A non-equilibrium internal exchange of energy and matter and its Onsager's-type variational theory of relaxation

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Abstract

An opinion is sometimes heard that the Onsagerian description of heat and mass exchange is not compatible with the commonly used engineering approach based on the hydrodynamic theory of boundary layer, with transfer coefficients and driving forces. However, in this work we prove the compatibility of both descriptions for the same driving forces. Applying a general approach based on the minimum of entropy production to a lumped relaxing system with simultaneous heat and mass transfer between two subsystems, we find the canonical (Hamilton's) structure of the non-equilibrium dynamics, and show a general self-consistent way of derivation of these dynamics.

The relaxation dynamics is derived from a 'thermodynamic Lagrangian' L_σ which uses two dissipation functions: a rate dependent one Φ^*; and a state dependent one Ψ. Two possible variational approaches are compared: the first, which uses dependent variables of state connected by constraints stemming from conservation laws (DVA); and the second, in which the constraints are eliminated in advance, so that the model contains only independent variables (IVA). The first approach is novel, the second is basically an integral version of Onsager's approach in a two-phase context. Both approaches are analyzed via methods of optimal control theory, and make use of ideas based on the Hamilton–Jacobi–Bellman equation (H–J–B theory). It is shown that the DVA has a number of virtues with respect to the IVA: it can deal with the non-truncated thermodynamic entropy and with absolute values of thermodynamic adjoints $(T^{-1}, T^{-1}\mu_i)$, and it gives a complementary relaxation picture for these adjoints, as governed by the relaxation matrix K^{T}, the transpose of the state relaxation matrix K.

Other new physical results elucidate a general optimal-control scheme to construct a non-equilibrium thermodynamic entropy S as the principal function which satisfies an autonomous H–J–B equation and the related Hamilton–Jacobi theory under the constraint of a vanishing thermodynamic Hamiltonian $H_\sigma = \Phi - \Psi$, necessary for S to be a state function. The properties of this entropy are herein analyzed, and it is concluded that the proper non-equilibrium S is that evaluated additively over the homogeneous subsystems. This result, along with the proven Lagrangian or Hamiltonian dynamics of the heat and mass exchange, enhances our confidence to the Onsager's theory. © 1999 Elsevier Science Ltd. All rights reserved.

Nomenclature

A action, area
DVA   dependent variable approach
e internal energy in the thermodynamic relaxation process

E energy or energy-like function in terms of velocities and state coordinates
$H(\mathbf{x}, \mathbf{u}, \mu', \mathbf{p}, t)$ generalized Hamiltonian function adjoining local constraints in a rate form
$H(\mathbf{x}, \mathbf{u}, \mathbf{p}, t)$ Pontryagin's Hamiltonian function of a general continuous process
$H_\sigma = \Phi - \Psi$ dissipative Hamiltonian function of thermodynamic system
IVA   independent variable approach
J performance criterion to be extremized
K^N N-stage cost, a measure of the total intensity of entropy production in a discrete process

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K state relaxation matrix, matrix of the products of the transfer area A and transport coefficients

L Lagrangian, rate of entropy generation

$L_\sigma = \Phi^* + \Psi$ dissipative kinetic potential of a thermodynamic system

L, **L**$^\gamma$ overall conductance matrix and partial conductance matrix of the subsystem γ, respectively

M_i molar mass of i-th component

n vector of mole numbers in thermodynamic process

p_i^γ absolute transfer potentials, derivatives of entropy with respect to energy and mole numbers

p$^\gamma$ vector of absolute transfer potentials in subsystem γ, with coordinates p_i^γ

p^0 equilibrium vector of absolute transfer potentials, with coordinates p_i^0

p* interface vector of absolute transfer potentials, with coordinates p_i^*

P^n single-stage cost, a measure of the local intensity of entropy production in a discrete process

P_s power criterion in the entropy representation

R universal gas constant

R, **R**$^\gamma$ overall resistance matrix and partial resistance matrix of the subsystem γ, respectively

s specific entropy, number of species in the mixture

s_σ state function describing minimal dissipated entropy in the system

S, S thermodynamic entropy and Onsager's restricted entropy, respectively

$S(\mathbf{x}, t)$ optimal entropy-like performance function in terms of the current state and current time

t physical time, time-like variable

T absolute temperature

$\mathbf{u} = (\mathbf{u}, \mu')$ extended control vector including the Lagrange multipliers of local constraints

U region of an admissible control

v_0 entropy production rate in a general process, rate of cost production

$\mathbf{v} = \dot{\mathbf{x}}$ rate vector of a general thermodynamic process

V volume of the physical system

$\mathbf{W} \equiv \Gamma \mathbf{L} \Gamma$ symmetric matrix of second dissipation function

x_0 thermal coordinate (whose extremum is S)

x state vector of a general process with coordinates x_0, **x** and t

$\mathbf{x}^i$, $\mathbf{x}^f$ initial and final space-time vector of the general process, respectively

$\mathbf{X} = \mathbf{p}^\gamma - \mathbf{p}^\delta$ interphase thermodynamic force as difference of potentials **p** in both phases

$\mathbf{X} = (\mathbf{X}^\gamma, \mathbf{X}^\delta)$ thermodynamic forces as deviations of transfer potentials from equilibrium.

Greek symbols

α vector of independent non-equilibrium variables in standard Onsager's theory

Γ^γ thermostatic matrix of subsystem γ based on negative entropy Hessian

$\Gamma = \Gamma^\gamma + \Gamma^\delta$ overall thermostatic matrix of the system

δ variational operator

$\zeta_i^\gamma, \zeta_i^\delta$ Planck potentials of ith component in subsystems γ and δ, respectively

Λ_σ dissipative thermodynamic Lagrangian adjoining the system constraints

μ_i molar chemical potential of ith species

μ_a' Lagrange multipliers of local constraints in the rate form

σ_s entropy production

$\phi_a(\mathbf{x}, t)$ constraining function, ath component of the vector ϕ

$\phi_a'(\mathbf{x}, t)$ time derivative of constraining function, ath component of the vector ϕ'

Φ, Φ^* first dissipation function and its Legendre transform, respectively

Ψ second dissipation function

∇ nabla differential operator.

Subscripts

e energy

i ith component

s entropy, entropy representation

σ dissipative quantity

$'$ derivative related quantity.

Superscripts

f final state

i initial state

T transpose matrix

γ phase γ, gamma subsystem

δ phase δ, delta subsystem

0 final state of equilibrium

$*$ interface value, Legendre transform

$\sim$ enlarged state.

1. Introduction

In spite of many thermodynamic approaches applied recently to chemical engineering problems, the theory of the coefficients of heat and mass transfer and the exchange equations which contain them [1, 2] are most frequently derived from hydrodynamics of real fluids, in particular from the boundary layer theory. By itself, this fact would be no disadvantage, but opinions are sometimes expressed that the basic thermodynamic theory, Onsager [3], Keizer [4] and Lavenda [5], is not compatible with the classical hydrodynamic outcome, and, consequently a restrictiveness of thermodynamics of irreversible processes is suggested. It is shown in this work, however, that this is actually not the case, i.e. not only the two approaches, hydrodynamic and thermodynamic, are compatible, but the thermodynamic approach can contribute much to the rectification and extension of classical results of the theory of heat and mass transfer.

As these extensions can lead to non-linear generalizations of the phenomenological equations, the subject matter is worth investigation. Here we present the analysis of the problem based on deterministic variational principles of irreversible thermodynamics.

Consider a non-equilibrium system shown in Fig. 1. It is a composition of two homogeneous subsystems γ and δ separated by an interface with negligible thermodynamic properties. To present the basic concepts of this paper in a transparent way, we neglect surface phenomena by treating the interface as just a mathematical surface, possibly involving discontinuities of concentrations, enthalpy etc., but not of the temperature and the chemical potentials as the interface is still assumed to be non-dissipative. However, a generalization including surface effects and surface dissipation can still be worked out and it will be the topic of a future work. The subsystems are not in thermodynamic equilibrium, which means that they differ in the values of their intensive parameters, the temperature reciprocals and the Planck potentials. In principle, we assume that both subsystems constitute an isolated system, yet a few remarks will be made throughout the work about the non-adiabatic case. Working within the purely deterministic framework, we revisit here the classical problem of irreversible thermodynamics, which is the relaxation of the overall lumped process to equilibrium.

The difference in the subsystems intensive parameters causes the simultaneous heat and mass transfer between them. We analyze the dynamics of energy and mole numbers during the subsystem's relaxation to equilibrium, with special attention paid to the particular process description, the one with dependent state coordinates connected by the conservation laws, $\phi = 0$. Putting these constraints into a standardized rate form (the form with $\phi' \equiv \mathrm{d}\phi/\mathrm{d}t = 0$), we show the significance of an approach which adjoints the balance constraints to the total intensity of dissipation through Lagrange multipliers in ther-

modynamic functionals. The method resembles Liu's method of thermodynamic multipliers [6], the basic difference being, however, that our method works involving equality constraints, not inequality as in Liu's. Thus, we do not make predictions of inequalities implied by the second law of thermodynamics, but rather we derive the kinetic equations of the process as thermodynamic equalities. They are associated with the minimum of dissipation and hold for a definite model of dissipation contained in the optimized dissipation functionals.

A basic approach to irreversible dynamics is applied here using the integral criterion of minimum entropy production and the corresponding local principles. The optimal control theory and variational calculus help establish a general theoretical scheme governing the phenomenological equations which are the dynamical equations characterizing the behavior of a relaxation process. In fact, our variational approach used not only derives the standard dynamics of exchange processes [1, 2] but also leads to the corresponding representation of Onsagerian irreversible thermodynamics [3, 7]. These dynamics are shown to be Lagrangian or Hamiltonian. They are governed by the thermodynamic entropy S as the principal function of the variational problem, satisfying the basic equation of H–J–B of the optimal control and the related Hamilton–Jacobi equation. The conditions for the principal function S to represent the thermodynamic entropy are established as the additivity and autonomicity of the dissipative Lagrangian L_σ and vanishing of its Legendre transformation H_σ (the dissipative Hamiltonian). Once the two homogeneous subsystems (γ and δ), which differ with values of the transport potentials $(T^{-1}, T^{-1}\mu_i)$, are brought in contact at an initial time t^i, an initial entropy of an isolated system S^i is defined additively over its subsystems ($S^i = S^{i\gamma} + S^{i\delta}$). Knowledge of S^i at an initial time t^i and state x^i allows one to find the final entropy S^f for a given final time t^f (final state x^f) as the sum $S^i + s_\sigma$, where s_σ is the minimal entropy production. The s_σ can be found by any optimization method, in particular by the dynamic programming (Sections 5 and 6 and Appendix). The system entropy S remains additive for each future time instant ($S = S^\gamma + S^\delta$) due to the additivity of the dissipation over subsystems ($L_\sigma = L_\sigma^\delta + L_\sigma^\gamma$). Each method (variational calculus, H–J–B equation or Hamilton–Jacobi theory) lead to the same dynamics and the same governing entropy. These results show that the principles of irreversible heat and mass transfer are consistent with basic laws of dynamics and optimal control, thus enhancing our confidence to the Onsager's theory.

Yet, it should be stressed that the variational principles considered here refer to the so-called first-order systems, meaning that the effects of the kinetic energy are neglected in them. Taking these effects into account would require us to use functionals with second-order derivatives [8–10]. While the optimal control theory
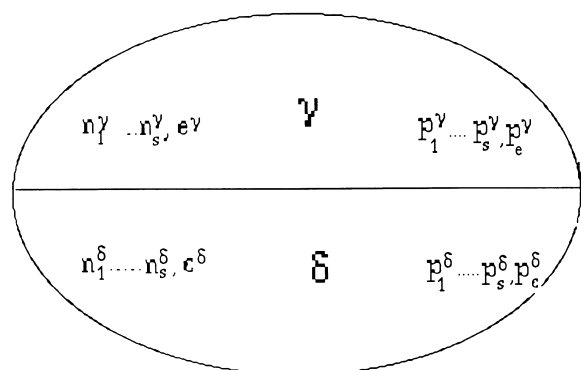

Fig. 1. A non-equilibrium system composed of the two phases γ and δ with the physical properties differing in the values of intensive thermodynamic parameters (transfer potentials).

approach [11, 12], that we use here, works with such systems as well, the structure of the mathematical problem and its analysis are complicated by the simultaneous presence of reversible and dissipative terms, as, for example, encountered in equations of the Cattaneo type [13]. The related analysis would have been then more complicated and would have obscured the main conceptual line of this paper which is the presentation of the entropy S as a potential generated along kinetic paths; thus, this analysis is delegated to a future paper. Equally omitted is a generalization dealing with 'real' thermodynamic surfaces as opposed to our 'mathematical' interfaces. Moreover, we need to emphasize that in this work we do not add any random components to the phenomenological equations as it was done, for example, in the classical work by Onsager and Machlup [8]. Despite working with forward and backward algorithms of dynamic programming as mathematical tools, our dynamics are restricted to relaxation processes only, i.e. we do not consider dynamics of fluctuations and effects of time reversal. Yet, an evaluation can be made of the magnitude and probability of statistical fluctuations in the system on the purely thermodynamic ground [14] based on evaluation of the difference between the non-equilibrium entropy (as an additive quantity over homogeneous subsystems) and the limiting equilibrium entropy.

The state variables of the process are components of the vector variable, $\mathbf{x}^\gamma$ and $\mathbf{x}^\delta$, which describe the 'charges' of energy and mass in the subsystems γ and δ:

$$\mathbf{x}^\gamma = (n_1^\gamma - n_1^{\gamma 0}, n_2^\gamma - n_2^{\gamma 0}, n_s^\gamma - n_s^{\gamma 0}, e^\gamma - e^{\gamma 0}) \tag{1a}$$

$$\mathbf{x}^\delta = (n_1^\delta - n_1^{\delta 0}, n_2^\delta - n_2^{\delta 0}, n_s^\delta - n_s^{\delta 0}, e^\delta - e^{\delta 0}). \tag{1b}$$

The subscripts refer to the species and the energy as the transferred entities. The superscripts refer to two subsystems. While $\mathbf{x} = (\mathbf{x}^\gamma, \mathbf{x}^\delta)$ are our basic variables, we shall also occasionally use the original state vector, $\tilde{\mathbf{n}} = (\mathbf{n}, e)$. The superscript zero refers to the equilibrium which is the thermodynamic equilibrium reached within each of the two subsystems at infinite time under global (system-wise) adiabatic conditions. Clearly, the two subsystems can (but do not have to) represent the same thermodynamic phase. We will report the equation that applies for the first subsystem γ only, if the equation for the second subsystem can be trivially obtained by exchanging γ with δ.

The balance constraints follow from the mass and energy balances expressed in terms of the mole numbers and energies of both subsystems:

$$\phi(\mathbf{x}^\gamma, \mathbf{x}^\delta) = \mathbf{x}^\gamma + \mathbf{x}^\delta = 0. \tag{2}$$

While this is an extremely simple structure, and one of the two vectors, say $\mathbf{x}^\delta$, could be immediately eliminated, we shall not do this as we want to treat all state variables on an equal footing. Another argument against the state variables elimination is that the simplicity of the constraint follows from the use of the conserved quantities
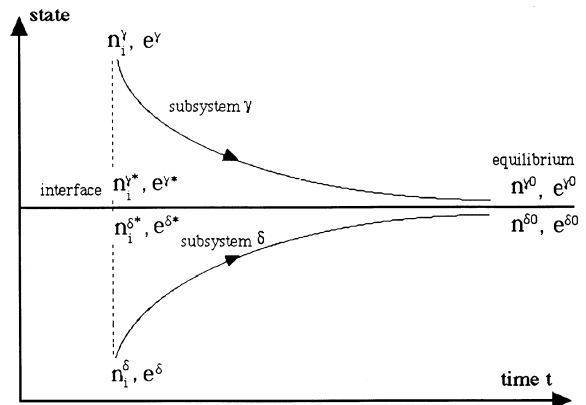

Fig. 2. Relaxation of original state variables in the considered system.

(n_i^γ, e^γ, n_i^δ and e^δ) in a non-reacting system, as the most natural variables in thermodynamics. Should one decide to use arbitrary state variables the constraint equation could be complex, and, in particular, non-linear. The Lagrangian multiplier method, which we use here, is capable of handling more complicated constraints as well. Still we use here the above simple form of the constraint for illustrative purposes. Thus, we will use and compare two approaches to the same thermodynamic problem: the dependent (or constrained) variable approach (DVA); and the independent (or unconstrained) variable approach (IVA).

