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Perturbational dynamics of thermal processes and chemical reactions in distributed systems

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Abstract—A perturbation analysis of diffusion–reaction systems exposes the effect of local thermal equilibrium as an extremal property of systems which minimize dissipation. The effect is also shown to be sufficient for stability of small perturbations relaxing towards steady-states close to equilibrium. Several variational principles are constructed for perturbations in chemically reacting systems with simultaneous transfer of heat, mass and electric charge. The underlying physical principle, which substantiates the joint role of thermodynamic potentials and intensity of dissipation, is invariance of the energy dissipation. The formulations of perturbed dynamics include: a nonstationary extension of Onsager's principle, gradient representations with a perturbed vector of thermal displacement, perturbed potentials of thermal field, and functional Hamiltonian formalism. Each formalism works with the assumption of local thermal equilibrium which, in our analyses, is a common property of asymptotic states of various orders. An important result is inclusion of chemical reactions into perturbational dynamics, with chemical nonlinearities governed by the standard kinetics of mass action law. We also present a novel method, based on equivalent variational problems, which implies transformations between various thermodynamic potentials at nonequilibrium.

1. INTRODUCTION

Chemical perturbations relaxing towards nonequilibrium steady states obey nonlinear laws of chemical kinetics, the most popular being the mass action law. In this work, we consider these perturbations coupled with transfer of the heat, mass and electric charge, in systems which are in mechanical equilibrium. Through variational principles for the state perturbations we investigate the effect of the local thermal equilibrium which, in our analysis, appears as a unique property of both transients and steady states of various orders. The uniqueness of the effect manifests through a common property of various asymptotic states in which the Lagrangian multipliers of balance constraints coincide with the Gibbsian derivatives of the governing thermodynamic potential.

There have been numerous approaches to generalized extremum principles for nonstationary nonlinear evolutions. The classical works of Onsager [1–4] and Prigogine [5] dealt with linear irreversible processes. Gyarmati's quasi-linear generalizations [6–8] while of a considerable generality, belong to the class of restricted principles of Rosen's type [9], or local potential type [10], where some variables and/or derivatives are subjectively 'frozen' to ensure a correct result. Essex [11] has proved a potential of minimum entropy theorems to yield nonlinear balance equations for radiative transfer. Mornev and Aliev [12] have formulated a functional extension of the local Onsager's principle. Using a caloric coordinate Grmela and Teichman [13] stated an *H* theorem as a proper setting for the maximum entropy in Lagrangian coordinates. Grmela [14–17] and Grmela and Lebon [18] have worked out an efficient two-bracket formalism, with Poissonian brackets and dissipative brackets, the latter being a functional extension of the Rayleigh dissipation function [19]. With applications to rheology, bracket approaches have systematically been exposed in a recent book [20]. However, two-bracket theorems are not associated with an extremum of a definite physical quantity; for that purpose the single Poissonian bracket and a Hamiltonian system are necessary. Yet Nyiri's [21] approach has introduced certain potentials, similar to those known in the electromagnetic field theory, and related integrals which were subject to extremization. Their application to nonreacting systems has proved to be of considerable utility [22–24], although the inclusion of chemical reactions has required treating chemical sources as given functions of time and position.

This work deals with the inclusion of chemical reactions into perturbational formulation of the second law, in which Lagrange multipliers handle balance constraints. Similar formulations have so far been restricted to nonreacting systems, both parabolic [25, 26] and hyperbolic. These approaches may been seen as being of the type of Liu's multiplier method, but since they deal with an explicit dissipation formula and the second law in an equality form, they lead to

NOMENCLATURE

$\mathbf{A}$	vector of chemical affinities
$\mathbf{a}$	matrix of thermostatic capacitances
$\mathbf{C}$	column vector of densities, equation (4)
c_i	molar concentration of *i*th component
e_v	molar energy of unit volume
$\mathbf{H}_i$	Biot vector associated with flux $\mathbf{J}_i$
H_σ	dissipative (thermodynamic) Hamiltonian
i	molar flux density of electric current
$\mathbf{J}$	column matrix of independent fluxes, equation (1)
J_e	density of total energy flux
J_i	molar flux density of *i*th component
J_s	density of entropy flux
k	thermal conductivity
$\mathbf{L}$	Onsagerian matrix of phenomenological coefficients
L_σ	dissipative (thermodynamic) Lagrangian
M_k	molar mass of *k*th component
P	power criterion
$\mathbf{R}$	resistance matrix
S, S^T	total entropy and its Legendre transform, respectively
s_v	entropy of unit volume
T	temperature
t	time
$\mathbf{u}$	Gibbsian vector of independent thermodynamic intensities, equation (5)
V	volume
$\mathbf{w}$	Onsager's vector of independent transport intensities or Lagrangian multiplier of conservation laws
$\mathbf{X}$	vector of independent thermodynamic forces, equation (6).

Greek symbols

Λ_σ	Lagrangian density of dissipative field
∇	nabla operator
δ	perturbation operator
ν	extended stoichiometric matrix
ϕ	electric potential
μ_k	molar chemical potential of *k*th component
$\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$	transfer potential of *k*th component ($\mu'_k \equiv -\tilde{\mu}_k$)
σ	production terms per unit volume.

Subscripts

e	total energy
i	*i*th component
s	entropy
σ	dissipative property.

Superscripts

s	entropy representation
T	transpose matrix, Legendre transform; transformed quantity
$'$	free-energy representation.

quantitative rather than qualitative results. Chemical systems could also be treated by Anthony's variational method [29–33] which uses a 'field of thermal excitation', a thermal counterpart of quantum wave function, and certain reaction potentials, at the expense however of undefined physical origin of these potentials and their relation to the mass action law. Otherwise, our variational method, which is applied here to the state perturbations rather than to any unperturbed dynamics, uses only classical quantities, the most essential being the nonlinear chemical resistance [35–38]. With chemical resistances, nonlinear variational and extremum formulations for lumped systems are possible [37–41]. In the present work they are applied to *perturbed* reaction–diffusion fields in the Eulerian representation of transport phenomena.

Whenever irreversibility enters into the issue, the admissibility of a variational formulation needs a solid substantiation. As it has already been explained [25, 26], we only briefly recapitulate here the argument. A system of differential equations admits a variational formulation if and only if it is self-adjoint [42–47], the property which requires that stringent conditions for the related differential operator are satisfied. The typical equations of irreversible processes are, as a rule, not self-adjoint [46, 48], which means that they do not admit variational formulation in the state-space spanned on their own dependent variables. However, the so-called composite principles, in the extended space spanned on the original state variables and certain new variables (state adjoints), are always possible [42, 47]. In fact, all successful variational formulations for irreversible systems do involve a space expansion. This also refers to formulations which use higher order functionals [21–24], which can be broken down to those based on the first order functionals in enlarged spaces. These properties are also shared by many action-based approaches for irreversible and reversible processes [31, 49–55]. Reviews and books on this subject are available, see refs. [56–61]. With these findings, the conservation laws and the idea of the minimum dissipation in the case of physical fields described by thermodynamic potentials [62, 63], here we develop a perturbational thermodynamics of the diffusion–reaction systems around nonequilibrium steady-states. We assume that a steady-state is sufficiently close to equilibrium so that the Onsagerian reciprocity still may be assumed.

For the standard set of the balance constraints (with balances of the energy, momentum and species), in the entropy generation functional the new or adjoint variables are a type of the transport intensities [27]. The distinction between the classical Gibbsian intensities **u** (the temperature reciprocal and Planck chemical potentials or the partial derivatives of entropy with respect to energy and mole numbers), and their transport counterparts **w** (Lagrangian multipliers of balance equations), is essential in order to distinguish between arbitrary macroscopic states and thermodynamic states (of asymptotic nature) in both continuous [27] and lumped [64] systems. While both **u** and **w** play a role in thermodynamic functionals, their distinction is appropriate off local thermodynamic states ('local thermal equilibria') when a dynamic behavior is considered, as only then local or instantaneous potentials of transfer are not necessary thermodynamic quantities. The distinction is neither necessary nor possible for descriptions which ignore any dynamic development, such as typical formulations of the maximum entropy formalism [65] with the Lagrange multipliers referring to the final state of equilibrium rather than to a variety of intermediate states. Yet, the distinction is appropriate in perturbational dynamics studied here, although, due to the commonness of the asymptotic (thermodynamic) states in physical systems, the two vectors **u** and **w** coincide for large majority of physical situations so that the condition $\mathbf{u} = \mathbf{w}$ should *a posteriori* be imposed for most models of heat and mass transport. When $\mathbf{u} = \mathbf{w}$, the equations of change are equations dependent on the conservation laws and phenomenological equations. On the other hand, when **u** and **w** differ, the equations of change follow independently of the conservation laws and phenomenological equations.

The hypothesis of the stable 'local equilibrium' is substantial in classical nonequilibrium thermodynamics. As that theory extrapolates methods of statistical mechanics to nonequilibrium situations, one has to assume that, at any time, each region of the system is in a macroscopic status so that it can be completely defined by a set of macroscopic or thermodynamic variables (those of a Gibbs equation). To call this status 'the local equilibrium' as it is commonly done is rather misleading, firstly because one should rather speak about the 'local thermal equilibrium' or 'restricted equilibrium' when only some degrees of freedom relax instantly. For reacting systems, especially, it is more appropriate to speak about the local *thermal* equilibria corresponding with the situation when relaxation of thermal degrees of freedom is immediate. A true local equilibrium would be a more restrictive situation, the one with vanishing reaction rates at a particular point of the system, which is, in fact not a case for real nonequilibrium systems. Secondly, since there is not a *a priori* any requirement of vanishing chemical affinities for chemical potentials obtained from the Gibbs equation, this equation is, in fact, an equation of nonequilibrium thermodynamics, and, in the case of chemical systems, the local thermodynamic equilibrium is not satisfied even in classical thermodynamics. In fact, what is actually satisfied for a large majority of macroscopic systems is a thermodynamic-limit property of the energy and other thermodynamic potentials which depend on a small number of macroscopic variables (including rates or fluxes in extended thermodynamic systems).

