Pergamon

Int. J. Heat Mass Transfer. Vol. 39, No. 15, pp. 3293–3303, 1996

0017–9310/96 $15.00+0.00

0017–9310(95)00387–8

Perturbational thermodynamics of coupled electrochemical heat and mass transfer

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(*Received* 12 *September* 1994)

Abstract—Local equilibrium effect in systems with transport of energy, matter and electric charge is shown to be sufficient for local stability of the processes which satisfy a dissipative variational formalism for perturbations relaxing to a steady state. It is postulated that the effect is an extremal property of those thermodynamic systems which minimize dissipation and whose evolution is governed by an extremum principle describing their natural tendency to fast local relaxations. A pertinent principle extends that of Onsager's [1] to nonstationary quasilinear regime and electrochemical transport. Its resulting form describes an extremum of a functional structure related to grand thermodynamic potential, the Legendere transform of entropy. The principle is set in the physical space–time rather than in the three-dimensional (3D) space and, as such, it substantiates the joint role of thermodynamic potentials and intensity of dissipation. For isolated systems the principle implies a least possible growth of entropy under constraints imposed by conservation laws, whereas for nonequilibrium steady-states its perturbational form implies minimum of a work potential at the steady state. Phenomenological equations, equations of change and bulk overvoltage properties can be derived in complex electrochemical systems. Nonequilibrium temperatures and chemical potentials are interpreted in terms of the Lagrangian multipliers of conservation constraints. These quantities converge to the classical thermodynamic intensities when the local equilibrium is attained. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION

We consider the dynamics of perturbations relaxing towards nonequilibrium steady states in systems with coupled transfer of the heat, mass and electric charge. The transients may occur in the bulk of an electrochemical cell or electrolyser. In the context of a variational principle we testify the meaning and consequences of the assumption that the system is in local thermal equilibrium. The system is a multicomponent one with various transport phenomena in the bulk. The macroscopic motion of the system is neglected by the choice of the vanishing barycentric frame and assumption about the constancy of the system density, ρ, consistent with the mechanical equilibrium assumption. This mechanical equilibrium assumption is a simplification which makes the effects considered more transparent. With this simplification, which is sufficient for a large number of cells encountered in the practice, the total mass density, ρ, is a constant parameter rather than the state variable, and a reference frame in which the whole system rests easily follows.

In spite of large number of works, the proper theoretical setting for entropy and other thermodynamic potentials in nonequilibrium systems is still not clear. Since Onsager's syntheses and his original extremum principle [1–4] there have been numerous attempts to construct variational and extremum principles for irreversible processes, aimed, in particular, on nonlinear generalizations of the theory. Prigogine's [5] reformulation has focused on the entropy production rather than thermodynamic potentials and didn't expose necessity of using of two dissipative potentials, which emerges in all schemes associated with Fokker–Planck equation. On the other hand, for mechanical systems Yang and Song [6] have formulated general theorems of minimum energy and energy dissipation rate. The latter asserts that for a closed and dissipative system in stable dynamic equilibrium its total rate of the energy dissipation is at its minimum value which is compatible with the constraints applied to the system. Essex [7] however has stressed a potential of minimum entropy theorems to yield the nonlinear balance equations for radiative transfer. By introduction of an original concept of caloric coordinate Grmela and Teichman [8] have been able to state a negative-entropy-based H theorem in Lagrangian coordinates, thus showing that, perhaps, this may be a more proper setting for the theorem of maximum entropy S than

NOMENCLATURE

A	cross-sectional area
$\mathbf{b}$	Lagrangian multiplier of relaxation term
$\mathbf{C}$	column vector of molar densities, equation (8)
c_i	molar concentration of the *i*th component
e_v	internal energy of unit volume
$\mathbf{H}_i$	Biot vector associated with flux $\mathbf{J}_i$
h_i	partial molar enthalpy of *i*th component
$\mathbf{i}$	molar flux density of electric current
$\mathbf{J}$	column matrix of independent fluxes, equation (7)
$\mathbf{J}_e$	density of effective energy flux. equation (4)
$\mathbf{J}_q$	density of heat flux
$\mathbf{J}_i$	molar flux density of *i*th component
$\mathbf{J}_s$	density of entropy flux
$\mathbf{J}_u$	density of internal energy flux
M_k	molar mass of *k*th component
$\mathbf{L}$	Onsagerian matrix of phenomenological coefficients
$\mathbf{q}$	vector of generalized state comprising $\mathbf{u}$, $\mathbf{J}$ and $\mathbf{w}$
$\mathbf{r}$	radius vector of spatial coordinates
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 (13)
$\mathbf{w}$	Onsagerian vector of independent transport intensities or Lagrangian multiplier of conservation laws
V	volume
$\mathbf{X}$	vector of independent thermodynamic forces, equation (14).

Greek symbols

∇	nabla operator
δ	first differential, first-order perturbation
δ^2	second differential, second-order perturbation
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
σ	entropy production of unit volume.

Subscripts

q	heat
e	total energy
i	*i*th component
s	entropy
u	internal energy.

Superscripts

T	transpose matrix, Legendre transform
t	time.

various Eulerian frames. Recent microscopic approach of Evans and Baranyi [9] transfers the problem to phase space by postulating that, subject to externally imposed constraints, the rate of decrease of the volume of phase space, which is accessible to the system, is a local minium. However no general strategy has been worked out until now which could allow one to systematically handle nonequilibrium thermodynamic potentials in various irreversible processes.

On the other hand, difficulties in finding exact variational formulations for irreversible processes are still very serious. The well-known Gyarmati's principle [10–13] and some related approaches [14] while of a considerable generality admitting generalizations to quasi-linear processes, belong to the class of the restricted variational principles of Rosen's type [15] or local potential type [16] where some variables and/or derivatives are subjectively 'frozen' to yield a relevant result. Bypassing of older approaches to minimum entropy production [17] seems to be implied in a novel general approach of Nyiri [18] based on construction of certain potentials similar to those known in the theory of electromagnetic field. The difficulties have been especially strong in situations when the irreversible phenomena accompany the dynamical ones, the latter being representative for various partial differential equations of physics [19].