The rates of change of the coordinates $\mathbf{x}^\gamma$ and $\mathbf{x}^\delta$, $\mathbf{v}^\gamma = \mathrm{d}\mathbf{x}^\gamma/\mathrm{d}t$ and $\mathbf{v}^\delta = \mathrm{d}\mathbf{x}^\delta/\mathrm{d}t$, may be regarded as the control variables for the optimal control problem in which the total dissipation is minimized (Section 4). However, within the framework of the variational calculus no reference to a control action needs to be made. These two viewpoints are compared throughout this work. The rates satisfy the balance constraint in the rate form

$$\phi'(\mathbf{x}, \mathbf{v}) = \mathbf{v}^\gamma + \mathbf{v}^\delta = 0. \tag{3}$$

One can associate the above model with an exchange process in an ideally mixed, batch exchanger in which two immiscible dispersed liquids or two different phases (e.g. solid and gas) exchange energy and species between themselves. Another simple interpretation of this model is the steady-state cocurrent flow of two adjacent streams exchanging heat and matter through an interface. Still another example is the system of two interpenetrating continua which differ in their potentials (T^{-1}, $T^{-1}\mu_i$) at the same point in space.

2. Thermodynamic performance criteria for two descriptions of exchange processes between subsystems

Onsager [3] has shown that the physical formulation of the relaxation thermodynamics in terms of independent
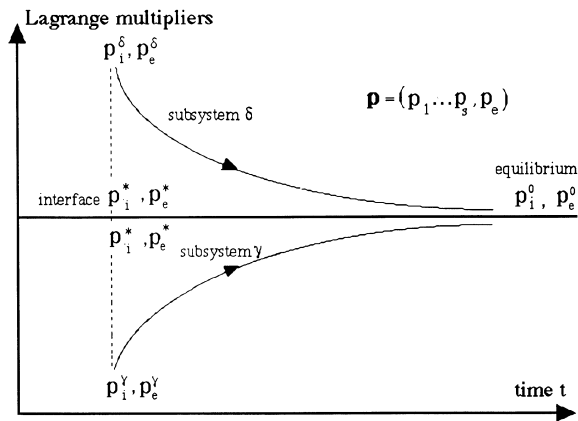
Fig. 3. Relaxation of Lagrange multipliers or thermodynamic adjoints in the considered system. Thermodynamic adjoints are transport potentials for the energy and mass exchange.

variables, α ($\alpha = \mathbf{x}^\gamma = -\mathbf{x}^\delta$ in the above example), involves the minimization of the entropy production, σ_s, given, by definition, as the sum of two dissipation functions, Φ^* and Ψ. The first dissipation function, Φ^*, depends on the process rates $d\alpha/dt$ and possibly on the state α, whereas the second dissipation function, Ψ (called sometimes the generating function), depends only on the state of the process which, however, may involve the second derivatives of the state in those complex models in which not only rates but also state accelerations play a role. These complex processes are called the second-order processes, and are not considered here. This means that we restrict ourselves to processes in which the second dissipation function is a function of the state variables only.

Dealing with a description of irreversible relaxation processes in terms of a set of independent variables, α, Onsager [3] proposed a restricted extremum principle in which the phenomenological equations are obtained by the variations of the rates in the expression which involves the difference between the quadratic dissipation function $\Phi^*(d\alpha/dt)$ and the total derivative of entropy, $dS/dt = (\partial S/\partial \alpha) \, d\alpha/dt$, under the assumption of the fixed state vector, α:

$$P_s \equiv \frac{1}{2}\mathbf{R}:\dot\alpha\dot\alpha - \frac{\partial S(\alpha)}{\partial \alpha}\cdot\dot\alpha. \tag{4}$$

Equation (4) is reminiscent of the structure which appears in the dynamic programming method and the theory of the H–J–B equation [12]. In thermodynamics, equation (4) represents what is sometimes called the 'power expression' [5]. Since this is obtained in the entropy representation, the subscript s is added to distinguish it from similar expressions in the free energy representations, where the related P has a dimension of the mechanical power. Use of the entropy representation is more suitable

for a description of non-isothermal relaxation processes, which we want to study here. In the original Onsager's treatment, the positive definite matrix $\mathbf{R}$, which is called the resistance matrix, was assumed to be state independent. The nature of the restricted extremum of P_s with respect to the rates $\dot\alpha$ at the fixed state α was recognized to be minimum. (This is, of course, easy to confirm by computing the matrix of the second derivatives of P_s which is just $\mathbf{R}$.) Thus, it is the minimization of the power expression (4) with respect to the rates $\mathbf{v} = \dot\alpha$ which leads to the relaxation dynamics

$$\frac{\partial P_s}{\partial \dot\alpha} = \mathbf{R}\dot\alpha - \frac{\partial S(\alpha)}{\partial \alpha} = 0. \tag{5}$$

In terms of the symmetric conductance matrix $\mathbf{L} = \mathbf{R}^{-1}$ the above equation takes its popular form

$$\frac{d\alpha}{dt} = \mathbf{L}\frac{\partial S(\alpha)}{\partial \alpha}. \tag{6}$$

Clearly, due to the requirement of the 'frozen' α, this extremum principle is not a variational principle but a local extremum condition. One can, therefore, ask several basic questions, for example:

- Is this local extremum condition related to any exact variational principle?
- If the answer is yes, what role does equation (5) play in a complete set of extremum conditions describing irreversible motions to equilibrium, and which are the Euler–Lagrange equations of the variational problem?
- What is the generalization of the underlying variational principle to the case when the state variables are not independent? This is the case in which there are physical constraints linking the coordinates of the state vector, such as the simple balance constraints (2) or (3).
- What is the physical meaning of the non-equilibrium entropy S? (the question which is still not answered clearly enough despite the mathematical exactness of Onsager's theory).

We shall show here that an exact variational principle can indeed be associated with the local extremum principle (5) for the non-equilibrium entropy S defined as the sum of the entropies of equilibrium subsystems, $\mathsf{S} = \mathsf{S}^\gamma + \mathsf{S}^\delta$, and that this variational principle expresses the second law of thermodynamics for the whole system in the form which uses a Lagrangian representation of the total entropy production, $\sigma_s = \sigma_s^\delta + \sigma_s^\gamma$. The Lagrangian of the system is the sum of the two dissipation functions, $L_\sigma \equiv \Phi^* + \Psi$, of which the first is rate (and possibly state-)dependent and the second is only state-dependent; L_σ contains contributions of all subsystems to the total dissipation. The subscript σ in L_σ stresses the dissipative nature of this quantity. The variational principle shows that, starting with any non-equilibrium state, an entropy coordinate of an isolated system grows in time with such a rate so that to make its final value a

minimum subject to the conservation constraints for any process duration. These constraints can be taken into account before the variational procedure, in which case the dependent state variables are eliminated, or they can be treated explicitly within the variational procedure, in the rate form (3).

In each approach (dependent or independent variables; DVA or IVA), the restricted nature of the Onsager's extremum principle represents an analog of the H–J–B equation for the minimum of the generated entropy functional. For the Onsager's unconstrained formulation (with independent variables α; IVA) the minimized functional is:

$$J = \int_{t_1}^{t_2} L_\sigma \, dt = \int_{t_1}^{t_2} [\Phi^*(\alpha, \dot{\alpha}) + \Psi(\alpha)] \, dt. \tag{7}$$

The asterisk superscript means that the first dissipation function Φ^* is regarded as the Legendre transform of an original function Φ that appears in the Hamiltonian of the problem. The distinction between Φ^* and Φ is important only in the case that the dissipation is non-quadratic with respect to the rates $\dot{\alpha} = d\alpha/dt$.

On the other hand, for the case of dependent variables (DVA), a minimum of the following function can be considered:

$$J = \int_{t^1}^{t^2} \Lambda_\sigma(\mathbf{x}, \dot{\mathbf{x}}, \mu', t) \, dt \equiv \int_{t^1}^{t^2} [\Phi^*(\mathbf{x}, \dot{\mathbf{x}})$$
$$+ \Psi(\mathbf{x}, t) + \mu' \cdot (\dot{\mathbf{x}}^\gamma + \dot{\mathbf{x}}^\delta)] \, dt \tag{8}$$

where $\mathbf{x} = (\mathbf{x}^\gamma, \mathbf{x}^\delta)$ and the dissipative Lagrangian Λ_σ contains the constraints adjoined via the vector of the Lagrange multipliers, μ'. The presence of time t in Ψ means that the above formulation admits the explicit presence of time in Λ_σ in the case of driven (non-isolated) systems. Analytical forms of the dissipation functions may differ in either case (constrained and unconstrained), and the state constraints cause some equations to be interdependent. In general, the knowledge of both dissipation functions is necessary. While (as we shall see later) Φ and Ψ are numerically equal along extremals of an isolated system, taking $L_\sigma \equiv \sigma_s$ as 2Φ or 2Ψ in the integrand expression would be erroneous, since it is the analytical form of the functional minimized which essentially influences the result of extremization.

We shall compare the principal functions, associated dynamics, dissipative Lagrangians and necessary extremum conditions for the functionals (7) and (8) when the same physical system is described in terms of either the dependent or independent variables. For isolated systems the principal function obtained via minimization of a pertinent quadratic Lagrangian is the change of the system entropy between the initial and the final instant of time. The second-order approximation of the entropy itself

$$S(\mathbf{x}, \mathbf{n}^0, e^0) = S^0(\mathbf{n}^{\gamma 0}, e^{\gamma 0}, \mathbf{n}^{\delta 0}, e^{\gamma 0}) + \mathbf{p}^0 \cdot (\mathbf{x}^\gamma + \mathbf{x}^\delta)$$

$$-\tfrac{1}{2}\Gamma^\gamma : \mathbf{x}^\gamma \mathbf{x}^\gamma - \tfrac{1}{2}\Gamma^\delta : \mathbf{x}^\delta \mathbf{x}^\delta \tag{9}$$

is a suitable potential function for linear dynamics. As it contains the linear term, the ('non-truncated') entropy of an initial state is assumed involving two systems at equilibrium, but not with respect to each other, in terms of that corresponding to the final common equilibrium state and the deviations, $\mathbf{x}$. When dealing with such non-truncated S, the optimal control approach shows the important property of DVA: the Lagrange multipliers of the rate constraints, $\dot{\mathbf{x}} = \mathbf{v}$, are the co-state variables in the Gibbs equation, the transfer potentials $\mathbf{p}$.

3. Thermodynamic driving forces and the entropy production

The $s+1$-dimensional vector $\mathbf{p}^0$ represents the common value of the equilibrium transfer potentials in each subsystem, or the derivatives of the entropy around the equilibrium

$$\mathbf{p}^0 \equiv \frac{\partial S^{\gamma 0}(\mathbf{n}^{\gamma 0}, e^{\gamma 0})}{\partial(\mathbf{n}^{\gamma 0}, e^{\gamma 0})} = \frac{\partial S^{\delta 0}(\mathbf{n}^{\delta 0}, e^{\delta 0})}{\partial(\mathbf{n}^{\delta 0}, e^{\delta 0})}$$
$$= (\zeta_1^0, \zeta_2^0, \dots, \zeta_s^0, T^{0^{-1}}). \tag{10}$$

The potentials are the Planck potentials (the ratios of the chemical potentials and the temperature), and the reciprocals of the temperature. Of equilibrium, the potentials are different for each subsystem. In the interacting phases, the potentials are designated by ζ_i^γ and ζ_i^δ for the Planck potentials and by $T^{\gamma^{-1}}$ and $T^{\delta^{-1}}$ for the reciprocals of the temperature. For the subsystem γ they satisfy, by definition, the equations

$$\mathbf{p}^\gamma \equiv \frac{\partial S^\gamma(\mathbf{n}^\gamma, e^\gamma)}{\partial(\mathbf{n}^\gamma, e^\gamma)} = (\zeta_1^\gamma, \zeta_2^\gamma, \dots, \zeta_s^\gamma, T^{\gamma^{-1}}). \tag{11}$$

An analogous equation holds for the subsystem δ. The deviations of $\mathbf{p}$ from equilibrium values constitute the so-called thermodynamic forces, $\mathbf{X} = (\mathbf{X}^\gamma, \mathbf{X}^\delta)$, in the approach using the dependent variables. For the subsystem γ

$$\mathbf{X}^\gamma \equiv \mathbf{p}^\gamma - \mathbf{p}^0 = \frac{\partial S^\gamma(\mathbf{n}^\gamma, e^\gamma)}{\partial(\mathbf{n}^\gamma, e^\gamma)} - \frac{\partial S^{\gamma 0}(\mathbf{n}^{\gamma 0}, e^{\gamma 0})}{\partial(\mathbf{n}^{\gamma 0}, e^{\gamma 0})}$$

$$= (\zeta_1^\gamma - \zeta_1^0, \zeta_2^\gamma - \zeta_2^0, \dots, \zeta_s^\gamma - \zeta_s^0, T^{\gamma^{-1}} - T^{0^{-1}}) \tag{12}$$

and analogous expressions are valid for $\mathbf{X}^\delta \equiv \mathbf{p}^\delta - \mathbf{p}^0$.

In the framework of the linear dynamical theory, governed by the quadratic approximation of the entropy, equation (9), the forces $\mathbf{X} = (\mathbf{X}^\gamma, \mathbf{X}^\delta)$ can be evaluated as linear functions of the state variables $\mathbf{x}$. The force $\mathbf{X}^\delta$ equals

$$\mathbf{X}^\gamma \equiv \mathbf{p}^\gamma - \mathbf{p}^0 = \frac{\partial^2 S^{\gamma 0}(\mathbf{n}^{\gamma 0}, e^{\gamma 0})}{\partial(\mathbf{n}^{\gamma 0}, e^{\gamma 0}) \, \partial(\mathbf{n}^{\gamma 0}, e^{\gamma 0})} \mathbf{x}^\gamma \tag{13}$$

and $\mathbf{X}^\delta \equiv \mathbf{p}^\delta - \mathbf{p}^0$, the subsystem δ, satisfies the same definition. Thus, defining the constant matrices Γ^γ and Γ^δ as the negative entropy Hessians at equilibrium

$$\Gamma^\gamma \equiv -\frac{\partial^2 S^{\gamma 0}(\mathbf{n}^{\gamma 0}, e^{\gamma 0})}{\partial(\mathbf{n}^{\gamma 0}, e^{\gamma 0})\,\partial(\mathbf{n}^{\gamma 0}, e^{\gamma 0})}; \tag{14}$$

$$\Gamma^\delta \equiv -\frac{\partial^2 S^{\delta 0}(\mathbf{n}^{\delta 0}, e^{\delta 0})}{\partial(\mathbf{n}^{\delta 0}, e^{\delta 0})\,\partial(\mathbf{n}^{\delta 0}, e^{\delta 0})}$$

one writes the thermodynamic forces in the simple forms

$$\mathbf{X}^\gamma \equiv \mathbf{p}^\gamma - \mathbf{p}^0 = -\Gamma^\gamma \mathbf{x}^\gamma; \quad \mathbf{X}^\delta \equiv \mathbf{p}^\delta - \mathbf{p}^0 = -\Gamma^\delta \mathbf{x}^\delta. \tag{15}$$

This leads to evaluation of the transfer potentials $\mathbf{p}$ as functions of non-equilibrium state variables $\mathbf{x}$ in the framework of the linear theory

$$\mathbf{p}^\gamma \equiv \frac{\partial S^\gamma(\mathbf{n}^\gamma, e^\gamma)}{\partial(\mathbf{n}^\gamma, e^\gamma)} = \mathbf{p}^0 - \Gamma^\gamma \mathbf{x}^\gamma; \tag{16}$$

$$\mathbf{p}^\delta \equiv \frac{\partial S^\delta(\mathbf{n}^\delta, e^\delta)}{\partial(\mathbf{n}^\delta, e^\delta)} = \mathbf{p}^0 - \Gamma^\delta \mathbf{x}^\delta.$$

On the other hand, the independent variable approach uses the differences $\mathbf{X}^\gamma - \mathbf{X}^\delta$ which are equal to the differences $\mathbf{p}^\gamma - \mathbf{p}^\delta$ of the transfer potentials (11) in both phases. These should be contrasted with the single-phase deviations of $\mathbf{p}$ described by $\mathbf{X}^\gamma$ and $\mathbf{X}^\delta$.

The second-order approximation of the thermodynamic entropy expressed by the dependent variables $\mathbf{x}$, equation (9), and the Onsagerian form of entropy expressed by the independent variables α, equation (24) below, can be compared. Each entropy is based on the equilibrium entropies of the (two) subsystems, $S = S^\gamma + S^\delta$, but, as explained below, involves different variables. Also the entropy production appears in two forms.