In our theory, the local thermal equilibrium is a unique property of various thermodynamic states, which manifests through the common asymptotic property of macroscopic states for which the Lagrangian multipliers of balance constraints **w** coincide with the Gibbsian derivatives, **u**. The behavior of **u** and **w** separates the local equilibrium and local disequilibrium situations in continua in a natural way. The limiting equality $\mathbf{u} = \mathbf{w}$ is valid for both steady-state thermodynamic processes and for those which are not necessarily stationary. For steady states, it holds regardless of whether only some of all the species (e.g. first N' species) diffuse (whereas the system boundaries are closed to diffusion of remaining species), or all the species are allowed to freely diffuse in and out of the system ($N' = N$). These different situations correspond to various steady states, of different order N'. The unifying equality $\mathbf{u} = \mathbf{w}$ is the only general relationship obeyed on various limiting manifolds representing various steady states, and importantly, it holds for both parabolic and hyperbolic equations of the heat and mass transfer [27]. In this respect, the equality of two sorts of intensities replaces with improved precision the vague meaning of 'local equilibrium', by showing that this traditional meaning is not entirely proper for nonequilibrium steady states with a nonvanishing difference or 'slip' between the transfer velocities of moving species. The presence of the slip in these systems means that they admit only certain 'pseudo-local-equilibrium' structures, those with some production of entropy, which still satisfy the equality $\mathbf{u} = \mathbf{w}$, but in which the thermodynamic behavior is different that at equilibrium (in particular, the role of inertial terms is different).

Dealing with a perturbed continuum one should consistently use a model containing the perturbations of both the state variables and their adjoints. An excess of dissipation intensity with respect to a steady state is described by two perturbed dissipation functions of Onsager's type, $\delta^2\Phi$ and $\delta^2\Psi$, expressed in terms of the extended state $(C, \mathbf{J})$ [or $(\mathbf{u}, \mathbf{J})$], its perturbations, δC and δJ, and the derivatives of perturbations, $\partial \delta C/\partial t$, $\nabla \delta C$, etc. An excess entropy four-vector $(\delta s_v, \delta J_s)$, may depend on excesses of both the classical (static) variables δC and fluxes δJ and the excesses of the Lagrange multipliers δw. We show that by implying a least increase of the integral representing the excess entropy production during a transient relaxation to a steady-state in a nonisolated chemical system, one can derive the perturbed equations of change and perturbed phenomenological equations under the given (perturbed) dissipation potentials and the well known information contained in the (perturbed) conservation laws. These results are exposed through a few variational principles for perturbations, in several new and important contexts, such as:

- Gradient representations which use Biot's vector of thermal displacement [66] and thermal potentials introduced recently [21–24].
- Chemical nonlinearities governed by the mass action kinetics [34]. Their variational formulation is of a special importance as it makes it possible to solve complex models of reaction–diffusion processes by direct variational methods [67].
- Nonequilibrium thermodynamic potentials for inhomogeneous systems and their relation to basic statistical mechanics [68].
- The link between Lagrangian and Hamiltonian descriptions of perturbations.

The system considered is with various chemical reactions and transport phenomena in the bulk. Mechanical equilibrium, consistent with the constancy of the total mass density ρ and vanishing barycentric velocity in a suitable reference frame, is assumed. The system, which may be electrochemical, is composed of components, reacting, but neutral [69–71], obeying the phase rule [72]. As shown by Sundheim [69] this setting leads to the independent fluxes of mass, energy and electric current. For an ionic description see ref. [73].

2. PERTURBED NONREACTING FIELDS WITH HEAT AND MASS TRANSFER

To acquaint the reader briefly with the various variational methods which one might use in analysis of perturbations we consider first (Sections 2 and 3) nonreacting systems. Then we will choose a suitable method and pass to reacting systems, which is the main goal of this paper. Under assumptions of negligible convection, absence of viscosity terms, and electroneutrality, the perturbed conservation laws which describe transients of energy, mass and electric current, are in the matrix notation

$$\frac{\partial \delta C}{\partial t}+\nabla\cdot\delta\mathbf{J}=0. \qquad (1)$$

The immediate relaxation of the electric current follows as consequence of the electroneutrality effect incorporated in the model, nonetheless we will use equation (1) in its nontruncated form, to allow the common description of all involved quantities and generalizations to some complex cases. In equation (1), $\mathbf{J}$ is the matrix of independent fluxes

$$\mathbf{J}=(J_e, J_1, J_2, \ldots, J_{n-1}, i)^{\mathrm{T}} \qquad (2)$$

(the superscript T means transpose of the matrix) J_e is the total energy flux defined as

$$J_e = J_u+\phi i = J_q+\sum_1^n h_i J_i+\phi i. \qquad (3)$$

The corresponding column vector of densities $\mathbf{C}$ is

$$\mathbf{C}(e_v, c_1, c_2, \ldots, c_{n-1}, c_{el})^{\mathrm{T}}. \qquad (4)$$

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

$$\mathbf{u}=(T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots, \tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1}) \qquad (5)$$

with $\tilde{\mu}_k=\mu_n M_k M_n^{-1}-\mu_k$. Their gradients $\mathbf{X}=\nabla\mathbf{u}$ are independent forces

$$\mathbf{X}\equiv\nabla\mathbf{u}=(\nabla T^{-1}, \nabla(\tilde{\mu}_1 T^{-1}),$$
$$\nabla(\tilde{\mu}_2 T^{-1}), \ldots, \nabla(\tilde{\mu}_{n-1} T^{-1}), -\nabla(\phi T^{-1}))^{\mathrm{T}}. \qquad (6)$$

The densities, equation (4) and the transfer potentials equation (5) are the two sets of variables in the Gibbs equation for the entropy density $s_v=\rho s$ of an incompressible system with the mass density $\rho=\Sigma M_i c_i$.

Our analysis of perturbed dynamics differs from that encountered in the classical analysis of thermodynamic stability [10], which uses the entropy differentials

$$\delta s_v=\mathbf{u}\cdot\delta\mathbf{C};\quad \mathrm{d}^2 s_v=\delta\mathbf{u}\cdot\delta\mathbf{C}\leqslant 0. \qquad (7)$$

Instead, following the method developed earlier for nonreacting systems [26], one may consider the perturbations of the entropy four-vector, $[s_v(\mathbf{C}), J_s(\mathbf{J}, \mathbf{C})]$, where $J_s(\mathbf{J}, \mathbf{C})=\mathbf{J}\cdot\mathbf{u}=\mathbf{J}\cdot\partial s_v/\partial\mathbf{C}$. One then obtains the quantities $\delta(s_v, J_s)$ and $1/2\delta^2(s_v, J_s)$ describing the once-perturbed and twice-perturbed entropy four-flux. The four-divergence of the second differential of the entropy four-vector $1/2\delta^2(\partial_t s_v, \nabla\cdot J_s)$ combined with once-perturbed conservation laws, equation (1), yields the excess entropy production $1/2\delta^2\sigma$. The superiority of this method over the classical one follows from the notion that the second-order perturbation of the entropy four-flux yields the excess of the entropy production in the general case, without traditional restrictions related to the fixed state at the system boundaries or purely dissipative nature of the process. In terms of the conserved fluxes, for nonreacting systems

$$\partial_t(\tfrac{1}{2}\delta^2 s_v)+\nabla\cdot(\tfrac{1}{2}\delta^2 J_s)\equiv\tfrac{1}{2}\delta^2\sigma=\delta J_e\cdot\nabla\delta T^{-1}$$
$$-\sum_{i=1}^{n}\delta J_i\cdot\nabla\delta(\mu_i T^{-1})-\delta i\cdot\nabla\delta(\phi T^{-1})=\delta J_e\cdot\nabla\delta T^{-1}$$
$$+\sum_{i=1}^{n-1}\delta J_i\cdot\nabla\delta(\tilde{\mu}_i T^{-1})-\delta i\cdot\nabla\delta(\phi T^{-1}) \qquad (8)$$

with

$$J_s \equiv T^{-1}\left(J_e - \sum_1^n \mu_k J_k - \phi i\right) = T^{-1}\left(J_e + \sum_1^{n-1} \tilde{\mu}_k J_k - \phi i\right). \qquad (9)$$

These equations contain (in the perturbed and unperturbed forms, respectively), the matrix of independent fluxes $\mathbf{J}$, equation (2), the vector of the transport potentials $\mathbf{u}$, equation (5), and the associated vector of the independent thermodynamic forces $\mathbf{X} = \nabla\mathbf{u}$ equation (6). The kinetic coefficients implicit in equation (8) are assumed to be constants (steady states close to equilibrium).

The perturbed conservation laws, equation (1) are built into the entropy functional, equation (10) below, with the help of the perturbed vector of the Lagrangian multipliers $\delta\mathbf{w} = (\delta w_0, \delta w_1, \delta w_2, \ldots, \delta w_{n-1}, \delta w_n)$. The *extremum* value of the multiplier $\delta\mathbf{w}$ in the entropy functional (10) is the vector of the *kinetic* conjugates of the perturbed extensities δC, equation (4). On the extremal surfaces of the entropy functional, equation (10), the vector $\mathbf{w}$ coincides with the transport potential vector $\mathbf{u}$, equation (5), in the limiting situation of the local equilibrium. This coincidence, which also takes place for the perturbations $\delta\mathbf{u} = \delta\mathbf{w}$, does not occur off any extremal non-equilibrium solution and, therefore, $\mathbf{w}$ and $\mathbf{u}$ as well as $\delta\mathbf{u}$ and $\delta\mathbf{w}$ are generally two distinctive sorts of the field variables in the entropy functional, equation (10). As long as the constraint $\mathbf{w} = \mathbf{u}$ is not imposed, they constitute two fields independent of each other. The quantities $\mathbf{w}$ and $\mathbf{u}$ 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 $\mathbf{w} = \mathbf{u}$ and $\delta\mathbf{u} = \delta\mathbf{w}$, meaning that the extremal Lagrangian multipliers $\delta\mathbf{w}$ coincide with the components of the entropy gradient in the state space of δC_i. In a limiting (local equilibrium) situation w_i and δw_i converge respectively to the classical intensities, equation (5), and their perturbations. In the extended thermodynamics models these quantities converge to certain flux-dependent intensities that are still the partials of an extended entropy although they then depend on both C_i and J_i. The equalities $\mathbf{w} = \mathbf{u}$ and $\delta\mathbf{u} = \delta\mathbf{w}$ also hold in these extended situations. One may consider that a 'pseudo-local-equilibrium' situation is created at stable steady states far from equilibrium, and then $\mathbf{w}$ may converge to the above mentioned, non-equilibrium intensities $\mathbf{u}$. On stable extremal solutions $\delta\mathbf{w} = \delta\mathbf{u}$ and both tend to vanish at $t \to \infty$.