In this work an extremum principle following from an excess entropy balance is formulated for irreversible electrochemical transport. The possibility of variational formulation calls however for substantiation in case when irreversibility enters into the issue. It is already well recognized, that the system of the differential equations admits a variational formulation if and only if it is selfadjoint [20–27]. This means that stringent conditions involving the partial derivatives of the related differential operator must be identifically specified. It is also well known that the typical equations of irreversible processes are, as a rule, not self-adjoint [24, 27, 28], so that one can doubt in the existence of the variational formulation in our case. A suitable substantiation is: 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 non-self adjointness applies), a variational formulation in the extended space spanned on these state variables and certain new variables, called state adjoints, is always possible [27]. This substantiates the so-called composite variational principles, with functionals which are scalar products of the original differential equations and adjoint variables [20, 27, 28]. With this concept, and having a dissipation expression and physical conservation laws (for energy, momentum and species), we are searching here for an extremum of a nonequilibrium potential around a steady state as well as its limiting classical case of extremum of a thermodynamic potential [29]. We assume that the steady state is sufficiently close to equilibrium so that the Onsagerian reciprocity still may be assumed. This limitation is not severe for the transfer processes considered, in which the applicability range of the Onsager symmetries is quite vast, nonetheless, since the limitation is quite fundamental, it will be relaxed in a future work along this line.

In fact, a majority of successful recent variational formulations for irreversible continua involve the space expansion. This is clear if one takes into account that (by suitable substitutions) the formulations which use higher order functionals [18, 30–33] can be broken down into those based on the first-order functionals in an enlarged space. The role of the additional variables has also been appreciated in various action-based approaches to irreversible [34] and reversible continua [35–42] where conservation laws can be derived as independent results. A crucial role of new variables has already been firmly established. Some older variational principles which didn't introduce new variables, had to operate with an exponential factor containing explicitly the time, to preserve the 'time arrow', but they have turned out to be too restrictive [43, 44]. A synthetic analysis of these older approaches has been summarized in reviews [43–45], whereas those novel ones, operating in enlarged spaces, are still waiting for their formal adoption in extended thermodynamics [46, 47].

For the standard set of the balance equations (with balances of the energy, momentum and species) and with the entropy generation criterion, the new or adjoint variables are sort of the nonequilibrium thermodynamic intensities [48]. For a stable local equilibrium they tend to the well-known equilibrium intensities: temperature reciprocal, Planck potentials, etc. Then, the states of the whole system become constrained to reside on the Gibb's equilibrium manifold (where the Gibb's fundamental equation holds), and both state and adjoint variable are connected by that equation.

Nonetheless, at nonequilibrium the state and adjoint variables are no longer dependent. They both span an extended space of the (dependent) thermodynamic variables. As follows from an earlier analysis [48] [see also equations (26)–(28)], any pertinent description without local equilibrium assumption must consistently use a model comprising both the state variables and the adjoints. We show here that such a physical picture is consistent with a variational principle of minimum dissipation which governs relaxations to a steady state, and simplifies to that of Onsager in case of the equilibrium steady-state.

An excess of dissipation intensity with respect to a steady-state, equation (21), is described by two perturbed dissipation functions, $\delta^2\Phi$ and $\delta^2\Psi$, of Onsager's type, expressed in terms of the extended state $(\mathbf{C}, \mathbf{J})$ [or $(\mathbf{u}, \mathbf{J})$], its perturbations, $\delta\mathbf{C}$ and $\delta\mathbf{J}$, and the derivatives of perturbations, $\partial\delta\mathbf{C}/\partial t$, $\nabla\delta\mathbf{C}$., etc. An excess entropy four-vector $(\delta s_v, \delta\mathbf{J}_s)$, whose four-divergence is generated by motions along extremal paths of the variational solution, pertains, as a rule, to an excess of a *kinetic* entropy, which may involve both the classical (static) variables $\mathbf{C}$ and fluxes $\mathbf{J}$. This entropy and its excess are therefore certain nonequilibrium (extended) quantities. A distinction between the static (Gibbsian) and the kinetic (Onsagerian, evolution related) entropies manifests in such situations in an explicit way. The distinction, and the related difference between the thermodynamic and kinetic transfer potentials ($\mathbf{u}$ and $\mathbf{w}$), is a general physical property, one which has a nontrivial significance for the nonequilibrium thermodynamic theory.

2. TOWARDS MINIMIZING THE EXCESS ENTROPY PRODUCTION

For conservative systems the evolution of an isolated system with gradients in temperature T and concentrations c_i follows the path which minimizes the final entropy of the system, under the system constraints which include the conservation laws [48]. While entropy grows, its growth is the least possible one under the system constraints. This statement emphasizes the role of the entropy itself rather than the entropy production. Here, the relaxation towards a state state is in question, but an analogous while a more general reasoning applies. By implying a least increase of the integral representing the excess entropy production during a transient relaxation to a steady state (a nonisolated system) one can derive 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.

The above concept is here verified for electrochemical systems. It turns out to be useful, since the stability of the quasilinear heat, mass and electric charge transfer follows directly from equation (21), for constant potentials at the space–time boundary (under assumption of the negligible convection and absence of viscosity). The extension is also interesting because it shows explicitly the role of the electric work perturbation in the perturbed balances of mass, energy and electric charge, equations (1)–(3), (5), and also in excess equations for thermodynamic potentials, equations (9), (11) and (24). This analysis sheds also a new light towards understanding earlier results which deal with the conservative wave (hyperbolic) heat and mass transfer [48]. It should be noted that the present paper analyses the (parabolic) electrochemical systems which are, in fact, nonconservative, due to the work of the external electric field, and it is only the potential property of this work which makes the direct extension of previous variational results possible. The principle, however, will need reformulation whenever the role of the magnetic effects and/or deviations from Onsagerian symmetries become essential.

As distinguished from ref. [48] the working formulae of the present paper use purposely the definition of state in terms of thermostatic intensities rather than densities, to show explicitly that the consequence of the independence of the state variables and the adjoint variables is the existence of two different temperatures. They may be called the Gibbsian (thermodynamic) temperature and Onsagerian or transfer temperature, and they coincide only at the local equilibrium. Analogous effect pertains to the chemical potentials. The present extension uses the perturbation of an effective energy flux $\delta \mathbf{J}_e$ which includes the transfer of the electric energy. The electric charge conservation yields the divergence property for the electric work which makes use of $\mathbf{J}_e$ admissible, $\mathrm{d}W/\mathrm{d}t = \mathbf{i}\cdot\mathbf{E} = -\mathbf{i}\cdot\operatorname{grad}\phi = -\operatorname{div}(\mathbf{i}\phi)$. This property is valid when the role of the electromagnetic vector potential $\mathbf{A}$ in the electric field $\mathbf{E}$ can be neglected.

