

Action-Type Variational Principles For Hyperbolic and Parabolic Heat & Mass Transfer

Stanislaw SIENIUTYCZ
The Faculty of Materials Science and Technology (WMiTO),
Pulaski Technical University
Department of Environmental Protection,
Division of Process and Environmental Engineering
27 Chrobrego Street (room 316), 26-600 Radom, Poland
E-mail: sieniutycz@ichip.pw.edu.pl

Abstract

For the field or Eulerian description of heat conduction, a method is discussed associated with description of thermal fields by a variational principle involving suitably constructed potentials rather than original physical variables. The considered processes are: simple hyperbolic heat transfer and coupled parabolic transfer of heat, mass and electric charge. By using various gradient or nongradient representations of original physical fields in terms of potentials, which are quantities of similar sort as those which Clebsch used in his representation of hydrodynamic velocity, suitable action-type criteria can be found, and corresponding Lagrangian and Hamiltonian formalisms can be developed. Symmetry principles can also be considered and components of energy-momentum tensor can be evaluated for a gauged lagrangian. The limiting reversible case appears as a suitable reference frame. The results suggest that thermodynamic irreversibility does not change neither kinetic potential nor action functional; it only complicates potential representations of physical fields in comparison with those describing the reversible evolution.

Key words: variational principles, least action, extended irreversible thermodynamics

1. Introduction

The evolution of an irreversible thermodynamic system can sometimes be described in terms of a variational principle. When a variational formulation is known, a suitable numerical solving procedure can be applied which is based on direct variational methods (Kantorovich and Krylov, 1958). Two novel approaches, closely related to classical variational principles, have attracted attention of researchers in recent years.

In the first approach, Grmela and coworkers have worked out an important two-bracket formalism (Grmela, 1985; Grmela and Lebon, 1990; Grmela and Ottinger, 1997; Ottinger and Grmela, 1997). It produces evolution equations of a dissipative system via Poissonian and dissipative brackets, the latter being the functional extension of the Rayleigh dissipation function (Rayleigh, 1945). With applications to

rheology, bracket approach have systematically been exposed in a recent book (Beris and Edwards, 1994). Yet two-bracket theorems are not associated with an extremum of a definite physical quantity; for that purpose the single Poissonian bracket and a Hamiltonian system are necessary.

In the second approach, which does not avoid extremizing procedure, the process description is transferred to a different, suitable space, and a variational formulation is found in this space. This is made by introducing certain potentials, similar to those known in the theory of electromagnetic field (Nyiri, 1991; Marcus and Gambar, 1991). Their application to nonreacting systems has proved considerable utility and Lagrangian-Hamiltonian formalisms for irreversible thermodynamics of heat and mass transfer (Gambar and Markus, 1994; Van and Nyiri, 1999). Yet, the inclusion of chemical reactions

has required treating of sources as given functions of time and position, and the choice of potentials reminded slightly mysterious. Recent action approaches to various processes of thermo-hydrodynamics, with Lagrange multipliers absorbing balance constraints for mass and entropy, have proved crucial role of these multipliers in constructing potential representations of physical fields for the purpose of variational principles (Sieniutycz and Berry, 1989, 1993; Sieniutycz, 1994).

The admissibility of a variational formulation calls for substantiation in case when irreversibility enters into the issue. A system of differential equations admits a variational formulation if and only if it is selfadjoint, i.e. when stringent conditions for partial derivatives of the related differential operator are satisfied (Finlayson, 1972; Atherton and Homsy, 1975; Santilli, 1977; Caviglia, 1988; Vazquez et al., 1996). It is also known that typical equations of irreversible processes are, as a rule, not self-adjoint (Finlayson, 1972). A pertinent argument is valid though: while equations of irreversible processes do not admit variational formulation in the state space spanned on their own dependent variables (this is the situation where the non-self-adjointness holds), the so-called composite variational principles in the extended space spanned on these state variables and certain new variables, called state adjoints, is always possible (Atherton and Homsy, 1975; Caviglia, 1988). In fact, all successful recent variational formulations for irreversible continua always involve the space expansion. This claim refers also to the second group of formulations discussed above, which use higher order functionals, because, by suitable substitutions, they can be broken down to those based on the first order functionals in an enlarged space. In this paper we formulate composite functionals of action type in order to obtain field variational principles for two examples: hyperbolic heat transfer and parabolic coupled heat and mass transfer. In the first case we consider the process description in terms of phenomenological and balance equations. In the second case we restrict ourselves to the process description in terms of equations of change.

