm{e} - TJ_\mathrm{s}$, the relation which also follows from equation (59). The following definitions apply:

$$\mathbf{J}' = (J_1, J_2, \ldots, J_{n-1}, i)^{\mathrm{T}} \tag{64}$$

$$\mathbf{c}' = (c_1, c_2, \ldots, c_{n-1}, 0)^{\mathrm{T}} \tag{65}$$

$$\mathbf{u}' = (\tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, \phi) \tag{66}$$

($\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$). In the linear theory, the matrices $\mathbf{L}'$, $\mathbf{u}'$ etc., of this representation are obtained from the matrices $\mathbf{L}'$, $\mathbf{u}'$ of the energy representation by rejection of entries corresponding to the entropy. However, in any nonlinear descriptions they are functions of the temperature T and contain T as a parameter. This is the frame where many practical kinetic relationships is imbedded. The variation of the above functional leads to the equations of diffusion, Ohm's law of electrical conductivity and chemical kinetics in isothermal systems.

The Euler–Lagrange equations of the free energy functional, equation (63), with respect to the variables $\mathbf{w}'$, $\mathbf{J}'$, $\mathbf{r}$ and $\mathbf{u}'$ are, respectively,

$$\frac{\partial \mathbf{c}'(\mathbf{u}')}{\partial t} + \nabla \cdot \mathbf{J}' - v'\mathbf{r} = 0 \tag{67}$$

$$\mathbf{L}'(\mathbf{u}')^{-1} \cdot \mathbf{J}' = \nabla\mathbf{w}' \tag{68}$$

$$\mathbf{R}(\mathbf{u}') \cdot r = v'^{\mathrm{T}}\mathbf{w}' \tag{69}$$

$$g(\mathbf{u}') \frac{\partial \mathbf{w}'}{\partial t} = \nabla \cdot (\mathbf{L}'\nabla\mathbf{u}') - v'\mathbf{R}^{-1}\mathbf{A}(\mathbf{u}')$$

$$\underset{\mathbf{u}'=\mathbf{w}'}{\Rightarrow} \nabla \cdot (\mathbf{L}'\nabla\mathbf{u}') - v'\mathbf{r}. \tag{70}$$

Here $g = \partial \mathbf{c}'(\mathbf{u}')/\partial \mathbf{u}$ is the positive Hessian of the isothermal free energy, and $\mathbf{A} = v'^{\mathrm{T}}\mathbf{u}'$. The isothermal transport equations, Ohm's law for electric current, and isothermal chemical kinetics are contained in these equations. Provided that local thermal equilibrium holds, i.e. $\mathbf{u}' = \mathbf{w}'$, and the chemical resistances $\mathbf{R}' = \mathbf{R}T$ [where $\mathbf{R}$ satisfies equation (29)], equation (69) represents Ohm's law for chemical reactions, equivalent to the mass action kinetics of Guldberg and Waage.

6. DISSIPATIVE HAMILTONIANS AND POISSONIAN BRACKETS

For the rest of this text, it will be sufficient to only consider cases with a constant state at the system boundaries: thus, any possible surface terms in the functionals used will be ignored. Thermodynamic functionals gauged by subtraction of the four-divergence ($\partial/\partial t, \nabla\cdot$) of a vector, here $\partial/\partial t(w_k c_k) + \nabla \cdot (w_k J_k)$, or linear combinations of such four-divergences, have found some useful applications [11, 72]. In the case of fields, they lead directly to dissipative Hamiltonians, identical with those of Onsager's discrete theory, thus making possible related Hamiltonian formalisms and bracket formulations with only one type of bracket (Poissonian brackets). This seems interesting and important, since the bracket approaches, which stem from dissipative generalizations of concepts of ideal continua, use two sorts of brackets [27, 28, 30], and, as such, are not directly associated with extrema of definite physical quantities.

In the entropy representation, the thermodynamic functional, gauged as described above, has the general structure

$$S_\sigma^{\mathrm{T}} = \int_{t_1,V}^{t_2} \Lambda_\sigma^{\mathrm{T}}(\mathbf{J}, \mathbf{u}, \mathbf{r}, \mathbf{w})\, \mathrm{d}V \mathrm{d}t. \tag{71}$$

It takes into account all balance constraints. For the present model, the 'thermodynamic Lagrangian' $\Lambda_\sigma^{\mathrm{T}}$ is

$$\Lambda_\sigma^{\tau}(\mathbf{J}, \mathbf{u}, \mathbf{r}, \mathbf{w}) \equiv \frac{1}{2} \mathbf{L}^{-1}(\mathbf{u}) : \mathbf{JJ}$$

$$+ \frac{1}{2} \mathbf{L}(\mathbf{u}) : \nabla\mathbf{u}\nabla\mathbf{u} + \frac{1}{2} \mathbf{R}^{-1} : (v'^{\mathrm{T}}\mathbf{u})(v'^{\mathrm{T}}\mathbf{u})$$

$$+ \frac{1}{2} \mathbf{R} : \mathbf{rr} - \mathbf{w}^{\mathrm{T}}\mathbf{v}'\mathbf{r} - \mathbf{C}(\mathbf{u}) \frac{\partial \mathbf{w}}{\partial t} - \mathbf{J} \cdot \nabla\mathbf{w}. \tag{72}$$

The (**w**-indepedent) quantity containing the sum of two dissipation functions for transports and chemical reactions:

$$L_\sigma(\mathbf{J}, \mathbf{u}, \mathbf{r}) \equiv \tfrac{1}{2} \mathbf{L}^{-1}(\mathbf{u}) : \mathbf{JJ} + \tfrac{1}{2} \mathbf{L}(\mathbf{u}) : \nabla\mathbf{u}\nabla\mathbf{u}$$

$$+ \tfrac{1}{2} \mathbf{R}^{-1} : (v'^{\mathrm{T}}\mathbf{u})(v'^{\mathrm{T}}\mathbf{u}) + \tfrac{1}{2} \mathbf{R} : \mathbf{rr} \tag{73}$$

is also used which, *per analogiam* with its classical mechanical counterpart, plays the role of a kinetic potential of the process.

