On the structure of the Governing Principle of Dissipative Processes

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Abstract

The Governing Principle of Dissipative Processes (GPDP) is the most widely applied variational principle in non-equilibrium thermodynamics. It is not a usual 'hamiltonian type' principle, therefore there are a lot of misunderstandings and misconceptions regarding its applicability and completeness. In this paper its structure and domain of applicability is investigated and cleared up.

1 Introduction

Thermodynamics is a special area of physics where we find a lot of different variational principles. The reason is that an investigation based on a mathematical theorem shows that the basic differential equations of (irreversible) thermodynamics, the transport equations cannot be derived from a usual 'hamiltonian type' variational principle. Let us consider a differential equation. If there exists a hamiltonian type variational principle whose Euler-Lagrange equation is the differential equation, than we call that equation (and the corresponding differential operator) *potent*. We call the equation *non-potent* if there exists no such a principle. Several principles and methods were born to circumvent the mentioned theorem, to construct variational principles for non-potent operators using different techniques. We can distinguish four main groups:

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- The method of *additional variables (or dual principles)* introduces new variables to make the corresponding operator potent.
- The method of *integrating operator* is a generalization of the method of integrating multipliers. A special case of this trick is the method of *least* squares.
- In the method of *transformation of variables* we introduce 'potentials' like the scalar and vector potential in the Maxwell equations.
- Using the *method of modifications* we modify the corresponding operator or function space in an appropriate way to get a potent operator.

A more detailed treatment and a survey of the variational principles and methods in thermodynamics is given in [1, 2, 3]. For the same non-potent equation (e.g. heat conduction equation) one can find and apply several variational principles each based on a different method. Moreover after having grasped the essence of the corresponding method one can easily *construct* different principles for almost any differential (or integral or any other) equation.

Some principles mix different methods to solve the problem caused by different non-potent terms of the equation. The Governing Principle of Dissipative Processes (GPDP) is one of them. This principle exploits the special structure of transport equations of irreversible thermodynamics; introduces the thermodynamical currents as additional variables (here the additional variables have a physical meaning!); has a Gaussian form resembling the method of least squares and modifies the original function space.

In the following chapter we consider shortly the method of least squares and the method of modifications for non-potent differential operators. In the third one we treat the structure of the GPDP. The fourth chapter is dealing with the special case of 'pure dissipative processes'. The last chapter contains some discussion.

2 Methods of constructing variational principles for non-potent operators

In the following a mapping (or a function) is called an **operator**, if its domain and its range are spaces of functions. A mapping is called a **functional**, if its domain is a function space and its range a linear space of real (or complex) numbers.

It was mentioned in the introduction that the basic theorem of the inverse problem of calculus of variation results in a strict mathematical condition for constructing a variational principle of a given (usually differential) operator. This condition was known essentially by Helmholtz and was after him reconsidered and generalized by several authors (see Havas, Santilli and Tonti on historical aspects [4, 5, 6]). A modern and general formulation and a proof that it is a necessary and sufficient condition for the existence of a variational principle is due to Vainberg [7]. This theorem can be considered as a (not simple) generalization of the well known fact that a force field is conservative, if its curl vanishes. This classical condition splits the group of equations (more properly operators) into two groups:

- 1. **potent** operators for which a variational principle can be constructed in this rigorous sense,
- 2. **non-potent** operators for which a variational principle does not exist in this classical, 'hamiltonian' sense.

Most of the differential equations of physics are non-potent, so the inverse problem of calculus of variation was a great challenge for physicists, which resulted in a huge amount of methods for constructing variational principles for non-potent operators or equations. Three of them will be treated in this chapter, because they are incorporated in the GPDP.

The general notation for any differential or integral equation will be $\hat{\Theta}(\varphi) = 0$ where $\hat{\Theta}$ is an (integral or differential, linear or nonlinear) operator mapping from the function space of φ functions to an other function space. The corresponding spaces are usually normed. For the sake of simplicity we allways will speak of Hilbert spaces. The corresponding scalar product will be denoted by $\langle -, - \rangle$. Some important aspects on the - not only mathematical - question of the relation between normed and Hilbert spaces in the inverse problem of calculus of variation is discussed in [1, 2].