2. Field Potentials and Action Functional for Hyperbolic Heat Transfer

In this section we exemplify the technique of potential representations by constructing a variational formulation for the linear process of pure heat conduction (heat flux \mathbf{q}) in a rigid solid at rest. We assume that the process is described by the Cattaneo equation and energy conservation law. These equations are respectively

$$-\frac{\partial \mathbf{q}}{c_0^2 \partial t} + \frac{\mathbf{q}}{c_0^2 \tau} + \nabla \rho_e = 0 \quad (1)$$

and

$$\frac{\partial \rho_e}{\partial t} + \nabla \cdot \mathbf{q} = 0 \quad (2)$$

where the density of the thermal energy ρ_e satisfies $d\rho_e = \rho C dT$, c_0 is propagation speed for the thermal wave, τ is thermal relaxation time, and the product $\mathcal{D} \equiv c_0^2 \tau$ is the thermal diffusivity. An action functional which absorbs constraints (1) and (2) by the Lagrange multipliers, the vector ψ and the scalar ϕ , is tested in the form

$$A = \int_{t_{1,v}}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2} \mathbf{q}^2 c_0^{-2} - \frac{1}{2} \rho_e^2 + \psi \cdot \left(-\frac{\partial \mathbf{q}}{c_0^2 \partial t} + \frac{\mathbf{q}}{c_0^2 \tau} + \nabla \rho_e \right) + \phi \left(\frac{\partial \rho_e}{\partial t} + \nabla \cdot \mathbf{q} \right) \right\} dV dt \quad (3)$$

where ε is the density of equilibrium energy at a reference state, the constant which assures the action dimension for A , but otherwise is unimportant. We shall call the multiplier-free term of the integrand (3)

$$L \equiv \frac{1}{2} \varepsilon^{-1} c_0^{-2} \mathbf{q}^2 - \frac{1}{2} \varepsilon^{-1} \rho_e^2$$

the kinetic potential. It has usual units of the energy density. In Eq. (3) the kinetic potential of an indefinite sign is chosen as the structure suitable from the viewpoint of the energy conservation in a limiting reversible process (see further considerations). Vanishing variations with respect to multipliers ψ and ϕ recover constraints, whereas those with respect to state variables \mathbf{q} and ρ_e yield the following representations of state variables in terms of ψ and ϕ

$$\mathbf{q} = \frac{\partial \psi}{\partial t} - \frac{\psi}{\tau} + c_0^2 \nabla \phi \quad (4)$$

and

$$\rho_e = -\nabla \cdot \psi - \frac{\partial \phi}{\partial t} \quad (5)$$

In a limiting reversible process (undamped or wave heat conduction for $\tau \rightarrow \infty$) the process is described by pure gradient representations; the representation for \mathbf{q} has then the structure of the electric field \mathbf{E} expressed in terms of electromagnetic potentials.

The action A, Eq. (3), in terms of the potentials ψ and ϕ is

$$A = \int_{t_{1,v}}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2c_0^2} \left(\frac{\partial \psi}{\partial t} - \frac{\psi}{\tau} + c_0^2 \nabla \phi \right)^2 - \frac{1}{2} \left(\nabla \cdot \psi + \frac{\partial \phi}{\partial t} \right)^2 \right\} dV dt \quad (6)$$

Its Euler-Lagrange equations with respect to ψ and ϕ are respectively

$$\frac{\partial}{\partial \alpha} \left\{ \frac{1}{c_0^2} \left(\frac{\partial \psi}{\partial \alpha} - \frac{\psi}{\tau} + c_0^2 \nabla \phi \right) \right\} + \frac{1}{c_0^2} \left(\frac{\partial \psi}{\partial \alpha} - \frac{\psi}{\tau} + c_0^2 \nabla \phi \right) - \nabla \cdot \left(\nabla \cdot \psi + \frac{\partial \phi}{\partial \alpha} \right) = 0 \quad (7)$$

and

$$-\frac{\partial}{\partial \alpha} \left(\nabla \cdot \psi + \frac{\partial \phi}{\partial \alpha} \right) + \nabla \cdot \left(\frac{\partial \psi}{\partial \alpha} - \frac{\psi}{\tau} + c_0^2 \nabla \phi \right) = 0 \quad (8)$$

It is easy to see that these, Eqs. (1) and (2), are equations of the thermal field in terms of the potentials ψ and ϕ . Their equivalent simplified form shows the damped wave nature of the transfer process. For the Cattaneo equation (1)

$$\frac{\partial^2 \psi}{c_0^2 \partial t^2} - \frac{1}{\tau c_0^2} \frac{\partial \psi}{\partial t} + \frac{\nabla \phi}{\tau} - \nabla \cdot (\nabla \cdot \psi) = 0 \quad (9)$$

and, for the energy conservation equation (2)

$$-\frac{\partial^2 \phi}{\partial t^2} - \frac{\nabla \cdot \psi}{\tau} + c_0^2 \nabla^2 \phi = 0 \quad (10)$$