The minimum of the functional, equation (71), with respect to the fluxes J and r, or the corresponding Euler–Lagrange equations, yields the representations (in terms of **w**) of certain flux adjoints. Quantities of this sort were, to our knowledge, first investigated by Vojta [87], although for a different L_σ. They may be called the 'dissipative' or 'thermodynamic' momenta:

$$p_{\sigma} \equiv \frac{\partial L_{\sigma}}{\partial \mathbf{J}} = \mathbf{L}^{-1}\mathbf{J} = \nabla w \tag{74}$$

$$\pi_{\sigma} \equiv \frac{\partial L_{\sigma}}{\partial \mathbf{r}} = \mathbf{R}\mathbf{r} = \tilde{\nu}^{\mathrm{T}}\mathbf{w}. \tag{75}$$

At a local thermal equilibrium, both of these quantities become thermodynamic forces, transports driving gradients of u and chemical affinities, equation (34). One can also define the 'thermodynamic Hamiltonian', a quantity related to the entropy production, as the time component G^{tt} of the energy–momentum tensor associated with the gauged Lagrangian $\Lambda_{\sigma}^{\mathrm{T}}$:

$$H_{\sigma} \equiv \frac{\partial \Lambda_{\sigma}^{\mathrm{T}}}{\partial \dot{\mathbf{w}}} \cdot \dot{\mathbf{w}} - \Lambda_{\sigma}^{\mathrm{T}}. \tag{76}$$

For $\Lambda_{\sigma}^{\mathrm{T}}$ of equation (72), via extremum conditions (74) and (75), an extremal H_{σ} follows from equation (76). Such an extremal quantity is represented by the second line of equation (77). It is the field generalization of the Onsager's thermodynamic Hamiltonian [88], which includes the nonlinear chemical kinetics:

$$\begin{aligned} H_{\sigma} = {} & -\tfrac{1}{2}\mathbf{L}^{-1}(\mathbf{u}):\mathbf{J}\mathbf{J} - \tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u} \\ & -\tfrac{1}{2}\mathbf{R}^{-1}:(\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u}) \\ & -\tfrac{1}{2}\mathbf{R}:\mathbf{r}\mathbf{r} + \mathbf{w}^{\mathrm{T}}\nu'\mathbf{r} + \mathbf{J}\cdot\nabla\mathbf{w} \\ = {} & \tfrac{1}{2}\mathbf{L}^{-1}(\mathbf{u}):\mathbf{J}\mathbf{J} - \tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u} + \tfrac{1}{2}\mathbf{R}:\mathbf{r}\mathbf{r} \\ & -\tfrac{1}{2}R^{-1}:(\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u}). \end{aligned} \tag{77}$$

Clearly, this dissipative Hamiltonian vanishes at local equilibrium, as does its Onsagerian counterpart. In terms of the canonical variables

$$\begin{aligned} H_{\sigma} = {} & \tfrac{1}{2}\mathbf{L}(\mathbf{u}):p_{\sigma}p_{\sigma} - \tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u} \\ & +\tfrac{1}{2}\mathbf{R}^{-1}:\pi_{\sigma}\pi_{\sigma} - \tfrac{1}{2}\mathbf{R}^{-1}:(\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u}). \end{aligned} \tag{78}$$

The direct imbedding of Onsager's H_{σ} in the context of thermodynamic fields with nonlinear chemical kinetics and quasilinear transports is meaningful. To achieve this goal, it was more efficient to use the gauged structure, equation (72), than the original functional, equation (28). Also note that the extremal Lagrangian $\Lambda_{\sigma}^{\mathrm{T}}$, equation (72), in terms of the extremal H_{σ} acquires the Hamilton–Jacobi structure

$$\Lambda_{\sigma}^{\mathrm{T}}(\mathbf{J},\mathbf{r},\mathbf{u},\mathbf{w}) = -\mathbf{C}(\mathbf{u})\frac{\partial \mathbf{w}}{\partial t} - H_{\sigma}(\mathbf{J},\mathbf{r},\mathbf{u}). \tag{79}$$

which is essential for direct development of *functional* canonical equations of the field theory [see equations (84), (86), (96) and (98)].

It follows from the definition of L_{σ}, equation (73), that the dissipative functions H_{σ} and L_{σ} are connected by the Legendre transformation

$$\begin{aligned} H_{\sigma}(p_{\sigma},\pi_{\sigma},\mathbf{u}) &= \frac{\partial L_{\sigma}}{\partial \mathbf{J}}\mathbf{J} + \frac{\partial L_{\sigma}}{\partial \mathbf{r}}\mathbf{r} - L_{\sigma}(\mathbf{J},\mathbf{r},\mathbf{u}) \\ &= \frac{\partial L_{\sigma}}{\partial \mathbf{v}}\mathbf{v} + \frac{\partial L_{\sigma}}{\partial \mathbf{r}}\mathbf{r} - L_{\sigma}(\mathbf{v},\mathbf{r},\mathbf{u}) \end{aligned} \tag{80}$$

where the momenta at p_{σ} and π_{σ} satisfy equations (74) and (75), whereas $\mathbf{v}$ is the velocity matrix whose entries $v_{\alpha i} = J_{\alpha i}/C_i$ are transport velocities related to the fluxes J_i. As in mechanics, only the rate-type variables are subject to the Legendre transformation, whereas the static state $\mathbf{u}$ plays the role of a parameter vector. This is also in analogy with the lumped system thermodynamics, where rates are not fields, but rather time derivatives of certain generalized displacements [13, 88].

However, for variational dynamics of fields, a particular representation of H_{σ} is essential in which the momenta are eliminated on account of the (gradients of) Lagrange multipliers of balance constraints [11, 72]. This is just the representation suitable for direct development of canonical equations and functional Poissonian brackets. Similar multipliers, which are used in the theory of perfect fluids (in the context of action approaches though), are known as the velocity potentials or Clebsch variables [3, 62]. In the present case, the pertinent variables of H_{σ} are the coordinates of the *static* thermodynamic state ($\mathbf{u}$ or $\mathbf{C}$) and Lagrange multipliers $\mathbf{w}$. From equations (74), (75) and (78)

$$\begin{aligned} H_{\sigma} = {} & \tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{w}\nabla\mathbf{w} - \tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u} \\ & +\tfrac{1}{2}\mathbf{R}^{-1}:(\nu'^{\mathrm{T}}\mathbf{w})(\nu'^{\mathrm{T}}\mathbf{w}) - \tfrac{1}{2}\mathbf{R}^{-1}:(\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u}). \end{aligned} \tag{81}$$

In terms of the above Hamiltonian, the thermodynamic integrals S_{σ}^{T}, equations (37), (71) and (82), conform to the general structure of the field-theory actions having the Hamilton–Jacobi expressions as their integrands:

$$S_{\sigma}^{\mathrm{T}} = -\int\left[H_{\sigma}(\mathbf{u},\mathbf{w},\nabla\mathbf{u},\nabla\mathbf{w}) + \mathbf{C}(\mathbf{u})\cdot\frac{\partial w}{\partial t}\right]\mathrm{d}x\,\mathrm{d}t. \tag{82}$$