In the first case (DVA) all the (dependent) state variables are treated on an equal footing, and then, since the parameters of the adiabatic equilibrium state are constant and S is not explicitly dependent on time t, we have:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\partial S}{\partial t} + \frac{\partial S}{\partial \mathbf{x}^\gamma} \cdot \mathbf{v}^\gamma + \frac{\partial S}{\partial \mathbf{x}^\delta} \cdot \mathbf{v}^\delta$$

$$= \mathbf{p}^\gamma(\mathbf{x}^\gamma) \cdot \mathbf{v}^\gamma + \mathbf{p}^\delta(\mathbf{x}^\delta) \cdot \mathbf{v}^\delta. \tag{17}$$

This equation can also be written in the form

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \zeta_1^\gamma \frac{\mathrm{d}n_1^\gamma}{\mathrm{d}t} + \zeta_2^\gamma \frac{\mathrm{d}n_2^\gamma}{\mathrm{d}t} \cdots + T^{\gamma^{-1}} \frac{\mathrm{d}e^\gamma}{\mathrm{d}t}$$

$$+ \zeta_1^\delta \frac{\mathrm{d}n_1^\delta}{\mathrm{d}t} + \zeta_2^\delta \frac{\mathrm{d}n_2^\delta}{\mathrm{d}t} \cdots + T^{\delta^{-1}} \frac{\mathrm{d}e^\delta}{\mathrm{d}t} \tag{18}$$

which uses the original state variables $\tilde{\mathbf{n}} = (\mathbf{n}, e)$ rather than their deviations, $\mathbf{x}$.

Accordingly, for the linear dynamics, associated with the quadratic approximation of the entropy, equation (9), the rate of entropy production in terms of the dependent variables $\mathbf{x}$ is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = (\mathbf{p}^0 - \Gamma^\gamma \mathbf{x}^\gamma) \cdot \mathbf{v}^\gamma + (\mathbf{p}^0 - \Gamma^\delta \mathbf{x}^\delta) \cdot \mathbf{v}^\delta. \tag{19}$$

Each of equations (17)–(19) will be applied in the H–J–B equation of the system with dependent state variables, which will write down later. The form explicit in $\mathbf{x}$, equation (19), uses the definition of the transfer potentials $\mathbf{p}$, equation (12), in terms of $\mathbf{x}$, in the framework of the linear theory.

In the second case (IVA) the dependent state variables are eliminated by using the constraining equations in advance, a procedure which leads to the use of independent variables. Then the rate of entropy production exploits in advance the link between the state coordinates, and consequently has the form

$$\sigma_s = \mathbf{p}^\gamma \cdot \mathbf{v}^\gamma + \mathbf{p}^\delta \cdot \mathbf{v}^\delta = (\mathbf{p}^\gamma - \mathbf{p}^\delta) \cdot \dot{\alpha}$$

$$= (\zeta_1^\gamma - \zeta_1^\delta)\frac{\mathrm{d}n_1^\gamma}{\mathrm{d}t} + (\zeta_2^\gamma - \zeta_2^\delta)\frac{\mathrm{d}n_2^\gamma}{\mathrm{d}t} \cdots + (T^{\gamma^{-1}} - T^{\delta^{-1}})\frac{\mathrm{d}e^\gamma}{\mathrm{d}t} \tag{20}$$

where $\dot{\alpha} \equiv \mathbf{v}^\gamma = -\mathbf{v}^\delta$ are the Onsagerian rates. Of course, the equation suggests that, in order to satisfy the second law of thermodynamics, in a simplest case, the fluxes of matter and energy to a definite phase should be proportional to the difference between the instantaneous value of the transport potential $\mathbf{p}$ in this phase and that in the second phase. However, this need not apply when there are discontinuities of the extensive variables through the interface. That difficulty is avoided in the approach involving dependent variables. This is an important feature of DVA which shows its superiority over the IVA.

Under the approximation of linear dynamics and a quadratic entropy function, the constraint-incorporating entropy production, equation (20), assumes the form

$$\sigma_s = \mathbf{p}^\gamma \cdot \mathbf{v}^\gamma + \mathbf{p}^\delta \cdot \mathbf{v}^\delta$$

$$= (\mathbf{p}^0 - \Gamma^\gamma \mathbf{x}^\gamma) \cdot \mathbf{v}^\gamma + (\mathbf{p}^0 - \Gamma^\delta \mathbf{x}^\delta) \cdot \mathbf{v}^\delta$$

$$= -(\Gamma^\gamma \mathbf{x}^\gamma) \cdot \dot{\mathbf{x}}^\gamma - (\Gamma^\delta \mathbf{x}^\delta) \cdot \dot{\mathbf{x}}^\delta = -((\Gamma^\gamma \mathbf{x}^\gamma) + (\Gamma^\delta \mathbf{x}^\delta)) \cdot \dot{\mathbf{x}}^\gamma \tag{21}$$

where the last equality uses the condition $\mathbf{x}^\gamma + \mathbf{x}^\delta = 0$ since the $\mathbf{x}$ represents deviations.

In the formulae (20) and (21) we have taken the coordinates of one subsystem, $\mathbf{x}^\gamma$, as the set of the independent variables, and the state constraint along with its rate representation have been used to pass to the entropy production in terms of these independent variables. Using the traditional notation, i.e. making the identification $\alpha \equiv \mathbf{x}^\gamma$, one gets the entropy production in terms of the Onsager's independent variables α:

$$\sigma_s \equiv \frac{\mathrm{d}S}{\mathrm{d}t} = -\alpha \cdot (\Gamma^\gamma + \Gamma^\delta) \cdot \dot{\alpha} \equiv -\alpha \cdot \Gamma \cdot \dot{\alpha} \tag{22}$$

where by definition $\Gamma = \Gamma^\gamma + \Gamma^\delta$, the positive matrix. The product $-\Gamma\alpha$ equals the difference $\mathbf{X} = \mathbf{p}^\gamma - \mathbf{p}^\delta$ between

the potentials **p** in both phases which from equation (22) can also be identified as $\partial S/\partial \alpha$. This difference is the interphase driving force, which is not the same as the driving force $\mathbf{X}^\gamma$, equation (15). Note that the IVA is not capable of treating any surface discontinuities of the extensive variables in multiphase systems, and this is where the superiority of DVA shows up.

Equation (22) describes the total time derivative of the entropy function (entropy production) in which the state constraint, resulting from the conservation laws, has been incorporated a priori. It is important that this equation defines an entropy S which is a different mathematical function than S of equation (9), not only because it contains the reduced set of non-equilibrium variables (the independent coordinates $\alpha \equiv \mathbf{x}^\gamma$), but also, and more importantly, because it does not contain any linear terms since such terms have been eliminated a priori, through the application of the conservation-law constraint. The quadratic approximation for such an entropy can be obtained from equation (9) in which the state constraint $\mathbf{x}^\gamma + \mathbf{x}^\delta = 0$ is applied, thus yielding

$$S(\alpha, \mathbf{n}^0, e^0) = S(\mathbf{n}^{\gamma 0}, e^{\gamma 0}, \mathbf{n}^{\delta 0}, e^{\gamma 0}) - \tfrac{1}{2}\Gamma : \alpha\alpha \tag{23}$$

where $\Gamma \equiv \Gamma^\gamma + \Gamma^\delta$ contains additive contributions of each phase to the overall coefficient. This result shows that the classical Onsagerian description may be regarded as the particular case of a two-phase IVA when either of two subsystems (of different **p**) has identical properties, in which case $\Gamma^\gamma = \Gamma^\delta$ and $\Gamma = 2\Gamma^\gamma$. Yet, in the general case, the subsystem properties may be different in either IVA or DVA. An analysis shows a greater lucidity of DVA than IVA when physical interpretations of coefficients are essential.

In contrast to the above entropy function, the genuine entropy function in equation (9) does contain linear terms. Therefore, while $S(\mathbf{x})$ is the complete (non-truncated) entropy function of the non-equilibrium two-phase system, the Onsagerian entropy $\mathsf{S}(\alpha)$ should be regarded as the restricted entropy function or a pseudoentropy. To point out the distinction between these functions we use different fonts, (Times) S for the non-truncated thermodynamic entropy and (Geneva) S for the restricted Onsagerian entropy. The restricted entropy resembles the well-known availability function divided by the (equilibrium) temperature of environment, except for one difference. Namely, in the case of the traditional availability, a definite medium is assumed present in an infinite amount as an environment, hence the equilibrium temperature is just the constant temperature of this environment. However, in the case considered, both phases are present in finite amounts, hence the equilibrium temperature is that obtained when the internal (adiabatic) equilibrium is reached between them.

The distinction between $S(\mathbf{x})$ and $\mathsf{S}(\alpha)$ cannot be ignored, as such ignorance can lead to essential errors. While $S(\mathbf{x})$ and $\mathsf{S}(\alpha)$ coincide in the subspaces of vari-

ables satisfying the conservation constraints, their partial derivatives with respect to the state variables differ substantially; $\partial S/\partial \mathbf{x} = \mathbf{p}$ and $\partial \mathsf{S}/\partial \alpha = \mathbf{X} = \mathbf{p}^\gamma - \mathbf{p}^\delta$. Equation (22) proves that the two-phase model considered is consistent with the well-known classical expression for the rate of the entropy production as the product of the thermodynamic flows and forces

$$\sigma_s = \frac{\mathrm{d}\mathsf{S}(\alpha)}{\mathrm{d}t} = \dot\alpha \cdot \frac{\partial \mathsf{S}}{\partial \alpha} = \dot\alpha \cdot \mathbf{X}. \tag{24}$$

From Onsager's [3] basic theory, the evolution of the variables α_i in time, governed by the linear dynamics $\dot\alpha = -\mathbf{K}\alpha$, is related to the gradient of S by the flux–force relation

$$\dot\alpha = \mathbf{L}\frac{\partial \mathsf{S}}{\partial \alpha} = -\mathbf{R}^{-1}\Gamma\alpha \quad (\equiv -\mathbf{K}\alpha) \tag{25}$$

in which the conductance matrix $\mathbf{L} = \mathbf{K}\Gamma^{-1}$ or its inverse, the resistance matrix $\mathbf{R} = \Gamma K^{-1}$, are symmetric matrices. Through its relation to Hessians of the thermodynamic entropy in each phase, the static matrix Γ is also symmetric. However, northing can be said about the symmetry properties of the relaxation matrix $\mathbf{K}$. Therefore, physical theories are usually formulated in terms of the matrices Γ and $\mathbf{R}$, or Γ and $\mathbf{L}$, in terms of which $\mathbf{K} = \mathbf{R}^{-1}\Gamma = \mathbf{L}\Gamma$.

With the opportunity of mentioning the flux–force relationship (25) as the main relationship describing the dissipation dynamics considered here, it is also important to mention the fact that this relationship is completely equivalent, to the lowest order of approximation, with the dynamics described by the (more traditional to engineering application) continuum unsteady diffusion equation. Indeed, if, for simplicity, we consider as our two subsystems, two infinite layers of thickness Δl brought at contact at time $t = 0$, then it is straightforward to show (i.e., using a piecewise parabolic approximation for the spacial dependence of concentration) that if α represents the average (in space) concentration difference before the two sublayers, i.e., $\alpha \equiv \bar c^\gamma - \bar c^\delta$, then it obeys to a lowest-order approximation a dynamic equation exactly as the provided by equation (25) with $\mathbf{R}^{-1}\Gamma \equiv D/3(\Delta x)^2$, where D is the (assumed constant) continuum diffusivity. Thus, the dynamic equations considered here are fully compatible with the traditional partial differential equations describing dissipation through diffusion, and the assumption of constant material properties within each subsystem is consistent with the spatial averages assuming a continuum transport model.

With these adjustments, we are now ready to compare the two approaches to the non-equilibrium thermodynamics, the DVA which treats all non-equilibrium variables **x** on an equal footing, associated with the use of Lagrange multipliers, and the (more traditional) IVA which deals with the independent variables α. This will be done by using the framework of the optimal control

theory as most basic and suitable. As the DVA is a new idea, our analysis focuses mostly on the derivation of DVA equations, from which the IVA equations can be found by elimination of properties of a definite phase (i.e. applying the balance constraint).

4. Adjoining rate constraints and the optimal control formulation

Note that in the optimal control formulation, the control space of rates $\mathbf{v} = (\mathbf{v}^\gamma, \mathbf{v}^\delta)$ is introduced as independent of the state space $\mathbf{x} = (\mathbf{x}^\gamma, \mathbf{x}^\delta)$. As the rates are dependent, our approach adjoins the product of the Lagrange multiplier μ' and the total derivative $d\phi/dt$ of the constraint, equation (3), to the thermodynamic Lagrangian, L_σ, which is the sum of two dissipation functions. In the theory, the function L_σ can thus be quite arbitrary, yet in our examples we assume that L_σ has the quadratic form with respect to rates

$$L_\sigma(\mathbf{x}, \mathbf{v}, t) = \tfrac{1}{2}\mathbf{R}^\gamma(\mathbf{x}):\mathbf{v}^\gamma\mathbf{v}^\gamma + \tfrac{1}{2}\mathbf{R}^\delta(\mathbf{x}):\mathbf{v}^\delta\mathbf{v}^\delta + \Psi(\mathbf{x}^\gamma, \mathbf{x}^\delta, t)$$

(26)

where $\mathbf{x} = (\mathbf{x}^\gamma, \mathbf{x}^\delta)$ and $\mathbf{v} = (\mathbf{v}^\gamma, \mathbf{v}^\delta)$ satisfy the simple differential constraints

$$\dot{\mathbf{x}}^\gamma = \mathbf{v}^\gamma; \quad \dot{\mathbf{x}}^\delta = \mathbf{v}^\delta.$$

(27)

At this point it is unnecessary to make more specific assumptions abut the second dissipation function Ψ, thus, equation (26) admits an arbitrary general form of Ψ.

To treat the balance constraints, the augmented Lagrangian is formed which adjoins the constraints in the rate form (3) to the original Lagrangian, L_σ, equation (26):

$$\Lambda_\sigma(\mathbf{x}, \mathbf{v}, \mu', t) = L_\sigma(\mathbf{x}, \mathbf{v}, t) + \mu'(\mathbf{v}^\gamma + \mathbf{v}^\delta)$$
$$= \tfrac{1}{2}\mathbf{R}^\gamma(\mathbf{x}):\mathbf{v}^\gamma\mathbf{v}^\gamma + \tfrac{1}{2}\mathbf{R}^\delta(\mathbf{x}):\mathbf{v}^\delta\mathbf{v}^\delta$$
$$+ \Psi(\mathbf{x}^\gamma, \mathbf{x}^\delta, t) + \mu'(\mathbf{v}^\gamma + \mathbf{v}^\delta).$$

(28)

The sum $L_\sigma = \Phi^* + \Psi$ is sometimes called the dissipative kinetic potential. The global Lagrangian Λ_σ, which adjoins the constraints, is the integrand of the general dissipation integral, equation (29) below, which has to be minimized subject to the differential constraints (27). For arbitrary Φ^* and Ψ the functional (29) is merely a mathematical construct, without any physical relation to the second law of thermodynamics. However, as long as a certain stringent condition is fulfilled for Φ^* and Ψ, which requires a time-independent Ψ to be equal to Φ, or the Legendre transform of Φ^* [see equations (74)–(76) below], the functional (29) describes the second law in a non-equilibrium system between the two time instants, t^1 and t^2:

$$J = \int_{t^1}^{t^2} \Lambda_\sigma(\mathbf{x}, \mathbf{v}, \mu', t)\,dt$$

$$\equiv \int_{t^1}^{t^2} [\Phi^*(\mathbf{x}, \mathbf{v}) + \Psi(\mathbf{x}, t) + \mu'\cdot(\mathbf{v}^\gamma + \mathbf{v}^\delta)]\,dt$$

$$= \int_{t^1}^{t^2} \left[\tfrac{1}{2}\mathbf{R}^\gamma(\mathbf{x}):\mathbf{v}^\gamma\mathbf{v}^\gamma + \tfrac{1}{2}\mathbf{R}^\delta(\mathbf{x}):\mathbf{v}^\delta\mathbf{v}^\delta + \Psi(\mathbf{x}^\gamma, \mathbf{x}^\delta, t) \right.$$

(29)

$$\left. + \mu'\cdot(\mathbf{v}^\gamma + \mathbf{v}^\delta) \right]\,dt.$$

This is the process performance index which should be minimized subject to the rate-defining constraints, equation (27), and for the arbitrary fixed duration $t^f - t^i$. An arbitrary initial time t^i (e.g., $t^i = 0$) can be assumed admissible for an autonomous system. The first line of this equation describes a general structure proper for the optimal control formulation, whereas the second line refers to the example with a quadratic dissipation function Φ^*. Clearly, representations with rates as the derivatives of state variables [as in equation (8)] are forms pertinent for direct use of the variational calculus [15] and the methods of classical mechanics [16]. On the other hand, the optimal control formulations, in particular the dynamic programming, which we use here as a basis for any representation of the problem (DVA or IVA), requires the minimization of J, equation (29), subject to the simple equations of state (27).