Interpreting τ as an average time between the collisions, we can regard the reversible process (with $\tau \rightarrow \infty$) as the collisionless one. This is a particular case in which vector potential ψ is only necessary. To prove this statement let us start with action (3) in the single-potential but still irreversible case of a finite τ

$$A = \int_{t_{1,v}}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2} \mathbf{q}^2 c_0^{-2} - \frac{1}{2} \rho_e^2 + \psi \cdot \left(\frac{\partial \mathbf{q}}{c_0^2 \partial t} + \frac{\mathbf{q}}{c_0^2 \tau} + \nabla \rho_e \right) \right\} dV dt \quad (11)$$

The stationarity condition of this A with respect to \mathbf{q} are the representations

$$\mathbf{q} = \frac{\partial \psi}{\partial t} - \frac{\psi}{\tau} \quad (12)$$

$$\rho_e = -\nabla \cdot \psi \quad (13)$$

which constitute a truncated form of general representations (4) and (5). The truncated representations are invalid in the irreversible case. Indeed, while the ψ representation of functional (11), or

$$A = \int_{t_{1,v}}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2c_0^2} \left(\frac{\partial \psi}{\partial t} - \frac{\psi}{\tau} \right)^2 - \frac{1}{2} (\nabla \cdot \psi)^2 \right\} dV dt \quad (14)$$

assures the correct Cattaneo equation (1) for Eqs. (12) and (13), the energy conservation formula (2) is violated by these representations. In fact, they imply the source term $\nabla \cdot \psi / \tau = -\rho_e / \tau$ for the four-divergence of energy. If, however, the process is reversible ($\tau \rightarrow \infty$) the simplest gradient representations $\mathbf{q} = \partial \psi / \partial t$ and $\rho_e = -\nabla \cdot \psi$ hold, which apply the so-called Biot's heat vector (Biot, 1970). They correspond with Cattaneo equation (1) without the irreversible \mathbf{q} term and with a collisionless limit of action (14)

$$A = \int_{t_{1,v}}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2c_0^2} \left(\frac{\partial \psi}{\partial t} \right)^2 - \frac{1}{2} (\nabla \cdot \psi)^2 \right\} dV dt \quad (15)$$

With the simplest (Biot's) representations, the energy conservation is satisfied identically. Functional (15) then refers to undamped thermal waves which propagate with the speed c_0 and satisfy d'Alembert's equation for the energy density ρ_e and temperature T, such as Eq. (10) for $\tau \rightarrow \infty$. Here Biot's potentials are either generalized or replaced by other potentials. As this is in the context of the classical variational formulation, our result is stronger than Biot's.

It should be noted that the choice of the kinetic potential with the plus sign at ρ_e^2 in Eqs. (3) or (11) would result in representations violating energy conservation even in the reversible case, should the Cattaneo equation be taken as the sole adjoined constraint. This substantiates our choice of the kinetic potential in Eq. (3). In fact, the accepted structure of the kinetic potential is Hamiltonian. Yet, large flexibility in choosing the kinetic potential should be stressed when both constraints (1) and (2) are adjoined. This issue is also discussed in Section 4.

3. Energy-Momentum Tensor for Wave Heat Transfer

It is well known that physical actions of reversible processes yield components of the so-called energy momentum tensor G^{jk} , also called the tensor of matter. Taking into account its basic role in conservation laws, we shall outline a

procedure which leads to the energy-momentum tensor from the truncated functional (3) in the case when $\psi = 0$. Subtleties associated with the derivation of balance laws directly from irreversible functionals (3) or (6) are relegated to a separate publication. In any case gauging of the lagrangian Λ plays most essential role when searching for physical components of the tensor. Yet, conservation laws are unaffected by irreversibility, thus they can be derived from reversible lagrangians Λ (without τ terms).

The first Nöther's theorem yields the invariance conditions for the action $A[v(\chi)]$ with respect to the parallel translations of space and time coordinates (Sieniutycz, 1994). In absence of external fields these invariance conditions are conservation equations

$$\sum_k \left(\frac{\partial G^{jk}}{\partial \chi^k} \right) = 0 \quad (16)$$

for the energy-momentum tensor defined as

$$G^{jk} \equiv \sum_1 \frac{\partial v_l}{\partial \chi^j} \left[\frac{\partial \Lambda}{\partial \left(\frac{\partial v_l}{\partial \chi^k} \right)} \right] - \delta^{jk} \Lambda \quad (17)$$

where δ^{jk} is the Kronecker delta and $\chi = (\mathbf{x}, t)$ comprises the spatial coordinates and time. The conservation laws (16) follow directly from the condition that the external fields are absent and Λ does not contain any coordinate χ^k explicitly. Eq. (16) constitutes the concise formulation of the conservation laws for the momentum ($j = 1, 2, 3$) and the energy ($j = 4$). In absence of external fields they describe the vanishing four-divergences ($\text{div}, \partial/\partial t$) of G^{jk} .