For the heat and mass transfer theory, equation (82), and its particular form, equation (83), have a meaning analogous to that which the Hamilton–Jacobi equation has in the mechanics of particle motion. Through the gradient and time derivative of the 'eiconal' $\mathbf{w}$, these equations describe the relation between the 'wave fronts' and the 'rays', the trajectories of the heat and mass diffusion. An equation of thermal rays is in our case the first Fourier–Fick law, equation (74), contained in equation (84). The temperature reciprocal T^{-1} and the tilde Planck potentials are the velocity potentials for the thermal rays. For a thermally inhomogeneous, chemically reacting fluid field, a working form of the thermodynamic integral, equation (82), is

$$S_\sigma^{\mathrm{T}} = -\int\Big[\mathbf{C}(\mathbf{u})\cdot\frac{\partial \mathbf{w}}{\partial t} + \frac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{w}\nabla\mathbf{w}$$

$$-\frac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\mathbf{u}\nabla\mathbf{u} + \frac{1}{2}\mathbf{R}^{-1}(\nu'^{\mathrm{T}}\mathbf{w})(\nu'^{\mathrm{T}}\mathbf{w})$$

$$-\frac{1}{2}\mathbf{R}^{-1}:(\nu'^{\mathrm{T}}\mathbf{u})(\nu'^{\mathrm{T}}\mathbf{u})\Big]\mathrm{d}x\,\mathrm{d}t. \quad (83)$$

From the viewpoint of the local equilibrium effect ($\mathbf{u} = \mathbf{w}$), the state variables $\mathbf{u}$ used in this equation along with the Clebsch-like variables $\mathbf{w}$ describe the process in the simplest way possible.

With the Hamiltonian, equation (81), the first canonical equation is obtained by taking the variational (Volterra) derivative for the above action integral with respect to the intensity vector:

$$-\mathbf{a}(\mathbf{u})\frac{\partial w}{\partial t} = -\frac{\delta H_\sigma}{\delta \mathbf{u}} = -\nabla\cdot(\mathbf{L}\nabla\mathbf{u}) + \mathbf{v}'\mathbf{R}^{-1}\mathbf{A}^{\mathrm{s}}(\mathbf{u}). \quad (84)$$

This is the vector representation of all equations of change. In the special case of pure heat transfer in a nonreacting continuum, one can introduce an energy diffusivity $D_e = La^{-1}$. Since $L = kT^2$ and $a = \rho c_v T^2$, in the local equilibrium limit, the quantity D_e is the standard heat diffusivity: $D_e = k/(\rho c_v)$. Moreover, since $\mathbf{w}$ approximates T^{-1}, the partial derivatives obey $\partial w/\partial t \cong -T^{-2}\partial T/\partial t$ and $\nabla^2 w \cong -T^{-2}\nabla^2 T$. Thus in the local equilibrium situation

$$\frac{\partial T}{\partial t} = D_e \nabla^2 T \quad (85)$$

which is the second Fourier's law. Note that the variational principle yields an inherently nonequilibrium description, with $\mathbf{w}$ and $\mathbf{u}$ as independent variables. As previously, the local equilibrium assumption is the necessary extra postulate in the limiting transition to the second Fourier's law in its traditional form. For unstable situations, with diverging $\mathbf{w}$ and $\mathbf{u}$, such a postulate may be unacceptable.

The second canonical equation or the stationarity condition of the integral S_σ^{T} with respect to the vector $\mathbf{w}$ is the set of conservation equations for energy, mass and electric charge:

$$\frac{\partial \mathbf{C}(\mathbf{u})}{\partial t} = \frac{\delta H_\sigma}{\delta \mathbf{w}} = -\nabla\cdot(\mathbf{L}\nabla\mathbf{w}) + \nu'\mathbf{R}^{-1}(\nu'^{\mathrm{T}}\mathbf{w})$$

$$= -\nabla\cdot\mathbf{J} + \nu'\mathbf{r} \quad (86)$$

where equations (74) and (75) have been exploited. The presence of the state-dependent properties in L_σ or H_σ gives rise to nonlinear behavior. Note that the two canonical equations (84) and (86) coincide at the local equilibrium, and the resulting equation can be written in terms of the state variables $\mathbf{u}$ only, as the following nonlinear equation of change:

$$\mathbf{a}(\mathbf{u})\frac{\partial \mathbf{u}}{\partial t} = \nabla\cdot(\mathbf{L}\nabla\mathbf{u}) - \mathbf{v}'\mathbf{R}^{-1}\mathbf{A}^{\mathrm{s}}(\mathbf{u}). \quad (87)$$

It incorporates the Fourier–Onsager transports, Ohm's electric conductivity and nonlinear chemical kinetics of Guldberg and Waage. In effect, a quasi-canonical Poissonian bracket form

$$-\mathbf{a}(\mathbf{u})\frac{\partial \mathbf{w}}{\partial t} = \{\mathbf{w}, H_\sigma\} = -\frac{\delta H_\sigma}{\delta \mathbf{u}} \quad (88)$$

and

$$\frac{\partial \mathbf{C}(\mathbf{u})}{\partial t} = \{\mathbf{u}, H_\sigma\} = \frac{\delta H_\sigma}{\delta \mathbf{w}} \quad (89)$$

is valid for transports with chemical reactions described by the thermodynamic Hamiltonian, equation (81). Consider equation (82) to conclude that an exact canonical form does involve densities C_k rather than intensities u_k. In the limiting state of a local equilibrium, the two equations (88) and (89) become identical, thus converging into the classical diffusion–reaction system described by *nonlinear* partial differential equations. Through transformations of the Hamiltonian matrix the theory of Poissonian brackets allows transformations of the above field equations into various equivalent sets governed by noncanonical Poissonian brackets [89].