One of the main reasons for using variational approaches (leaving apart, of course, their computational virtues) is our general research direction towards extending Callen's postulational thermodynamics to inhomogeneous thermodynamic systems. To simplify the notation we use the single-integral symbols for multiplied integrals in the physical space-time. The governing functional describes the dynamics of small perturbations between the two fixed times t_1 and a subsequent t_2

$$\frac{1}{2}\delta^2 S(t_2) = \min\left\langle \frac{1}{2}\delta^2 S(t_1) + \int_{t_1,\mathbf{A}}^{t_2} -\frac{1}{2}\delta^2 J_s(\delta\mathbf{J}, \delta\mathbf{u}) \cdot \mathrm{d}\mathbf{A}\,\mathrm{d}t + \int_{t_1,V}^{t_2} \left\{\frac{1}{2}\mathbf{L}^{-1}(\mathbf{u}) : \delta\mathbf{J}\delta\mathbf{J} + \frac{1}{2}\mathbf{L}(\mathbf{u}) : \nabla\delta\mathbf{u}\nabla\delta\mathbf{u} + \delta\mathbf{w}\left(\frac{\partial\delta\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J}\right)\right\}\mathrm{d}V\,\mathrm{d}t \right\rangle \qquad (10)$$

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 [27, 40]. By direct application of the divergence theorem to the $\mathbf{w}$ term in the unperturbed counterpart of equation (10) it can also be 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 which leads to the kinetic equations (as the only result) through the restricted variation of fluxes (at the constant thermodynamic forces $\mathbf{X}$). At a steady-state, when only $\mathbf{J}$ is varied and $\mathbf{w}$ converges to $\mathbf{u}$ on the extremal surfaces, the Onsager's functional and his kinetic equation $\mathbf{J} = \mathbf{L}\cdot\nabla\mathbf{u}$ follow from the unperturbed counterpart of equation (10) as the only steady-state formulae.

However, in the unsteady situation, for the perturbed states, equation (10) yields, as the Euler–Lagrange equations with respect to the variables $\delta\mathbf{u}$, $\delta\mathbf{J}$ and $\delta\mathbf{w}$, a more general result. It is a quasilinear set representing (at $\mathbf{w} = \mathbf{u}$ and $\delta\mathbf{u} = \delta\mathbf{w}$) 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 small perturbations $\delta\mathbf{w}$, $\delta\mathbf{J}$ and $\delta\mathbf{u}$ around a steady state which is close to equilibrium are respectively

$$\frac{\partial\delta\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J} = 0 \qquad (1)$$

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

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

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 we use, i.e. the integrand of space-time integral in equation (10), does a good job since it leads to *all* pertinent equations, the property which is essentially not obeyed for previous models. The perturbed conservation laws, equation (1), are recovered; the other results are the perturbed phenomenological equations and the equations of change. The last equation is the perturbed Fourier–Kirchhoff type matrix equation of change which links the fields of the temperature, chemical potentials and electrical potential. At the local equilibrium, when all states of the system are located on Gibbs manifold, the equalities $\mathbf{w} = \mathbf{u}$ and $\delta\mathbf{w} = \delta\mathbf{u}$ hold, and the three equations (1), (11) and (12) become dependent. This is the well-known classical situation, in which only a subset of possible solutions is realized in practice.

Otherwise, it may be shown that equation (10) is capable of describing situations in which the potentials $\mathbf{u}$ and $\mathbf{w}$ differ, in particular those which, perhaps, may be referred to case of inherent local nonequilibria and instabilities. Since however the reference state is not varied, the functional, equation (10) cannot predict neither equality $\mathbf{u} = \mathbf{w}$ nor other properties of reference state, as e.g. the function $\mathbf{L}(\mathbf{u})$. As the properties of the background (steady-) state, they must be assumed or evaluated from the unperturbed dynamical model in which the rates as set to zero at the reference state. This is typical in the stability analyses. The corresponding equality $\delta\mathbf{w} = \delta\mathbf{u}$ has also been assumed.

3. PERTURBATIONS IN GRADIENT INVARIANT FUNCTIONALS

We now propose a different variational formulation which makes use of the perturbations of so-called Biot's [66] thermal displacement vector, $\mathbf{H}_e$, in the integrand of the entropy functional. Actually, as long as the system is multicomponent, one has to apply a set of such vectors, associated with the energy flux, component fluxes and electric current,

$$\mathbf{H} = (\mathbf{H}_e, \mathbf{H}_1, \mathbf{H}_2, \ldots, \mathbf{H}_{n-1}, \mathbf{H}_{el})^{\mathrm{T}}. \qquad (13)$$

They refer to each vector component of the matrices (2) and (4). Since the perturbation of each flux and each density satisfy the gradient representations

$$\delta\mathbf{J} = \frac{\partial\delta\mathbf{H}}{\partial t} \qquad (14)$$

and

$$\delta\mathbf{C} = -\nabla\cdot\delta\mathbf{H} \qquad (15)$$

the perturbed conservation laws are identically satisfied. Indeed, the addition of the divergence of equation (14) to the partial time derivative of equation (15) yields equation (1).

To obtain the Euler–Lagrange equations for perturbations from a functional based on the representations (14) and (15) it suffices to substitute these equations into the production part of the entropy functional (10). Restricting to linear perturbations (the case of constant coefficients) yields

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

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

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

The Euler–Lagrange equation for the functional (16) describes the matrix $\delta\mathbf{H}$ composed of the perturbed Biot's vectors

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

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

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

Equation (19) holds with the conservation laws, equation (1) contained in equations (14) and (15). 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 elimination of the multipliers $\delta\mathbf{w}$ from equations (11) and (12).) However, when one wants to obtain the set of equation (1), (11) and (12) from this model than a more general equation set is admitted by equations (14), (15) and (19)

$$\frac{\partial\delta\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J} = 0 \qquad (1)$$

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

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

where $\delta\mathbf{c}(\mathbf{x}) = 0$, but $\delta h(t)$ is an arbitrary perturbation. With this result, one couldn't *a priori* judge if the model of the process transients should be described by equations (1), (20) and (21) with non-vanishing $\delta h(t)$ or by equations (1), (11) and (12). The only reasonable way to resolve the dilemma is to restrict the structure of independent equations to the range implied by an experiment or microscopic transport theories. This in turn means their dependence associated with taking $\mathbf{w} = \mathbf{u}$ (implying $\delta\mathbf{u} = \delta\mathbf{w}$) along with $\delta\mathbf{c}(\mathbf{x}) = 0$, and $\delta h(t) = 0$. Thus, it is the physics of the problem which requires one to restrict to the case when $\delta\mathbf{c}(\mathbf{x}) = 0$, $\delta h(t) = 0$ and $\mathbf{w} = \mathbf{u}$.

For the same parabolic problem the so-called transfer potentials introduced in Nÿiri's [21] approach can be used in case of linear transients. Gamber and Ma'rkus [24] have constructed a dissipative Lagrangian obtained through squaring the variational adjoint of the equation of change. For perturbed dynamics this is equation (12) at $\delta\mathbf{u} = \delta\mathbf{w}$. The variational adjoint, which is next identified with the perturbation $\delta\mathbf{u}$, is, in our notation

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

(their $\rho S_{ik} = -a_{ik}^{-1}$). The perturbations of the thermal potentials, $\delta\phi$, are described by the second order Lagrangian

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

This Lagrangian yields the Euler–Lagrange equation for transients

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

which is satisfied by equation (22) in the form

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

This is a form of the Fourier–Kirchhoff equation in terms of transients. The approach based on thermal potentials has resulted in a number of original interpretations and a field theory of nonequilibrium thermodynamic systems [22–24]. These ingenious analyses provide equations of change, and extra physical conditions, obtained from certain invariance requirements, should be satisfied to obtain the kinetic equations or conservation laws from equation (23). This conforms with our earlier conclusion that 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 $f(x, t)$

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

provided that the perturbation $\delta f(x, t)$ obeys the equation

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

Consider a one-potential process with $f = 1/2x^2 - 3t$ as an example. In the present approach, the representations, equation (26) are, however, rejected on account of the simpler representations, equation (22) which are regarded as 'more physical' since they obey the gradient invariance. One may argue that the adjoint quantities are 'non-physical' anyhow, so there is no matter which representation, equation (22) or equation (26) is used. However, the restrictions imposed on definition of potentials may have physical reasons. Consider, for example, restrictions on electromagnetic potentials [74]. Another example are momenta of classical mechanics, which are adjoints of coordinates. Therefore, physical limitations must accompany the representations of transients expressed in terms of the potentials.