The tensor $\mathbf{G} = G^{jk}$ has the following general structure

$$\mathbf{G} = \begin{bmatrix} \mathbf{T} & -\mathbf{\Gamma} \\ \mathbf{Q} & \mathbf{E} \end{bmatrix} \quad (18)$$

where \mathbf{T} is the stress tensor, $\mathbf{\Gamma}$ is the momentum density, \mathbf{Q} is the energy flux density, and \mathbf{E} is the total energy density. The components of this tensor are well known for the adiabatic fluid in which heat flow is absent ("perfect fluid"; Sieniutycz, 1994). The case of fluids with finite thermal conductivities is the most difficult; thus any subsequent implications for lagrangian of Eq. (15), which refers to fluid conducting heat ideally, may be of interest.

When external fields are present, the lagrangian Λ contains explicitly some of

coordinates χ^j . Then only balance equations result. Explicitly they are

$$\sum_k \left(\frac{\partial G^{jk}}{\partial \chi^k} \right) + \frac{\partial \Lambda}{\partial \chi^j} = 0 \quad (16')$$

for $j, k = 1, 2, 4$. Eq. (16') is the formulation of balance equations for momentum ($j = 1, 2, 3$) and energy ($j = 4$).

We shall now calculate components of energy-momentum tensor G^{jk} for a solid heat conductor according to a method developed earlier (Sieniutycz 1994). To eliminate the influence of sources, calculations proceed for the reversible truncation of the original lagrangian Λ [i.e. by taking $\tau \rightarrow \infty$ and $\psi = 0$ in Eq. (3)] after it is gauged by subtracting the four-divergence of energy flow. Thus the following "gauged action" is applied

$$A_g = \int_{t_1, v}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2} q^2 c_0^{-2} - \frac{1}{2} \rho_e^2 - \rho_e \frac{\partial \phi}{\partial t} - q \cdot \nabla \cdot \phi \right\} dV dt \quad (19)$$

With this action we evaluate components G^{jk} from the general formula, Eq. (16), in terms of fields v as coordinates of vector $\mathbf{v} \equiv (q_1, q_2, q_3, \rho_e, \phi)$. Greek indices stand for the spatial components, $G^{\alpha\beta}$ ($\alpha, \beta = 1, 2, 3$). Using the gauged lagrangian Λ and stationarity conditions of Eq. (19) we find for components of stress tensor

$$\begin{aligned} T^{\alpha\beta} &= \sum_1 \left[\frac{\partial v^1}{\partial \chi^\alpha} \frac{\partial \Lambda}{\partial \left(\frac{\partial v^1}{\partial \chi^\beta} \right)} \right] - \delta^{\alpha\beta} \Lambda = \\ &= -\varepsilon^{-1} \frac{\partial \phi}{\partial t} q^\beta - \delta^{\alpha\beta} \Lambda = -\varepsilon^{-1} c_0^{-2} q^\alpha q^\beta + \\ &\varepsilon^{-1} \delta^{\alpha\beta} \left(\frac{1}{2} q^2 c_0^{-2} - \frac{1}{2} \rho_e^2 \right) \end{aligned} \quad (20)$$

where Λ pertains to its stationary value equal to the negative of L . Note that quantity (20) represents stresses caused by the pure heat flow; it vanishes at equilibrium as the heat flux itself. However, these are not usual thermal stresses as the solid is rigid. Rather, they are associated with the heat inertia.

Similarly, the momentum density, $\Gamma^\alpha = -G^{\alpha 4}$, is

$$\begin{aligned} -G^{\alpha 4} &= \Gamma^\alpha = -\sum_1 \frac{\partial v_1 \partial \Lambda}{\partial \chi^\alpha \partial \left(\frac{\partial v_1}{\partial t} \right)} \\ &= \varepsilon^{-1} \frac{\partial \phi}{\partial \chi^\alpha} \rho_e = c_0^{-2} \frac{\rho_e}{\varepsilon} q^\alpha \end{aligned} \quad (21)$$

for $\alpha = 1, 2, 3$. This shows that the heat flow carries a finite momentum defined by the components of the heat flux density, \mathbf{q} , and the derivatives of the heat potential ϕ with respect to spatial coordinates. Again, the momentum of heat vanishes at equilibrium as the heat itself.

The vector $G^{4\beta}$, designated Q^β , is the density of the energy flux. It equals

$$G^{4\beta} = Q^\beta = \sum_{l=1}^3 \left(\frac{\partial v_l}{\partial t} \frac{\partial \Lambda}{\partial (\partial v_l / \partial \chi^\beta)} \right) = \frac{\partial \phi}{\partial t} \frac{\partial \Lambda}{\partial (\partial \phi / \partial \chi^\beta)} = -\varepsilon^{-1} \mathbf{q}^\beta \frac{\partial \phi}{\partial t} = \varepsilon^{-1} \rho_e \mathbf{q}^\beta \quad (22)$$

for $\beta = 1, 2, 3$. This shows the selfconsistency of the description with accuracy to second-order terms of energy-momentum tensor.