7. THERMOMECHANICS OF CHEMICAL REACTIONS IN DISPLACEMENT FIELDS

Consider now an example in which the chemical reactions are coupled with mechanical processes, and the velocity of mechanical motion in a suitable frame, $\mathbf{v}$, is an unknown variable which should be found along with the chemical progress variables. In the case of muscle contraction, the velocity refers to the frame of thin filaments. The concentrations and chemical advancement coordinates that are most commonly used in chemistry are the molar concentrations c_i, and the progress variables ξ_j, which are related to the former. However, the search has substantiated the suitability of the concentrations defined as moles per unit mass of the mixture $x_i = c_i/\rho$ and the related progress variables (chemical coordinates) $\kappa_j = \xi_j/\rho$ as those variables which are the most suitable in the analysis. For the standard formalism which uses as the field variables the reaction rate r_j and the molar concentrations c_i, the basic equations of constraint are those describing the mass balances of the species:

$$f_i = \frac{\partial c_i}{\partial t} + \nabla\cdot(c_i \mathbf{v}_i) - \sum_{j=1}^{N} \nu_{ij} r_j = 0 \quad (90)$$

However, a formalism will be used tracing chemical changes in terms of progress or chemical coordinates ζ_j, and then

$$f_i = \frac{\partial c_i}{\partial t} + \nabla\cdot(c_i\mathbf{v}_i) - \sum_{j=1}^{N} \nu_{ij}\left(\frac{\partial \xi_j}{\partial t} + \nabla\cdot(\xi_j\mathbf{v}_i)\right) = 0. \tag{91}$$

The quantities ξ_j refer to the unit volume, and they should be distinguished from their global counterparts used in the lumped systems. Using the continuity equation for the whole mixture one can write equation (91) in an alternative form:

$$\rho\left(\frac{\partial c_i/\rho}{\partial t} + \mathbf{v}\cdot\nabla(c_i/\rho)\right) + \nabla\cdot\left[(\mathbf{v}_i - \mathbf{v})\left(c_i - \sum_{j=1}^{N}\nu_{ij}\xi_j\right)\right] - \sum_{j=1}^{N}\left[\nu_{ij}\rho\left(\frac{\partial \xi_j/\rho}{\partial t} + \mathbf{v}\cdot\nabla(\zeta_j/\rho)\right)\right] = 0 \tag{92}$$

which proves the integrability of equation (91) along a Lagrangian path whenever the diffusion effects can be ignored, i.e. for $\mathbf{v} = \mathbf{v}_i$. Restricting to this case, the following integral is found:

$$c_i/\rho - \sum_{j=1}^{N}(\nu_{ij}\zeta_j)/\rho = c_i^0/\rho^0 - \sum_{j=1}^{N}(\nu_{ij}\xi_j^0)/\rho^0 \tag{93}$$

for each point on the Lagrangian path of a diffusionless process. This equation substantiates the use of the concentrations $x_i = c_i/\rho$ (mol kg^{-1}) and the chemical advancement coordinates $\kappa_j = \xi_j/\rho$ (mol kg^{-1}) as the most suitable variables in the description. This is the first constraining equation of the thermomechanical process.

Further constraints preserve the identity of the fluid elements, for the fluid taken as a whole. They are known from the field theory of perfect fluids in the form expressing the constancy of its initial set of Lagrangian coordinates, $\mathrm{d}\mathbf{X}/\mathrm{d}t = 0$, or

$$\frac{\partial \mathbf{X}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{X} = 0. \tag{94}$$

(Possible 'partial identity constraints' are ignored.) When equation (94) is combined with the mass conservation law

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0 \tag{95}$$

(the mass density $\rho = \Sigma c_i M_i$ and the velocity $\mathbf{v} = \rho^{-1}\Sigma c_i M_i \mathbf{v}_i$) a canonical form of equation (94) can be obtained:

$$\frac{\partial \Gamma}{\partial t} + \nabla\cdot(\Gamma\mathbf{u}) = 0 \tag{96}$$

where $\Gamma = \rho\mathbf{X}$ is the initial density related to $\mathbf{X}$. The set of densities contains c_i, ξ_j, and $\Gamma = \boldsymbol{\varepsilon}\mathbf{X}$. We also use the density $\gamma = \rho\mathbf{x}$, such that the mass flux density $\mathbf{J} = \rho\mathbf{v}$ is the four-divergence of γ.

The mechanical displacement vector for the ith species is

$$\boldsymbol{\varepsilon}_i(\mathbf{x}, t) = \mathbf{x} - \mathbf{X}_i(\mathbf{x}, t). \tag{97}$$

If $\kappa_j = \xi_j/\rho$ is the chemical progress coordinate of the jth reaction, introduced on the basis of equation (93), then its initial or reference value, $K_j = \xi_j^0/\rho^0$, is a function of the initial Lagrangian coordinates of the species, $\mathbf{X}_i$. Since $\mathbf{X}_i = \mathbf{X}_i(\mathbf{x}, t)$, an initial field $K_j(\mathbf{x}, t)$ of κ_j can be introduced. One can then define the chemical displacement field $\chi_j(\mathbf{x}, t)$ for the jth reaction:

$$\chi_j(\mathbf{x}, t) = \kappa_j(\mathbf{x}, t) - K_j(\mathbf{x}, t). \tag{98}$$

With $x_i = c_i/\rho$ and $\kappa_j = \xi_j/\rho$, the integrated constraint, equation (93), can be written as

$$x_i - \sum_{j=1}^{N}(\nu_{ij}\chi_j) \equiv x_i^0. \tag{99}$$

In a general case of a compressible medium, on the basis of the continuity equation (95)

$$\rho\frac{\mathrm{d}\chi_j}{\mathrm{d}t} = \rho\frac{\mathrm{d}(\rho^{-1}\xi_j)}{\mathrm{d}t} = \rho\left(v\frac{\mathrm{d}\xi_j}{\mathrm{d}t} + \xi_j\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(v\frac{\mathrm{d}\xi_j}{\mathrm{d}t} + v\xi_j\nabla\cdot\mathbf{v}\right) = \frac{\partial \xi_j}{\partial t} + \nabla\cdot(\xi_j\mathbf{v}) \tag{100}$$

where $v = \rho^{-1}$ is the specific volume. Accordingly, two representations of chemical rates, per unit volume and per unit mass, can be considered. They are linked by the formula

$$r = \rho r' = \rho\left(\frac{\partial \chi_j}{\partial t} + \mathbf{v}\cdot\nabla\chi_j\right) = \frac{\partial \xi_j}{\partial t} + \nabla\cdot(\xi_j\mathbf{v}). \tag{101}$$

For the new resistances $R_j'(\mathbf{x})$, defined as $R_j'(\mathbf{x}) = \rho R_j(\mathbf{c})$ the chemical Ohm's law expressed by displacements χ_j holds in the same form as the original:

$$r' = \mathrm{d}\chi_j/\mathrm{d}t = A_j/R_j' = -\sum_{j=1}^{N}\nu_{ij}\mu_i/R_j' \quad j = 1, \ldots, N \tag{102}$$

where $R_j'(\mathbf{x}) = \rho R_j(\mathbf{c})$ is associated with R given by equation (4). This redefinition of resistances also follows from the preservation of the classical Raleigh's dissipation formula.