4. TRANSIENTS IN NONLINEAR REACTION–DIFFUSION SYSTEMS

In reacting systems, in terms of the conserved fluxes and associated forces, the excess entropy production takes the form

$$\begin{aligned}
\partial_t(\tfrac{1}{2}\delta^2 s_v) + \nabla\cdot(\tfrac{1}{2}\delta^2 J_s) &\equiv \tfrac{1}{2}\delta^2\sigma = \delta J_e\cdot\nabla\delta T^{-1} \\
&\quad - \sum_{i=1}^{n}\delta J_i\cdot\nabla\delta(\mu_i T^{-1}) - \delta i\cdot\nabla\delta(\phi T^{-1}) + \delta\mathbf{A}^s\cdot\delta r \\
&= \delta J_e\cdot\nabla\delta T^{-1} + \sum_{i=1}^{n-1}\delta J_i\cdot\nabla(\delta\tilde{\mu}_i T^{-1}) \\
&\quad + \delta i\cdot\nabla(-\delta\phi T^{-1}) + \delta\mathbf{A}^s\cdot\delta r = \delta J\cdot\nabla\delta\mathbf{u} \\
&\quad + \delta\mathbf{A}^s\cdot\delta\mathbf{r}.
\end{aligned} \tag{28}$$

This expression, which generalizes equation (8), is consistent with the classical theory of nonequilibrium thermodynamics and equation (9) for the entropy flux. A generalized form of the functional, equation (10) which uses the excess entropy production should be applied for chemically reacting systems to describe transient behavior of small perturbations. Two perturbed chemical dissipation functions should be introduced into equation (10) and the balance expression must contain the chemical sources of each species in all reactions. Around the steady states which are close to equilibrium.

$$\begin{aligned}
\frac{1}{2}\delta^2 S(t_2) = \min\Big\langle &\frac{1}{2}\delta^2 S(t_1) \\
&+ \int_{t_1,\mathbf{A}}^{t_2} -\frac{1}{2}\delta^2 J_s(\delta\mathbf{J}, \delta\mathbf{u})\cdot\mathrm{d}\mathbf{A}\,\mathrm{d}t \\
&+ \int_{t_1,V}^{t_2}\Big\{\frac{1}{2}\mathbf{L}^{-1}(\mathbf{u}):\delta\mathbf{J}\delta\mathbf{J} + \frac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\delta\mathbf{u}\nabla\delta\mathbf{u} \\
&+ \frac{1}{2}\mathbf{R}:\delta r\delta r + \frac{1}{2}\mathbf{R}^{-1}:(v'^{\mathrm{T}}\delta\mathbf{u})(v'^{\mathrm{T}}\delta\mathbf{u}) \\
&+ \delta\mathbf{w}\cdot\left(\frac{\partial\delta\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J} - v'\delta\mathbf{r}\right)\Big\}\mathrm{d}V\,\mathrm{d}t\Big\rangle.
\end{aligned} \tag{29}$$

The term $v'^{\mathrm{T}}\delta\mathbf{u}$ represents the perturbation of an extended vector of the chemical affinities in the entropy representation, $\mathbf{A}^s$, which is defined below. Both $\mathbf{R}$ terms refer to chemical dissipation described by the nonlinear chemical resistance $\mathbf{R}$. It is important that the background reference state may be highly nonlinear. This property follows from nonlinear chemical resistances (of the entropy representation) which are consistent with the mass action law of Guldberg and Waage [34]. They obey the logarithmic formula [35–38]

$$R_j(\mathbf{C}) = \frac{\mathrm{R}\ln\left[\left(k_j^f \prod_{i=1}^{N} a_i^{\nu_{ij}^f}\right) \Big/ \left(k_j^b \prod_{i=1}^{N} a_i^{\nu_{ij}^b}\right)\right]}{k_j^f \prod_{i=1}^{N} a_i^{\nu_{ij}^f} - k_j^b \prod_{i=1}^{N} a_i^{\nu_{ij}^b}}. \tag{30}$$

Here $a_i = a_i(\mathbf{C})$ are the activities expressed as functions of the reference state, and R is the gas constant.

We now use the mass conservation law for each chemical reaction $\nu^{\mathrm{T}}M = 0$ and an appropriately extended stoichiometric matrix

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

where the rows for $k = 0$ and $k = n$ vanish corresponding with vanishing stoichiometric coefficients for the energy and electricity, to be consistent with the conservation laws. With the independent transfer potentials, equation (5), and independent mass fluxes the classical affinity of the jth reaction (the index n refers here to the last mass component)

$$\mathbf{A}_j = -\sum_{i=1}^{n} \nu_{ij}\mu_i = -(\nu^{\mathrm{T}}\mu)_j \tag{32}$$

can be transformed into its entropy-representation counterpart which operates with the reduced (tilde) chemical potentials. In the present formalism the latter are the thermodynamic forces of mass transfer and satisfy the definitive equation

$$\tilde{\mu}_i \equiv \mu_n M_i M_n^{-1} - \mu_i. \tag{33}$$

The standard affinity can then be extended (mark $\Rightarrow$ in equation (34)) to an expression which can deal with all components of the transfer potential vector, equation (5)

$$\begin{aligned} \mathbf{A}_j^{\mathrm{s}} &= -\sum_{i=1}^{n} T^{-1}\nu_{ij}\mu_i = -\sum_{i=1}^{n} T^{-1}\nu_{ij}(\mu_n M_i M_n^{-1} - \tilde{\mu}_i) \\ &= \sum_{i=1}^{n-1} T^{-1}\nu_{ij}\tilde{\mu}_i \Rightarrow (\upsilon'^{\mathrm{T}}\mathbf{u})_j. \end{aligned} \tag{34}$$

The explicit formula for the transpose of the extended matrix of stoichiometry is

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

where the component index changes from 0 (energy), through $1, 2 \ldots n-1$ (independent mass components), to n (electric current). To verify how the extended vector $\mathbf{A}_j^{\mathrm{s}}$ works, one can multiply the transformed stoichiometric matrix (35) by the transport potential vector, equation (5). As long as all the extra stoichiometric coefficients ν_{0j} and ν_{nj} vanish, the considered product is the vector $\mathbf{A}/T$ whose components are ratios of the usual affinities $\mathbf{A}_j$ and the temperature T. This justifies the use of extension, (34) in the variational principle for perturbations, associated with the minimum of the integral (28). A gauged functional, obtained by applying the divergence theorem to the **w** term of equation (28) can also be used

$$\begin{aligned} \frac{1}{2}\delta^2 S_\sigma^{\mathrm{T}} = \int_{t_1,V}^{t_2} \Big\{ & \frac{1}{2}\mathbf{L}^{-1}(\mathbf{u}) : \delta\mathbf{J}\delta\mathbf{J} + \frac{1}{2}\mathbf{L}(\mathbf{u}) : \nabla\delta\mathbf{u}\nabla\delta\mathbf{u} \\ & + \frac{1}{2}\mathbf{R}^{-1} : (\nu'^{\mathrm{T}}\delta\mathbf{u})(\nu'^{\mathrm{T}}\delta\mathbf{u}) + \frac{1}{2}\mathbf{R} : \delta\mathbf{r}\delta\mathbf{r} - \delta\mathbf{C}(\mathbf{u})\frac{\partial\delta\mathbf{w}}{\partial t} \\ & - \delta\mathbf{J}\cdot\nabla\delta\mathbf{w} - \delta\mathbf{w}\cdot\upsilon'\delta\mathbf{r} \Big\} \mathrm{d}V\,\mathrm{d}t. \end{aligned} \tag{36}$$

This functional has been shown to be more suitable than the original integral, equation (28), for setting the Hamiltonian formalism.

The necessary extremum conditions or the Euler–Lagrange equations are the same for the functionals (28) or (36). With respect to the perturbations $\delta\mathbf{w}$, $\delta\mathbf{J}$, δr and δu they are respectively

$$\frac{\delta\partial\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J} = \upsilon'\delta\mathbf{r} \tag{37}$$

$$\mathbf{L}(\mathbf{u})^{-1}\cdot\delta\mathbf{J} = \nabla\delta w \tag{38}$$

$$\mathbf{R}(\mathbf{u})\cdot\delta\mathbf{r} = \nu'^{\mathrm{T}}\delta\mathrm{w} \tag{39}$$

$$\begin{aligned} \mathbf{a}(\mathbf{u})\frac{\partial\delta\mathbf{w}}{\partial t} &= \nabla\cdot(\mathbf{L}\nabla\delta\mathbf{u}) - \nu'\mathbf{R}^{-1}\delta\mathbf{A}^{\mathrm{s}}(\mathbf{u}) \\ &\underset{u=\mathbf{w}}{\Rightarrow} \nabla\cdot(\mathbf{L}\nabla\delta\mathbf{u}) - \nu'\delta\mathbf{r} \end{aligned} \tag{40}$$

where $\mathbf{a}(\mathbf{u}) \equiv -\partial\mathbf{C}(\mathbf{u})/\partial\mathbf{u}$ and $\mathbf{A}^{\mathrm{s}} = \upsilon'^{\mathrm{T}}u$. The perturbed conservation laws, equation (37) 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 are absent because these quantities are conserved. The perturbed transport is described by equation (38) whereas the perturbed chemical Ohm's law is represented by equation (39). The perturbed equation of change (40), which links the perturbations of the temperature, chemical potentials and electrical potential, does contain the perturbations of sources. We recall at this point that the numerator of equation (30) is an expression for the chemical affinity $\mathbf{A}^{\mathrm{s}} = \upsilon'^{\mathrm{T}}\mathbf{u}$ [37]. Thus, provided that the 'local thermal equilibrium' limit takes place, i.e. $\mathbf{u} = \mathbf{w}$, and the chemical resistances satisfy equation (30), equation (39) is the perturbed mass action kinetics of Guldberg and Waage. The limiting ('local equilibrium') perturbations of sources in equations (37) and (40) are described by the vector

$$\delta\boldsymbol{\sigma} = \begin{bmatrix} v_{01} & \ldots v_{0j} & \ldots v_{0N} \\ \ldots & \ldots & \ldots \\ v_{i1} & \ldots v_{ij} & \ldots v_{iN} \\ \ldots & \ldots & \ldots \\ v_{n1} & \ldots v_{nj} & \ldots v_{nN} \end{bmatrix} \begin{bmatrix} \delta r_1 \\ \ldots \\ \delta r_j \\ \ldots \\ \delta r_N \end{bmatrix} = \begin{bmatrix} 0 \\ \ldots \\ \Sigma\, v_{ij}\delta r_j \\ \ldots \\ 0 \end{bmatrix}. \tag{41}$$

It is interesting 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 (37). An analysis using the relativistic equivalence of the inertial mass and the energy leads then to the conclusion that an effective temperature reciprocal (with tilde sign) should replace the usual temperature reciprocal T^{-1}

$$\tilde{T}^{-1} \equiv T^{-1}(1+\mu_n M_n^{-1}/c^2). \tag{42}$$

This means that 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 electrical potential

$$\tilde{\phi} = \phi - \mu_n M_{\mathrm{el}} M_n^{-1} \tag{43}$$

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. It is easy to see, however, that these corrections are negligible, and our basic description which ignores them is sufficiently exact.