As opposed to the traditional methods, quoted above, a most popular version of the dynamic programming, the so-called backward algorithm [17–21], generates a minimum value of the functional J (or a minimum of a final entropy coordinate; Section 5) as a function of initial states and initial times, for an arbitrary but fixed final state and final time

$$s_\sigma(\mathbf{x}^{\gamma i}, \mathbf{x}^{\delta i}, t^i) \equiv \min J = \min \int_{t^i}^{t^f} \Lambda_\sigma\,dt.$$

(30)

A dual of the same problem, the so-called forward algorithm, for the same quantity $s_\sigma \equiv \min J$, generates s_σ as a function of final states and final times (for an arbitrary but fixed initial state and initial time), and this refers to a maximum of an initial entropy coordinate, Section 5. We stress that both backward and forward algorithms deal here with the same physical process of relaxation understood as the 'forward-in-time' approach of the system to the equilibrium, and they have nothing in common with the time-inverted dynamics which should be attributed to the fluctuations around the equilibrium. Once the initial and final states and the initial (non-equilibrium) entropy of the system are assumed at a fixed initial time instant t^i, the minimization principle described by equation (30) leads to the final non-equilibrium entropy $S^f = S^i + s_\sigma$ at the fixed final time instant t^f. Yet, due to a possible dependence of J on the process duration,

the extremal function s_σ need not always be an increment of the thermodynamic entropy, which has to be a time-independent state function. In general, the integration of equation (30) along extremal paths generates s_σ as the increment of the entropy function or its time-dependent generalization. The former is obtained for the quadratic and time-independent dissipation functions Φ^* and Ψ, and for Ψ being the Legendre transformation of Φ^* expressed in terms of the state $\mathbf{x}$. These conditions assure vanishing of the 'thermodynamic Hamiltonian' $\Phi - \Psi$ and the time-independent s_σ and S.

The time dependent generalizations of entropy and other thermodynamic potentials are not merely theoretical constructs. Indeed it was recently shown [22] that such generalized quantities play the role of governing criteria in open thermodynamic networks, especially those with time-dependent external sources. However, we will not discuss here details of this issue.

5. A generalized control scheme and the H–J–B approach

Taking $\mathbf{x} = (x_0, \mathbf{x}, t)$, where $\mathbf{x} = (\mathbf{x}^\gamma, \mathbf{x}^\delta)$, as the enlarged state vector, and the derivatives dx_k/dt, as the controls v_k, one can regard the thermodynamic entropy or its generalization, S, as the minimum of a new (zeroth) coordinate x_0 in a general optimal control model applied to our thermodynamic problem. The variable x_0 satisfies $dx_0/d\sigma = \Lambda_\sigma(\mathbf{x}, \mathbf{v})$, where σ is the independent variable of a general description. Depending on the model σ may be the time t, a length parameter l, or even a monotonic variable of state x_j. Whenever $\sigma = t$, the unconstrained part of the Lagrangian, $L_\sigma(\mathbf{x}, \mathbf{v})$, equals the sum of two dissipation functions $\Phi^* + \Psi$, in other cases $L_\sigma = (\Phi^* + \Psi)\,dt/d\sigma$. Usually we will take $\sigma = t$, yet it is useful to develop a general scheme, for arbitrary σ. We will write the generic differential constraints in the form $d\mathbf{x}/dt = \mathbf{v}$, meaning $d\mathbf{x}^\gamma/dt = \mathbf{v}^\gamma$ and $d\mathbf{x}^\delta/dt = \mathbf{v}^\delta$, where $\mathbf{v} = (\mathbf{v}^\gamma, \mathbf{v}^\delta)$, are the process rates.

In this formalism, a problem of the minimum entropy coordinate x_0 at the instant $\sigma = \sigma^f$ can be written as $x_0(\sigma^f) = $ minimum, subject to the differential constraint $dx_0/d\sigma = L_\sigma(\mathbf{x}, \mathbf{v})$ and all remaining constraints, $d\mathbf{x}/dt = \mathbf{v}$ and $\mathbf{v}^\gamma + \mathbf{v}^\delta = 0$. Of course, the minimum of $x_0(\sigma^f)$ is the value of the (generalized) entropy S^f at the final instant, σ^f. In all optimal control formulations, it is natural that the rates $\mathbf{v}$ and L_σ are regarded as functions of the state $\mathbf{x}$ and certain controls, $\mathbf{u}$, i.e., that one deals with functions $L_\sigma(\mathbf{x}, \mathbf{u})$ and $\mathbf{v}(\mathbf{x}, \mathbf{u})$. Also the dimensionality of the control vector $\mathbf{u}$ can be different than that of the state vector $\mathbf{x}$ in the optimal control formulations. Yet, for most common descriptions of relaxation (as ours and Onsagerian), the control type variables are identical with the process rates, i.e. $\mathbf{u} = \mathbf{v}$. This means that the

dimensionalities of the original state vector $\mathbf{x}$ and that of the control vector $\mathbf{v}$ are the same. It will be occasionally useful to apply the generalized scheme and draw conclusions in the framework of this generalization. Thus, in the case of arbitrary controls $\mathbf{u}$, those should appear in dynamics of the form $d\mathbf{x}/dt = \mathbf{v}(\mathbf{x}, \mathbf{u})$, and the balance constraints will have the form $\mathbf{v}^\gamma(\mathbf{x}, \mathbf{u}) + \mathbf{v}^\delta(\mathbf{x}, \mathbf{u}) = 0$. However, there may also be some extra inequality constraints on the path, caused by a 'configurational obstacle', say $O(\mathbf{x}) \leqslant 0$; then the original function $L_\sigma(\mathbf{x}, \mathbf{u})$ must be modified by also taking these constraints into account. Here we will assume that such inequality constraints are not present, nonetheless an augmented Lagrangian $\Lambda_\sigma(\mathbf{x}, \mathbf{u})$ is still needed because of the constraint $\mathbf{v}^\gamma(\mathbf{x}, \mathbf{u}) + \mathbf{v}^\delta(\mathbf{x}, \mathbf{u}) = 0$.

The constrained path problem can be formulated mathematically as follows. Consider a control system of the $n + 2$ state equations

$$\frac{dx_\beta}{d\sigma} = v_\beta(\mathbf{x}, \mathbf{u}) \quad \beta = 0, \quad 1, \ldots, n, n+1 \qquad (31)$$

where $\mathbf{x} = (x_0, \mathbf{x}, t)$. The index range, $n = s + 1$, comprises all s components and the energy. Equation (31) is the enlarged system for an original set of equations

$$\frac{dx_i}{d\sigma} = v_i(\mathbf{x}, t, \mathbf{u}); \quad \frac{dt}{d\sigma} = v_{n+1}(\mathbf{x}, t, \mathbf{u}) \quad i = 1, \ldots, n \qquad (32)$$

in which $x_{n+1} = t$. The entropy S is the extremum of the extra (zero-th) coordinate of the enlarged state vector, $\mathbf{x}$. As the model does not contain explicitly the independent variable, σ, this is a parameter, and there is no need to introduce it as an $(n+2)$-th coordinate. (The quantity σ could only play a role in descriptions with explicit 'aging' or 'activation' in which case a formal rate expression, $dx_{n+2}/d\sigma = v_{n+2}(\mathbf{x}, t, \sigma) = 1$, should be included.) In agreement with all the above, the constrained entropy variable, x_0, satisfies the equation

$$\frac{dx_0}{d\sigma} = L_\sigma(\mathbf{x}, \mathbf{u}) + \mu' \cdot \phi'(\mathbf{u}) \equiv \Lambda_\sigma(\mathbf{x}, \mathbf{u}, \mu') \equiv v_0(\mathbf{x}, \mathbf{u})$$

$$(33)$$

with the rate type constraining function $\phi' \equiv d\phi/d\sigma$. The associated Lagrangian multipliers are μ'. The control system (31) includes the original vector $(\mathbf{x}, t)$ into the enlarged state vector, $\mathbf{x} = (x_0, \mathbf{x}, t)$, and the Lagrange multipliers of the local constraints into the enlarged control vector $\mathbf{u} = (\mathbf{u}, \mu')$. When t is explicitly present in $\mathbf{v}$, the system is non-autonomous (frequently it is 'driven' in this case), else there exists an energy-like constant (in fact the Hamiltonian, H_σ) associated with the invariance of the (transition related) entropy production functional J with respect to the translation of time. The L_σ part in equation (33) refers to the locally-unconstrained Lagrangian. Because of the form $\phi' = 0$, the constraint-related part of the expression in equation (33) (i.e. the μ' term) does always vanish.

The extremum value of the entropy variable x_0 equals S, and its optimal change is s_σ, the minimal 'entropy production'. In the constrained case, the minimal entropy change $s_\sigma(\mathbf{x}_0, \mathbf{x}_1) = \min J[=\min(x_0^f - x_0^i)]$ should be understood as a transition index associated with the augmented Lagrangian $\Lambda_\sigma(\mathbf{x}, \mathbf{u})$ rather than with the original Lagrangian $L_\sigma(\mathbf{x}, \mathbf{u})$. This also applies, for example, to the situation when a 'thermal ray' slides over a 'configurational obstacle' in the state space. In this case, the optimal trajectories (rays) may be composed of parts located within the αth constraint boundary ($O_\alpha < 0$, $\mu'_\alpha = 0$) or on the boundary ($O_\alpha = 0, \mu'_\alpha \geqslant 0$). The condition $O_\alpha(\mathbf{x}) = 0$ thus imposes a way of handling the boundary paths [20, 23].

Here we apply the dynamic programming method in its two versions (backward and forward), which altogether constitute an efficient tool in the optimal control theory of thermodynamic processes [24]. The power of the dynamic programming lies in that regardless of the presence of local constraints (which change the control vector $\mathbf{u}$ into $\mathbf{u}$, the latter containing the Lagrange multipliers μ'_α), the extremal performance functions work with the same state variables as in the case of the unconstrained problem. Only the control sets are different, but those are absent in the optimal performance functions. Hence, regardless of specific constraints, the basic problem of the minimal final entropy (and associated minimum of entropy production) is governed by the characteristic function of the following structure

$$\min_{\{\mathbf{u}, \mu'\}} x_0^f \equiv S^f(x_0^i, \mathbf{x}^i, t^i, \mathbf{x}^f, t^f) = x_0^i + s_\sigma(\mathbf{x}^i, t^i, \mathbf{x}^f, t^f) \qquad (34)$$

where s_σ is the minimum of J, the constrained entropy production or its time-dependent generalization. The function S^f (equal to the sum of $S^{\gamma^f} + S^{\delta^f}$ because of the additivity of dissipation over subsystems) does not contain the variable x_0^f. S^f may be associated with the expansion of the final entropy around the complete initial nonequilibrium state of the process. The partial derivatives of the extremal function S^f with respect to its 'working state' [here the initial state $(t^i, \mathbf{x}^i)$] and those of a 'wavefront function', defined as $V^f \equiv S^f - x_0^f$, do coincide. One can thus use the partial derivatives $(\partial V^f/\partial \mathbf{x}^i, \partial V^f/\partial t^i)$ instead of $(\partial S^f/\partial \mathbf{x}^i, \partial S^f/\partial t^i)$ in any equation of the backward DP algorithm (the standard algorithm in which the initial state $x_0^i, \mathbf{x}^i, t^i$ is varied).

However, one can also state a dual problem of a maximal initial coordinate of entropy, $\mathbf{x}_0^i$, when the final entropy coordinate $\mathbf{x}_0^f$ is fixed. This formulation is particularly suitable for thermodynamics as the final entropy of the equilibrium point attained in an adiabatic system at the limit of infinite time is constant by nature. Yet we do not assume here that the final state must be an equilibrium state as we admit finite time transitions. The maximum of x_0^i is described by the extremal performance function

$$\max_{\{\mathbf{u}, \mu'\}} x_0^i \equiv S^i(x_0^f, \mathbf{x}^f, t^f, \mathbf{x}^i, t^i) = x_0^f - s_\sigma(\mathbf{x}^i, t^i, \mathbf{x}^f, t^f). \qquad (35)$$

The partial derivatives of the extremal performance function S^i with respect to its 'working state' [the final state $(t_1, \mathbf{x}_1)$] and those of $V^i \equiv x_0^i - S^i$ coincide only modulo the sign. One may therefore, use the negative partial derivatives $(-\partial V^i/\partial \mathbf{x}^f, -\partial V^i/\partial t^f)$ instead of $(\partial S^f/\partial \mathbf{x}^f, \partial S^f/\partial t^f)$ in any equation of the forward DP algorithm (the algorithm where the final state $\mathbf{x}^f$, t^f is varied). Yet it should be realized that V^i and V^f, as defined above, represent the same function

$$V(x_0^i, \mathbf{x}^i, t^i, x_0^f, \mathbf{x}^f, t^f) = x_0^i - x_0^f + s_\sigma(\mathbf{x}^i, t^i, \mathbf{x}^f, t^f) \qquad (36)$$

which vanishes along any extremal path. These properties are exploited below. While both S and V refer to nonequilibrium situations, it should be kept in mind that only under special conditions, which preserve the time-independence of S, the function S is the thermodynamic entropy. One of the necessary conditions is the autonomicity of the Lagrangian, another is the vanishing of a corresponding Hamiltonian function (Section 8).

With the distinction in mind between the entropy coordinate x_0 and an entropy S as an extremum property of x_0, in order to find the equations of dynamic programming (DP), we apply here Bellman's optimality principle [11, 17, 19], for a control $\mathbf{u}$ in a set U which makes the (constrained) final entropy coordinate $x_0^f(\sigma^f)$ a minimum for a fixed $x_0^i(\sigma^i)$ or an initial entropy coordinate $x_0^i(\sigma^i)$ a maximum for a fixed $x_0^f(\sigma^f)$. By doing this, we use the optimality principle in a rather seldom context which shows the link between the original and dual optimization problem. The principle states that the optimal final value of an optimized quantity is a function of the initial state, equation (34), whereas the optimal initial value of the optimized quantity is a function of the final state, equation (35). See also Fig. 4. [As a generalized optimized quantity one could consider instead of the x_0 a criterion $A(x_0, \mathbf{x}, t) \equiv A(\mathbf{x})$ which works with the same structure of the associated Hamiltonian.] We thus apply the original and dual statement of the optimality principle for the initial and final part of a thermodynamic ray, to show that the conclusions stemming from DP equations can be read in terms of a single, common wave-front function $V(x_0^i, \mathbf{x}^i, t^i, x_0^f, \mathbf{x}^f, t^f) \equiv V(\mathbf{x}^i, \mathbf{x}^f)$ which treats the initial and final states in the space time on an equal footing. Of diverse possible parameters σ, the simplest ones as the time t or the length l are favored. While we derive here the DP equations for the functions $S^f(\mathbf{x}^i)$ or $S^i(\mathbf{x}^f)$, a formula for the extremal entropy production or its non-autonomous generalization, $s_\sigma(\mathbf{x}^i, t^i, \mathbf{x}^f, t^f)$ in the narrowed space $(\mathbf{x}, t)$, follows immediately from the condition $V(\mathbf{x}^i, \mathbf{x}^f) \equiv 0$.