Finally, the component G^{44} is the energy density,

$$G^{44} = E = \sum_I \frac{\partial v_I \partial \Lambda}{\partial t \partial (\partial v_I / \partial t)} - \Lambda = \frac{\partial \phi \partial \Lambda}{\partial t \partial (\partial \phi / \partial t)} - \Lambda = \varepsilon^{-1} \rho^2 e - \Lambda = \frac{1}{2} \varepsilon^{-1} c_0^{-2} \mathbf{q}^2 + \frac{1}{2} \varepsilon^{-1} \rho^2 e \quad (23)$$

Note that this is only the nonequilibrium part of the total energy of the system. Should one accept a slight modification of the original kinetic potential in the form

$$L^{\text{tot}} \equiv \frac{1}{2} \varepsilon^{-1} c_0^{-2} \mathbf{q}^2 - \frac{1}{2} \varepsilon^{-1} \rho^2 e - \frac{1}{2} \varepsilon$$

then stationary Λ would equal $-L^{\text{tot}} - \varepsilon$ and total energy density would follow as

$$G^{44} = E^{\text{tot}} = \frac{1}{2} \varepsilon^{-1} c_0^{-2} \mathbf{q}^2 + \frac{1}{2} \varepsilon^{-1} \rho^2 e + \frac{1}{2} \varepsilon \quad (24)$$

where the sum of two last terms well approximates ρ_e when the system is close to equilibrium. Clearly, this modification of L is acceptable as it does not change the representations of the physical fields, \mathbf{q} and ρ_e in terms of the potentials. These results prove that the kinetic potentials accepted here, whose structures conform with Hamilton's structures encountered in various mechanical action principles, can be used to successfully describe processes of heat flow.

4. Adjoined Constraints and Potential Representations of Equations of Change

Here we shall briefly outline an analogous procedure applied for a set of vector equations of

change which describe fields of temperature and chemical potentials in a coupled process of heat and mass transfer. The procedure may involve diverse gradient or non-gradient representations for the considered set of physical fields; thus it constitutes a versatile tool to test various evolution functionals. Again, its basic principle rests on observation that extremizing of an arbitrary criterion subject to given constraints yields automatically a set of equations for Lagrange multipliers of these constraints which is adjoint with respect to the set of constraints. The following example below illustrates the procedure.

A multicomponent, nonisothermal system is now considered, which is composed of components undergoing various transport phenomena in the bulk. The components are neutral (Sundheim, 1964; Ekman et al., 1978; Forland et al., 1989) obeying the phase rule (Van Zeggeren and Storey, 1970). As shown by Sundheim (1964) this setting leads to the independent fluxes of mass, energy and electric current. For the alternative ionic description see Newman (1973). The macroscopic motion of the system is eliminated by choice of the vanishing barycentric frame and assumption about the constancy of the system density, ρ , consistent with the mechanical equilibrium assumption. This assumption makes the effects considered more transparent. With this, the total mass density, ρ , is a constant parameter rather than the state variable, and a reference frame in which the whole system rests easily follows. In this example we ignore effects of finite propagation speed, i.e. we assume traditional form of transfer equations.

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

$$\frac{\partial \mathbf{C}}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (25)$$

This is the matrix notation (de Groot and Mazur, 1984) of all conservation laws consistent when \mathbf{J} is the matrix of independent fluxes

$$\mathbf{J} = (\mathbf{J}_e, \mathbf{J}_1, \mathbf{J}_2, \dots, \mathbf{J}_{n-1}, \mathbf{i})^T \quad (26)$$

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

$$\mathbf{C} = (\rho_e, c_1, c_2, \dots, c_{n-1}, 0)^T \quad (27)$$

The n -th mass flux \mathbf{J}_n has been eliminated by using the condition $\sum \mathbf{J}_i M_i = 0$ for $i = 1, 2, \dots, n$.

The last component of \mathbf{C} vanishes because of the

electroneutrality. The independent transfer potentials are

$$\mathbf{u} = \left(T^{-1}, \tilde{\mu}_1 T^{-1}, \tilde{\mu}_2 T^{-1}, \dots, \tilde{\mu}_{n-1} T^{-1}, -\phi T^{-1} \right) \quad (28)$$

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

$$\mathbf{X} \equiv \nabla \mathbf{u} = \left(\nabla T^{-1}, \nabla(\tilde{\mu}_1 T^{-1}), \nabla(\tilde{\mu}_2 T^{-1}), \dots, \dots, \nabla(\tilde{\mu}_{n-1} T^{-1}), -\nabla(\phi T^{-1}) \right)^T \quad (29)$$

The phenomenological equation for coupled parabolic heat and mass transfer is

$$\mathbf{J} = \mathbf{LX} \equiv \mathbf{L}\nabla\mathbf{u} \quad (30)$$

The densities (27) and the transfer potentials (28) are the two sets of variables in the Gibbs equation for the entropy density $s_v = \rho s$ of the incompressible system with the mass density $\rho = \Sigma M_i c_i$

$$ds_v = \mathbf{u} \cdot d\mathbf{C} \quad (31)$$

The second differential of the entropy involves the derivatives $h^{ik} = d^2 s_v / \partial c_i \partial c_k$, which are components of the symmetric Hessian matrix. These derivatives play the role in partial differential equations describing transfer potentials \mathbf{u} .