5. PERTURBED THERMODYNAMIC POTENTIALS AND COMMON EXCESS DISSIPATION

An important feature of the four-divergence of the entropy four-vector perturbation $\delta^2\sigma$ leads one to the excess entropy production without any limitations related to the system behavior at its boundary. Moreover, in place of the four-vector of the entropy, a four-vector of another thermodynamic potential can be used, which is obtained from the former via Legendre transformation for each vector component, and the four-divergence of the second differential of that new four-vector again yields the same excess entropy production. This can be shown in case of the local equilibrium (where $J_s = \mathbf{J}\cdot\mathbf{u}$) for the four-vector of the thermodynamic grand potential $(s_v^{\mathrm{T}}, \mathbf{J}_s^{\mathrm{T}})$ which is the following set of the four Legendre transforms for the entropy four-vector (s_v, J_s)

$$s_v^{\mathrm{T}} = s_v - \frac{\partial s_v}{\partial \mathbf{C}}\cdot\mathbf{C} - \frac{\partial s_v}{\partial \mathbf{J}}\cdot\mathbf{J} \tag{44'}$$

$$\mathbf{J}_s^{\mathrm{T}} = J_s - \frac{\partial J_s}{\partial \mathbf{C}}\cdot\mathbf{C} - \frac{\partial J_s}{\partial \mathbf{J}}\cdot\mathbf{J}. \tag{44''}$$

Computing of the pertinent four-divergence yields

$$\begin{aligned} &-\{\partial_t(\tfrac{1}{2}\delta^2 s_v^{\mathrm{T}}) + \nabla\cdot(\tfrac{1}{2}\delta^2 J_s^{\mathrm{T}})\} = \tfrac{1}{2}\partial_t(\delta\mathbf{C}\cdot\delta\mathbf{u} + \delta\mathbf{J}\cdot\delta s_{v,\mathbf{J}}) \\ &+\tfrac{1}{2}\nabla\cdot(\delta\mathbf{C}\cdot\delta\mathbf{J}_{s,\mathbf{C}} + \delta\mathbf{J}\cdot\delta\mathbf{J}_{s,\mathbf{J}}) = \tfrac{1}{2}\partial_t(\delta\mathbf{C}\cdot\delta\mathbf{u}) \\ &+\tfrac{1}{2}\nabla\cdot[\delta\mathbf{C}\cdot\delta\cdot(\mathbf{J}\cdot\mathbf{u}_{\mathrm{c}}) + \delta\mathbf{J}\cdot\delta\mathbf{u})] = \delta\mathbf{u}\cdot\partial_t\delta\mathbf{C} \\ &+\tfrac{1}{2}\nabla\cdot[\delta\mathbf{C}\cdot\delta\cdot(\mathbf{J}\cdot\mathbf{u}_{\mathrm{c}})] + \delta\mathbf{u}\cdot\nabla\cdot\delta\mathbf{J} = \delta\mathbf{J}\cdot\delta\nabla\mathbf{u} \\ &+\delta\mathbf{u}\cdot v'\delta\mathbf{r} = \delta\mathbf{J}\cdot\delta\nabla\mathbf{u} + \delta(v'^{\mathrm{T}}\mathbf{u})\cdot\delta\mathbf{r} = \partial_t(\tfrac{1}{2}\delta^2 s_v) \\ &+\nabla\cdot(\tfrac{1}{2}\delta^2 J_s) \end{aligned} \tag{45}$$

where $s_{v,\mathbf{J}} = 0$ and, due to the conservation laws, equation (37), the last line represents the same excess entropy production as that obtained in equations (8) and (28) with the help of the entropy. In the above transformations the relation $J_s = \mathbf{J}\cdot\mathbf{u}$ was used to determine the partial derivatives $J_{s,\mathbf{C}} = \partial J_s/\partial\mathbf{C} = \mathbf{J}\cdot\partial\mathbf{u}/\partial\mathbf{C}$; $\mathbf{J}_{s,\mathbf{J}} = \partial J_s/\partial\mathbf{J} = \mathbf{u}$. Equation (45) describes equivalence of the thermodynamic potential of the entropy and its Legendre transform as a criterion describing the perturbation dynamics.

From a variational expression describing the second law [or the unperturbed counterpart of the functional (28)] written in the form of the vanishing integral

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

one can pass to various thermodynamic potentials associated with appropriate constraints. For any new thermodynamic potential, in the functionals like that of equation (46), there is no Lagrange multiplier before the perturbed four-divergence of the second differential of that thermodynamic potential. Hence, one can obtain 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. However, there are some practical limitations for this rule since the concentrations of individual components are not really suitable to be new potentials due to the source terms they contain. The balances of energy-type quantities, such as energy, free energy, etc., are suitable. Writing the integrand of equation (46) as follows

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

one can pass to the energy representation of thermodynamics. 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. With the entropy flux expression, equation (9), written in the form

$$J_{\mathrm{e}} = TJ_{\mathrm{s}} + \sum_{1}^{n} \mu_k J_k + \phi i = TJ_{\mathrm{s}} - \sum_{1}^{n-1} \tilde{\mu}_k J_k + \phi i \tag{48}$$

($\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$) the transport part of the excess entropy production σ_{s}^{t} transforms as follows

$$\sigma_s^t = \mathbf{J} \cdot \nabla \mathbf{u} = -T^{-1} \left\{ J_{\mathrm{e}} \cdot T^{-1} \nabla T \right.$$
$$\left. - \sum_{i=1}^{n-1} J_i \cdot T\nabla(\tilde{\mu}_i T^{-1}) + i \cdot T\nabla(\phi T^{-1}) \right\}$$
$$= -T^{-1} \left\{ \left(TJ_{\mathrm{s}} - \sum_{1}^{n-1} \tilde{\mu}_k J_k + \phi i \right) \cdot T^{-1} \nabla T \right.$$
$$\left. - \sum_{i=1}^{n-1} J_i \cdot T\nabla(\tilde{\mu}_i T^{-1}) + i \cdot T\nabla(\phi T^{-1}) \right\} \tag{49}$$

thus yielding, in terms of the primed fluxes and forces

$$\sigma_{\mathrm{s}}^t = \mathbf{J} \cdot \nabla \mathbf{u} = -T^{-1} \left\{ \mathbf{J}_{\mathrm{s}} \nabla T - \sum_{1}^{n-1} J_k \nabla \tilde{\mu}_k + i \cdot \nabla \phi \right\}$$
$$= -T^{-1} \mathbf{J}' \cdot \nabla \mathbf{u}'. \tag{50}$$

Inclusion of the chemical reaction contribution into equation (50) and taking the second-order perturbations leads to the total excess entropy production in the two forms

$$\tfrac{1}{2}\sigma_{\mathrm{s}}^2 \equiv \delta \mathbf{J} \cdot \nabla \delta \mathbf{u} + \delta A^{\mathrm{s}} \cdot \delta \mathbf{r}$$
$$= -T^{-1} \tfrac{1}{2} \sigma_{\mathrm{e}}^2 = T^{-1} (\delta \mathbf{J}' \cdot \nabla \delta \mathbf{u}' + \delta \mathbf{A} \cdot \delta \mathbf{r}). \tag{51}$$

The second line expression contains actually the excess of the energy dissipation

$$\tfrac{1}{2}\sigma_{\mathrm{e}}^2 \equiv -\delta \mathbf{J}' \cdot \nabla \delta \mathbf{u}' - \delta \mathbf{A} \cdot \delta \mathbf{r}. \tag{52}$$

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 (32). The two sets of the phenomenological equations are the non-primed and primed forms of the relations $\mathbf{J} = \mathbf{L} \cdot \nabla \mathbf{u}$ and $\mathbf{r} = \mathbf{R} \cdot \mathbf{A}$ with the positive transport conductances $\mathbf{L}$ and $\mathbf{L}'$ and positive chemical resistances $\mathbf{R}$ and $\mathbf{R}'$. These coefficients, which may depend on the reference state, are linked respectively by $\mathbf{L}' = T\mathbf{L}$ and $\mathbf{R}' = \mathbf{R}T$.

With the components of the entropy four-flux $(s_{\mathrm{v}}, \mathbf{J}_{\mathrm{s}})$ as independent variables, the matrix of independent fluxes is

$$\mathbf{J}' = (J_{\mathrm{s}}, J_1, J_2, \ldots, J_{n-1}, i)^{\mathrm{T}} \tag{53}$$

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

$$\mathbf{C}' = (s_{\mathrm{v}}, c_1, c_2, \ldots, c_{n-1}, c_{\mathrm{el}})^{\mathrm{T}}. \tag{54}$$

Again, $c_{\mathrm{el}} = 0$ (electroneutrality). The new independent transfer potentials are

$$\mathbf{u}'(-T, \tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, -\phi) \tag{55}$$

($\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$). their gradients are independent forces of the transport processes. The Gibbs differential for the governing potential, which is now the energy density $e_{\mathrm{v}} = \rho e$, is written in the form

$$\delta e_{\mathrm{v}} = -\mathbf{u}' \cdot \delta \mathbf{C}'; \quad \delta e_{\mathrm{v}}^2 = -\delta \mathbf{u}' \cdot \delta \mathbf{C}' \geqslant 0. \tag{56}$$

In order not to change signs of the Lagrange multipliers a new vector $\mathbf{u}'$ has been defined in equation (55) so that it appears with minus sign in equation (56). This definition also ensures a conformal invariance of the two production expressions in equation (51).