3. PERTURBED BALANCE EQUATIONS AND IRREVERSIBLE THERMODYNAMICS

Assuming negligible convection, absence of viscosity terms, and electroneutrality of the solution, the perturbed conservation equations which characterize transients of mass, electric current, and energy are

$$\frac{\partial \delta c_i}{\partial t} + \nabla\cdot\delta\mathbf{J}_i = 0 \tag{1}$$

$$\nabla\cdot\delta\mathbf{i} = 0 \tag{2}$$

$$\frac{\partial \delta e_v}{\partial t} + \nabla\cdot\delta\mathbf{J}_u = -\delta(\mathbf{i}\cdot\nabla\phi). \tag{3}$$

Here c_i, and e_v are the molar concentrations and internal energy per unit volume, and $\mathbf{J}_i$, $\mathbf{J}_u$, and $\mathbf{i}$ are respectively the flux densities of independent component fluxes, internal energy flux and electric current. The immediate relaxation of the electric current is the consequence of the electroneutrality effect incorporated in the model, yet we will keep equation (2) in the above form, to allow generalizations to the form of equation (1) in some involved cases. (The same remark applies to some other formulas with nonvanishing $\delta\mathbf{i}$ in the further part of the text.) The components are neutral [49–52], set according to the Gibbs phase rule [52, 53]. As clarified by Sundheim [49] this setting leads to the independent thermodynamic fluxes. The description of electrochemical systems in terms of neutral components should be distinguished from the conventional ionic description [17, 54]. The visible similarity of the electrochemical model to the standard model of the simultaneous heat and mass transfer (without electric current) is the consequence of using merely component description instead of the ionic description. Yet, in spite of this similarity, the role of the electric current $\mathbf{i}$ in the component-based model is quite nontrivial and the model, equations (1)–(28), describes ionic systems as precisely as the conventional ionic model as long as the charge separation effects can be neglected. This property makes model applicable to the transport in the bulk, where the electroneutrality holds. For $i = \nabla\phi = 0$ all properties of the classical thermal diffusion systems are recovered. A proof of the equivalence between the two descriptions is available [49]. We stress that the use of the component description has several important operational advantages that have been appreciated in full only recently. These are: omission of the troublesome thermodynamic properties of ions, use of the pure chemical (not electrochemical) potentials, working with sets of independent thermodynamic fluxes, explicit electric current in place of partial ionic flows, use of operational electric potentials, and an easy, natural description of electro-mechanical couplings [50–52]. Recent thermo-electrochemistry uses the component formalism quite commonly and successfully, in particular to highly nonisothermal cells and electrolysers with fused salts [51, 52].

The energy equation (3) contains the perturbation of the electric power term $-\mathbf{i}\cdot\nabla\phi$ and the divergence of the perturbed energy flux $\delta\mathbf{J}_u$. The energy flux $\mathbf{J}_u = \mathbf{J}_q + \Sigma h_i \mathbf{J}_i$ where $\mathbf{J}_q$ is the heat flux. Introducing the effective energy flux

$$\mathbf{J}_e = \mathbf{J}_u + \phi\mathbf{i} = \mathbf{J}_q + \sum_1^n h_i\mathbf{J}_i + \phi\mathbf{i} \tag{4}$$

and using the charge conservation law in equation (3) the perturbed energy equation (with the electric work incorporated) becomes sourceless

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

Thus, all perturbed balance constraints take the form of the vanishing space–time divergences and can be written in a common matrix notation [17]

$$\frac{\partial \delta C}{\partial t} + \nabla\cdot\delta\mathbf{J} = 0. \tag{6}$$

The above equation describes the perturbation of the conservation laws with respect to arbitrary reference state. In our case it is a steady-state. Equation

(6) should be used with the matrix of independent fluxes **J**

$$\mathbf{J} = (\mathbf{J}_e, \mathbf{J}_1, \mathbf{J}_2, \ldots \mathbf{J}_{n-1}, \mathbf{i})^{T} \tag{7}$$

(the superscript T means transpose of the matrix) and for the corresponding column vector of densities **C**

$$\mathbf{C} = (e_v, c_1, c_2, \ldots c_{n-1}, 0)^{T}. \tag{8}$$

The nth mass flux $\mathbf{J}_n$ has been eliminated by using the condition $\Sigma \mathbf{J}_i M_i = 0$ for $i = 1, 2, \ldots n$. The last component of **C** equals zero because of the electroneutrality.

Now we need to find an equation describing the perturbation of the entropy four-vector, $\delta(s_v, \mathbf{J}_s)$. Since the derivation proceeds in the way analogous to that known while deriving the standard expression for the entropy production [17, 51] we only adduce here the final result. After combining the twice-perturbed classical Gibbs equation [equation (17) for $\mathbf{a} = 0$] with perturbed conservation laws (6), the four-divergence of the second differential of the entropy four-vector $\delta^2\sigma$ is obtained. Two alternative forms can be used, each based on the classical, local equilibrium entropy.

The first form deals with the traditional variables

$$\begin{aligned}\partial_t(\tfrac{1}{2}\delta^2 s_v) + \nabla\cdot(\tfrac{1}{2}\delta^2\mathbf{J}_s) &\equiv \tfrac{1}{2}\delta^2\sigma \\ &= \delta\mathbf{J}_u\cdot\nabla\,\delta T^{-1} - \sum_{i=1}^{n}\delta\mathbf{J}_i\cdot\nabla\,\delta(\mu_i T^{-1}) \\ &\quad -\delta(T^{-1}\mathbf{i})\cdot\nabla\,\delta\phi \\ &= -T^{-1}\left(\delta\mathbf{J}_q\cdot\nabla\,\delta\ln T + \sum_{i=1}^{n}\delta\mathbf{J}_i\cdot\nabla_T\,\delta\mu_i + \delta\mathbf{i}\cdot\nabla\,\delta\phi\right)\end{aligned} \tag{9}$$

and the perturbation of the entropy flux, $\delta\mathbf{J}_s$, expressed as

$$\delta\mathbf{J}_s \equiv T^{-1}\left(\delta\mathbf{J}_u - \sum_{1}^{n}\mu_k\,\delta\mathbf{J}_k\right) = T^{-1}\left(\delta\mathbf{J}_u + \sum_{1}^{n-1}\tilde{\mu}_k\,\delta\mathbf{J}_k\right) \tag{10}$$

where $\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$. The unperturbed quantities pertain to the reference steady state.