Let us now consider the minimum problem for the final entropy coordinate, x_0^f. We assume differentiability of the optimal function $S^f(\mathbf{x}^i)$ and consider the (enlarged) control $\mathbf{u}$ in intervals $\langle \sigma^i, \sigma^i + \Delta\sigma \rangle$ and $\langle \sigma^i + \Delta\sigma, \sigma^f \rangle$,
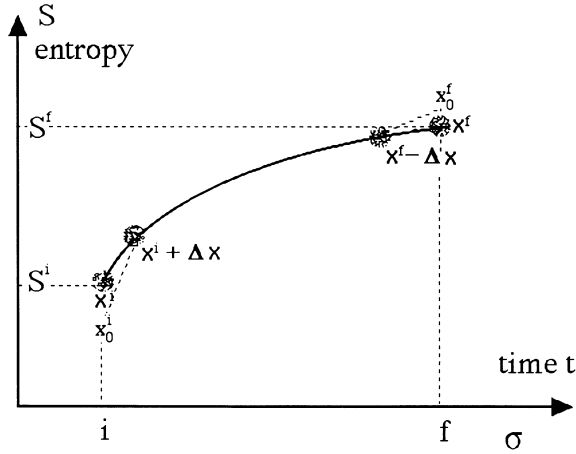
S
entropy

Fig. 4. Duality for dynamic programming formulation. The final entropy S^f generated in terms of the initial states $\mathbf{x}^i$ as the minimum of the final entropy coordinate x_0^f. The initial entropy S^i is generated in terms of the final states $\mathbf{x}^f$ as the maximum of the initial entropy coordinate x_0^i.

where $\Delta\sigma$ is a small quantity. Working with a fixed initial state in $S^f(\mathbf{x}^i)$, we assume that the 'long', final segment of an optimal trajectory, for σ in the interval $\langle\sigma^i+\Delta\sigma, \sigma^f\rangle$, is optimal. The performance index of this optimal segment is $S^f(\mathbf{x}^i+\Delta\mathbf{x})$. Thus, for the whole trajectory in the interval $\langle\sigma^i, \sigma^f\rangle$, the final entropy is the minimum of the expression

$$x_0^f = S^f(\mathbf{x}^i+\Delta\mathbf{x})$$
$$\equiv S^f(x_0^i+\Delta x_0, \mathbf{x}^i+\Delta\mathbf{x}, t^i+\Delta t). \qquad (37)$$

The expression in the second line of equation (37) is associated with the split of the space–time vector $\mathbf{x}^i$ into its parts x_0^i, $\mathbf{x}^i$ and t^i. The minimization in question is with respect to the control vector $\mathbf{u}^i$ for the small initial (non-optimal) part of the path. It is performed at the constant $\mathbf{x}^i = (x_0^i, \mathbf{x}^i, t^i)$ subject to all constraints, i.e. including the differential transformations (31). Restricting the Taylor expansion of S^f, equation (37), to linear terms one finds (summation convention is used)

$$x_0^f = S^f(\mathbf{x}^i)+\frac{\partial S^f}{\partial x \mathbf{x}_\beta}\Delta x_\beta+0(\varepsilon^2)$$
$$\equiv S^f(x_0^i, \mathbf{x}^i, t^i)+\frac{\partial S^f}{\partial x_0^i}\Delta x_0+\frac{\partial S^f}{\partial x_k^i}\Delta x_k+\frac{\partial S^f}{\partial t^i}\Delta t+0(\varepsilon^2). \qquad (38)$$

In equation (38) the symbol $0(\varepsilon^2)$ means the second-order and higher terms. They possess the property $\lim[0(\varepsilon^2)/\Delta\sigma]\to 0$ when the parameter increment tends to zero, $\Delta\sigma\to 0$.

Likewise, for the dual problem of maximum initial

entropy coordinate, x_0^i, one is working with a fixed final coordinate of the state vector $\mathbf{x} = \mathbf{x}^f$ and assumes that a 'long' initial segment of the trajectory is optimal. The performance index of this optimal segment equals $S^i(\mathbf{x}^f-\Delta\mathbf{x})$. In this case the control $\mathbf{u} = \mathbf{u}^f$ should be properly adjusted along a 'short' non-optimal final part of the path. For the whole path in the interval $\langle\sigma^i, \sigma^f\rangle$, the initial entropy is the maximum of

$$x_0^i = S^i(\mathbf{x}^f-\Delta\mathbf{x})$$
$$\equiv S^i(x_0^f-\Delta x_0, \mathbf{x}^f-\Delta\mathbf{x}, t^f-\Delta t). \qquad (39)$$

The maximization is at the constant $\mathbf{x}^f = (x_0^f, \mathbf{x}^f, t^f)$ subject to the constraints (31). Restricting to the linear terms the expansion of S^i, equation (39), in the Taylor series, one obtains

$$x_0^i = S^i(\mathbf{x}^f)-\frac{\partial S^i}{\partial \mathbf{x}_\beta^f}\Delta x_\beta+0(\varepsilon^2)$$
$$= S^i(x_0^f, \mathbf{x}^f, t^f)-\frac{\partial S^i}{\partial x_0^i}\Delta x_0-\frac{\partial S^i}{\partial x_k^f}\cdot\Delta x_k-\frac{\partial S^i}{\partial t^f}\Delta t+0(\varepsilon^2). \qquad (40)$$

In equations (38) and (40) the state changes are linked with controls $\mathbf{u}$ by the state equations (31), hence for small $\Delta\sigma$:

$$\Delta x_\beta = v_\beta(\mathbf{x}, \mathbf{u})\Delta\sigma+0(\varepsilon^2). \qquad (41)$$

After substituting equation (41) into equations (38) and (40), and performing the appropriate extremizations one obtains in terms of the coordinates of the initial point

$$\min_{\mathbf{u}} x_0^f = \min_{\mathbf{u}}\left\{S^f(\mathbf{x}^i)+\frac{\partial S^f}{\partial x_\beta^i}v_\beta(\mathbf{x}^i, \mathbf{u}^i)\Delta\sigma+0(\varepsilon^2)\right\} \qquad (42)$$

and, in terms of the coordinates of the final point

$$\max_{\mathbf{u}} x_0^i = \max_{\mathbf{u}}\left\{S^i(\mathbf{x}^f)-\frac{\partial S^i}{\partial x_\beta^f}v_\beta(\mathbf{x}^f, \mathbf{u}^f)\Delta\sigma+0(\varepsilon^2)\right\}. \qquad (43)$$

Based on the definition of the optimal functions S^f and S^i, equations (34) and (35), equations (42) and (43) can be simplified next as each S is independent of the control $\mathbf{u}$. After reduction of S^f and S^i and division of both sides of equations (42) and (43) by $\Delta\sigma$, the passage to the limit $\Delta\sigma\to 0$ subject to the condition $\lim[0(\varepsilon^2)/\Delta\sigma]\to 0$ yields, respectively, the backward and forward H–J–B equations of the optimization problem, i.e.

$$\min_{\mathbf{u}}\left\{\frac{\partial S^f}{\partial x_\beta}v_\beta(\mathbf{x}^i, \mathbf{u}^i)\right\}$$
$$= \min_{\mathbf{u}}\left\{\frac{\partial S^f}{\partial x_0^i}\frac{dx_0^i}{d\sigma}+\frac{\partial S^f}{\partial x_k^i}\frac{dx_k^i}{d\sigma}+\frac{\partial S^f}{\partial t^i}\frac{dt^i}{d\sigma}\right\}$$
$$= \min_{\mathbf{u}}\left(\frac{dS^f}{d\sigma^i}\right) = \min_{\mathbf{u}}\left(\frac{dV}{d\sigma^i}\right) = 0 \qquad (44)$$

and

$$\max_{\mathbf{u}} \left\{ -\frac{\partial S^{\mathrm{i}}}{\partial x_\beta^{\mathrm{f}}} v_\beta(\mathbf{x}^{\mathrm{f}}, \mathbf{u}^{\mathrm{f}}) \right\}$$

$$= \max_{\mathbf{u}} \left\{ -\frac{\partial S^{\mathrm{i}}}{\partial x_0^{\mathrm{f}}} \frac{\mathrm{d}x_0^{\mathrm{f}}}{\mathrm{d}\sigma} - \frac{\partial S^{\mathrm{i}}}{\partial x_k^{\mathrm{f}}} \frac{\mathrm{d}x_k^{\mathrm{f}}}{\mathrm{d}\sigma} - \frac{\partial S^{\mathrm{i}}}{\partial t^{\mathrm{f}}} \frac{\mathrm{d}t^{\mathrm{f}}}{\mathrm{d}\sigma} \right\}$$

$$= \max_{\mathbf{u}_1} \left(-\frac{\mathrm{d}S^{\mathrm{i}}}{\mathrm{d}\sigma^{\mathrm{f}}} \right) = \max_{\mathbf{u}} \left(\frac{\mathrm{d}V}{\mathrm{d}\sigma^{\mathrm{f}}} \right) = 0. \quad (45)$$

In the expressions appearing in the second line of the above equations, which link the H–J–B equations with the properties of the total derivative of the wave-front function V, the space-time vector $\mathbf{x}$ has been split into its parts related to $\mathbf{x}$, t and s. The property $V = S^{\mathrm{f}} - x_0^{\mathrm{f}} = x_0^{\mathrm{i}} - S^{\mathrm{i}}$ has been used in the second lines of the above equations. The first lines of equations (44) and (45) prove that, in the optimization, the rate $\mathrm{d}x^{\mathrm{i}}/\mathrm{d}\sigma$, $\mathrm{d}t/\mathrm{d}\sigma$, etc. in the second lines must be expressed in terms of the state variables and all actual controls, i.e. including the Lagrange multipliers of the local constraints. Hence, the presence of the multiplier μ' in the expression $\mathrm{d}x_0/\mathrm{d}\sigma = \Lambda_\sigma(\mathbf{x}, t, \mathbf{u}, \mu')$ for the restricted rate of the entropy production. The optimal wave motion always maximizes the speed of the advancing wave-front $\mathrm{d}V/\mathrm{d}\sigma^{\mathrm{f}}$ or the speed of the retreating wave-front $\mathrm{d}V/\mathrm{d}(-\sigma^{\mathrm{i}})$. This result holds even if there are certain local constraints caused by a 'configurational obstacle'.

When the parameter $\sigma = t$, $\mathrm{d}t/\mathrm{d}\sigma = v_t \equiv 1$ is the $n+2$-th rate equation in the above H–J–B equations. Equations (44) and (45) resemble the Hamilton–Jacobi expressions with the extremization sign before their Hamiltonian-type expressions, which are the scalar products of the process rates and the corresponding partial derivatives of S^{f}, S^{i}, s_σ or V. In the language of the wave-propagation theory these equations state that the wavelet is always located on one side of its tangent hyperplane or that the optimal control is always chosen in order to maximize the velocity of the wave-front. This statement is equivalent to Pontryagin's maximum principle [20, 21].

6. H–J–B equation for the minimum entropy production in the original space and the power criterion

The absence of the entropy coordinate x_0 in all rate functions enables one to return to the ordinary or reduced space of the state variables $(\mathbf{x}, t)$. Since equations (34) and (35) are valid, $S^{\mathrm{f}} = x_0^{\mathrm{i}} + s_\sigma(\mathbf{x}^{\mathrm{i}}, t^{\mathrm{i}}, \mathbf{x}^{\mathrm{f}}, t^{\mathrm{f}})$ and $S^{\mathrm{i}} = x_0^{\mathrm{f}} - s_\sigma(\mathbf{x}^{\mathrm{i}}, t^{\mathrm{i}}, \mathbf{x}^{\mathrm{f}}, t^{\mathrm{f}})$, the forward and backward H–J–B equations (44) and (45) read in terms of the Lagrangian Λ_σ and the optimal entropy production $s_\sigma(\mathbf{x}^{\mathrm{i}}, t^{\mathrm{i}}, \mathbf{x}^{\mathrm{f}}, t^{\mathrm{f}})$

$$\min_{\mathbf{u},\mu'} \left\{ \frac{\partial s_\sigma}{\partial t^{\mathrm{i}}} + \frac{\partial s_\sigma}{\partial x_k^{\mathrm{i}}} v_k(\mathbf{x}, \mathbf{u}) + \Lambda_\sigma^{\mathrm{i}}(\mathbf{x}, t, \mathbf{u}, \mu') \right\}$$

$$= 0 \quad \left\{ \equiv \max_{\mathbf{u}} \left(\frac{\mathrm{d}V}{\mathrm{d}(-t^{\mathrm{i}})} \right) \right\} \quad (46)$$

and

$$\max_{\mathbf{u},\mu'} \left\{ \frac{\partial s_\sigma}{\partial t^{\mathrm{f}}} + \frac{\partial s_\sigma}{\partial x_k^{\mathrm{f}}} v_k(\mathbf{x}, \mathbf{u}) + \Lambda_\sigma^{\mathrm{f}}(\mathbf{x}, t, \mathbf{u}, \mu') \right\}$$

$$= 0 \quad \left\{ \equiv \max_{\mathbf{u}} \left(\frac{\mathrm{d}V}{\mathrm{d}(t^{\mathrm{f}})} \right) \right\}. \quad (47)$$

Each of these equations refers to the minimum of integral J, equation (30). Note that in equations (46) and (47) $\mathbf{v}$ is the original (not enlarged) vector of rates and $\mathbf{u}$ is the original (not enlarged) control vector. (In our thermodynamic examples they are identical, i.e., $\mathbf{v}(\mathbf{x}, \mathbf{u}) \equiv \mathbf{u}$.) As it may be shown that $\partial s_\sigma/\partial x^{\mathrm{f}} = -\partial s_\sigma/\partial x^{\mathrm{i}}$, equations (46) and (47) represent in essence the same relationship. In what follows we will deal with the 'forward' equation, equation (47), and will neglect the superscript f of the final state. Thus, within the optimal control framework, the H–J–B equation for the minimization problem of the entropy production integral J is

$$\max_{\mathbf{v}^\gamma, \mathbf{v}^\delta, \mu'} \left\{ \frac{\partial s_\sigma}{\partial t} + \frac{\partial s_\sigma}{\partial \mathbf{x}^\gamma} \mathbf{v}^\gamma + \frac{\partial s_\sigma}{\partial \mathbf{x}^\delta} \mathbf{v}^\delta - \mathbf{R}^\gamma(\mathbf{x}): \mathbf{v}^\gamma \mathbf{v}^\gamma \right.$$

$$\left. - \frac{1}{2} \mathbf{R}^\delta(\mathbf{x}^\gamma): \mathbf{v}^\delta \mathbf{v}^\delta - \Psi(\mathbf{x}^\gamma, \mathbf{x}^\delta, t) - \mu' \cdot (\mathbf{v}^\gamma + \mathbf{v}^\delta) \right\} = 0 \quad (48)$$

where $\mathbf{v}^\gamma$ and $\mathbf{v}^\delta$ are the two dependent controls and the second line represents the thermodynamic Lagrangian, Λ_σ. Of course, $\partial s_\sigma/\partial t = 0$ for adiabatic thermodynamics. As the presence of the Lagrange multiplier μ' allows us to treat the controls as unconstrained, i.e., to apply the stationary extremum conditions, equation (48) is equivalent to the set of the following equations:

$$\frac{\partial s_\sigma}{\partial t} + \frac{\partial s_\sigma}{\partial \mathbf{x}^\gamma} \mathbf{v}^\gamma + \frac{\partial s_\sigma}{\partial \mathbf{x}^\delta} \mathbf{v}^\delta - \Lambda_\sigma(\mathbf{x}, \mathbf{v}, \mu', t) = 0$$

$$\frac{\partial s_\sigma(\mathbf{x}, t)}{\partial \mathbf{x}^\gamma} = \frac{\partial \Lambda_\sigma(\mathbf{x}, \mathbf{v}, \mu', t)}{\partial \mathbf{v}^\gamma};$$

$$\frac{\partial s_\sigma(\mathbf{x}, t)}{\partial \mathbf{x}^\delta} = \frac{\partial \Lambda_\sigma(\mathbf{x}, \mathbf{v}, \mu', t)}{\partial \mathbf{v}^\delta} \frac{\partial \Lambda_\sigma(\mathbf{x}, \mathbf{v}, \mu', t)}{\partial \mu'} \quad (49)$$

$$= \phi'(\mathbf{x}, \mathbf{v}) = \mathbf{v}^\delta + \mathbf{v}^\delta = 0$$

with the unknowns: s_σ, $\mathbf{v}$ and μ'.

Note that evaluation of the total derivatives $\mathrm{d}(\partial \Lambda/\partial \mathbf{v}^\gamma)/\mathrm{d}t$ and $\mathrm{d}(\partial \Lambda/\partial \mathbf{v}^\delta)/\mathrm{d}t$ of the two middle equations of the above set, with the help of the first equation to eliminate s_σ, leads to the Euler–Lagrange equations. Indeed, one obtains

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \Lambda_\sigma}{\partial v_i^\gamma} \right) = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial s_\sigma}{\partial x_i^\gamma} \right) = \frac{\partial^2 s_\sigma}{\partial t \partial x_i^\gamma} + \sum_j \frac{\partial^2 s_\sigma}{\partial x_j^\gamma \partial x_i^\gamma} v_j^\gamma$$

$$= \frac{\partial}{\partial x_i^\gamma}\left(\frac{\partial s_\sigma}{\partial t} + \sum_j \frac{\partial s_\sigma}{\partial x_j^\gamma}v_j^\gamma\right) = \frac{\partial \Lambda_\sigma}{\partial x_i^\gamma} \qquad (50)$$

where the vanishing first line of equation (49) has been exploited. This derivation also holds for the variables $\mathbf{x}^\delta$. Moreover, it is worth stressing that equation (50) can be interpreted as the extremum condition of the power criterion $P_s = \dot{s}_\sigma - \Lambda_\sigma$ [the first line of equation (49)] with respect to the state of the system, i.e. by applying $\partial P_s/\partial x_i^\gamma = \partial P_s/\partial x_i^\delta = 0$.