It is quite essential that due to the change of constraints to those involving the entropy, and 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 (47) becomes

$$\min \int_{t_1,V}^{t_2} T^{-1} \left\langle \left\{ \frac{1}{2} \mathbf{L}'^{-1}(\mathbf{u}') : \mathbf{J}'\mathbf{J}' + \frac{1}{2} \mathbf{L}'(\mathbf{u}') : \nabla\mathbf{u}'\nabla\mathbf{u}' \right.\right.$$
$$+ \frac{1}{2} \mathbf{R}' : \mathbf{rr} + \frac{1}{2} \mathbf{R}'^{-1} : (v'^{\mathrm{T}} \mathbf{u}')(v'^{\mathrm{T}} \mathbf{u}')$$
$$+ \left(\frac{\partial e_{\mathrm{v}}(\mathbf{u}')}{\partial t} + \nabla \cdot J_{\mathrm{e}}(\mathbf{J}', \mathbf{u}') \right)$$
$$+ \sum_{k=1}^{n} w_k' \cdot \left(\frac{\partial c_k(u')}{\partial t} + \nabla \cdot J_k' - (v'\mathbf{r})_k \right)$$
$$\left.\left. + w_0' \left(\frac{\partial s_{\mathrm{v}}(\mathbf{u}')}{\partial t} + \nabla \cdot J_{\mathrm{s}}' \right) \right\} \mathrm{d}V \mathrm{d}t \right\rangle = 0. \tag{57}$$

Here $w'_0 = -T$ and $J_e = -\mathbf{J}'\mathbf{u}'$ and in agreement with equation (48). The transformations of the Onsager's conductance and capacitance matrices, $\mathbf{L}$ and $\mathbf{a}$, follow the established rule, $\mathbf{L}' = P\mathbf{L}P^{\mathrm{T}}$ and $\mathbf{a}' = P\mathbf{a}P^{\mathrm{T}}$, when the transformation of fluxes is of the form $\mathbf{J}' = P\mathbf{J}$; see, e.g. [62]). As in the entropy representation, the introduction of dummy stoichiometric coefficients, such 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 (60)), is

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

$$= \sum_{i=1}^{n-1} v_{ij}\tilde{\mu}_i \Rightarrow (v'^{\mathrm{T}}\mathbf{u}')_j. \tag{58}$$

In the extended affinity of the energy representation, $\mathbf{A}'_j \equiv (v'^{\mathrm{T}}u')_j$, the component index changes from 0 (entropy) through 1, 2 ... $n-1$ (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 (57) is now assigned to the total energy. It follows from equation (57) 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 large brackets $\langle\,\rangle$ of equation (57) it is clear that an analogous integral, obtained by taking T^{-1} off the integral, equation (57), vanishes on its extremal surfaces as well; this observation shows how one is lead to the energy functional. Such a functional contains, as its integral, the energy dissipated plus the product of the new Lagrange multiplier vector and the appropriate balance constraints. The perturbed form of the energy integral is

$$-\frac{1}{2}\delta^2 E(t_2) = \min\Bigg\langle -\frac{1}{2}\delta^2 E(t_1)$$

$$+\int_{t_1,\mathbf{A}}^{t_2} \frac{1}{2}\delta^2 J_e(\delta\mathbf{J}', \delta\mathbf{u}')\cdot \mathrm{d}\mathbf{A}\,\mathrm{d}t$$

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

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

$$+\delta\mathbf{w}'\cdot\left(\frac{\partial\delta\mathbf{C}'(\mathbf{u}')}{\partial t} + \nabla\cdot\delta\mathbf{J}' - v'\delta\mathbf{r}\right)\Bigg\}\mathrm{d}V\,\mathrm{d}t\Bigg\rangle. \tag{59}$$

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 [63] postulational thermodynamics to nonequilibrium, spatially inhomogeneous systems. The perturbed constraints, which now comprise the balances of mass, electric charge and the sourceless entropy, have been multiplied by $\delta\mathbf{w}'$ rather than by $-\delta\mathbf{w}'$. This assures the identification $\delta\mathbf{w}' = \delta\mathbf{u}'$ rather than $-\delta\mathbf{w}' = \delta\mathbf{u}'$ at local equilibrium. New perturbed balances are build into the energy functional, equation (59), with the help of the vector of the Lagrangian multipliers $\delta\mathbf{w}' = (\delta w'_0, \delta w'_1, \delta w'_2, \ldots, \delta w'_{n-1}, \delta w'_n)$. The *extremum* value of the multiplier $\delta\mathbf{w}'$ in the energy function, equation (59) is the perturbed vector of the *kinetic* conjugates $\delta\mathbf{u}'$ of the densities $\mathbf{C}'$, equation (54). On the extremal surfaces of the energy functional, equation (59), the vector $\delta\mathbf{w}'$ coincides with the transport potential vector $\delta\mathbf{u}'$, equation (55), in the limiting situation of the local thermal equilibrium

$$\mathbf{w}' = \mathbf{u}' = (-T, \tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, -\phi). \tag{60}$$

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

$$\mathbf{w} = \mathbf{u} = (T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots,$$

$$\tilde{\mu}_{n-1}T^{-1}, -\phi T^{-1}). \tag{5}$$

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

It follows from equation (57) 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 the 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 we won't discuss here. A simplified free-energy representation, applicable to thermally homogeneous systems, is still quite useful. From equation (57), the perturbed functional of the thermally homogeneous free-energy is

$$-\frac{1}{2}\delta^2 F(t_2) = \min\Bigg\langle -\frac{1}{2}\delta^2 F(t_1)$$

$$+\int_{t_1,\mathbf{A}}^{t_2} \frac{1}{2}\delta^2 J_f(\delta\mathbf{J}', \delta\mathbf{u}')\cdot \mathrm{d}\mathbf{A}\,\mathrm{d}t$$

$$+\int_{t_1,V}^{t_2} \Bigg\{\frac{1}{2}\mathbf{L}'^{-1}(\mathbf{u}') : \delta\mathbf{J}'\delta\mathbf{J}'$$

$$+\frac{1}{2}\mathbf{L}'(\mathbf{u}') : \nabla\delta\mathbf{u}'\nabla\delta\mathbf{u}' + \frac{1}{2}\mathbf{R}' : \delta\mathbf{r}\delta\mathbf{r}$$

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

$$\cdot\left(\frac{\partial\delta\mathbf{c}(\mathbf{u}')}{\partial t} + \nabla\cdot\delta J' - v'\delta\mathbf{r}\right)\Bigg\}\mathrm{d}V\,\mathrm{d}t\Bigg\rangle, \tag{61}$$

with $J_f = J_e - TJ_s$, as follows from equation (57). The following definitions apply

$$\mathbf{J}' = (J_1, J_2, \ldots, J_{n-1}, i)^{\mathrm{T}} \qquad (62)$$

$$\mathbf{c}' = (c_1, c_2, \ldots, c_{n-1}, c_{\mathrm{el}})^{\mathrm{T}} \qquad (63)$$

$$\mathbf{u}' = (\tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, -\phi) \qquad (64)$$

($\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$). In the linear theory, the matrices $\mathbf{L}'$, $\mathbf{u}'$, etc., of the representation are obtained from the matrices $\mathbf{L}'$, $\mathbf{u}'$ of the energy representation by rejection of entries corresponding to the entropy. Yet, 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 embedded. The Euler–Lagrange equations of equation (61) with respect to the perturbations $\delta\mathbf{w}'$, $\delta\mathbf{J}'$, and δr and $\delta\mathbf{u}'$ describe the perturbed dynamics of isothermal reaction–diffusion

$$\frac{\partial \delta \mathbf{c}'(\mathbf{u}')}{\partial t} + \nabla \cdot \delta \mathbf{J}' - v' \delta \mathbf{r} = 0 \qquad (65)$$

$$\mathbf{L}'(\mathbf{u}')^{-1} \cdot \delta \mathbf{J}' = \nabla \delta \mathbf{w}' \qquad (66)$$

$$\mathbf{R}(\mathbf{u}') \cdot \delta \mathbf{r} = v'^{\mathrm{T}} \delta w' \qquad (67)$$

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

$$\underset{\mathbf{u}'=\mathbf{w}'}{\Rightarrow} \nabla \cdot (\mathbf{L}' \nabla \delta \mathbf{u}') - v' \delta \mathbf{r}. \qquad (68)$$

Here $\mathbf{g} = \partial \mathbf{c}'(\mathbf{u}')/\partial \mathbf{u}$ is the positive hessian of the isothermal free energy and $\mathbf{A} = \mathbf{v}'^{\mathrm{T}} \mathbf{u}'$. The perturbed transport and rate equations of thermally homogeneous systems are contained in these formulae.

6. DISSIPATIVE CANONICAL EQUATIONS FOR PERTURBATIONS

Unperturbed 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 to describe irreversible dynamics in terms of a Hamiltonian [60]. In the case of fields, these functionals lead directly to dissipative Hamiltonians identical with those of Onsager's discrete theory, thus making possible related canonical formulations with only one type of brackets (Poissonian brackets). Here we extend these formalisms to perturbations. This seems important since the bracket approaches which stem from dissipative generalizations of concepts of ideal continua use two sorts of brackets [15, 16, 18, 20] and, as such, are not directly associated with extrema of definite physical quantities.

Let us outline the approach for the free energy functional, equation (61), gauged as described above. (Gauging and transpose matrices are designated by the superscript T over the corresponding thermodynamic quantities.) Using in the gauged functional the kinetic equations for perturbations, equation (66) and (67), the following functional is obtained

$$\frac{1}{2}\delta^2 F_\sigma^{\mathrm{T}} = -\iint \Big[\delta c(\mu') \cdot \frac{\partial \delta \mathbf{w}'}{\partial t} + \frac{1}{2} \mathbf{L}'(\mu') : \nabla \delta \mathbf{w}' \nabla \delta \mathbf{w}'$$

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

$$- \tfrac{1}{2} \mathbf{R}'^{-1} : (v^{\mathrm{T}} \delta \mu')(v'^{\mathrm{T}} \delta \mu') \Big] \mathrm{d}x \, \mathrm{d}t \qquad (69)$$

where

$$\mu' \equiv (\mu'_1, \mu'_2, \ldots, \mu'_{n-1}, \phi)$$

$$= -\mathbf{u}' = -(\tilde{\mu}_1, \tilde{\mu}_2, \ldots, \tilde{\mu}_{n-1}, -\phi). \qquad (5')$$

Here, to comply with the popular definitions of diffusivity in equation (70) and (79), we have modified our previous designations replacing the tilde transfer potentials $\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$, by the primed potentials $\mu'_k \equiv \mu_k - \mu_n M_k M_n^{-1}$, with inverted signs. The local equilibrium corresponds with the equalities $\mathbf{w}' = \mathbf{u}'$ or $\mathbf{w}' = -\mu'$. The temperature T is the constant parameter in the above equation.