2.1 The method of least squares

For equations with a bounded linear operator \hat{A} we can construct the variational action functional

$$\hat{S}(\varphi) = \frac{1}{2} \langle \hat{A}\varphi, \hat{A}\varphi \rangle.$$

This would be considered as a generalization of the method of least squares for functions in Hilbert spaces. Formally we can derive that the corresponding Euler-Lagrange equation is $\hat{A}^* \hat{A} \varphi = 0$. Here * denotes the adjoint of the operator. The solutions of this equation is a subset of the solutions of the equation $\hat{A}\varphi = 0$. However it is easy to see that the range of \hat{A} should be in the domain of its adjoint. A detailed investigation and a proper generalization of this method for every nonlinear operator (bounded or unbounded) is given by Tonti [6].

The two other methods used in the GPDP are usually treated together and are sometimes referred as quasi-variational, or 'restricted' principles [8, 9, 10].

2.2 Modified operators

By this method the operator $\hat{\Theta}$ is modified in such a way that the transformed operator $\hat{\Theta}_m$ will be potent. The domain of the modified operator is the same as for the original one. Of course, in this case variational potentials exist only for the modified operator, not for the original one.

"Variational principles" coming from the method of modified operators are usually believed to be valid in a more general sense than they really are. For instance, the resulting Euler-Lagrange equations are transformed to get back the original operator. Sometimes the method is interpreted as application of a "restriction" because the modification is usually a restriction of the original operator, as it is shown in the following example. However, well applicable numerical methods can be elaborated with the help of this procedure to solve the *original* equation.

Example: The typical example is the stationary heat conduction equation with a temperature-dependent heat conduction: $\hat{\Theta}(T) = \nabla(\lambda(T)\nabla T)$. This operator is generally non-potent. The usual modification is the following $\hat{\Theta}_m(T) =$ $\nabla(\lambda_0 \nabla T)$. Here λ_0 is a positive real number.

This trick was applied among others by Glansdorff and Prigogine and his co-workers in the method of local potentials [11, 12].

2.3 Modified function spaces

In this case the domain of the original operator is restricted, so that the originally non-potent operator becomes potent on the restricted domain. With other words the operator is modified by restricting its domain $(Dom\hat{\Theta}_m \subset Dom\hat{\Theta})$ and not its 'shape'.

The modification of function spaces leads to well defined extremum problems on an appropriate 'restricted' function space for a differential equation. Thus Finlayson is wrong declaring that this method is out of the framework of the calculus of variation [9, p342-343]. Moreover, in case of usual initial-boundary value problems this procedure can lead to well manageable numerical methods for the *original* equation, too [12, 13].

In practice this method is applied most frequently to obtain a variational principle for differential equations containing first order time derivatives. A more detailed mathematical treatment of this special case can be found in the Appendix. In non-equilibrium thermodynamics it is used in the method of local potentials [11, 12] or in different forms of the Gyarmati principle [14, 15].

Remark: If we find the hint: "the time derivative must be held fixed during the variation", then a modified function space is introduced for the variation.

3 The GPDP

The Governing Principle of Dissipative Processes of Gyarmati [14, 15] is one of the most widely applied variational principle of irreversible thermodynamics [16]-[30]. It is not a hamiltonian variational principle and its structure initiated several papers [15, 33] [9, p342-343][31, 32] with some misunderstandings and misinterpretations among them. As far as physics is concerned, it is formulated to incorporate the whole domain of non-equilibrium thermodynamics.

From the original form of the Gyarmati principle the basic equations of the Onsager's irreversible thermodynamics are derivable and its formulation extensively exploits the special structure of these equations. To describe the principle in a sufficiently general form I should expound the whole structure of equations of continuum physics. Although completely objective, reference frame independent form can be given [34, 35, 36] we restrict ourself to the usual frame dependent description.