The second form is expressed in terms of the conserved fluxes

$$\begin{aligned}\tfrac{1}{2}\delta^2\sigma &= \delta\mathbf{J}_e\cdot\nabla\,\delta T^{-1} - \sum_{i=1}^{n}\delta\mathbf{J}_i\cdot\nabla\,\delta(\mu_i T^{-1}) \\ &\quad -\delta\mathbf{i}\cdot\nabla\,\delta(\phi T^{-1}) \\ &= \delta\mathbf{J}_e\cdot\nabla\,\delta T^{-1} + \sum_{i=1}^{n-1}\delta\mathbf{J}_i\cdot\nabla\,\delta(\tilde{\mu}_i T^{-1}) \\ &\quad -\delta\mathbf{i}\cdot\nabla\,\delta(\phi T^{-1})\end{aligned} \tag{11}$$

and

$$\begin{aligned}\delta\mathbf{J}_s &\equiv T^{-1}\left(\delta\mathbf{J}_e - \sum_{1}^{n}\mu_k\,\delta\mathbf{L}_k - \phi\,\delta\mathbf{i}\right) \\ &= T^{-1}\left(\delta\mathbf{J}_e + \sum_{1}^{n-1}\tilde{\mu}_k\,\delta\mathbf{J}_k - \phi\,\delta\mathbf{i}\right).\end{aligned} \tag{12}$$

These equations contain (in the perturbed form) the vector of the transport potentials **u**, the matrix of independent fluxes **J**, equation (7) and the associated vector of the independent thermodynamic forces $X = \nabla u$

$$\mathbf{u} = (T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \ldots \tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1}) \tag{13}$$

$$\begin{aligned}\mathbf{X} \equiv \nabla\mathbf{u} = (&\nabla T^{-1}, \nabla(\tilde{\mu}_1 T^{-1}), \nabla(\tilde{\mu}_2 T^{-1}), \\ &\ldots\nabla(\tilde{\mu}_{n-1} T^{-1}), -\nabla(\phi T^{-1}))^{T}.\end{aligned} \tag{14}$$

In the matrix notation introduced, the perturbations of the conserved currents obey the simple relations

$$\delta\mathbf{J}_s = \mathbf{u}\cdot\delta\mathbf{J} \Rightarrow \mathbf{u}\cdot\mathbf{L}\cdot\nabla\,\delta\mathbf{u} \tag{15}$$

$$\tfrac{1}{2}\delta^2\sigma = \delta\mathbf{J}\cdot\nabla\,\delta\mathbf{u} \Rightarrow \mathbf{L} : \nabla\,\delta\mathbf{u}\nabla\,\delta\mathbf{u}. \tag{16}$$

The arrows lead the reader to the corresponding expressions obeyed on the extremal surfaces of the governing functional (21); clearly, the **L** terms in equations (15) and (16) are not a starting formula but rather an outcome of our variational formulation for perturbations. Yet the positiveness of the excess entropy production in equation (11) is associated with the standard phenomenology, whose perturbed form is indicated in equation (16) by arrow. We admit that the Onsager's matrix **L** may depend on the thermodynamic state (represented by the vector **C** or **u**). This pertains to the so-called quasilinear description [12] which is more realistic and useful than the standard linear theory.

The state space of a nonequilibrium system is spanned on both the classical variables and the fluxes. Consequently (in an incompressible system with constant density $\rho = \Sigma M_i c_i$) the entropy density $s_v = \rho s$ should satisfy an extended Gibbs equation

$$\mathrm{d}s_v = \bar{\mathbf{u}}\cdot\mathrm{d}\mathbf{C} + \mathbf{a}\cdot\mathrm{d}\mathbf{J} \tag{17}$$

where $\bar{\mathbf{u}} = \partial s_v/\partial\mathbf{C}$ and $\mathbf{a} = \partial s_v/\partial\mathbf{J}$ are corresponding adjoints of the density **C** and flux **J**. It is only at the genuine equilibrium limit (at the Gibbs surface) when $\bar{\mathbf{u}} = \mathbf{u}$, where **u** is defined by equation (13). This limit involves the equilibrium entropy obeying $\mathrm{d}s_v^{eq} \equiv \mathrm{d}s_v = \mathbf{u}\cdot\mathrm{d}\mathbf{C}$, and its derivatives $\mathbf{u} = \partial s_v^{eq}/\partial\mathbf{C}$ which depend on the classical variables only. These limiting quantities characterize the classical, static entropy at the local equilibrium and define the corresponding transport potentials **u**, equation (13), in terms of this static entropy. Clearly, equations (9)–(16) describe merely this equilibrium limit, which, while restricting the system behavior severely, is nonetheless unusually common. Our analysis of relaxing perturbations in

Sections 4 and 5 shows how this limit is approached by the system.

Undiscovered until now, important features of the four-divergence of the entropy four-vector perturbation $\delta^2\sigma$ are worth stressing. These properties have caused our preference in using this quantity instead of the standard time derivative of the second differential of the entropy [16]. As shown by equations (9) and (11), the former leads to the excess entropy production without any limitations related to the system behavior at its boundary, whereas the latter does this job only for (sometimes too subjectively assumed) vanishing boundary perturbations of the extended state $(\mathbf{C}, \mathbf{J})$. 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 will again yield the same excess entropy production.

Let us verify the above statement in case of the local equilibrium (where $\mathbf{J}_s = \mathbf{J}\cdot\mathbf{u}$) for the four-vector of the thermodynamic grand potential $(s_v^\Gamma, \mathbf{J}_s^\Gamma)$, which is defined as the following set of the four Legendre transforms written down for the entropy four-vector $(s_v, \mathbf{J}_s)$

$$s_v^{\mathrm{T}} = s_v - \frac{\partial s_v}{\partial \mathbf{C}}\cdot\mathbf{C} - \frac{\partial s_v}{\partial \mathbf{J}}\cdot\mathbf{J} \tag{18a}$$

$$\mathbf{J}_s^\Gamma = \mathbf{J}_s - \frac{\partial \mathbf{J}_s}{\partial \mathbf{C}}\cdot\mathbf{C} - \frac{\partial \mathbf{J}_s}{\partial \mathbf{J}}\cdot\mathbf{J}. \tag{18b}$$

Computing of the pertinent four-divergence yields

$$\begin{aligned}
&\partial_t(\tfrac{1}{2}\delta^2 s_v^{\mathrm{T}}) + \nabla\cdot(\tfrac{1}{2}\delta^2\mathbf{J}_s^{\mathrm{T}})\\
&= \tfrac{1}{2}\partial_t(\delta\mathbf{C}\cdot\delta\bar{\mathbf{u}} + \delta\mathbf{J}\cdot\delta\mathbf{a}) + \tfrac{1}{2}\nabla\cdot(\delta\mathbf{C}\cdot\delta\mathbf{J}_{s,C} + \delta\mathbf{J}\cdot\delta\mathbf{L}_{s,J})\\
&= \tfrac{1}{2}\partial_t(\delta\mathbf{C}\cdot\delta\mathbf{u}) + \tfrac{1}{2}\nabla\cdot[\delta\mathbf{C}\cdot\delta\cdot(\mathbf{J}\cdot\mathbf{u}_c) + \delta\mathbf{J}\cdot\delta\mathbf{u})]\\
&= \delta\mathbf{u}\cdot\partial_t\,\delta\mathbf{C} + \tfrac{1}{2}\nabla\cdot[\delta\mathbf{C}\cdot\delta\cdot(\mathbf{J}\cdot\mathbf{u}_c)] + \delta\mathbf{u}\cdot\nabla\cdot\delta\mathbf{J}\\
&= \delta\mathbf{J}\cdot\delta\,\nabla\mathbf{u}
\end{aligned} \tag{19}$$