For practical purposes however, a modified form of equation (69) is suitable, which uses as state variables the concentrations c' instead of the primed chemical potentials μ'. With the former variables, the four-dimensional functional describing the free energy excess is

$$\frac{1}{2}\delta^2 F_\sigma^{\mathrm{T}} = -\iint \Big[\delta c' \cdot \frac{\partial \delta \mathbf{w}'}{\partial t} + \frac{1}{2} \mathbf{L}'(c') : \nabla \delta \mathbf{w}' \nabla \delta \mathbf{w}'$$

$$- \frac{1}{2} \mathbf{W}'(c') : \nabla \delta c' \nabla \delta c' + \frac{1}{2} \mathbf{R}'^{-1} : (v'^{\mathrm{T}} \delta \mathbf{w}')(v'^{\mathrm{T}} \delta \mathbf{w}')$$

$$- \frac{1}{2} \mathbf{R}'^{-1} : (v'^{\mathrm{T}} \delta \mu'(c'))(v'^{\mathrm{T}} \delta \mu'(c')) \Big] \mathrm{d}x \, \mathrm{d}t \qquad (70)$$

where $\mathbf{W}' = (\partial \mu'/\partial c')^{\mathrm{T}} \mathbf{L}' (\partial \mu'/\partial c')$ is a symmetric matrix which contains the isothermal diffusivity matrix, $\mathbf{D}' = \mathbf{L}' \, \partial \mu'/\partial c'$. The functional, equation (70) incorporates the perturbed Hamiltonian

$$\tfrac{1}{2}\delta^2 H_\sigma = \int \big[\tfrac{1}{2} \mathbf{L}'(c') : \nabla \delta \mathbf{w}' \nabla \delta \mathbf{w}'$$

$$+ \tfrac{1}{2} \mathbf{R}'^{-1} : (v'^{\mathrm{T}} \delta \mathbf{w}')(v'^{\mathrm{T}} \delta \mathbf{w}') - \tfrac{1}{2} \mathbf{W}'(c') : \nabla \delta c' \nabla \delta c'$$

$$- \tfrac{1}{2} \mathbf{R}'^{-1} : (v'^{\mathrm{T}} \delta \mu'(c'))(v'^{\mathrm{T}} \delta \mu'(c')) \big] \, \mathrm{d}x. \qquad (71)$$

This is the Hamiltonian of Onsager's type since it contains the difference of the two perturbed dissipation functions. In terms of the Hamiltonian (71) the Euler–Lagrange equation for the perturbed free-energy (70) with respect to the perturbation $\delta c'_k$ is the first canonical equation

$$\frac{\partial \delta w'_k}{\partial t} = -\frac{\delta(\frac{1}{2}\delta^2 H_\sigma)}{\delta c'_k} = -\nabla\cdot(\mathbf{W}'\nabla\delta c')_k + [(\partial\mu'/\partial c')v\mathbf{R}'^{-1}\delta\mathbf{A}(c')]_k. \quad (72)$$

The symbols $\delta/\delta c'_k$ refers to the functional derivatives in the three-dimensional physical space. Otherwise, the extremum conditions of $1/2\delta^2 F^{\mathrm{T}}_\sigma$ with respect to the adjoints $\delta w'_k$ are

$$\frac{\partial \delta c'_k}{\partial t} = \frac{\partial\frac{1}{2}\delta^2 H_\sigma}{\partial w'_k} = -\nabla\cdot\left(\sum_{k=1}^{n} L'_{ik}\nabla\delta w'_k\right) + \sum_{j=1}^{N}\mathbf{R}_j^{-1}v_{kj}\delta A_j(\mathbf{w}') = -\nabla\cdot(\mathbf{v}_k\delta c'_k) + \sum_{j=1}^{N} v_{kj}\delta\mathbf{r}_j(\mathbf{w}'). \quad (73)$$

Here the representations of perturbed fluxes $\delta\mathbf{J}$ and δr in terms of δw_k have been exploited. The two vector canonical equations (72) and (73) coincide at the local equilibrium, when $\mathbf{w}' = \mathbf{u}' = -\mu'$. Then a common equation set follows which can be written exclusively in terms of the perturbed state variables $\delta c'_k$, as the set of *linear* equations of change for perturbations in a diffusion–reaction system

$$\frac{\partial \delta c'_i}{\partial t} = \nabla\cdot\left(\sum_k D'_{ik}\nabla\delta c'_k\right) + \sum_{j=1}^{N} v_{ij}\delta r_j(\mathbf{c}') \left(= -\frac{\delta\frac{1}{2}\delta^2 H_\sigma}{\delta\mu'_i}\right). \quad (74)$$

Equation (74) stems from the nonlinear equations of unperturbed dynamics, with incorporated laws of the isothermal Onsager–Ohm transports and nonlinear chemical kinetics of Guldberg and Waage. The cases when linear or quasilinear equations of change lead in narrowing subspaces to nonlinear equations are known from the analytical theory of energy and mass transfer [75]. A comparison of the approach based on perturbations of thermodynamic potentials with the action-related approaches, which use two sorts of brackets, Poissonian and dissipative bracket, is in progress [76].

8. LOCAL EQUILIBRIUM AS THE SUFFICIENT CONDITION FOR LOCAL STABILITY

Is the 'local thermal equilibrium' effect sufficient for stability? Since the phenomenological equations hold on the extremal surfaces of the functional, equation (29), then, for the vanishing boundary perturbations, the partial time derivative of the three-dimensional integral extracted from equation (29) to be tested as a Liapounov criterion is

$$\begin{aligned}\frac{\partial}{\partial t}\left(\frac{1}{2}\delta^2 P\right) &\equiv \frac{\partial}{\partial t}\left\{\int_{\mathrm{v}}\left[\frac{1}{2}\mathbf{L}:(\nabla\delta\mathbf{u}\nabla\delta\mathbf{u}+\nabla\delta\mathbf{w}\nabla\delta\mathbf{w}) + \frac{1}{2}\mathbf{R}^{-1}:((v'^{\mathrm{T}}\delta\mathbf{w})(v'^{\mathrm{T}}\delta\mathbf{w})+(v'^{\mathrm{T}}\delta\mathbf{u})(v'^{\mathrm{T}}\delta\mathbf{u}))\right]\mathrm{d}V\right\}\\ &= \int_{\mathrm{v}}\{\mathbf{L}:[\nabla\delta\mathbf{u}\nabla\,\partial_t(\delta\mathbf{u})+\nabla\delta\mathbf{w}\nabla\,\partial_t(\delta\mathbf{w})] + \mathbf{R}^{-1}:((v'^{\mathrm{T}}\delta\mathbf{w})(v'^{\mathrm{T}}\,\partial_t\delta\mathbf{w})+(v'^{\mathrm{T}}\delta\mathbf{u})(v'^{\mathrm{T}}\,\partial_t\delta\mathbf{u}))\}\,\mathrm{d}V\\ &= \int_{\mathrm{v}}\{-\nabla\cdot(\mathbf{L}\nabla\delta\mathbf{u})\,\partial_t(\delta\mathbf{u})-\nabla\cdot(\mathbf{L}\nabla\delta\mathbf{w})\,\partial_t(\delta\mathbf{w}) + \mathbf{R}^{-1}:((v'^{\mathrm{T}}\delta\mathbf{w})(v'\,\partial_t\delta\mathbf{w})+(v'^{\mathrm{T}}\delta\mathbf{u})(v'^{\mathrm{T}}\,\partial_t\delta\mathbf{u}))\}\,\mathrm{d}V\end{aligned} \quad (75)$$

where the divergence theorem was used and the boundary term with vanishing perturbations was set to zero. From the last integral of equation (75), with the help of equation (40), the affinity definition, equation (34), and the condition $\mathbf{u} = \mathbf{w}$, the basic inequality follows

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\delta^2 P\right) = -\int_{\mathrm{v}} 2\mathbf{a}:\partial_t(\delta\mathbf{u})\,\partial_t(\delta\mathbf{u})\,\mathrm{d}V \quad (76)$$

where $\mathbf{a}(\mathbf{u}) \equiv -\partial\mathbf{C}(\mathbf{u})/\partial\mathbf{u}$ is the negative of the entropy hessian. Since $\mathbf{a} \geqslant 0$, the condition known from the classical thermodynamics, the above time derivative is negative whenever $\mathbf{u} = \mathbf{w}$. Now let us note that the excess entropy production $V = \frac{1}{2}\delta^2 P$ in the form given by the first integral of equation (75) is locally positive, whenever the constancy of the transport coefficients and chemical resistances can be assumed, corresponding with small perturbations. Then, on the basis of the Liapounov second theorem applied to the positive potential function $V = \frac{1}{2}\delta^2 P$ and its negative time derivative, $1/\,\mathrm{d}\delta^2 P/\mathrm{d}t \leqslant 0$, the local equilibrium, which means that both equalities $\mathbf{u} = \mathbf{w}$ and $\delta\mathbf{u} = \delta\mathbf{w}$ hold, is sufficient for the local asymptotic stability of the steady state close to equilibrium. Yet, neither the 'local thermodynamic limit' nor the 'local thermal equilibrium' in the form of the condition $\mathbf{u} = \mathbf{w}$ (and $\delta\mathbf{u} = \delta\mathbf{w}$) need necessarily follow for a stable process. For large perturbations, however, the terms associated with the change of the transport and rate coefficients with state may be essential and the stability cannot be proven. Thus, it is precisely the nonlinearity property of the transport coefficients and (especially) chemical resistances which may cause violation of stability of chemically reacting fields at large perturbations even at 'local equilibrium'. The similar conclusion has been obtained for lumped systems [76]. This approach adds therefore an important ingredient to the earlier linear stability analyses. In particular, the methods developed here can be extended to the linear wave systems [77, 78]. The conclusions can be compared with those drawn when other methods are applied to stability of nonlinear chemical systems, such as normal modes approach [79] and the energy method [80]. The thermodynamic approach applied here has the unique virtue of easy handling the process constraints, the point which may be difficult to accomplish by other methods.