The dissipation function of the Lagrangian picture of motion, and in coordinates $\mathbf{x}$ and κ, is

$$\Phi' = \frac{1}{2}B'(x, \dot{\mathbf{x}}, \mathbf{x})(\partial\mathbf{x}_j/\partial t)^2_{K,\mathbf{X}} + \sum_{j=1}^{N}\frac{1}{2}R_j'(x)(\partial\kappa_j/\partial t)^2_{K,\mathbf{X}} \tag{103}$$

where $\mathbf{x} = (x, y, z)$, $\kappa = \xi/\rho$, and $x = \mathbf{c}/\rho$. As associated function can be formed in terms of the displacements ε and χ of these coordinates, equations (97) and (98).

However, instead of using an entropy functional similar to those of previous sections, which would use the dissipation function (103) and its transformation, we shall here apply a different approach. This is a dissipative action approach in which the irreversibility effect is represented by the exponential term $\exp(t/\tau)$, the multiplicator of reversible Lagrangians. This term, which contains the average time between the collisions, τ, increases in time when the system memory fades. Below is presented a Lagrangian and its corresponding action integral of an isothermal mechanochemical motion. Next, its application to the mechanochemistry of muscle contraction in the reference frame of the stationary thin filament is considered.

The starting Lagrangian of the thermomechanochemical field has the general structure

$$\Lambda = \Bigg\{L(\mathbf{v}, \mathbf{c}, \xi, \Gamma, \dot{\mathbf{v}}, \dot{\mathbf{c}}, \dot{\xi}, \dot{\Gamma}, \nabla\mathbf{v}, \nabla\mathbf{c}, \nabla\xi, \nabla\Gamma, \mathbf{x}, t) + \sum_{k=1}^{n}\left[\phi_k\left(\frac{\partial c_k}{\partial t}+\nabla\cdot(\mathbf{v}c_k)-\sum_{j=1}^{n}\left[\nu_{kj}\left(\frac{\partial \xi_j}{\partial t}+\nabla\cdot(\mathbf{v}\xi_j)\right)\right]\right.\right. + \left.\sum_{l=n+1}^{n+3}\phi'_l\left(\frac{\partial \Gamma_l}{\partial t}+\nabla\cdot(\mathbf{v}\Gamma_l)\right)\right]\Bigg\}e^{t/\tau} \tag{104}$$

where the nonprimed ϕ_k ($k = 1, 2, \ldots, n$) refer to the multipliers of the mass constraints (partial actions), and the primed ϕ'_l ($l = 1, 2, 3$) to the particles identity. The above functional contains the kinetic potential density L in the form

$$L = \rho^{-1}(\mathbf{c})\frac{\mathbf{J}^2}{2}+\frac{1}{2}\mathbf{I}(\mathbf{c}):\mathbf{rr}-F(\mathbf{c}, \nabla\mathbf{c}, \Gamma, \nabla\Gamma, \mathbf{x}, t). \tag{105}$$

The functional (104) should be varied subject to the extra constraint $\Sigma M_k x_k = 1$. However, this constraint and the related multiplier Ω' were eliminated by using the kinetic potential of unit mass in the modified form

$$L' = \frac{1}{2}\sum_{k=1}^{N} M_k x_k(\mathbf{v}^2+\mathbf{I}':(\dot{\chi}+\mathbf{v}\cdot\nabla\chi))(\dot{\chi}+\mathbf{v}\cdot\nabla\chi))-F'. \tag{106}$$

An advantage of using L' instead of L is that the correct value of the chemical potential for the moving continuum is achieved only when L is augmented to the constraint-absorbing form $L_c = L-\Omega'(1+\Sigma M_k x_k)$, whereas for the Lagrangian L' this property holds in any case. In the latter case, the constraint $\Sigma M_k x_k = 1$ can be taken into account after the procedure is completed. However, the extremum conditions for $L = sL'$ not L' are displayed below, since the former are more general, and the latter follow from the former as the special case when $\Omega' = 0$.

The extremum conditions of the four-dimensional action integral based on the Lagrangian (104) and the kinetic potential (106) are

$$\delta\rho: \quad \frac{\partial(\rho L')}{\partial\rho}-\sum_{k=1}^{n}\left[\left(x_k-\sum_{j=1}^{N}\nu_{kj}\chi_j\right)\times\left(\frac{\partial\phi_k}{\partial t}+\frac{\phi_k}{\tau}+\mathbf{v}\cdot\nabla\phi_k\right)\right] - \sum_{l=n+1}^{n+3}\left[X_l\left(\frac{\partial\phi'_l}{\partial t}+\frac{\phi'_l}{\tau}+\mathbf{v}\cdot\nabla\phi'_l\right)\right] - \Omega'\left(1-\sum_{i=1}^{n}M_i x_i\right) = 0 \tag{107}$$

$$\delta\mathbf{v}: \quad \frac{\delta L'}{\delta\mathbf{v}}-\sum_{k=1}^{n}\left[\left(x_k-\sum_{j=1}^{N}\nu_{kj}\chi_j\right)\nabla\phi_k\right] - \sum_{l=n+1}^{n+3}X_l\nabla\phi'_l = 0 \tag{108}$$

$$\delta x_k: \quad \frac{\delta L'}{\delta x_k}-\frac{\partial\phi_k}{\partial t}-\frac{\phi_k}{\tau}-\mathbf{v}\cdot\nabla\phi_k+\Omega' M_k = 0 \tag{109}$$

$$\delta\chi_j: \quad \frac{\delta L'}{\delta\chi_j}+\sum_{k=1}^{n}\nu_{kj}\left(\frac{\partial\phi_k}{\partial t}+\frac{\phi_k}{\tau}+\mathbf{v}\cdot\nabla\phi_k\right) = 0 \tag{110}$$

$$\delta\phi_k: \quad \frac{\partial}{\partial t}\rho\left(x_k-\sum_{j=1}^{N}\nu_{kj}\chi_j\right) + \nabla\cdot\left[\rho\mathbf{v}\left(x_k-\sum_{j=1}^{N}\nu_{kj}\chi_j\right)\right] = 0 \tag{111}$$

$$\delta X_l: \quad \frac{\delta L'}{\delta X_l}-\frac{\partial\phi'_l}{\partial t}-\frac{\phi'_l}{\tau}-(\mathbf{v}\nabla)\phi'_l = 0 \tag{112}$$

$$\delta\phi_l: \quad \frac{\partial(\rho X_l)}{\partial t}+\nabla\cdot(\rho X_l) = 0 \tag{113}$$

$$\delta\Omega: \quad 1-\sum_{i=1}^{N}M_i x_i = 0. \tag{114}$$

They contain the correct result for the classical chemical potentials $\mu k = \mu_k^{\mathrm{eq}}-M_k\mathbf{u}^2/2$, regardless of the thermodynamic potential used [8–10]. This correct result is obtained only when the Lagrangian L' used to define μ_k is modified by the constraint $-\Omega'(1-\Sigma M_k x_k)$. However, in the present case, one has to work in general with the *extended* chemical potentials

$$\mu_k \equiv -\frac{\delta L'}{\delta x_k} = -\left\{\frac{\partial L'}{\partial x_k}-\frac{\partial}{\partial t}\left(\frac{\partial L'}{\partial \dot{x}_k}\right) - \tau^{-1}\frac{\partial L'}{\partial \dot{x}_k}-\frac{\partial}{\partial \mathbf{x}}\left(\frac{\partial L'}{\partial x_{k,x}}\right)\right\}. \tag{115}$$