where due to the conservation laws (6), the last line represents the same excess entropy production as that in equations (9), (11) and (16) with the help of the entropy. In the above transformations the relation $\mathbf{J}_s = \mathbf{J}\cdot\mathbf{u}$ was used to determine the partial derivatives $\mathbf{J}_{s,C} = \partial\mathbf{J}_s/\partial\mathbf{C} = \mathbf{J}\cdot\partial\mathbf{u}/\partial\mathbf{C}$; $\mathbf{J}_{s,J} = \partial\mathbf{J}_s/\partial\mathbf{J} = \mathbf{u}$.

The above result solves the long-standing difficulty of apparent nonequivalence between various thermodynamics potentials, observed if the second order differentials of thermodynamic densities are used in the linear stability approaches [16]. The equivalence shown here occurs only in the range of small perturbations (linear stability, interchangeability operations). It is associated with the equality of the small changes of thermodynamic potentials around equilibrium, known in statistical mechanics [29].

4. ENTROPY EXCESS FUNCTIONAL, EXTREMUM CONDITIONS AND LINK WITH ONSAGER'S CRITERION

We will show that the perturbed dynamics follow from a variational principle for the perturbed entropy four-vector give conservation laws, equation (6). The variational principle, equation (21) below, describes the second law in terms of the two excess dissipation functions. The first is flux dependent and the second is force dependent. Use of both functions is necessary for validity of the variational formulation.

The conservation laws perturbations (6) are built into the entropy functional (21) with the help of the perturbed vector $\delta\mathbf{w}$ which represents the vector of associated Lagrangian multipliers, $\delta\mathbf{w} = (\delta w_0, \delta w_1, \delta w_2, \ldots, \delta w_{n-1}, \delta w_n)$. This vector constitutes an adjoint of the vector differential operator appearing on the left hand side of equation (6). The inclusion of constraints does not change the numerical value of the entropy functional but influences its extremum properties which then correspond to the free (unconstrained) extremum. The physical meaning of $\delta\mathbf{w}$ follows from formal properties of the Lagrangian multipliers, which characterize the change of the optimization criterion with change in the value of the constraint. The extremum value of $\delta\mathbf{w}$ is a vector of kinetic conjugates of the perturbations $\delta\mathbf{C}$ and $\delta\mathbf{J}$ in equation (6), corresponding with the excess entropy function generated by the functional (21). In the local equilibrium limit, on the extremal surfaces of the functional (21) the vector $\mathbf{w}$ and its perturbation $\delta\mathbf{w}$ coincide with the corresponding Gibbsian quantities $\mathbf{u}$ and $\delta\mathbf{u}$, equation (13), and, in a stable process, both perturbations tend to vanish

$$\lim_{t\to\infty}\delta\mathbf{w} = \lim_{t\to\infty}\delta\mathbf{u} = \lim_{t\to\infty}[\delta T^{-1}, (\delta\tilde{\mu}_1/T), (\delta\tilde{\mu}_2/T), \ldots \delta(\tilde{\mu}_n/T), -\delta(\phi T^{-1})] = 0. \tag{20}$$

The coincidence $\mathbf{w}$ and $\mathbf{u}$ does not occur however off any limiting equilibrium solution and, therefore, $\mathbf{w}$ and $\mathbf{u}$ are generally two distinctive sorts of the field variables in the entropy functional extremized. As long as no constraint linking $\mathbf{w}$, $\mathbf{u}$, $\delta\mathbf{w}$ and $\delta\mathbf{u}$ is imposed, $\mathbf{w}$ and $\mathbf{u}$ constitute two fields independent of the other. They may be interpreted, respectively, as the transfer (Onsagerian) intensities and thermodynamic (Gibbsian) intensities, which coincide in a stable limiting situation whenever a sort of local equilibrium emerges. When the limiting manifold is that of Gibbs (genuine equilibrium manifold) strong conditions $\nabla\mathbf{u} = 0$ and $\mathbf{J} = 0$ hold, but they are unnecessary at stable nonequilibrium steady states where only sustainability of a inhomogeneous state in time is realized. Any unperturbed transfer intensity is the Lagrangian multiplier of the unperturbed conservation law, whereas any Gibbsian intensity, equation (13), is the appropriate partial derivative of the entropy with respect to the adjoint extensity. On stable extremal solution $\delta\mathbf{w}$ tends to $\delta\mathbf{u}$ and both tend to vanish at $t \to$

∞. One may regard that a pseudo local-equilibrium situation is created at stable steady states far from equilibrium, and then $\mathbf{w}$ may converge to non-equilibrium intensities $\bar{\mathbf{u}}$, equation (17), that are still the partials of an extended entropy although they then depend on both C_i and J_i (extended thermodynamics).

The governing functional describes the behavior of the perturbed entropy vector between the two fixed times t_1 and a subsequent t_2

$$\begin{aligned}\tfrac{1}{2}\delta^2 S(t_2) = \min\Big\langle \frac{1}{2}\delta^2 S(t_1) \\ + \int_{t_1,A}^{t_2} -\tfrac{1}{2}\delta^2 \mathbf{J}_s(\delta\mathbf{J},\delta\mathbf{u})\,\mathrm{d}\mathbf{A}\,\mathrm{d}t \\ + \int_{t_1,\mathrm{v}}^{t_2} \Big\{ \tfrac{1}{2}\mathbf{L}^{-1}(\mathbf{u}):\delta\mathbf{J}\,\delta\mathbf{J} + \tfrac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\,\delta\mathbf{u}\nabla\,\delta\mathbf{u} \\ + \delta w\cdot\left(\frac{\partial\delta\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J}\right)\Big\}\mathrm{d}V\,\mathrm{d}t\Big\rangle \end{aligned} \qquad (21)$$