A continuum has a velocity field $\mathbf{v} \in C^2(\mathbb{R} \times \mathbb{R}^3, \mathbb{R}^3)$. We will call **balance**

equation of the specific physical quantity 'a' an equation of the shape

$$\underline{\varrho}\dot{a} + \nabla \cdot \mathbf{J}_a = \sigma_a. \tag{1}$$

Here ρ is the mass density, \mathbf{J}_a is the conductive current density of a, and σ_a is its source density. The dot denotes the substantial time derivative (derivative along a current line), $\nabla \cdot$ is the trace of the derivative with respect of the space variables according to a given observer.

Let us suppose that the behavior of the continuum in a given frame of reference can be described by 'n' quantities. We should remark that these quantities can be tensor valued functions of any order. The formal structure of the (1) balance equations does not change in case of quantities 'a' with different orders, but the differentiation should be interpreted properly. For the sake of simplicity we will suppose that 'a' is an 'n' component vector of scalar valued functions, and it is defined on a given $U \in \mathbb{R}^3$ compact set (space), and on a $[t_1, t_2]$ interval of time. Thus the corresponding source and current density have the same domain and an appropriate tensorial character.

For the mass density an independent balance equation is introduced, which does not fit into the scheme of (1) and called **equation of continuity**:

$$\dot{\varrho} + \varrho \nabla \cdot \mathbf{v} = 0, \tag{2}$$

where $\mathbf{v} : [t_1, t_2] \times U \to \mathbb{R}^3$ is the material velocity field of the continuum. The mentioned reference frame independent description, where the functions representing the physical quantities are defined in a space-time model, would enable a unified treatment of the balance equations, and a clearer insight into their structure, but it would require to define some more concepts which is out of the frame of this paper.

With these definitions (1) is not a differential equation that we could solve. We need relations which are called **material functions** and which contain different physical assumptions on the structure of the material. Let our basic variables be the components of the *n* component vector valued function Γ . Its components usually represent different thermostatically intensive or extensive physical quantities. We give the material functions in the following forms

$$\sigma: \mathbb{R}^n \to \mathbb{R}^n; \quad \Gamma \qquad \mapsto \sigma(\Gamma), \tag{3}$$

$$a: \mathbb{R}^n \to \mathbb{R}^n; \ \Gamma \longmapsto a(\Gamma),$$
 (4)

$$\mathbf{J}: \mathbb{R}^n \times \left(\mathbb{R}^n \otimes \mathbb{R}^3\right) \to \mathbb{R}^n \otimes \mathbb{R}^3; \quad (\Gamma, \nabla \Gamma) \quad \mapsto \mathbf{J}(\Gamma, \nabla \Gamma) = \mathbf{L}(\Gamma) \cdot \nabla \Gamma,$$
(5)

where $\mathbf{L} : \mathbb{R}^n \to (\mathbb{R}^n \otimes \mathbb{R}^3) \otimes (\mathbb{R}^n \otimes \mathbb{R}^3), \Gamma \mapsto \mathbf{L}(\Gamma)$ is a symmetric nondegenerate matrix (in a given reference frame) which is called **conductivity matrix**. Formula (4) is called as **state function (state equation)**; (5) is the **constitutive function (constitutive equation)**.

This model of a continuum is quite a restricted one; here the main assumptions are

- local equilibrium, in the sense that we assumed that the traditional equilibrium physical quantities are sufficient for the description of the continuum also in non-equilibrium, and the state functions known from thermostatics describe the relationships among them;
- the constitutive functions are of the shape (5), the thermodynamic forces have a gradient form ($\nabla\Gamma$), and σ depends only on the variables determined in (3);
- Onsager's reciprocity relations.

These assumptions can be weakened, the validity of the GPDP can be extended to more general continuum models:

- the assumption of the local equilibrium is not necessary [37];
- there are several extensions of the principle to different non-linear constitutive equations [14, 38, 39, 40, 41];
- there are efforts to extend the validity of the principle for Casimir type reciprocity relations, i. e. if the conductivity matrix has antisymmetric parts [40, 41, 42].