The Euler–Lagrange equations, for each subsystem

$$\frac{d}{dt}\left(\frac{\partial \Lambda_\sigma}{\partial \mathbf{v}^\gamma}\right) = \frac{\partial \Lambda_\sigma}{\partial \mathbf{x}^\gamma}; \quad \frac{d}{dt}\left(\frac{\partial \Lambda_\sigma}{\partial \mathbf{v}^\delta}\right) = \frac{\partial \Lambda_\sigma}{\partial \mathbf{x}^\delta} \qquad (51)$$

along with the constraint $\phi' = 0$ [the last equation of the set (49)], define the thermodynamic motion. One is thus assured that the H–J–B equation contains the full information which can be derived from the (constrained) variational calculus, so it is sufficient to proceed with an H–J–B equation of the problem. Numerical solutions are effective for small dimensions of the state even in the presence of complex constraints ϕ'. They are based on transformation of a continuous H–J–B equation into its discrete counterpart which is the Bellman's recurrence equation. We refer the reader to many books in which such recurrence equations are derived and their computer solutions are found by an iterative procedure [11, 19, 17, 24]. Otherwise, we are dealing here with the analytical approach to the problem.

Now we will make an essential assumption that the function s_σ is known [as the component of the solution to the set (49)]. The H–J–B equation (48) can then use this known optimal s_σ and the related known entropy function S [equation (35) with $x_0^f = S$ and $\mathbf{x}^f = \mathbf{x}$] to define the rates $\mathbf{v}$ in terms of $\partial S/\partial \mathbf{x}$ from equation (49). The entropies of final states S can be substituted into this equation as sums of the productions s_σ and the known initial entropies S^i. This procedure is admissible due to explicit independence of the model, equations (47)–(49), of the (final) thermal coordinate x_0^f. The change of the generalized entropy S is

$$S(\mathbf{x}^\gamma, \mathbf{x}^\delta, t, \mathbf{x}^{\gamma i}, \mathbf{x}^{\delta i}, t^i) = s_\sigma(\mathbf{x}^\gamma, \mathbf{x}^\delta, t, \mathbf{x}^{\gamma i}, \mathbf{x}^{\delta i}, t^i) + S^i \qquad (52)$$

where the superscript i refers to the initial state and the variable final states are considered. For the 'thermodynamic' dissipation functions Ψ and s_σ, that is when it can be assumed that the model is time-independent and sufficiently exact to regard s_σ as the change of the physical entropy, equation (52) takes the special form

$$S(\mathbf{x}^\gamma, \mathbf{x}^\delta) = s_\sigma(\mathbf{x}^\gamma, \mathbf{x}^\delta, \mathbf{x}^{\gamma i}, \mathbf{x}^{\delta i}) + S^i. \qquad (53)$$

When this is substituted to equation (48) and the derivative $\partial S/\partial t$ is set to zero, the power criterion P_s follows in the time-independent form proposed by Onsager [3] but generalized to constrained state variables

$$P_s(\mathbf{x}^\gamma, \mathbf{x}^\delta, \mathbf{v}^\gamma, \mathbf{v}^\delta, \mu') \equiv \left\{-\frac{\partial S}{\partial \mathbf{x}^\gamma}\mathbf{v}^\gamma - \frac{\partial S}{\partial \mathbf{x}^\delta}\mathbf{v}^\delta + \frac{1}{2}\mathbf{R}^\gamma(\mathbf{x}):\mathbf{v}^\gamma\mathbf{v}^\gamma\right.$$
$$\left. + \frac{1}{2}\mathbf{R}^\delta(\mathbf{x}^\gamma):\mathbf{v}^\delta\mathbf{v}^\delta + \Psi(\mathbf{x}^\gamma, \mathbf{x}^\delta) + \mu'(\mathbf{v}^\gamma + \mathbf{v}^\delta)\right\}. \qquad (54)$$

In adiabatic systems this applies to a time-independent S and with $P_s = 0$. The partial derivative $\partial S/\partial t$, implied by equation (48), vanishes whenever one restricts the thermodynamic entropies. In non-adiabatic systems, even for autonomous dissipation functions and related Lagrangians, the derivative $\partial S/\partial t$ and the power criterion P_s are non-vanishing whenever $H_\sigma = \Phi - \Psi$ is non-vanishing; then only certain generalizations of the thermodynamic entropy are represented by S. Yet the derivative $\partial S/\partial t$ can still be ignored in the power criterion $\mathbf{P}_s$ as not influencing the extremum conditions of equation (38) with respect to the rates $\mathbf{v}$.

Thus, the H–J–B theory proves that, in order to assure the minimum of the second law integral (29), one has to maximize the Hamiltonian expression in equation (48), or equivalently, to minimize the power criterion (54). This extremization is valid for each time instant of the process, and results in dynamical equations which link the rates $\mathbf{v}$ with the state variables $\mathbf{x}$ and the derivatives $\partial S/\partial \mathbf{x}$, which are just the 'phenomenological equations' of irreversible thermodynamics. Our general form of the principle of minimum power

$$\min_{\mathbf{v}^\gamma, \mathbf{v}^\delta, \mu'} P_s(\mathbf{x}^\gamma, \mathbf{x}^\delta, \mathbf{v}^\gamma, \mathbf{v}^\delta, \mu') = 0 \qquad (55)$$

is a generalization of the Onsager's local-extremum principle to the case of DVA. This criterion is especially useful to two-phase systems and interpenetrating continua.

In conclusion, power criteria of non-equilibrium thermodynamics stem from Hamiltonians of suitable H–J–B equations for problems of minimum entropy generation (with two dissipation functions). The essential difference between an H–J–B equation and a related power criterion P_s is that the function S in an H–J–B equation is unknown and it should be found for a definite Lagrangian, L_σ, whereas the function S in a power criterion P_s is a given thermodynamic function. The fact that an H–J–B is not restricted to classical S makes generalizations possible. See Section 9 for examples of dynamics satisfying the above criteria.

7. Phenomenological equations of DVA from the power criterion

Now we shall implement our approach based on dependent variables which allows us the non-truncated function of the entropy in its original form, with linear terms. Let us apply the criterion (48) or (54) to obtain equations of irreversible dynamics. As distinguished from the IVA (where partial derivatives of the principal func-

tion are differences of pertinent potentials), here the partial derivatives of the potential function S are the absolute potentials, i.e., the Planck potentials, ζ_i^γ and ζ_i^δ, and the temperature reciprocals $T^{\gamma^{-1}}$ and $T^{\delta^{-1}}$, expressed in terms of the deviations $\mathbf{x}$, equation (11):

$$\frac{\partial S^\gamma(\mathbf{x}^\gamma)}{\partial \mathbf{x}^\gamma} = \mathbf{p}^\gamma(\mathbf{x}^\gamma) = (\zeta_1^\gamma, \zeta_2^\gamma, \ldots, \zeta_s^\gamma, T^{\gamma^{-1}}). \tag{11'}$$

In effect, the variation of P_s with respect to all control variables, the rates $\mathbf{v}^\gamma$, $\mathbf{v}^\delta$ and the multiplier μ', yields expressions equivalent with the phenomenological equations of heat and mass exchange

$$\delta\mathbf{v}^\gamma: \quad \mathbf{p}^\gamma = \partial L_\sigma/\partial \mathbf{v}^\gamma + \mu' \tag{56}$$

$$\delta\mathbf{v}^\delta: \quad \mathbf{p}^\delta = \partial L_\sigma/\partial \mathbf{v}^\delta + \mu' \tag{57}$$

$$\delta\mu': \quad \mathbf{v}^\gamma + \mathbf{v}^\delta = 0 \tag{58}$$

where $L_\sigma = \Phi^* + \Psi$ is the dissipative kinetic potential. These equations should be solved with respect to $\mathbf{v}^\gamma$, $\mathbf{v}^\delta$ and μ'. Based on the above set, one may interpret the Lagrange multiplier μ' as an interphase transfer potential, and use further the new symbol $\mathbf{p}^*$ for μ'.

For the dissipation function Φ^* quadratic with respect to rates (R_{ij} independent of $\mathbf{v}$, although it still may depend on $\mathbf{x}$), one gets the linear equations

$$\delta\mathbf{v}^\gamma: \quad \mathbf{p}^\gamma = \mathbf{R}^\gamma\mathbf{v}^\gamma + \mathbf{p}^* \tag{59}$$

$$\delta\mathbf{v}^\delta: \quad \mathbf{p}^\delta = \mathbf{R}^\delta\mathbf{v}^\delta + \mathbf{p}^* \tag{60}$$

along with equation (58) which links them. One can write this result in the Ohm's law form, which contains the symmetric resistance matrices $\mathbf{R}^\gamma$ and $\mathbf{R}^\delta$:

$$\frac{d\mathbf{x}^\gamma}{dt} = (\mathbf{R}^\gamma)^{-1}(\mathbf{p}^\gamma - \mathbf{p}^*) \cong -(\mathbf{L}\Gamma)^\gamma\mathbf{x}^\gamma \tag{61}$$

$$\frac{d\mathbf{x}^\delta}{dt} = (\mathbf{R}^\delta)^{-1}(\mathbf{p}^\delta - \mathbf{p}^*) \cong -(\mathbf{L}\Gamma)^\delta\mathbf{x}^\delta \tag{62}$$

$$\frac{d\mathbf{x}^\gamma}{dt} + \frac{d\mathbf{x}^\delta}{dt} = 0. \tag{63}$$

The physical approximations refer to the linear dynamics and the second-order expansion of S, equation (9), with the constant coefficients.

The above equations describe the energy and mass exchange for a state-dependent R_{ij}. It may be noted that when the first dissipation co-function, $\Phi^*(\mathbf{x}, \mathbf{v})$, is non-quadratic in the rates, the rates follow as non-linear functions of the potential differences $\mathbf{p} - \mathbf{p}^*$. Any non-linear extensions would make a number of resulting equations [such as, e.g., equation (64) below] more complex, yet the procedure would remain the same.

Substituting equations (61) and (62) into the constraint (63) yields

$$(\mathbf{R}^\gamma)^{-1}(\mathbf{p}^\gamma - \mathbf{p}^*) + (\mathbf{R}^\delta)^{-1}(\mathbf{p}^\delta - \mathbf{p}^*) = 0 \tag{64}$$

whence, the interphase transfer potential follows as

$$\mathbf{p}^* = \frac{(\mathbf{R}^\gamma)^{-1}\mathbf{p}^\gamma + (\mathbf{R}^\delta)^{-1}\mathbf{p}^\delta}{(\mathbf{R}^\gamma)^{-1} + (\mathbf{R}^\delta)^{-1}} = \frac{\mathbf{L}^\gamma\mathbf{p}^\gamma + \mathbf{L}^\delta\mathbf{p}^\delta}{\mathbf{L}^\gamma + \mathbf{L}^\delta} \tag{65}$$

where $\mathbf{L}^\gamma \equiv (\mathbf{R}^\gamma)^{-1}$ and $\mathbf{L}^\delta \equiv (\mathbf{R}^\delta)^{-1}$. This result makes it possible to eliminate the Lagrange multiplier $\mathbf{p}^*$ from the transfer equations (61) and (62). One thus obtains the kinetic equations which contain the overall transfer resistance matrix $\mathbf{R} = \mathbf{R}^\gamma + \mathbf{R}^\delta$ or the overall conductance matrix $\mathbf{L} \equiv \mathbf{R}^{-1}$ such that $\mathbf{L}^{-1} = (\mathbf{L}^\gamma)^{-1} + (\mathbf{L}^\delta)^{-1}$:

$$\frac{d\mathbf{x}^\gamma}{dt} = \mathbf{R}^{-1}(\mathbf{p}^\gamma - \mathbf{p}^\delta) \equiv \mathbf{L}\left(\frac{\partial S}{\partial\mathbf{x}^\gamma} - \frac{\partial S}{\partial\mathbf{x}^\delta}\right) \tag{66}$$

$$\frac{d\mathbf{x}^\gamma}{dt} = \mathbf{R}^{-1}(\mathbf{p}^\delta - \mathbf{p}^\gamma) \equiv \mathbf{L}\left(\frac{\partial S}{\partial\mathbf{x}^\delta} - \frac{\partial S}{\partial\mathbf{x}^\gamma}\right). \tag{67}$$

We see that the overall transfer resistance appears quite natural in the model with dependent state variables. The simplest special case described by the above equations refers to the pure heat exchange between phases as subsystems. For two subsystems, γ and δ, the dependent equations of the heat exchange may be written in the form

$$\frac{de^\gamma}{dt} = \frac{(T^\gamma)^{-1} - (T^\delta)^{-1}}{R} \tag{68}$$

and

$$\frac{de^\gamma}{dt} = \frac{(T^\delta)^{-1} - (T^\gamma)^{-1}}{R}. \tag{69}$$

Clearly, their sum vanishes (energy conservation). Both resistances may be the state dependent quantities. These are the correct result if the resistances are $R^\gamma = 1/(\kappa^\gamma A)$, where A is the exchange area and κ^γ are partial coefficients of heat exchange referred to the driving forces ΔT^{-1} rather than to ΔT. We thus have shown that the quadratic approximation to the entropy, equation (9), is the appropriate governing criterion for the linear irreversible dynamics.

8. IVA and correspondence with the Onsager's description

It may be seen that the correspondence between the two considered descriptions is assured. Indeed, for the IVA description (the independent variables $\alpha \equiv \mathbf{x}^\gamma$), one obtains from equations (20) and (66) the independent phenomenological equation in the Onsager form

$$\frac{d\alpha}{dt} = \mathbf{R}^{-1}(\mathbf{p}^\gamma - \mathbf{p}^\delta) \equiv \mathbf{L}\,\partial S/\partial\alpha. \tag{70}$$

This corresponds directly with equations (66) and (67) of DVA. The correspondence refers also to the entropy production, σ_s. In terms of Onsager's α, the quantity σ_s is given by equation (22) in which, by definition, $\Gamma = \Gamma^\gamma + \Gamma^\delta$ is the positive matrix and the product $-\Gamma\alpha$

is the interphase driving force $\mathbf{X} = \mathbf{p}^\gamma - \mathbf{p}^\delta$ or the difference of the driving forces $\mathbf{X}^\gamma$ and $\mathbf{X}^\delta$, equation (12). Thus, both entropy productions, equation (17) of DVA and equation (22) of IVA, are equal:

$$\sigma_s \equiv \frac{dS}{dt} = \dot{\mathbf{x}}^\gamma \cdot \mathbf{X}^\gamma + \dot{\mathbf{x}}^\delta \cdot \mathbf{X}^\delta = \dot{\alpha} \cdot \mathbf{X} = \frac{dS}{dt}. \qquad (71)$$

In the independent variables the minimized second law integral has the form

$$J = \int_{t^1}^{t^2} L_\sigma(\alpha, \dot{\alpha}) \, dt = \int_{t^1}^{t^2} [\Phi^*(\alpha, \dot{\alpha}) + \Psi(\alpha)] \, dt$$

$$= \int_{t^1}^{t^2} \left[\frac{1}{2} \mathbf{R}(\alpha) : \dot{\alpha}\dot{\alpha} + \Psi(\alpha) \right] dt. \qquad (72)$$

This expression contains the total resistance $\mathbf{R} = \mathbf{R}^\gamma + \mathbf{R}^\delta$ and is consistent with equation (29).

The H–J–B equation for the thermodynamic problem, written in the form of the corresponding power criterion and in terms of the final entropy rather than the entropy production s_σ, reads

$$\min_{\dot{\alpha}} \left\langle P_s(\alpha, \dot{\alpha}) \equiv -\frac{\partial S}{\partial \alpha} \dot{\alpha} + \mathbf{R}(\alpha) : \dot{\alpha}\dot{\alpha} + \Psi(\alpha) \right\rangle = 0 \qquad (73)$$

where the function $\mathbf{S}$ is Onsager's approximation to the non-equilibrium entropy, equation (23). This result represents the Onsager's restricted extremum principle in which the phenomenological equations are obtained from the variation of P_s with respect to the independent rates $\dot{\alpha}$ at the fixed state variables, α. The corresponding DVA result is equation (54). For arbitrary mathematical dissipation functions the variational procedure (and the power criterion P_s) does not generate changes of the thermodynamic entropy.