where for brevity single integral symbols have been used to multiple space-time integrals. See equation (19) for computation of the perturbation $(1/2)\,\delta^2\mathbf{J}_s(\delta\mathbf{J},\delta\mathbf{u})$ in the local equilibrium model. The derivation of the above functional structure from an error criterion has been omitted here as it is fully analogous to the derivation of the unperturbed structure given in an earlier work (for the conservative thermal processes [48]). Equation (21) states that, $(1/2)\,\delta^2 S(t_2) = \min[(1/2)\,\delta^2 S(t_1) + (1/2)\,\delta^2 S^{\mathrm{prod}} - (1/2)\,\delta^2 S^{\mathrm{exch}}]$. Here $\delta^2 S^{\mathrm{prod}}$ and $\delta^2 S^{\mathrm{exch}}$ are the production and exchange components of the second perturbation of entropy. (The change of entropy itself is obtained for the extremal surface of the unperturbed functional as $(S(t_2) = (S(t_1) + S^{\mathrm{prod}} - S^{\mathrm{exch}}))$, see [48].) For the functional minimum it is required that the first variation of (21) vanish for all free variations of perturbations $\delta\mathbf{u}$, $\delta\mathbf{J}$, their derivatives, $\nabla\,\delta\mathbf{u}$, $\nabla\,\delta\mathbf{J}$ and $\delta\mathbf{w}$ excluding those $\delta\mathbf{u}$ and $\delta\mathbf{J}$ which are frozen to zero at the system boundary. The set of Euler–Lagrange equations

variation derivatives $\delta\Lambda/\delta q^1 = 0$ or

$$\frac{\partial\Lambda}{\partial\mathbf{q}} - \nabla\cdot\frac{\partial\Lambda}{\partial\nabla\mathbf{q}} - \frac{\partial}{\partial t}\frac{\partial\Lambda}{\partial(\partial q/\partial t)} = 0 \qquad (22)$$

where Λ is the integrand of the functional extremized, holds for free variations of the steady-state perturbations $q^1 = (\delta\mathbf{u}, \delta\mathbf{J}$ and $\delta\mathbf{w})$ and for arbitrary fixed region of the physical space.

For the vanishing boundary perturbations [constant state parameters and/or flows at the system boundaries] the surface term in equation (21) can be ignored and the functional (21) can be 'gauged' by transforming it into an equivalent form which yields the same equations for relaxing perturbations. This is made by subtracting from equations (21) the space–time divergence $\partial\,\delta\mathbf{C}\,\delta\mathbf{w}/\partial t + \mathrm{div}(\delta\mathbf{J}\,\delta\mathbf{w})$. As it is well known from variational calculus subtracting such divergences does not change the extremum properties of the original functional, in particular the Euler–Lagrange equation (22) is still valid. The so-transformed functional shows an explicit correspondence to the classical Onsager's criterion [1] whereby the phenomenological laws follow from the restricted variation (frozen $\mathbf{u}$) of the expression

$$\min\int_{\mathrm{v}}(\tfrac{1}{2}\mathbf{L}^{-1}:\mathbf{J}\mathbf{J} - \mathbf{J}\cdot\nabla\mathbf{u})\,\mathrm{d}V \qquad (23)$$

with respect to the fluxes $\mathbf{J}$. This yields $\mathbf{J} = \mathbf{L}\cdot\nabla\mathbf{u}$ as the only outcome; no information about the thermodynamic densities $\mathbf{C}$ or intensities $\mathbf{u}$ is obtained. Extensions involving the conservation laws and equations of change were pursued later in many research groups (Prigogine [5]; de Groot and Mazur [17]; Glansdorff and Prigogine [16]; Gyarmati [11]) and coworkers of these authors.

Onsager's functional (23) can be obtained from our functionals (21) or (24) in the case of equilibrium reference state when $\delta\mathbf{J} = \mathbf{J}$ and the derivative $\partial\,\delta\mathbf{w}/\partial t = \partial\mathbf{w}/\partial t$ vanish. Then, when only $\delta\mathbf{J}$ is varied in equation (24) and $\mathbf{w}$ converges to $\mathbf{u}$ on the extremal surfaces (local equilibrium), the Onsager's functional (24) and his equation $\mathbf{J} = \mathbf{L}\cdot\nabla\mathbf{u}$ follow from equation (24) as the close-to-equilibrium formulae. This shows that Onsager's formulation is limited to equilibrium steady states where not only the matrix $\mathbf{L}$ is symmetric but also the reference state is homogeneous.

A modified or 'gauged' functional (21) has the form

$$\begin{aligned}\tfrac{1}{2}\delta^2\tilde{S} \equiv \min\int_{t_1,\mathrm{v}}^{t_2}\Big[\frac{1}{2}\mathbf{L}(\mathbf{u}):\nabla\,\delta\mathbf{u}\nabla\,\delta\mathbf{u} + \tfrac{1}{2}\mathbf{L}(\mathbf{u})^{-1}:\delta\mathbf{J}\,\delta\mathbf{J} \\ - \delta\mathbf{C}(\mathbf{u})\cdot\frac{\partial\delta\mathbf{w}}{\partial t} - \delta\mathbf{J}\cdot\nabla\,\delta\mathbf{w} \\ + \tfrac{1}{2}\mathbf{b}:(\delta\mathbf{w}-\delta\mathbf{u})(\delta\mathbf{w}-\delta\mathbf{u})\Big]\mathrm{d}V\,\mathrm{d}t. \end{aligned} \qquad (24)$$

The surface term has been omitted here, as it does not influence the partial differential equations for transients. To preserve the explicit convergence of the kinetic perturbations $\delta\mathbf{w}$ to thermodynamic ones $\delta\mathbf{u}$, a term $1/2\mathbf{b}$: $(\delta\mathbf{w}-\delta\mathbf{u})(\delta\mathbf{w}-\delta\mathbf{u})$ has been introduced under the integral of δS^{T} with $\mathbf{b}$ being the Lagrangian multiplier of the penalty constraint $(\delta\mathbf{w}-\delta\mathbf{u})^2 = 0$ which provides the equality $\delta\mathbf{w} = \delta\mathbf{u}$ satisfied by perturbations. The whole term may be interpreted as the excess entropy production of a lower-hierarchy, fast relaxation process which leads $\mathbf{w}$ to $\mathbf{u}$ (and $\delta\mathbf{w}$ to $\delta\mathbf{u}$). Note that the use of $\mathbf{b}$ excludes $\delta\mathbf{w}$ as a Lagrangian multiplier of the perturbed balance equations (6) which was originally assumed in equation (21). In effect equations (21) and (24) are not equivalent; equation (21) is more flexible and general, whereas equation (24) is more restrictive but pertains more accurately to those physical situations in which undoubtedly $\mathbf{u} = \mathbf{w}$ (local equilibria and stable pseudoequilibria at steady state manifolds). Otherwise, it may be shown that equation (21) is capable of describing situations in which potentials **u** and **w** differ, those which, perhaps, may be referred to case of inherent local nonequilibria associated with instabilities. Since however the reference state is not varied, the functional (24) cannot predict neither equality $\mathbf{u} = \mathbf{w}$ nor other properties of reference state, as e.g. the function $L(\mathbf{u})$. These properties must be assumed, which is typical in the stability analyses. Only the weaker condition $\delta\mathbf{w} = \delta\mathbf{u}$ results from equation (24) via variation of **b**, and the stronger one $\mathbf{u} = \mathbf{w}$ must be obtained from an unperturbed counterpart of equation (24), see [48].