In terms of the extended chemical potentials, equation (109) with $\Omega' = 0$ (as referred to L') reads

$$\mu_k+\dot{\phi}_k+\tau^{-1}\phi_k+\mathbf{v}\cdot\nabla\phi_k = 0 \quad k = 1, 2, \ldots, n. \tag{116}$$

On elimination of the component actions ϕ_k from equations (107)–(110) and using the continuity equation (95), the chemical rate is found in terms the affinity vector $\mathbf{A} = -\nu^{\mathrm{T}}\mu$ in the form

$$\rho \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathbf{I}'\mathbf{r}'}{\rho}\right) + \mathbf{R}'\mathbf{r}' = \mathbf{A} \tag{117}$$

where $\mathbf{r}'$ is the total time derivative of χ, equation (98), and the resistance matrix obeys $\mathbf{R}' = \mathbf{I}'/\tau$. The above equation belongs, of course, to the χ-representation. An equivalent form in the ξ-representation results immediately from the above result. Since $\mathbf{I}'\mathbf{r}' = \mathbf{Ir}$ and $\mathbf{R}'\mathbf{r}' = \mathbf{Rr}$, one finds the same structure as equation (117). On elimination of the actions ϕ from equations (107)–(110) [11], a fundamental equation of the mechanical motion follows:

$$\begin{aligned} &\frac{\partial\, \delta L'}{\partial t\, \delta \mathbf{v}} + \frac{1}{\tau}\frac{\delta L'}{\delta \mathbf{v}} + \nabla\left(\mathbf{v}\cdot\frac{\delta L'}{\delta \mathbf{v}}\right) - \mathbf{v}\times\nabla\times\left(\frac{\delta L'}{\delta \mathbf{v}}\right) \\ &\quad - \sum_{k=1}^{n}\left[x_k \nabla\left(\frac{\delta L'}{\delta x_k}\right)\right] - \sum_{j=1}^{N}\left[\chi_j \nabla\left(\frac{\delta L'}{\delta \chi_j}\right)\right] \\ &\quad - \sum_{1=n+1}^{n+3}\left[X_l \nabla\left(\frac{\delta L'}{\delta X_l}\right)\right] = 0. \end{aligned} \tag{118}$$

This result may be compared with a recent result [12] derived by a different approach using the dissipation functions in lumped systems:

$$I\ddot{\mathbf{x}} + \beta\dot{\mathbf{x}} + \sum_{i}^{n} n_i(\partial\mu_i/\partial\mathbf{x}) - F_{\mathrm{ext}} = 0 \tag{119}$$

where n_i are the mole numbers of the ith species in a lumped system. One may observe that the latter equation is a special case of the former when the classical Hamilton's expression for the kinetic potential of unit mass is taken for L' of equation (118), and the vector calculus is applied to pass from the Eulerian to the Lagrangian picture of motion.

The current task in muscle modeling tends to find a reasonable approximation of the above complex results, to make the formulae usable in biophysical applications.

Acknowledgements—This work was supported in parts by grants from the Polish Committee of National Research, grant 3 P405 037 04, and the Sweizerischer Nationalfounds zur Förderung der Wissenschaftliche Forschung. The author acknowledges the hospitality of the Physiology Department, University of Bern, Switzerland, and the invitation of Dr J. S. Shiner.

REFERENCES

1. Shiner, J. S., Algebraic symmetry in chemical reaction systems at stationary states arbitrarily far from equilibrium. *Journal of Chemical Physics*, 1987, **87**, 1089–1094.
2. Sieniutycz, S., From a least action principle to mass action law and extended affinity, *Chemical Engineering Science*, 1987, **42**, 2697–2711.
3. Seliger, R. L. and Whitham, G. B., Variational principles in continuum mechanics. *Proceedings of the Royal Society*, 1968, **302A**, 1–25.
4. de Groot, S. R. and Mazur, P., *Non-equilibrium Thermodynamics*. Dover, New York, 1984.
5. MacFarlane, A. G. J., *Dynamical System Models*. George G. Harrap, London, 1970.
6. Shiner, J. S., A Lagrangian formulation of chemical reaction dynamics far from equilibrium. In *Flow, Diffusion and Rate Processes, Advances in Thermodynamics Series* (Eds. S. Sieniutycz and P. Salamon), Vol. 6. Taylor & Francis, New York, 1992, pp. 248–282.
7. Jou, D., Casas-Vàzquez, J. and Lebon, G., Extended irreversible thermodynamics. *Report on Progress in Physics*, 1989, **51**, 1105.
8. Sieniutycz, S. and Berry, R. S., Field thermodynamic potentials and geometric thermodynamics with heat transfer and fluid flow. *Physics Review, A*, 1991, **43**, 2807.
9. Sieniutycz, S. and Berry, R. S., Canonical formalism, fundamental equation and generalized thermomechanics for irreversible fluids with heat transfer. *Physical Review, E*, 1992, **47**, 1765–1783.
10. Keizer, J., *Statistical Thermodynamics of Nonequilibrium Processes*. Springer, New York, 1987.
11. Sieniutycz, S. *Conservation Laws in Variational Thermohydrodynamics*. Kluwer Academic Publishers, Dordrecht, 1994.
12. Shiner, J. S. and Sieniutycz, S., The mechanical and chemical equations of motion of muscle contraction. *Progress in Biophysics and Molecular Biology*, submitted for publication.
13. Onsager, L., Reciprocal relations in irreversible processes, I. *Physical Review*, 1931, **37**, 405–426; II. *Physical Review*, 1931, **38**, 2265–2279.
14. Onsager, L. and Machlup, S., Fluctuations and irreversible processes. I. *Physical Review*, 1953, **91**, 1505–1512.
15. Machlup, S. and Onsager, L., Fluctuations and irreversible processes. II. Systems with kinetic energy, *Physical Review*, 1953, **91**, 1512–1515.
16. Hesse, D., Derivation of the transport equation for multicomponent diffusion through capillaries in the transition region between gas diffusion and Knudsen diffusion. *Berichte der Bunsen-Gesellschaft*, 1974, **78**, 276–279.
17. Prigogine, I., *Etude Thermodynamique des Phenomenes Irreversibles*. Desoer, Liege, 1947.
18. Gyarmati, I., On the "Governing principle of dissipative processes" and its extension to non-linear problems. *Annalen der Physik* (Leipzig), 1969, **23**, 353–375.
19. Gyarmati, I., *Non-equilibrium Thermodynamics*. Springer, Berlin, 1970.
20. Verhas, J., An extension of the "Governing principle of dissipative processes" to nonlinear constitutive equations. *Annalen der Physik* (Leipzig), 1983, **40**, 189–195.
21. Rosen, P., On the variation principles of irreversible processes. *Journal of Chemical Physics*, 1953, **21**, 1220–1222.
22. Glansdorff, P. and Prigogine, I., *The Thermodynamic Theory of Structure, Stability and Fluctuations*. Wiley, London, 1971.
23. Essex, Ch., Minimum entropy production in the steady state and the radiative transfer. *Astrophysical Journal*, 1984, **285**, 279–293.
24. Mornev, O. A. and Aliev, R. R., Local variational principle of minimum dissipation in dynamics of diffusion-reaction. *Russian Journal of Physical Chemistry*, 1995, **69**, 1325–1328.
25. Grmela, M. and Teichman, J., Lagrangian formulation of the Maxwell–Cattaneo hydrodynamics. *International Journal of Engineering Science*, 1983, **21**, 297–313.
26. Grmela, M., Bracket formulation for Navier–Stokes equations. *Physics Letters*, 1985, **111A**, 36–40.
27. Grmela, M., Thermodynamics of driven systems. *Physical Review, E*, 1993, **48**, 919–930.