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REFERENCES

1. Onsager, L., Reciprocal relations in irreversible processes, I and II. *Physics Review*, 1931, **37, 38,** 405–426, 2265–2279.
2. Onsager, L. and Machlup, S., Fluctuations and irreversible processes. I. *Physics Review*, 1953, **91,** 1505–1512.
3. Machlup, S. and Onsager, L., Fluctuations and irreversible processes. II. Systems with kinetic energy. *Physics Review*, 1953, **91,** 1512–1515.
4. Keizer, J., Variational principles in nonequilibrium thermodynamics. *Biosystems*, 1974, **8,** 219–226.
5. Prigogine, I., *Etude Thermodynamique des Phenomenes Irreversibles*. Desoer, Liege, 1947.
6. Gyarmati, I., On the "Governing principle of dissipative processes" and its extension to non-linear problems. *Annals of Physics* (Leipzig), 1969, **23,** 353–375.
7. Gyarmati, I., *Non-equilibrium Thermodynamics*. Springer, Berlin, 1970.
8. Verhas, J., An extension of the "Governing principle of dissipative processes" to nonlinear constitutive equations. *Annals of Physics* (Leipzig), 1983, **40,** 189–195.
9. Rosen, P., On the variational principles for irreversible processes. *Journal of Chemical Physics*, 1953, **21,** 1220–1222.
10. Glansdorff, P. and Prigogine, I., *The Thermodynamic Theory of Structure, Stability and Fluctuations*. Wiley, London, 1971.
11. Essex, Ch., Minimum entropy production in the steady state and the radiative transfer. *Astrophysics Journal*, 1984, **285,** 279–293.
12. 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.
13. Grmela, M. and Teichman, J., Lagrangian formulation of the Maxwell–Cattaneo hydrodynamics. *International Journal of Engineering Science*, 1983, **21,** 297–313.
14. Grmela, M., Bracket formulation for Navier–Stokes equations. *Physics Letters*, 1985, **111A,** 36–40.
15. Grmela, M., Thermodynamics of driven systems. *Physics Review E*, 1993, **48,** 919–930.
16. Grmela, M., Weakly nonlocal hydrodynamics. *Physics Review*, *E*, 1993, **47,** 351–365.
17. Grmela, M., Comments on the relation between Hamiltonian and Lagrangian formulations of mesoscopic dynamics. *Scientific Reports of Kieke Polytechnik, Mechanika*, 1995, **59,** 49–64.
18. Grmela, M. and Lebon, G., Hamiltonian extended thermodynamics. *Journal of Physics A*, 1990, **23,** 3341–3351.
19. Rayleigh, J. W. S., *The Theory of Sound*. Dover, New York, 1945.
20. Beris, A. N. and Edwards, B. J., *Thermodynamics of flowing Systems with Internal Microstructure*. Oxford University Press, Oxford, 1994.
21. Nyiri, B., On the construction of potentials and variational principles in thermodynamics and physics. *Journal of Non-Equilibrium Thermodynamics*, 1991, **16,** 39–55.
22. 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.
23. 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.
24. Gambàr, K. and Màrkus, F., Hamilton–Lagrange formalism of nonequilibrium thermodynamics. *Physics Review*, *E*, 1994, **50,** 1227–1231.
25. Sieniutycz, S. and Ratkje, S. K., Variational principle for entropy in electrochemical transport phenomena. *International Journal of Engineering Science*, 1996, **34,** 549–560.
26. Sieniutycz, S. and Ratkje, S. K., Perturbational thermodynamics of coupled electrochemical heat and mass transfer. *International Journal of Heat & Mass Transfer*, 1996, **39,** 3293–3303.
27. Sieniutycz, S. and Berry, R. S., Least-entropy generation: variational principle of Onsager's type for transient hyperbolic heat and mass transfer. *Physics Review*, *A*, 1992, **46,** 6359–6370.
28. I-Shih, Liu, Method of Lagrange multipliers for exploitation of the entropy principle. *Archives of Rational Mechanical Analysis*, 1972, **46,** 131–148.
29. 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.
30. Anthony, K.-H., Unification of continuum mechanics and thermodynamics by means a Lagrange formalism. *Archives of Mechanics*, 1989, **41,** 511–534.
31. Anthony, K.-H., Phenomenological thermodynamics of irreversible processes within Lagrange formalism. *Acta Physica Hungarica*, 1990, **67,** 321–340.
32. Kotowski, R., On the Lagrange functional for dissipative processes, *Archives of Mechanics*, 1989, **41,** 571–581.
33. Schoelle, M., Hydrodynamik im Lagrangeformalismus: Untersuchungen zur Wärmeleitung in idealen Flüssigkeiten. Diplomarbeit, University of Paderborn, 1994.
34. Guldberg, C. M. and Waage, P., *Etudes sur les Affinités Chimiques*. Brogger et Christie, Christiana, 1867.
35. Grabert, H., Hänggi P. and Oppenheim, I., Fluctuations in reversible chemical reactions. *Physica*, 1983, **117A,** 300–316.
36. Shiner, J. S., Algebraic symmetry in chemical reaction systems at stationary states arbitrarily far from equilibrium. *Journal of Chemical Physics*, 1987, **87,** 1089–1094.
37. Shiner, J. S., A Lagrangian formulation of chemical reaction dynamics far from equilibrium. In *Flow, Diffusion and Rate Processes, Advances in Thermodynamics Series*, Vol. 6, Taylor and Francis, New York, pp. 248–282.
38. Sieniutycz, S., From a least action principle to mass action law and extended affinity. *Chemical Engineering Science*, 1987, **42,** 2697–2711.
39. 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,** 149–182.
40. Sieniutycz, S. and Shiner, J. S., Variational and extremum principles of homogeneous chemical kinetics. II. Minimum dissipation approaches. *Open Systems Information Dynamics*, 1993, **1,** 327–348.
41. Shiner, J. S. and Sieniutycz, S., The chemical dynamics of biological systems: variational and extremal formulations. *Progress in Biophysics & Molecular Biology*, 1994, **62,** 203–221.
42. 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.

43. 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.
44. 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.
45. Perlick, V., The Hamiltonian problem from the global viewpoint. *Journal of Mathematical Physics*, 1992, **33,** 599–606.
46. Finlayson, B. A., *The Method of Weighted Residuals and Variational Principles*. Academic Press, New York, 1972.
47. Caviglia, G., Composite variational principles and the determination of conservation laws. *Journal of Mathematical Physics*, 1988, **29,** 812–816.
48. Morse, P. M. and Feshbach, H., *Methods of Theoretical Physics*. McGraw-Hill, New York, 1953.
49. Sieniutycz, S. and Berry, R. S., Canonical formalism, fundamental equation and generalized thermomechanics for irreversible fluids with heat transfer. *Physics Review, E*, 1993, **47,** 1765–1783.
50. Seliger, R. L. and Whitham, G. B., Variational principles in continuum mechanics. *Proceedings of the Royal Society*, 1968, **302A,** 1–25.
51. Serrin, J., Mathematical principles of classical fluid mechanics. In *Handbook der Physik*, Vol. VII/1, ed. S. Flugge, Springer, Berlin, 1959.
52. Jezierski, J. and Kijowski, J., Thermo-hydrodynamics as a field theory. In *Nonequilibrium Theory and Extremum Principles, Advances in Thermodynamics Series*, Vol. 3. Taylor and Francis, New York, 1990, pp. 282–316.
53. 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. M. Rubi. Springer, Berlin, 1986, pp. 149–174.
54. Sieniutycz, S., Hamiltonian energy-momentum tensor in extended thermodynamics of one-component fluid. *Inzynieria Chemiorno i Procesowa*, 1988, **4,** 839–861.
55. Sieniutycz, S. and Berry, R. S., Conservation laws from Hamilton's principle for nonlocal thermodynamic equilibrium fluids with heat flow. *Physics Review, A*, 1989, **40,** 348–361.
56. Muschik, W. and Trostel, R., Variational principles in thermodynamics. *ZAMM*, 1983, **63,** T190–T192.
57. Jou, D., Casas-Vàzquez, J. and Lebon, G., Extended irreversible thermodynamics: an overview of recent bibliography. *J. Non-Equilibrium Thermodynamics*, 1992, **17,** 383–396.
58. 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.
59. Salmon, R., Hamiltonian fluid mechanics. *Annual Mechanical Review*, 1987, **12,** 51–67.
60. Sieniutycz, S., *Conservation Laws in Variational Thermodynamics*. Kluwer Academic Publishers, Dordrecht, 1994.
61. Kupershmidt, B. A., *The Variational Principles of Dynamics*. World Scientific, New York, 1962.
62. de Groot, S. R. and Mazur, P., *Non-Equilibrium Thermodynamics*, Dover, New York, 1984.
63. Callen, H., *Thermodynamics and an Introduction to Thermostatistics*. Wiley, New York, 1988.
64. Sieniutycz, S. and Shiner, J. S., Variational dynamics of lumped thermal processes. (In preparation.)
65. Levine, R. D. and Tribus, M., *The Maximum Entropy Principle*. MIT Press, Cambridge, MA, 1979.
66. Biot, M., *Variational Principles in Heat Transfer*. Oxford University Press, Oxford, 1970.
67. Kantorovich, L. V. and Krylow, V. I., *Approximate Methods of Higher Analysis*. Nordhoff, Groningen, 1958.
68. Landau, L. D. and Lifshitz, E., *Statistical Physics*. Pergamon, Oxford, 1975.
69. Sundheim, B. R., Transport properties of liquid electrolytes. In *Fused Salts*, ed. B. R. Sundheim. McGraw–Hill, New York, 1964, pp. 165–264.
70. Ekman, A., Liukkonen, S. and Kontturi, K., Diffusion and electric conduction in multicomponent electrolyte systems. *Electrochemica Acta*, 1978, **23,** 243–250.
71. Forland, K. S., Forland, T. and Ratkje, S. K., *Irreversible Thermodynamics—Theory and Applications*. Wiley, Chichester, 1989.
72. Van Zeggeren, F. and Storey, S., *The Computation of Chemical Equilibria*, Cambridge University Press, Cambridge, 1970.
73. Newman, J., *Electrochemical Systems*. Prentice Hall, Englewood Cliffs, 1973.
74. Jackson, D., *Classical Electrodynamics*. Wiley, New York, 1975.
75. Luikov, A. V. and Mikhailov, Yu. A., *Theory of Energy and Mass Transfer*. Energia, Moscow, 1975.
76. Sieniutycz, S. and Shiner, J. S., Thermodynamic potentials and dissipative Lagrangian dynamics of non-equilibrium nonlinear networks. (In preparation.)
77. Sieniutycz, S., The thermodynamics stability of coupled heat and mass transfer described by linear wave equations. *Chemical Engineering Science*, 1981, **36,** 621–624.
78. Sieniutycz, S., The stability of coupled heat and mass transfer in presence of inertial (wave) effects. *Physics Letters*, 1981, **78A,** 433–436.
79. Fernandez, A. and Sinanoglu, O., Locally attractive normal modes for chemical processes. *Journal of Mathematical Physics*, 1984, **25,** 2576–2581.
80. Straughan, B., *The Energy Method, Stability and Nonlinear Convection*. Springer, New York, 1992.