These extensions would make our treatment unnecessarily complicated. Here we want to investigate the basic structure of the principle; that is why we restrict ourself to the generality of the original formulation.

If the material functions (3) and (4) are substituted into the balance (1) we can get the **quasi-balance equation**:

$$\rho \dot{a}(\Gamma) + \nabla \cdot \mathbf{J} = \sigma(\Gamma). \tag{6}$$

Here the independent variables are the components of the basic variable Γ and the current density **J**. If the constitutive function (5) is substituted into the quasi-balance (6) then we have the so called **transport equation**:

$$\rho \dot{a}(\Gamma) + \nabla \cdot (\mathbf{L}(\Gamma) \cdot \nabla \Gamma) = \sigma(\Gamma) \tag{7}$$

The transport equation is the dynamical equation of the continuum in the sense that together with the continuity equation (2) it is a well defined system of partial differential equations (as many variable as many function), that we can solve with given boundary and initial conditions and the solution result in the time and space development of the fields of the continuum.

The universal form of the Gyarmati principle provides a procedure to construct a variational potential for the (7) transport equation. It is well known and easy to check, that the operator of the equation (7) is non-potent, because the conductivity matrix depends on Γ and the first term is a time derivative of first order. Let us see how we can circumvent the usual conditions of the existence of a variational principle in the GPDP.

In GPDP the time derivatives are varied independently (thus according to the Appendix the function space is restricted to $X^3(U,g)$, the 'time parametric form' of the original one). Therefore the method of modified function spaces is applied. On the other hand the function space is enlarged by using additional variables to eliminate the problem that the conductivity matrix depends on Γ , and special subsidiary conditions are used to incorporate the source term to the variational principle.

The variational potential of Gyarmati, the 'action' functional of the principle can be written in its Gaussian form proposed by Nyíri [40, 41]:

$$S(\Gamma, \mathbf{J}) = -\int_{U} \frac{1}{2} (\mathbf{J} - \mathbf{L}(\Gamma) \cdot \nabla \Gamma) \cdot (\mathbf{L}^{-1}(\Gamma) \cdot \mathbf{J} - \nabla \Gamma) dV.$$
(8)

Here we are looking for the minimum of S on the restricted function space of the currents $\tilde{\mathbf{J}}(t)$ and independent variables $\Gamma(t)$, where $(\Gamma(t), \tilde{\mathbf{J}}(t)) \subset X^3(U, g) \times (X^3(U, g) \otimes X^3(U, g))$, using (6) as a subsidiary condition. In the following the $(\Gamma, \mathbf{J}$ functions and its 't' parametric forms $(\tilde{\Gamma}(t), \tilde{\mathbf{J}}(t))$ are denoted by the same letter according to the usual denotation.

It is suitable to put down the original form of the principle for further discussion:

$$S(\Gamma, \mathbf{J}) = \int_{U} \left(\sigma_s(\Gamma, \mathbf{J}) - \Phi(\Gamma, \mathbf{J}) - \Psi(\Gamma, \mathbf{J}) \right) dV, \tag{9}$$

where $\sigma_s(\Gamma, \mathbf{J}) = \mathbf{J} \cdot \nabla \Gamma$ is the **entropy production**, $\Phi(\Gamma, \mathbf{J}) = \frac{1}{2} \mathbf{J} \cdot \mathbf{L}^{-1}(\Gamma) \cdot \mathbf{J}$ and $\Psi(\Gamma, \mathbf{J}) = \frac{1}{2} \nabla \Gamma \cdot \mathbf{L}(\Gamma) \cdot \nabla \Gamma$ are the so-called **dissipation potentials**.

The derivation of the transport and constitutive equations, the application of the subsidiary conditions is usually executed in a quite special way [14, 15, 16] as follows.