28. Grmela, M., Weakly nonlocal hydrodynamics. *Physical Review, E*, 1993, **47**, 351–365.
29. Grmela, M., Comments on the relation between Hamiltonian and Lagrangian formulations of mesoscopic dynamics. Scientific Reports of Kielce Polytechnik, *Mechanika* **59**, 1995, 49–64.
30. Grmela, M. and Lebon, G., Hamiltonian extended thermodynamics. *Journal of Physics A*, 1990, **23**, 3341–3351.
31. Rayleigh, J. W. S., *The Theory of Sound*. Dover, New York, 1945.
32. Beris, A. N. and Edwards, B. J., *Thermodynamics of Flowing Systems with Internal Microstructure*. Oxford University Press, Oxford, 1994.
33. Nyiri, B., On the construction of potentials and variations principles in thermodynamics and physics. *Journal of Non-Equilibrium Thermodynamics*, 1991, **16**, 39–55.
34. Gambàr, K., Màrkus, F. and Nyiri, B., A variational principle for the balance and constitutive equations in convective systems. *Journal of Non-Equilibrium Thermodynamics*, 1991, **16**, 217–223.
35. Gambàr, K. and Màrkus, F., On the global symmetry of thermodynamics and Onsager's reciprocity relations. *Journal of Non-Equilibrium Thermodynamics*, 1993, **18**, 51–57.
36. Gambàr, K. and Màrkus, F., Hamilton–Lagrange formalism of nonequilibrium thermodynamics. *Physical Review, E*, 1994, **50**, 1227–1231.
37. Sieniutycz, S. and Ratkje, S. K., Variational principle for entropy in electrochemical transport phenomena. *International Journal of Engineering Science*, 1996, **34**, 529–560.
38. Sieniutycz, S. and Ratkje, S. K., Variational thermodynamics of coupled electrochemical heat and mass transfer. *International Journal of Heat and Mass Transfer*, 1996, **39**, 3239–3303.
39. Sieniutycz, S. and Berry, R. S., Least-entropy generation: variational principle of Onsager's type for transient hyperbolic heat and mass transfer. *Physical Review, A*, 1952, **46**, 6359–6370.
40. I-Shih, Liu, Method of Lagrange multipliers for exploitation of the entropy principle. *Archives for Rational Mechanics and Analysis*, 1972, **46**, 131–148.
41. Anthony, K.-H., A new approach describing irreversible processes. In *Continuum Models of Discrete Systems*, Vol. 4, ed. O. Brulin and R. K. T. Hsieh. North-Holland, Amsterdam, 1981, pp. 481–494.
42. Anthony, K.-H., Unification of continuum mechanics and thermodynamics by means of a Lagrange formalism. *Archives of Mechanics*, 1989, **41**, 511–534.
43. Anthony, K.-H., Phenomenological thermodynamics of irreversible processes within Lagrange formalism. *Acta Physica Hungarica*, 1990, **67**, 321–340.
44. Kotowski, R., On the Lagrange functional for dissipative processes. *Archives of Mechanics*, 1989, **41**, 571–581.
45. Schoelle, M., Hydrodynamik im Lagrangeformalismus: Untersuchungen zur Wärmeleitung in idealen Flüssigkeiten. Diplomarbeit, University of Paderborn, 1994.
46. Guldberg, C. M. and Waage, P., *Etudes sur les Affinités Chimiques*. Christiana, Brogger et Christie, 1867.
47. Grabert, H., Hänggi, P. and Oppenheim, I., Fluctuations in reversible chemical reactions. *Physica*, 1983, **117A**, 300–316.
48. Shiner, J. S. and Sieniutycz, S., Phenomenological macroscopic symmetry in dissipative nonlinear systems. In *Entropy and Entropy Generation: Fundamentals and Applications*, ed. J. S. Shiner. Kluwer, Dordrecht, 1996, pp. 139–158.
49. Shiner, J. S., Fassari, S. and Sieniutycz, S., Lagrangian and network formulations of nonlinear electrochemical systems. *Entropy and Entropy Generation: Fundamentals and Applications*, ed. J. S. Shiner. Kluwer, Dordrecht, 1996, pp. 221–239.
50. Sieniutycz, S., A variational approach to chemically reacting distributed systems. Scientific Reports of Kielce Polytechnik. *Mechanika* 59, 1995, 131–143.
51. Sieniutycz, S. and Shiner, J. S., Variational and extremum principles of homogeneous chemical kinetics. I. Lagrangian- and Hamiltonian-like formulations. *Open Systems Information Dynamics*, 1992, **1**(2), 149–182.
52. Sieniutycz, S. and Shiner, J. S., Variational and extremum principles of homogeneous chemical kinetics. II. Minimum dissipation approaches. *Open Systems Information Dynamics*, 1993, **1**(3), 327–348.
53. Shiner, J. S. and Sieniutycz, S., The chemical dynamics of biological systems: variational and extremal formulations. *Progress in Molecular Biophysics and Biology*, 1994, **62**, 203–221.
54. Atherton, R. W. and Homsy, G. M., On the existence and formulation of variational principles for nonlinear differential equations. *Studies in Applied Mathematics*, 1975, **54**, 31–80.
55. Bampi, F. and Morro, A., The inverse problem of the calculus of variations applied to continuum physics. *Journal of Mathematical Physics*, 1982, **23**, 2312–2321.
56. Santilli, R. M., Necessary and sufficient conditions for the existence of a Lagrangian in field theory. I. Variational approach to self-adjointness for tensorial field equations. *Annals of Physics* (NY), 1977, **103**, 354–408.
57. Perlick, V., The Hamiltonian problem from the global viewpoint. *Journal of Mathematical Physics*, 1992, **33**, 599–606.
58. Finlayson, B. A., *The Method of Weighted Residuals and Variational Principles*. Academic Press, New York, 1972.
59. Caviglia, G., Composite variational principles and the determination of conservation laws. *Journal of Mathematical Physics*, 1988, **29**, 812–816.
60. Morse, P. M. and Feshbach, H., *Methods of Theoretical Physics*. McGraw-Hill, New York, 1953.
61. Sieniutycz, S. and Berry, R. S., Canonical formalism, fundamental equation and generalized thermomechanics for irreversible fluids with heat transfer. *Physical Review, E*, 1993, **47**, 1765–1783.
62. Herivel, J. W., The derivation of the equations of motion of an ideal fluid by Hamilton's principle. *Proceedings of the Cambridge Philosophical Society*, 1955, **51**, 344–349.
63. Serrin, J., Mathematical principles of classical fluid mechanics. In *Handbook der Physik*, Vol. VII/1, ed. S. Flugge. Springer, Berlin, 1959.
64. Jezierski, J. and Kijowski, J., Thermo-hydrodynamics as a field theory. In *Nonequilibrium Theory and Extremum Principles, Advances in Thermodynamics Series* (Eds. S. Sieniutycz and P. Salamon), Vol. 3. Taylor & Francis, New York, pp. 282–316.
65. Nonnenmacher, T. F., Functional Poisson brackets for nonlinear fluid mechanics equations. In *Recent Developments in Nonequilibrium Thermodynamics: Fluids and Related Topics*, ed. J. Casas-Vàzquez, D. Jou and J. N. Rubi. Springer Berlin, 1986, pp. 149–174.
66. Sieniutycz, S., Hamiltonian energy-momentum tensor in extended thermodynamics of one-component fluid. *Inzynieria Chemiczna i Processowa*, 1988, **4**, 839–861.
67. Sieniutycz, S. and Berry, R. S., Conservation laws from Hamilton's principle for nonlocal thermodynamic equilibrium fluids with heat flow. *Physical Review, A*, 1989, **40**, 348–361.
68. Muschik, W. and Trostel, R. Variational principles in thermodynamics. *ZAMM*, 1983, **63**, T190-T192.
69. Jou, D., Casas-Vàzquez, J. and Lebon, G., Extended irreversible thermodynamics: an overview of recent bibliography. *Non-Equilibrium Thermodynamics*, 1992, **17**, 383–396.
70. Lebon, G., Variational principles in thermomechanics. In *Recent Developments in Thermomechanics of Solids*, ed. G. Lebon and P. Perzyna, CISM Courses and Lectures, Vol. 262. Springer, Vienna, 1986, pp. 221–415.
71. Salmon, R., Hamiltonian fluid mechanics. *Annual Mechanics Review*, 1987, **12**, 51–67.