The perfect differential of the extremal function for the integral J, equation (72),

$$ds_\sigma = \frac{\partial s_\sigma}{\partial \alpha} \cdot d\alpha + \frac{\partial s_\sigma}{\partial t} \, dt = \mathbf{X} \cdot d\alpha - H_\sigma \, dt$$

$$= \frac{\partial L_\sigma}{\partial \dot{\alpha}} \cdot d\alpha - \left(\frac{\partial L_\sigma}{\partial \dot{\alpha}} \cdot \dot{\alpha} - L_\sigma \right) dt \qquad (74)$$

shows that in order to assure the time independent potentials s_σ and $\mathbf{S}$, the thermodynamic Hamiltonian or the Legendre transform of the dissipative Lagrangian L_σ must vanish:

$$H_\sigma \equiv \frac{\partial L_\sigma}{\partial \dot{\alpha}} \cdot \dot{\alpha} - L_\sigma = \Phi(\alpha, \dot{\alpha}) - \Psi(\alpha) = 0 \qquad (75)$$

which means the equality of the kinetic and potential dissipation functions. This equation, along with the additivity of the momenta $\partial L / \partial \dot{\alpha}$ and the Hamiltonian H_σ over the subsystems are the physical constraints that assure the additive entropy, $S = S^\gamma + S^\delta$. For the Onsager's model, the generalized momenta are $\mathbf{X} = \mathbf{R}\dot{\alpha}$ and

$$H_\sigma = \frac{1}{2} \mathbf{R} : \dot{\alpha}\dot{\alpha} - \Psi(\alpha) = \frac{1}{2} \mathbf{L} : \mathbf{X}\mathbf{X} - \Psi(\alpha) = 0 \qquad (76)$$

where $\mathbf{L} = \mathbf{R}^{-1}$. This proves that $\Psi(\alpha)$ must be quadratic for his linear dynamics, equation (25). That dynamics is consistent with Ψ in the form $\Psi(\alpha) = \frac{1}{2}\mathbf{W} : \alpha\alpha$, where $\mathbf{W} = \Gamma \mathbf{R}^{-1} \Gamma$.

Because of the state function property of the thermodynamic entropies, S or $\mathbf{S}$, the time t cannot appear explicitly in any of the rate functions (especially in dissipation functions) as such explicit time dependence would exclude time-independent S and $\mathbf{S}$. Moreover, the conditions $\partial S / \partial t = 0$ and $\partial \mathbf{S} / \partial t = 0$ applied either in the governing H–J–B equations or in resulting Hamilton–Jacobi equations causing the vanishing (non-extremal) Pontryagin's Hamiltonian and classical (extremal) Hamiltonian in these equations, respectively. Accordingly, each power criterion and its corresponding Hamilton–Jacobi equation are time independent and do not contain the derivative $\partial S / \partial t$ [the time derivative is present only in general equations not restricted to adiabatic thermodynamic systems, such as equation (48) of DVA]. As the consequence of these limitations, the Hamilton–Jacobi equation for the IVA

$$\frac{1}{2} \sum_i \sum_k \mathbf{L}_{ik} \frac{\partial S_\sigma}{\partial \alpha_i} \frac{\partial S_\sigma}{\partial \alpha_k} - \Psi(\alpha) = 0 \qquad (77)$$

describes the vanishing property of the dissipative Hamiltonian, $H_\sigma = \Phi - \Psi$ [the Legendre transform of $L_\sigma = \Phi^* + \Psi$ for the quadratic $\Phi^* = (1/2)\mathbf{R} : \dot{\alpha}\dot{\alpha}$] in which the generalized momenta p_i are identified with the partial derivatives $\partial S_\sigma / \partial \alpha_i$. Note also that the Legendre transformation of a Lagrangian is explicit in all H–J–B equations and power criteria, in which $p_i = \partial S_\sigma / \partial \alpha_i = \partial S / \partial \alpha_i$ (IVA) or $p_i = \partial s_\sigma / \partial x_i = \partial S / / \partial x_i$ (DVA). Clearly, the entropy plays the role of an action, which is the 'thermodynamic action', in both approaches (DVA and IVA). As $\mathbf{S} = \mathbf{S}^i + \mathbf{S}_\sigma$, equation (77) governs both the optimal production function $s_\sigma \equiv \min J$ and the ('restricted') entropy function, $\mathbf{S}$ of equation (23). The use of $\mathbf{S}_\sigma = 1/2\Gamma : \alpha\alpha$ in equation (77), immediately defines the proper second dissipation function $\Psi(\alpha)$ for this problem as $(1/2)\alpha \cdot \mathbf{W} \cdot \alpha$, with the symmetric matrix $\mathbf{W} \equiv \Gamma \mathbf{L} \Gamma$.

We observe that it is the evaluation of the rates as the optimal control variables in the Hamiltonian expression of the H–J–B equation and the vanishing dissipative Hamiltonian which lead to the second dissipation function. Time independent second dissipation function is insufficient for the extremum dissipation integral to be the production of the thermodynamic entropy. It may be noted that the form of Ψ is inessential for the structure of the phenomenological equations in terms of the potentials $\mathbf{p}$. Nonetheless this form influences the Euler–Lagrange equations of the problem.

An extra conclusion stemming from the above analysis is that the phenomenological equations in their usual form, which links the coordinates of the entropy gradient and the process rates, do not necessarily follow as the Euler–Lagrange equations of the variational problem for

minimum dissipation. They may evolve rather as expressions that describe rates (controls) in terms of the state and state adjoints (gradients of S or S_σ) as the optimal rates maximizing the Pontryagin's Hamiltonian with respect to the rates as the control variables.

9. Euler–Lagrange structure of transfer and relaxation equations

Now we return to DVA and focus on its Euler–Lagrange equations, equation (51). As already explained in Section 6, the Euler–Lagrange equations of the thermodynamic problem arise as a transformation of the phenomenological equations. It is also worth remembering that the former can be derived from the extremum condition of the power criterion P_s with respect to the state $\mathbf{x}$ and using the equality $P_s = 0$. These properties hold for both DVA and IVA.

An expanded form of the first equation of the set, equation (51), is

$$\frac{d}{dt}\left(\frac{\partial[L_\sigma(\mathbf{x}^\gamma, \mathbf{v}^\gamma) + \mu' \cdot \phi']}{\partial \mathbf{v}^\gamma}\right) = \frac{\partial[L_\sigma(\mathbf{x}^\gamma, \mathbf{v}^\gamma) + \mu' \cdot \phi']}{\partial \mathbf{x}^\gamma} \qquad (78)$$

and the analogous equation for $\mathbf{x}^\delta$ plus the constraint equations. These equations stress explicitly the role of the Lagrange multipliers associated with the conservation laws.

As suggested by the IVA Hamiltonians in equations (76) and (77), one may test the above Euler–Lagrange equations by using the following second dissipation function:

$$\Psi(\mathbf{x}^\gamma, \mathbf{x}^\delta) = \tfrac{1}{2}\mathbf{W}^\gamma : \mathbf{x}^\gamma \mathbf{x}^\gamma + \tfrac{1}{2}\mathbf{W}^\delta : \mathbf{x}^\delta \mathbf{x}^\delta \qquad (79)$$

where $\mathbf{W}^\gamma \equiv (\mathbf{\Gamma L \Gamma})^\gamma$ and $\mathbf{W}^\delta \equiv (\mathbf{\Gamma L \Gamma})^\delta$ are the symmetric matrices. Indeed, note that when the equality $\mathbf{x}^\gamma = -\mathbf{x}^\delta$ is applied in equation (79), the description becomes the IVA and the generating function becomes Onsager's $\Psi(\alpha) = (1/2)\mathbf{W} : \alpha\alpha$, where $\mathbf{W} = \mathbf{\Gamma L \Gamma}$ contains the overall coefficients. Thus, equation (79) is essentially an Onsagerian structure [3, 7], but it refers to the DVA and partial transport and thermodynamic coefficients.

For an isolated system with quadratic dissipation function (79) and constant conductance matrices, the thermodynamic Euler–Lagrange equations of DVA are

$$\frac{d}{dt}(\mathbf{R}^\gamma \mathbf{v}^\gamma + \mathbf{p}^*) = \mathbf{W}^\gamma \mathbf{x}^\gamma; \quad \frac{d}{dt}(\mathbf{R}^\delta \mathbf{v}^\delta + \mathbf{p}^*) = \mathbf{W}^\delta \mathbf{x}^\delta \qquad (80)$$

where the Lagrange multipliers $\mathbf{p}^* \equiv \mu'$ are the interphase transfer potentials. This is an important result (Fig. 3). One may note that the left-hand-sides of these equations are time derivatives of the DVA transfer potentials (Planck potentials and temperature reciprocals). With equations (15), equation (80) may otherwise be written in a few alternative forms:

$$\frac{d\mathbf{p}^\gamma}{dt} = \mathbf{W}^\gamma \mathbf{x}^\gamma = \mathbf{\Gamma}^\gamma \mathbf{L}^\gamma \mathbf{\Gamma}^\gamma \mathbf{x}^\gamma = \mathbf{\Gamma}^\gamma \mathbf{L}^\gamma (\mathbf{p}^* - \mathbf{p}^\gamma)$$

$$= \mathbf{K}^{\mathrm{T}\gamma}(\mathbf{p}^* - \mathbf{p}^\gamma) \qquad (81)$$

where the matrix $\mathbf{K}^\gamma = \mathbf{L}^\gamma \mathbf{\Gamma}^\gamma$ is the state relaxation matrix and, simultaneously, the matrix of products of the transfer coefficients and the transfer area. The asterisk state variables do not appear due to the suitable definition of $\mathbf{x}$ as the deviations. An analogous equation holds for the adjoints $\mathbf{p}^\delta$ and the state variables $\mathbf{x}^\delta$. It follows that the Euler–Lagrange equations, equation (81), and the phenomenological equations (61) and (62) of the H–J–B theory describe the same dynamics, although the former does its job for the time derivatives of the absolute transfer potentials, $d\mathbf{p}^\gamma/dt$ and $d\mathbf{p}^\delta/dt$ and the latter work for the time derivatives of the state variables, $d\mathbf{x}^\gamma/dt$ and $d\mathbf{x}^\delta/dt$.

Indeed, after using equation (11) in equation (81) to express the dynamics in terms of $\mathbf{x}$:

$$\frac{d\mathbf{p}^\gamma}{dt} = -\mathbf{\Gamma}^\gamma \frac{d\mathbf{x}^\gamma}{dt} = \mathbf{K}^{\mathrm{T}\gamma}(\mathbf{p}^* - \mathbf{p}^\gamma) = \mathbf{\Gamma}^\gamma \mathbf{L}^\gamma \mathbf{\Gamma}^\gamma \mathbf{x}^\gamma = \mathbf{\Gamma}^\gamma \mathbf{K}^\gamma \mathbf{x}^\gamma$$

$$(81')$$

the state relaxation is extracted from the above formula in the form $d\mathbf{x}^\gamma/dt = -\mathbf{K}^\gamma \mathbf{x}^\gamma$, consistent with the relaxation of the thermodynamic adjoints $\mathbf{p}^\gamma$ and $\mathbf{p}^\delta$.

Summing up, in terms of the original state vector $\tilde{\mathbf{n}} = (\mathbf{n}, e)$, and for the Gibbs equation defining the non-equilibrium entropy as an additive quantity over the homogeneous subsystems

$$dS \equiv dS^\gamma + dS^\delta = \mathbf{p}^\gamma \cdot d\tilde{\mathbf{n}}^\gamma + \mathbf{p}^\delta \cdot d\tilde{\mathbf{n}}^\delta \qquad (82)$$

we have found the associated dynamics in the canonical form

$$\frac{d\tilde{\mathbf{n}}^\gamma}{dt} = \frac{\partial H_\sigma}{\partial \mathbf{p}^\gamma}; \quad \frac{d\mathbf{p}^\gamma}{dt} = -\frac{\partial H_\sigma}{\partial \tilde{\mathbf{n}}^\gamma} \qquad (83)$$

which, in the case of the linear dynamics, governed by the extremum Hamiltonian of the DVA

$$H_\sigma = \tfrac{1}{2}\mathbf{L} : (\mathbf{p}^\gamma - \mathbf{p}^\delta)(\mathbf{p}^\gamma - \mathbf{p}^\delta) - \tfrac{1}{2}\mathbf{W}^\gamma : \mathbf{x}^\gamma \mathbf{x}^\gamma - \tfrac{1}{2}\mathbf{W}^\delta : \mathbf{x}^\delta \mathbf{x}^\delta = 0 \qquad (84)$$

[compare equation (88) further], is consistent with the results of the hydrodynamic theory of the boundary layer.

$$\frac{d\tilde{\mathbf{n}}^\gamma}{dt} = -\mathbf{K}^\gamma \mathbf{x}^\gamma \equiv \mathbf{K}^\gamma(\tilde{\mathbf{n}}^\gamma * - \tilde{\mathbf{n}}^\gamma); \quad \frac{d\mathbf{p}^\gamma}{dt} = \mathbf{K}^{\mathrm{T}\gamma}(\mathbf{p}^* - \mathbf{p}^\gamma).$$

$$(83')$$

(The analogous dynamics hold for the phase δ.) Thus, in the present formalism, the relaxation equation for the co-state variables (thermodynamic adjoints) is a Euler–Lagrange equation. Otherwise the state relaxation equation stems either from the H–J–B equation, equation (48), or as the transformation of the Euler–Lagrange equation (81). We have also shown that the equation of

motion for the state variables $\tilde{\mathbf{n}}$ and their thermodynamic adjoints $\mathbf{p}$ constitute the canonical set (83). Our analysis has proven that the linear relaxation of the state variables is governed by the matrix $\mathbf{K}^\gamma = \mathbf{L}^\gamma\Gamma^\gamma$ and that of the thermodynamic adjoints by its transpose $\mathbf{K}^{\mathrm{T}\gamma} = \Gamma^\gamma\mathbf{L}^\gamma$. Only in the particular case when the matrix $\mathbf{K}$ is symmetric, the relaxation of state variables and their thermodynamic adjoints are governed by the same common matrix $\mathbf{K}$. The analysis also shows the coherence and elegance of the approach based on the dependent variables.

With the second dissipation function, equation (79) (consistent with the condition $H_\sigma = 0$ in an extremum H–J–B), the DVA, as opposed to the classical Onsager's approach, yields the standard equations of heat and mass exchange in a perfect symmetry for both the state variables and their thermodynamic adjoints. This property is lost in the classical approach, where the adjoints are not the absolute potentials $\mathbf{p}^\gamma$ and $\mathbf{p}^\delta$, but they are rather the differences $\mathbf{p}^\gamma - \mathbf{p}^\delta$. Consequently, the Euler–Lagrange equation of the Onsager theory deals not with the time derivatives $\mathrm{d}\mathbf{p}^\gamma/\mathrm{d}t$ and $\mathrm{d}\mathbf{p}^\delta/\mathrm{d}t$ but with the time derivatives of the thermodynamic forces $\mathrm{d}\mathbf{X}/\mathrm{d}t = \mathrm{d}(\mathbf{p}^\gamma - \mathbf{p}^\delta)/\mathrm{d}t$. The classical (Onsager's) result, while correct, is less suitable to use than the result established here, as the knowledge of local temperatures and chemical potentials along the path is more suitable than the knowledge of interphase differences for these quantities.

An analysis of equation (83') in the case of identical properties of subsystems yields the condition of the same relaxation matrix $\mathbf{L}^\gamma\Gamma^\gamma = \mathbf{L}^\delta\Gamma^\delta \equiv \mathbf{K}$, as the internal consistency condition for the linear DVA. This means that the relaxation matrices of the two interacting subsystems must be in agreement, to assure a common rate of the interlinked state variables. Another remarkable feature of the linear dynamical model is that the interphase potentials $\mathbf{p}^*$ are constants which coincide with the equilibrium potentials $\mathbf{p}^0$. The matrix $\mathbf{K}$ is related to the system size. A larger system is characterized by smaller matrices Γ^γ and Γ^δ and K than a smaller one [consider equations (14) and (84)], hence the relaxation times (entries of $\mathbf{K}^{-1}$) are larger in the larger system.

10. Hamilton–Jacobi equation with dependent variables

There are some subtleties in the problem using DVA, regarding the use of the Legendre transformation in the case when the dependent state variables are used, associated with the presence of the Lagrange multiplier. This is discussed below.