When the phenomenological equations and conservation laws are combined, the result is the vector equation of change for the transfer potentials \mathbf{u} . Its simplest representative is the Fourier-Kirchhoff type vector equation of change for pure heat transfer, which describes temperature in the energy representation or its reciprocal in the entropy representation. In the case when derivatives of state variables are small and thermodynamic and transport coefficients can be assumed as constants, equation of change is linear. It has then the form

$$-\mathbf{a} \frac{\partial}{\partial t} \mathbf{u} + \mathbf{L}\nabla^2 \mathbf{u} = 0 \quad (32)$$

where $\mathbf{a} \equiv -\partial \mathbf{C} / \partial \mathbf{u}$ is the thermodynamic capacitance matrix or the negative of the entropy hessian $h_{ik} = d^2 s_v / \partial c_i \partial c_k$. Eq. (32) contains two symmetric matrices, \mathbf{a} and \mathbf{L} . We shall consider a variational formulation for this equation in terms of potentials.

We shall show that in order to produce a variational principle for eq. (32) one can minimize a functional containing any positive integrand to which the constraint (32) is adjoined by a Lagrange multiplier. Consider, for example, functional (33) below with a symmetric positive matrix B

$$A = \int_{t_{1,v}}^{t_2} \left\{ \frac{1}{2} B : \mathbf{u}\mathbf{u} + \phi \left(-\mathbf{a} \frac{\partial}{\partial t} \mathbf{u} + \mathbf{L}\nabla^2 \mathbf{u} \right) \right\} dV dt \quad (33)$$

The Euler-Lagrange equation of this functional with respect to \mathbf{u} provides the following representation for the field vector \mathbf{u}

$$\mathbf{u} = -B^{-1} \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L}\nabla^2 \phi \right) \quad (34)$$

For $B = I$, the unit matrix, the representation of \mathbf{u} follows in terms of potentials found earlier (Nyiri, 1991; Markus and Gambar, 1991). In terms of ϕ action (33) becomes

$$\begin{aligned} A = & \int_{t_{1,v}}^{t_2} \left\{ \frac{1}{2} B^{-1} : \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L}\nabla^2 \phi \right) \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L}\nabla^2 \phi \right) \right\} dV dt + \\ & + \int_{t_{1,v}}^{t_2} \left\{ \phi \left(-\mathbf{a} B^{-1} \frac{\partial}{\partial t} \left(-\mathbf{a} \frac{\partial}{\partial t} \phi - \mathbf{L}\nabla^2 \phi \right) + \right. \right. \\ & \left. \left. + \mathbf{L} B^{-1} \nabla^2 \left(-\mathbf{a} \frac{\partial}{\partial t} \phi - \mathbf{L}\nabla^2 \phi \right) \right) \right\} dV dt \quad (35) \end{aligned}$$

or, since the constraint expression (32) must vanish as the result of the stationarity of A with respect to λ

$$A = \int_{t_{1,v}}^{t_2} \left\{ \frac{1}{2} B^{-1} : \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L}\nabla^2 \phi \right) \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L}\nabla^2 \phi \right) \right\} dV dt \quad (36)$$

Consequently, for any nonsingular B , vanishing vector constraint (32) is produced as Euler-Lagrange equations of functional (36). Indeed, varying Eq. (36) yields

$$B^{-1} \left\{ \mathbf{a} \frac{\partial}{\partial t} \left(\mathbf{a} \frac{\partial \phi}{\partial t} + \mathbf{L}\nabla^2 \phi \right) - \mathbf{L}\nabla^2 \left(\mathbf{a} \frac{\partial \phi}{\partial t} + \mathbf{L}\nabla^2 \phi \right) \right\} = 0 \quad (37)$$

which means that for any non-singular B vector Eq. (32) is satisfied in the form

$$\mathbf{a} \frac{\partial}{\partial t} \left(\mathbf{a} \frac{\partial \phi}{\partial t} + \mathbf{L}\nabla^2 \phi \right) - \mathbf{L}\nabla^2 \left(\mathbf{a} \frac{\partial \phi}{\partial t} + \mathbf{L}\nabla^2 \phi \right) = 0 \quad (38)$$

Whenever \mathbf{u} is represented by Eq. (34), the above equation is the original equation of change, Eq. (32). It describes the heat and mass transfer in terms of the potentials ϕ_k , the components of the vector ϕ . Thus we have shown that the variational principle for \mathbf{u} of Eq. (32) is represented by the minimum of the functional

$$A = \int_{t_{1,v}}^{t_2} \left\{ \frac{1}{2} B : \mathbf{u}\mathbf{u} \right\} dV dt \quad (39)$$

with

$$\mathbf{u} = -B^{-1} \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L} \nabla^2 \phi \right) \quad (34)$$

The result stating that the "representation of \mathbf{u} in terms of ϕ " is needed, as defined by Eq. (34), sets an analogy with the well-known variational principle of electromagnetic field, in which one uses the electromagnetic potentials (\mathbf{A} and ϕ) to state a variational principle for electric and magnetic fields (\mathbf{E} and \mathbf{B}) with their representations defined by the first pair of Maxwell equations (Jackson, 1975).