First of all the Euler-Lagrange equations of the variational potential (9) or (8) are constructed (on appropriate restricted function space) without the subsidiary conditions. The variation with respect to **J** results that:

$$\mathbf{L}^{-1}(\Gamma) \cdot \mathbf{J} - \nabla \Gamma = 0. \tag{10}$$

The variation with respect of Γ is:

$$\nabla \cdot \left[\mathbf{J} - \mathbf{L}(\Gamma) \cdot \nabla \Gamma\right] + \frac{1}{2} \mathbf{L}'(\Gamma) \left[\mathbf{L}^{-1}(\Gamma)\mathbf{J} + \nabla \cdot \Gamma\right] \cdot \left[\mathbf{L}^{-1}(\Gamma)\mathbf{J} - \nabla \Gamma\right] = 0 \quad (11)$$

Then we substitute the t-parametric quasi-balance equations into the first term of the left hand side of (11). The second term vanishes if we use equation (10). This latter fact is called the subsidiary theorem of Gyarmati [14]. In this way the transport equations (7) follow from (11) (of course in the narrower $X^{3}(U,g)$ function space!) and (10) is equivalent to the constitutive equations (5). The derivation of the constitutive and transport equations finished.

Let us examine this procedure a bit more closely. First of all we observe that (10) and (11) are not independent equations, since the solutions of (10) are the solutions of (11). Moreover, we know that the variational potential (9) has an extremum at the subsidiary condition (6). Now several questions arise. Why can be regarded (10) and (11) as independent equations? Why do not to apply the usual Lagrange multiplier method as usual in constrained extremum problems? The answers to these questions are quite straightforward after our preparations. First of all we must not confuse the concept of subsidiary condition with the concept of a constraint. In our case the subsidiary condition is the t parametric form of the quasi-balance equation. But the t parametric form of the \dot{a} time derivative in (6) is independent from the *t*-parametric form of *a*, therefore it is independent from the variables Γ and **J**. The differential equations (6) does not determine a constraint since it does not prescribe an additional condition for the original variables but gives the dependence of the new variable \dot{a} on the old variables! That is why the GPDP is called a variational principle with *subsidiary* condition, and not a variational principle with constraint. Let us recognize that

after the application of the subsidiary codition (6), our final equations (10) and (7) are independent becouse of the new variable. Furthermore, the usual procedure of the derivation of the Euler-Lagrange equations is correct, although the customary Lagrange multiplier method need not be applied, since we do not want to get an extremum on a subset of the original function space: our condition introduces a new variable. The 'time parametric' modified function space makes this simplified deduction of the Euler-Lagrange equations possible.

4 Purely dissipative systems

It is worth to mention the particular form of the Gyarmati principle valid for purely dissipative systems. In this case we suppose that convective mechanical motion does not occur, that is $\mathbf{v} = const.$, and we suppose that a and Γ represent the n component vector of thermostatically extensive and intensive variables, respectively. Therefore if $s : \mathbb{R}^n \to \mathbb{R}, a \mapsto s(a)$ is the entropy function, then the intensive variables $\Gamma(a) = Ds(a)$ are determined by the derivatives. Of course, in practise the situation is a bit more difficult. The usual intensive variables are not given by a simple derivation of the entropy, we can get only the so called *entropic intensive variables*. Remember, for example, that $\frac{\partial s}{\partial u} = \frac{1}{T}$ where u is the internal energy, T is the temperature. Because Gyarmati uses the extensive parameter a as an independent variable his variational potential can be transformed with the help of the entropy quasi-balance, which can be written in the next form:

$$\varrho \dot{s}(a) + \nabla \cdot \mathbf{J}_s = \sigma(\gamma, \mathbf{J}) = \varrho \Gamma(a) \cdot \dot{a} + \nabla \cdot \mathbf{J}_s,$$

where \mathbf{J}_s is the entropy current density.