In thermodynamic autonomous systems governed by a time-independent principal function, as the thermodynamic entropy function is, the second dissipation

function can be obtained from a general rule as the Legendre transform of its rate dependent part with respect to all rates (controls) to which the system dynamics are substituted as $\dot{\alpha}(\mathbf{x})$ [consider equation (75)]. Can this procedure be extended to the case of dependent variables in which the role of the Legendre transformation is not directly substantiated by the theory due to the presence of the linear control $\mu' = \mathbf{p}^*$?

Let us multiply equation (56) by $\mathbf{v}^\gamma$ and equation (57) by $\mathbf{v}^\delta$ and add the results taking the constraint (58) into account. Then, after using the definitions of the potentials $\mathbf{p}$ in terms of the entropy S:

$$\frac{\partial S}{\partial \mathbf{x}^\gamma}\cdot\mathbf{v}^\gamma + \frac{\partial S}{\partial \mathbf{x}^\delta}\cdot\mathbf{v}^\delta = \frac{\partial L_\sigma}{\partial \mathbf{v}^\gamma}\cdot\mathbf{v}^\gamma + \frac{\partial L_\sigma}{\partial \mathbf{v}^\delta}\cdot\mathbf{v}^\delta. \tag{85}$$

In a general case the dependent rates satisfy certain generalizations of equations (53) and (54). When these results are used in the H–J–B equation (48) [or in its generalized form for an arbitrary L_σ], one concludes that, while $\partial S/\partial \mathbf{x}$ is no longer equal to $\partial L_\sigma/\partial \mathbf{v}$, the Hamilton–Jacobi equation contains the same Legendre transform of L_σ as in the case of the IVA

$$\frac{\partial S}{\partial t} + \frac{\partial L_\sigma}{\partial \mathbf{v}^\gamma}\cdot\mathbf{v}^\gamma\left(\frac{\partial S}{\partial \mathbf{x}^\gamma}, \frac{\partial S}{\partial \mathbf{x}^\delta}, \mathbf{x}^\gamma, \mathbf{x}^\delta, t\right)$$

$$+ \frac{\partial L_\sigma}{\partial \mathbf{v}^\delta}\mathbf{v}^\delta\left(\frac{\partial S}{\partial \mathbf{x}^\gamma}, \frac{\partial S}{\partial \mathbf{x}^\delta}, \mathbf{x}^\gamma, \mathbf{x}^\delta, t\right)$$

$$- L_\sigma\left(\frac{\partial S}{\partial \mathbf{x}^\gamma}, \frac{\partial S}{\partial \mathbf{x}^\delta}, \mathbf{x}^\gamma, \mathbf{x}^\delta, t\right) = 0. \tag{86}$$

This also proves that the Hamilton–Jacobi equation preserves its standard form:

$$\frac{\partial S}{\partial t} + H_\sigma\left(\frac{\partial S}{\partial \mathbf{x}^\gamma}, \frac{\partial S}{\partial \mathbf{x}^\delta}, \mathbf{x}^\gamma, \mathbf{x}^\delta, t\right) = 0. \tag{87}$$

Of course, for an isolated thermodynamic system the time t does not appear in the Hamiltonian H_σ and in S, and the above equation has the form $H_\sigma = 0$.

Again, while $\partial S/\partial\mathbf{x} \neq \partial L_\sigma/\partial\mathbf{v}$, the perfect differential of the function S (which is the solution to this equation) satisfies equation (82). Accordingly, for the linear dynamics with the second dissipation function given by equation (79), the Hamilton–Jacobi equation of the DVA is

$$\frac{1}{2}\mathbf{L}:\left(\frac{\partial S}{\partial \mathbf{x}^\gamma} - \frac{\partial S}{\partial \mathbf{x}^\delta}\right)\left(\frac{\partial S}{\partial \mathbf{x}^\gamma} - \frac{\partial S}{\partial \mathbf{x}^\delta}\right) - \frac{1}{2}\mathbf{W}^\gamma:\mathbf{x}^\gamma\mathbf{x}^\gamma$$

$$- \frac{1}{2}\mathbf{W}^\delta:\mathbf{x}^\delta\mathbf{x}^\delta = 0 \tag{88}$$

where $\mathbf{W}^\gamma = (\Gamma\mathbf{L}\Gamma)^\gamma$, $\mathbf{W}^\delta = (\Gamma\mathbf{L}\Gamma)^\delta$ and $\mathbf{L}^{-1} = (\mathbf{L}^\gamma)^{-1} + (\mathbf{L}^\delta)^{-1}$. This equation is satisfied by the DVA entropy, equation (9). The modified form of equation (88) containing an unknown $\Psi(\mathbf{x})$ may serve to determine the second dissipation function in an exact

way, since the thermodynamic entropy $S(\mathbf{x})$ is frequently known with a considerable accuracy. This is the remarkable virtue of the DVA. For the linear dynamics, the quadratic function (9) is sufficient for that purpose.

An alternative way to find the generating function Ψ of the DVA is to deal with the global Lagrangian, Λ_σ, by inclusion of all formal controls ($\mu' \equiv \mathbf{p}^*$, $\mathbf{v}^\gamma$ and $\mathbf{v}^\delta$) into considerations. Let us verify that procedure for the pure heat transfer between the subsystems γ and δ. Consider the effect of all controls in the Lagrangian Λ_σ, equation (28), specialized for the case of the heat exchange.

In the case of quadratic dissipation, the Legendre transform of Λ_σ with respect to all control type variable $(\mathbf{v}, \mu')$ is identical with the original. For the heat exchange example, the constraint-adjoining Hamiltonian associated with Λ_σ follows in the form

$$H_\Lambda(\mathbf{x}, \mathbf{v}, \mu') = \tfrac{1}{2} R^\gamma(e^\gamma)(v^\gamma)^2 + \tfrac{1}{2} R^\delta(e^\delta)(v^\delta)^2$$
$$+ \mu'(v^\gamma + v^\delta) - \Psi(e^\gamma, e^\delta). \quad (89)$$

This Hamiltonian must vanish, which determines the second dissipation function whenever the dynamical equations are known. However, when the rates $\mathbf{v}$ are expressed in terms of the driving forces with the help of dynamics such as equation (61), for example:

$$\frac{de^\gamma}{dt} = \frac{(T^\gamma)^{-1} - (T^*)^{-1}}{R^\gamma} \quad (90)$$

the quantity Ψ satisfying the condition $H_\Lambda = 0$ contains the Lagrange multiplier $\mu' \equiv (T^*)^{-1}$:

$$\Psi(\mathbf{x}, \mu') = \tfrac{1}{2}(R^\gamma)^{-1}[(T^\gamma)^{-1} - (T^*)^{-1}]^2$$
$$+ \tfrac{1}{2}(R^\delta)^{-1}[(T^\delta)^{-1} - (T^*)^{-1}]^2 + (T^*)^{-1}(v^\gamma + v^\delta) \quad (91)$$

where the temperature differences are functions of the state variables, $x_e^\gamma = e^\gamma - e^{\gamma 0}$ and $x_e^\delta = e^\delta - e^{\delta 0}$. For the linear dynamical model the interphase potentials $\mathbf{p}^*$ coincide with the equilibrium potentials $\mathbf{p}^0$. Then applying equations (3) and (15) in equation (91) yields the second dissipation function

$$\Psi(\mathbf{x}) = \tfrac{1}{2} R^\gamma(\Gamma^\gamma)^2(x_e^\gamma)^2 + \tfrac{1}{2} R^\delta(\Gamma^\delta)^2(x_e^\delta)^2$$
$$= \tfrac{1}{2} W^\gamma(x_e^\gamma)^2 + \tfrac{1}{2} W^\delta(x_e^\delta)^2 \quad (92)$$

in which $x_e = e - e^0$. Equation (92) is the special case of equation (79). As this is the proper static function for the DVA, the suitability of the Hamiltonian function H_Λ, equation (89), is confirmed. Yet, by using in equation (91) the interphase relationship, equation (65), specialized to the form

$$(T^*)^{-1} = \frac{\mathbf{L}^\gamma(T^\gamma)^{-1} + \mathbf{L}^\delta(T^\delta)^{-1}}{\mathbf{L}^\gamma + \mathbf{L}^\gamma} \quad (93)$$

one can eliminate the Lagrange multiplier and simultaneously reduce the number of coordinates to those of the Onsager approach. This procedure yields

$$(T^\gamma)^{-1} - (T^*)^{-1} = \frac{R^\gamma}{R^\gamma + R^\delta}((T^\gamma)^{-1} - (T^\delta)^{-1}) \quad (94a)$$

$$(T^\delta)^{-1} - (T^*)^{-1} = -\frac{R^\delta}{R^\gamma + R^\delta}((T^\gamma)^{-1} - (T^\delta)^{-1}). \quad (94b)$$

Thus, after using the two above equations in equation (91):

$$\Psi(x_e) = \tfrac{1}{2}(R^\gamma)^{-1}R^{-2}[(T^\gamma)^{-1} - (T^\delta)^{-1}]^2$$
$$+ \tfrac{1}{2}(R^\delta)^{-1}R^{-2}[(T^\gamma)^{-1} - (T^\delta)^{-1}]^2$$
$$= \tfrac{1}{2}(R^\gamma + R^\delta)^{-1}[(T^\gamma)^{-1} - (T^\delta)^{-1}]^2$$
$$= \tfrac{1}{2}R^{-1}\Gamma^2\alpha_e^2 = \Psi(\alpha_e) \quad (95)$$

which is the classical result for the static dissipation function in terms of the independent variable α_e and overall coefficients $R = R^\gamma + R^\delta$ and $\Gamma = \Gamma^\gamma + \Gamma^\delta$.

11. Final remarks

This work has been motivated by the fact that the number of exchange equations, especially those for multiphase systems, have forms which seem at most only indirectly related to the Onsager's theory. The explanation of the origin of this feature has been the task of our work. Our mode of approach has involved comparison of the same process described in terms of the dependent and independent variables. Two approaches have been used: the DVA, or the dependent variables approach; and the IVA, or the independent variables approach (a two-phase counterpart of the integral Onsagerian description).

The virtue of the approach based on dependent variables is that it clarifies meanings of overall coefficients in terms of their one-phase components, a feature which is not considered in the Onsager's theory. We see that this approach yields phenomenological equations consistent with those of Onsager, yet it has the methodological virtue of using an original (non-truncated) entropy function, with the linear terms preserved. The Lagrange multipliers of DVA are the co-state variables in the Gibbs equation, the transfer potentials, $\mathbf{p}$. The DVA allows natural discontinuities of the state variables at the interface, and implies more correct partial transfer coefficients and partial driving forces instead of the (IVA-related) overall transfer coefficients and overall driving forces. The errors stemming from the use of overall coefficients can be especially large in non-isothermal systems with unidirectional or non-equimolar heat and mass transfer as shown by experiments [25–27].

Our approach shows that the classical irreversible thermodynamics uses, in fact, the restricted entropy function, **S**, which contains only terms quadratic or higher due to the prior elimination of linear terms from the original

entropy using the conservation laws. This restricted S is a function of the exergy type, as the latter also has the linear terms eliminated. The DVA approach, proposed here, allows the use of the genuine thermodynamic entropy and its finite-time extensions generated through the Bellman's method of dynamic programming.

The entropy (or its extensions) plays the role of action in any approach (IVA or DVA). The importance of the entropy and the related Lagrange equations is also seen when one passes to the path integrals associated with the stochastic formulation of the problem and the corresponding Fokker–Planck equation [8]. These problems have not been discussed here, but a future paper devoted to stochastic aspects of DVA is planned. This seems to be important since the information–theoretic counterpart of IVA has recently been derived in the context of the minimum relative Kullback entropy [28]; thus, a DVA-type extension should include explicit conservation laws and the absolute informational entropy. Analysis of the transition region between the gas diffusion and the Knudsen diffusion [29], has also been omitted as this might require changes in structure of the dissipation model. Yet, an application to continua with antisymmetric (Casimir) effects will be given in a future work, where a canonical Poisson bracket structure in the Lagrangian frames governed by the thermodynamic Hamiltonian H_σ will be used as the starting point to derive more complicated relaxation equations. The passage to Eulerian frames, Clebsch variables, and a resulting non-Poissonian structure will also be addressed, thus extending previous local-equilibrium results for continua [30, 31], to systems with inherent local disequilibrium caused by the internal variables. We expect that our theory will be appropriate for formulation of the dissipative component within the context of general non-equilibrium dynamics thus, after inclusion of Casimir's terms, the results will be compared with those found within the so-called functional two-bracket approaches [32, 33], which were recently transformed into the so-called generic formalism [34, 35]. Since our present theory is compatible with internal variable formulations in local equilibrium approximation [36, 37], the inclusion of Casimir's terms should add an important ingredient to the internal variable theory.

In conclusion, the thermodynamic theory of heat and mass transfer can be stated in terms of the global, classical variational principles, either as the DVA or (Onsager's) IVA. For the dependent variables (DVA case) we have established the power criterion from which a thermodynamic description complementary with respect to the Onsager case (IVA) follows. The new description involves: DVA variational principle; (dependent) phenomenological equations; DVA entropy production; DVA Lagrange and H–J–B equations; and the DVA Hamilton–Jacobi theory. The significance of these findings refers particularly to the heat and mass transfer processes in multiphase field systems and in interpenetrating continua.

Appendix: an outline of solving methods by discrete dynamic programming

The problem of constructing a generalized entropy function S or the related entropy production function s_σ in an arbitrary continuous or discrete system can be solved by the discrete method of Bellman's dynamic programming [11]. Both continuous and discrete control processes with a single independent variable can be treated in the frame of the common discrete formalism of dynamic programming. (For the continuous case prior discretization of the process equations is required.) Thus, it is enough to consider a multistage control process. Any additive positive quantity can be taken as a generalized cost of the process. At the stage n of a given duration Δt^n ($t^{n-1} = t^n - \Delta t^n$) a single-stage cost P^n is the measure of the local intensity of entropy production Λ_σ^n; $P^n \equiv \Lambda_\sigma^n \Delta t^n$. The total cost is then $K^N = \Sigma P^n = \Sigma \Lambda_\sigma^n \Delta t^n$, for $n = 1, 2, \ldots, N$. These data are entirely sufficient to develop a general theory for integrals or sums of quantities like P^n over cascade processes with an arbitrary number of stages. It is, however, important that P^n is properly expressed as a function of the state $\mathbf{x}^n$, and controls $\mathbf{u}^n$ at the stage n. The total cost K^N which should be minimized is the sum of P^n over the process stages 1, 2, \ldots, N. By definition of K^N, the entropy production function s_σ is the minimum value of the sum K^N.

For a given set of difference constraints and any cost function P^n, the function s_σ is found as the solution of a discrete functional equation or Bellman's equation of dynamic programming [11], which links the optimal functions s_σ^N, s_σ^{N-1} and the cost P^N of the process at stage N:

$$s_\sigma^N(\mathbf{x}^N) \equiv \min_{\mathbf{u}^N} \{P^N(\mathbf{x}^N, \mathbf{u}^N) + s_\sigma^0(\mathbf{x}^{N-1}(\mathbf{x}^N, \mathbf{u}^N))\}. \qquad (A1)$$

Here $\mathbf{x}^{N-1}(\mathbf{x}^N, \mathbf{u}^N)$ are given equality constraints describing the transformed state and time when passing from process stage $N-1$ to process stage N. The control vector $\mathbf{u}^N$ may include Lagrange multipliers of rate constraints in problems with dependent rates. The minimization in equation (A1) is made numerically for each node of the grid of the variables $\mathbf{x}^N$. For each node $\mathbf{x}^N$ the data of the optimal controls $\mathbf{u}^N$, optimal states $\mathbf{x}^{N-1}$ and the optimal function $s_\sigma^N(\mathbf{x}^N)$ are tabled. They are obtained as a solution of equation (A1) by an iterative procedure for the stages 1, 2, \ldots, N, starting from $N = 1$ and $s_\sigma^0 \equiv 0$. The function $s_\sigma^N(\mathbf{x}^N)$ represents a thermodynamic cost of the process related to the local intensity P^n and a finite dur-

ation $t^N - t^0$. Equation (A1) is true for any set of constraints imposed on intermediate states and controls. The optimal function $s_\sigma^N(\mathbf{x}^N)$ is in general a function of both the final state $\mathbf{x}^N$ and the number of stages N (final time t^N), even if the process is autonomous.

The relation between the optimal cost functions generated by dynamic programming and Pontryagin's maximum principle is now well understood [21]. The optimal trajectories of a thermodynamic problem are counterparts of mechanical trajectories in mechanics or light rays in optics. Otherwise, the dynamic programming cost functions describe certain generalized wave-fronts. The mathematics of these approaches is independent of the specific applications; they can be conducted first in the frame of the purely classical formulations and the experience gained can then be used to formulate and solve more involved problems of thermodynamics.

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