Let us treat the representation constraint by the Lagrange multiplier, say μ , instead of direct substitution. This requires determining the stationarity conditions for

$$A' = \int_{t_{1,v}}^{t_2} \left\{ \frac{1}{2} B : \mathbf{u} \mathbf{u} + \mu \left(\mathbf{u} + B^{-1} \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L} \nabla^2 \phi \right) \right) \right\} dV dt \quad (40)$$

Vanishing variations with respect to \mathbf{u} , ϕ and μ yield respectively

$$B \mathbf{u} + \mu = 0 \quad (41)$$

$$B^{-1} \left(-\mathbf{a} \frac{\partial}{\partial t} \mu + \mathbf{L} \nabla^2 \mu \right) = 0 \quad (42)$$

and

$$\mathbf{u} = -B^{-1} \left(\mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L} \nabla^2 \phi \right) \quad (34)$$

Eq. (42) is equivalent with Eq. (32). With Eq. (41) incorporated in the product $\mu \cdot \mathbf{u}$, the variational principle obtained from Eq. (40) describes a simple dual formulation: the maximum of the functional

$$A' = \int_{t_{1,v}}^{t_2} - \left\{ \frac{1}{2} B^{-1} : \mu \mu \right\} dV dt \quad (43)$$

subject to the following representation for μ

$$\mu = \mathbf{a} \frac{\partial}{\partial t} \phi + \mathbf{L} \nabla^2 \phi \quad (44)$$

The crucial role of Lagrange multipliers in constructing variational adjoints is well-known in Pontryagin's maximum principle, but seems to be overlooked in the literature of field variational principles. The results obtained here prove that an arbitrarily large number of diverse functionals and related variational principles can be found by this technique.

5. Conclusions

We have obtained here variational formulations based on action-type functionals, which differ substantially from formulations encountered in thermodynamics of Onsager and Prigogine. To our knowledge, no direct relation exists between these two types of variational settings. The results obtained here suggest that the theory of a limiting reversible process should serve as a basis and indicator when choosing a suitable kinetic potential. Its original, reversible structure should be left unchanged whenever any irreversible evolution is tested, and changes caused by the irreversibility should be defined as the necessity to adjoint to the kinetic potential both sort of equations: those describing irreversible kinetics and those representing conservation laws. Unnecessity of adjoining conservation laws in a limiting reversible process could, perhaps, be interpreted as the consequence of the fact that in a reversible evolution, where the physical information does not decrease, conservation laws should follow uniquely (as in mechanics) from dynamical equations of motion determined for a prearranged kinetic potential, or from symmetry principles with respect to time-space or phase translations, applied for the functional of extremal action. In irreversible situations, where the physical information is decaying, more constraints are necessary to be absorbed in the action functional. The thermodynamic irreversibility does not change neither the action nor the kinetic potential; it only complicates the potential representations of physical fields in comparison with the representations describing the reversible evolution.

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Nomenclature

A	action functional
\mathbf{a}	matrix of thermostatic capacitances
C	column vector of densities
c_i	molar concentration of i-th component
c_0	propagation speed of thermal wave
$\mathcal{D} \equiv c_0^2 \tau$	thermal diffusivity
E	total energy density
$e_v = \rho e$	internal energy per unit volume

G_{jk}	energy-momentum tensor;
H_i	Biot vector associated with flux J_i ;
H	Hamiltonian;
h	specific enthalpy
i	molar flux density of electric current;
J	matrix of independent fluxes; mass flux density
J_e	density of total energy flux in component description;
J_i	molar flux density of i-th component;
J_s	density of entropy flux;
k	thermal conductivity;
L	Onsagerian matrix of phenomenological coefficients;
L	kinetic potential;
M_k	molar mass of k-th component;
P	pressure;
Q	vector of energy flux density
q	density of pure heat flux;
S	entropy of the system;
s	entropy of unit mass;
T	temperature;
t	time;
u	vector of independent thermodynamic intensities;
v_l	l-th field variable
V	volume;
X	vector of independent thermodynamic forces.
Greek symbols	
δ	variational derivatives in space;
ε	density of thermal energy at equilibrium reference state
Λ	Lagrangian density;
λ	Lagrange multiplier;
μ_k	molar chemical potential of k-th component;
$\tilde{\mu}_k = \mu_n M_k M_n^{-1} - \mu_k$	transfer potential of k-th component; ($\mu_k \equiv -\tilde{\mu}_k$)
ρ	mass density
ρ_e	density of thermal energy
σ	production terms per unit volume;
τ	relaxation time;
ϕ	scalar potential of thermal or electromagnetic field;
ψ	vector potential of thermal field
Δ	nabla operator
Subscripts	
e	energy;
k	k-th component;
s	entropy;
v	per unit volume

Superscripts

s	entropy representation;
T	transpose matrix.