5. DISCUSSION OF EXTREMUM CONDITIONS AND LOCAL EQUILIBRIUM

The extremum condition of $(1/2)\,\delta^2\tilde{S}$ with respect to **b** is equation (25), or the constraint which preserves the equality of $\delta\mathbf{w}$ and $\delta\mathbf{u}$

$$\delta\mathbf{u} = \delta\mathbf{w}. \tag{25}$$

On stable paths each of these perturbations tends to vanish regardless of the local equilibrium ($\mathbf{u} = \mathbf{w}$), otherwise both remain finite in time. Other extremum conditions for $(1/2)\,\delta^2\tilde{S}$, equation (24), are equations (26)–(28), which follow the same for both functionals, equations (21) and (24). In the transient situation equations (21), (22) and (24) yield for free variations of $\delta\mathbf{u}$, $\delta\mathbf{J}$ and $\delta\mathbf{w}$ a quasilinear set representing (at $\delta\mathbf{w} = \delta\mathbf{u}$) the model of transients of heat, mass and electric charge

$$\frac{\partial\delta\mathbf{C}(\mathbf{u})}{\partial t} + \nabla\cdot\delta\mathbf{J} = 0 \tag{26}$$

$$\mathbf{L}(\mathbf{u})^{-1}\cdot\delta\mathbf{J} = \nabla\,\delta\mathbf{w} \tag{27}$$

$$\tilde{\mathbf{c}}(\mathbf{u})\cdot\frac{\partial\delta\mathbf{w}}{\partial t} = -\nabla\cdot(\mathbf{L}\cdot\nabla\,\delta\mathbf{u}) \tag{28}$$

where $\tilde{\mathbf{c}} = \partial\mathbf{C}/\partial\mathbf{u}$ is the thermodynamic capacity matrix or the entropy hessian. The extremum conditions for the functional (21) are equations (26)–(28) exclusively, corresponding to a broader physical situation.

Of the extremum conditions (26)–(28), the first equation is, of course, the perturbed vector of the conservation laws in the system whereas the second is the perturbed quasilinear kinetics with the reference-state dependent phenomenological matrix $\mathbf{L}(\mathbf{u})$. The last equation is the perturbed Fourier–Kirchhoff type matrix equation of change, that links the perturbed fields of the temperature, chemical potentials and electrical potential. An equation could also be obtained by eliminating the variable $\delta\mathbf{w}$ from the set, which is a valid result linking the state $\delta\mathbf{u}$ (or $\delta\mathbf{C}$) and the flux $\delta\mathbf{J}$, independent of the balance perturbations. For the special case of the pure heat transfer problem, one could thus eliminate the temperature perturbations from the (perturbed) first and the second Fourier's laws of heat conduction (in spite of the fact that such elimination does not add anything new to these *two classical* equations). In a more general situation, described by equation (21), equations (26)–(28) represent a generalization of the classical model. In practice, however, one assumes the local equilibrium and deals as a rule, with the two equations (27) and (28) rather than with combination of all of them. The theory developed generalizes Onsager's variational approach for the thermo-electrochemical relaxations towards the steady-states which are close to equilibrium. This steady state pertains to the situation when the Onsager's phenomenological coefficients L_{ik} may depend on the thermodynamic state of the system (T and c_i), yet the phenomenological equations remain linear with respect to the forces (gradients). This, nonetheless, can comprise a relatively vast class of systems. The nonlinear relations, which link the extensive and intensive thermodynamic quantities in the reference state, are satisfied due to the quasilinearity assumption which allows one to apply the exact (state dependent) functions $\mathbf{L}(\mathbf{u})$ and $\tilde{\mathbf{c}}(\mathbf{u})$.

A pseudo-local-equilibrium-linked transients and corresponding pseudo-local-equilibrium at a stable steady state can be obtained from equations (26)–(28) even without extra condition (25), as a limiting process. For an unperturbed counterpart of equations (26)–(28) it is well known that the Fourier–Kirchhoff law follows in the local equilibrium limit from the energy conservation equation and the Fourier law of conduction, i.e. the three these equations *are* dependent. Is this local equilibrium effect sufficient for stability? On the extremal surfaces of the functional (21), for the vanishing boundary perturbations, the partial time derivative of the four-dimensional integral of equation (21) is

$$\begin{aligned}
&\frac{\partial}{\partial t}\left(\tfrac{1}{2}\delta^2\Sigma\right)\\
&\quad\equiv \frac{\partial}{\partial t}\left\{\int_{t_1,V}^{t_2}\left[\tfrac{1}{2}\mathbf{L}(\mathbf{u}):(\nabla\,\delta\mathbf{u}\nabla\,\delta\mathbf{u}+\nabla\,\delta\mathbf{w}\nabla\,\delta\mathbf{w})\right]\mathrm{d}V\,\mathrm{d}t\right\}\\
&\quad= \int_{t_1,V}^{t_2}\mathbf{L}(\mathbf{u}):\left[\nabla\,\delta\mathbf{u}\nabla\,\partial_t(\delta\mathbf{u})+\nabla\,\delta\mathbf{w}\nabla\,\partial_t(\delta\mathbf{w})\right]\mathrm{d}V\,\mathrm{d}t\\
&\quad= \int_{t_1,V}^{t_2}\left[-\nabla\cdot(\mathbf{L}\nabla\,\delta\mathbf{u})\,\partial_t(\delta\mathbf{u})-\nabla\cdot(\mathbf{L}\nabla\,\delta\mathbf{w})\,\partial_t(\delta\mathbf{w})\right]\mathrm{d}V\,\mathrm{d}t
\end{aligned} \tag{29}$$

where the divergence theorem was used and the boundary term with vanishing perturbations was set to zero. With the help of equation (28), equation (29) yields

$$\begin{aligned}
\frac{\partial}{\partial t}\left(\tfrac{1}{2}\delta^2\Sigma\right) = \int_{t_1,V}^{t_2}&\left[\tilde{\mathbf{c}}:\partial_t(\delta\mathbf{w})\,\partial_t(\delta\mathbf{u})\right.\\
&\left.+\tilde{\mathbf{c}}^{-1}:\nabla\cdot(\mathbf{L}\nabla\,\delta\mathbf{w})\nabla\cdot(\mathbf{L}\nabla\,\delta\mathbf{u})\right]\mathrm{d}V\,\mathrm{d}t.
\end{aligned} \tag{30}$$