72. Sieniutycz, S. and Salamon, P., Eds., *Nonequilibrium Theory and Extremum Principles*. Taylor & Francis, New York, 1990.
73. Kupershmidt, B. A., *The Variational Principles of Dynamics*. World Scientific, New York, 1962.
74. Schechter, R. S., *The Variational Method in Engineering*. McGraw-Hill, New York, 1967 (see also references therein).
75. Callen, H., *Thermodynamics and an Introduction to Thermostatistics*. John Wiley, New York, 1988.
76. Sieniutycz, S. and Shiner, J. S., Variational dynamics of lumped thermal processes. Paper in preparation.
77. Levine, R. D. and Tribus, M., *The Maximum Entropy Principle*. MIT Press, Cambridge, MA, 1979.
78. Biot, M., *Variational Principles in Heat Transfer*. Oxford University Press, Oxford, 1970.
79. Kantorovich, L. V. and Krylow, V. I., *Approximate Methods of Higher Analysis*. Nordhoff, Groningen, 1958.
80. Landau, L. D. and Lifshitz, E., *Statistical Physics*. Pergamon Press, Oxford, 1975.
81. Sundheim, B. R., Transport properties of liquid electrolytes. In *Fused Salts*, ed. B. R. Sundheim. McGraw-Hill, New York, 1964, pp. 165–254.
82. Ekman, A., Liukkonen, S. and Kontturi, K., Diffusion and electric conduction in multicomponent electrolyte systems. *Electrochimica Acta*, 1978, **23**, 243–250.
83. Forland, K. S., Forland, T. and Ratkje, S. K., *Irreversible Thermodynamics—Theory and Applications*. Wiley, Chichester, 1989.
84. Van Zeggeren, F. and Storey, S., *The Computation of Chemical Equilibria*. Cambridge University Press, Cambridge, 1970.
85. Newman, J., *Electrochemical Systems*. Prentice-Hall, Englewood Cliffs, NJ, 1973.
86. Jackson, D., *Classical Electrodynamics*. Wiley, New York, 1975.
87. Vojta, G., Hamiltonian formalism in the thermodynamic theory of irreversible processes in continuous systems. *Acta Chimica Academiae Scientarum Hungariae*, 1967, **54**, 55–64.
88. Lavenda, B. H., *Nonequilibrium Statistical Thermodynamics*. Wiley, Chichester, 1985.
89. Kupershmidt, B. A., Hamiltonian formalism for reversible non-equilibrium fluids with heat flow. *Journal of Physics A: Mathematical and General*, 1990, **23**, L529–L532.