References

- Atherton, R. W., and Homsy, G. M., 1975, On the existence and formulation of variational principles for nonlinear differential equations, *Stud. Appl. Math.* **54**, 31-80
- Beris, A. N., and Edwards, B. J., 1994, *Thermodynamics of Flowing Systems with Internal Microstructure*, Oxford University Press, Oxford.
- Biot, M., 1970, *Variational Principles in Heat Transfer*, Oxford University Press, Oxford.
- Caviglia, G., 1988, Composite variational principles and the determination of conservation laws, *J. Math. Phys.* **29**, 812-816.
- De Groot, S. R., and Mazur, P., 1984, *Non-equilibrium thermodynamics*, Dover, New York.
- Ekman, A., Liukkonen, S., and Kontturi, K., 1978, Diffusion and electric conduction in multicomponent electrolyte systems, *Electrochimica Acta* **23**, 243-250.
- Finlayson, B. A., 1972, *The Method of Weighted Residuals and Variational Principles*, Academic Press, New York.
- Forland, K. S., Forland, T., and Ratkje, S. K., 1989, *Irreversible Thermodynamics-Theory and Applications*, Wiley, Chichester.
- Gambàr K., and F. Mårkus, F., 1994, on-Lagrange formalism of nonequilibrium thermodynamics, *Phys. Rev. E* **50**, 1227-1231.
- Grmela, M., 1985, Bracket formulation for Navier-Stokes equations, *Phys. Lett.* **111 A**, 36-40.
- Grmela M. and Lebon, G., 1990, Hamiltonian extended thermodynamics, *J. Phys. A* **23**, 3341-3351.
- Grmela, M. and Ottinger, H. C., 1997, Dynamics and thermodynamics of complex fluids. I. Development of a general formalism, *Phys. Rev. E* **56**, 6620-6632.
- Jackson, D., 1975, *Classical Electrodynamics*, Wiley, New York.
- Kantorovich, L. V., and Krylow, V. I., 1958, *Approximate Methods of Higher Analysis*, Nordhoff, Groningen.
- Markus F., and Gambar, K., 1991, A Variational Principle in Thermodynamics, *J. Non-Equilib. Thermodyn.* **16**, 27-31.
- Newman, J., 1973, *Electrochemical Systems*, Prentice Hall, Englewood Cliffs.

- Nyiri, B., 1991, On the construction of potentials and variational principles in thermodynamics and physics, *J. Non-Equilib. Thermodyn.* **16**, 39-55.
- Ottinger, H. C and Grmela, M., 1997, Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism, *Phys. Rev. E* **56**, 6633-6652.
- Rayleigh, J.W. S., 1945, *The Theory of Sound*, Dover, New York.
- Santilli, R. M., 1977, Necessary and sufficient conditions for the existence of a Lagrangian in field theory. I. Variational approach to self-adjointness for tensorial field equations, *Ann. Phys. (NY)* **103**, 354-408.
- Sieniutycz, S., and Berry, R. S., 1989, Conservation laws from Hamilton's principle for nonlocal thermodynamic equilibrium fluids with heat flow, *Phys. Rev. A* **40**, 348-361.
- Sieniutycz, S., and Berry, R. S., Canonical formalism, fundamental equation and generalized thermomechanics for irreversible fluids with heat transfer, *Phys. Rev. E* **47**, 1765-1783 (1993).
- Sieniutycz, S., 1994, *Conservation Laws in Variational Thermodynamics*, Kluwer Academic Publishers, Dordrecht.
- Sundheim, B. R., 1964, Transport properties of liquid electrolytes, in: *Fused Salts*, ed. B. R. Sundheim, pp. 165-254, Mc Graw Hill, New York.
- Van, P., and B. Nyiri, B., 1999, Hamilton formalism and variational principle construction, *Ann. Phys. (Leipzig)* **8**, 331-354.
- Van Zeggeren, F., and Storey, S., 1970, *The Computation of Chemical Equilibria*, Cambridge University Press, Cambridge.
- Vazquez, F., del Rio, J. A., Gambar, and Markus, F., 1996, Comments on the existence of Hamiltonian principles for non-selfadjoint operators, *J. Non-Equilibrium Thermodyn.* **21**, 357-360.