Since the entropy hessian $\tilde{\mathbf{c}} \leqslant 0$, the above time derivative is negative whenever $\delta\mathbf{u} = \delta\mathbf{w}$. Thus, the local equilibrium, which preserves both $\mathbf{u} = \mathbf{w}$ and $\delta\mathbf{u} = \delta\mathbf{w}$, is sufficient for the asymptotic stability of the steady state on the basis of the Liapounov second theorem applied to the positive potential function $V = \frac{1}{2}\delta^2\Sigma$ and its negative time derivative, equation (30), at $\mathbf{u} = \mathbf{w}$. However, the necessity of neither local equilibrium nor the conditions $\mathbf{u} = \mathbf{w}$ or $\delta\mathbf{u} = \delta\mathbf{w}$ for stability are not proven.

In any genuine disequilibrium situation, the variables $\mathbf{w}$ and $\mathbf{u}$ may differ. The distinction between $\mathbf{w}$ and $\mathbf{u}$ is allowed by equation (21) and the stationarity conditions, equations (26)–(28). Should one omit the $\mathbf{b}$ term in equation (24) the coincidence of $\mathbf{w}$ and $\mathbf{u}$ in some systems would not be secured in a general case, and an evolution through a set of disequilibrium states, with $\mathbf{w} \neq \mathbf{u}$, would be admitted. This might refer, in particular, to any system where a growing unstable behavior is observed. Yet, in most situations the equality of $\mathbf{w}$ and $\mathbf{u}$ and its weaker form $\delta\mathbf{w} = \delta\mathbf{u}$ are reasonable limitations, especially when one relies on use of the Onsager's potentials, which, ultimately, have this strong restriction incorporated in their derivation. Then, given conservation laws, the compatibility of kinetics with equilibrium can be attained without any further extra constraints [48, 55].

On the other hand, the possibility of independent $\mathbf{w}$ and $\mathbf{u}$ in a general case proves that an orthodox treatment of the entropy or any other thermodynamic function as function of the classical state $\mathbf{C}$ only is too restrictive. The entropy becomes a function of the extended state $(\mathbf{u}, \mathbf{J}, \ldots)$ in agreement with Truesdell's equipresence principle [56, 57] and extended thermodynamics [46]. This conclusion can be a suitable argument for generalization of the integrand of equation (21) to highly nonequilibrium phenomena, where the classical meaning of the temperature and other intensities is lost, in general when heat transfer or change of local thermodynamic variables occurs at a rate comparable to the internal relaxation of the system.

Our imbedding of the transient process in the four-dimensional space–time has resulted in the following benefits: physical insight to the related functionals in terms of the four-vector of the grand thermodynamic potential S^{T}, removal of subjectively 'frozen' fields, and, of course, the nonlinear background state. For an isolated distributed system approaching equilibrium, this theory implies the least possible increase of the system entropy between any two successive configurations. For steady-state processes (open systems), the principle implies the minimum of the functional (24) related on its extremum surfaces to thermodynamic grand potential, for constant perturbations at the system boundary. Its unperturbed counterpart goes over into the Onsagerian principle around equilibrium. The theory is integral, yet yielding all differential (local) phenomenology, and it does admit variations of all possible physical fields, for known thermodynamic and transport properties which may be nonlinear. The time-dependent functional replaces successfully three-dimensional integrals over physical space, considered in earlier works, which could only describe the properties of the entropy production, but neither the transient behavior nor the behavior of the thermodynamic potential in the sense of equations (18) and (19).

The possibility of more than one temperature in a nonequilibrium fluid has also been shown in the statistical way, in Karkheck's analysis of the Boltzmann kinetic equation, which was obtained from the maximum entropy formalism [58]. Also the Hamilton's action approach [40–42] (which is principally different from the approach used here) distinguish sharply between the static and kinetic intensities. Finally, such a distinction appears explicit in extended irreversible thermodynamics [46] and nonequilibrium molecular dynamics [59]. However, no unifying theory is known until now which could show the equivalence between various kinetic temperatures in all cases. This should be a task of further investigations which should, perhaps, exploit to a larger extent our conclusion that local equilibria are an effect of the reduction of the operational variables occurring on limiting (steady state) manifolds. Nonequilibrium molecular dynamics simulations (with Lennard–Jones particles) have shown [60] that the local thermodynamic functions in a system with severe gradients in temperature have the same value as they would have if the system were in equilibrium. A criterion compatible with this result for the state functions, was that the fluctuation in the temperature was 3% in a control volume. The magnitude of the control volume was so small that the temperature variation across the volume element was also around 3%. This means that we can take $\mathbf{w} = \mathbf{u}$ for most situations encountered in practice. However, this is, by no means, an argument against regarding the thermodynamic state and thermodynamic adjoints as variables independent of each other off the Gibb's equilibrium manifold.

This development, promoting the conclusion that the governing potential of open irreversible systems is related to the excess of the grand potential S^{T} taken in the form of its four-vector (S^{T} is the integral of a nonequilibrium ratio P/T over the volume, or the Legendre transform of the entropy) is in agreement with both classical equilibrium thermodynamics [29] and Grmela's recent results obtained for spatially inhomogeneous irreversible systems [35, 36, 38]. These latter works add also a valuable ingredient to the proof of the conclusion considered, which has therein been obtained by an entirely different approach which uses the powerful bracket formalism for dissipative systems. The present work is complementary to our earlier works [48, 61, 62]. However, those previous works have been directed towards variational formulation of the second law without explicitly defined manifold of attraction, which can be understood there as the equilibrium manifold. All these results call for use of thermodynamic potentials in irreversible processes on an equal footing, as in classical thermodynamics. However, such methodology is often rejected in many contemporary approaches to irreversible thermodynamics, sometimes even at the expense of the paradoxical assignment of the positive sign to the time derivative of entropy in open systems, see, e.g. equation (1.11) in [63]. Nonclassical stability criteria of nonequilibrium steady state, stemming from classical thermodynamics, are also explicit in recent work of Ross and his coworkers [64]. The formulation presented here has a natural change to originate further developments which will consider effects caused by violation of Onsagerian symmetry, for evolutions towards steady states which are located in the state space far from the Gibbs equilibrium surface.

Acknowledgements - This work was supported by a grant from SINTEF. One of the authors (S. S.) acknowledges the kind hospitality of the Laboratory of the Physical Chemistry, NTH, University of Trondheim, Norway.

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