We can change the variables of (11) with the help of the entropic intensive variables.

$$\begin{split} \hat{S}(a,\mathbf{J}) &= \hat{S}(\Gamma(a),\mathbf{J}) = \int_{U} \left(\sigma_{s}(\Gamma(a),\mathbf{J}) - \Phi(\Gamma(a),\mathbf{J}) - \Psi(\Gamma(a),\mathbf{J}) \right) dV = \\ &= \int_{U} \left(\varrho \Gamma(a) \dot{a} - \frac{1}{2} \left(\nabla \Gamma(a) \cdot \mathbf{L}(\Gamma(a)) \cdot \nabla \Gamma(a) + \mathbf{J} \cdot \mathbf{L}^{-1}(\Gamma(a)) \cdot \mathbf{J} \right) \right) dV + \\ &+ \oint_{\partial U} \mathbf{J}_{s} \cdot d\mathbf{A}. \end{split}$$

Here the entropy quasi-balance (4) and the definition of the dissipation potentials are used. In this case σ_s is divided into two parts, and the Lagrange density looses its quadratic character. As a result, Gyarmati's supplementary theorem looses its validity. Unfortunately, this fact implies the restriction of the variational principle to transport equations with strictly linear constitutive functions [14]. In this case **J** is not an independent variable anymore. Suppressing unnecessary terms we get the force representation of the Gyarmati principle [15], where the variational potential can be written as:

$$S_{force}(a) = \int_{U} \left(\varrho \Gamma(a) \dot{a} - \frac{1}{2} \nabla \Gamma(a) \cdot \mathbf{L} \cdot \nabla \Gamma(a) \right) dV.$$
(12)

Moreover, if we suppose that the quasi-balance equation considered does not have a source term, then the variational principle is valid without any subsidiary condition. This latter case is essentially equivalent with the principle of minimal entropy production (every function is time-parametric). In this case the corresponding Euler-Lagrange equation is:

$$\left[\varrho\dot{a} - \nabla \cdot (\mathbf{L} \cdot \nabla \Gamma(a))\right] \cdot D\Gamma(a) = 0.$$
⁽¹³⁾

Here $D\Gamma(a)$ is the second derivative of the entropy, so it must be a symmetric and negative definite function according to the basic principles of thermostatics. Therefore (13) is equivalent to the appropriate restricted transport equation (7).

However, other independent variables can be used, too. For example, we can keep the variable Γ , but in this case the Legendre transformed form of the entropy function $s_L(\Gamma) = a \cdot \Gamma - s(a)$ should be used to get the right result, since in this case $\dot{s}_L(\Gamma) = a(\Gamma) \cdot \dot{\Gamma}$. The previous variational potential can be modified as:

$$S_{Lforce}(\Gamma) = \int_{U} \left(\varrho a(\Gamma) \dot{\Gamma} - \frac{1}{2} \nabla \Gamma \cdot \mathbf{L} \cdot \nabla \Gamma \right) dV \tag{14}$$

and the Euler -Lagrange equation is as follows:

$$\varrho \frac{\partial a(\Gamma)}{\partial \Gamma} \dot{\Gamma} - \nabla \cdot (\mathbf{L} \cdot \nabla \Gamma) = 0, \qquad (15)$$

so the transport equation is derived directly and in the more usual Γ -variables.

The variational potential (12) was used by Gyarmati [14]. The other variational potential (14) was proposed by Lambermont and Lebon [31, 43] and these authors also criticized the validity of (12). However, after the previous paragraphs it can be seen that although the Legendre transformed form is really more comfortable it does not touch the validity of the original form and it is doubtful that the proposal of Lambermont and Lebon can be accepted as an independent variational principle. Furthermore the authors in the paper mentioned above also criticize the universal form of Gyarmati's principle. Here, it seems to me that they do not distinguish sharply the balance and transport equations so they misunderstand the role and the usage of the restrictions and subsidiary conditions in the principle.

It is worth mentioning that both forms of Gyarmati's principle valid for purely dissipative systems are in a close connection with the principle of minimal entropy production as far as of the application of the restriction of the variation to the time derivatives is concerned. The strength of Gyarmati's principle is in its applicability to *quasilinear* transport equations.

5 Remarks

We have seen what kind of techniques are used in the Governing Principle of Dissipative Processes to avoid the non-hamiltonian, non-potent character of the transport equations of classical irreversible thermodynamics. I hope that this investigation, the distinction of the different methods, make the right interpretation, the appropriate application and the generalization of the principle easier.

6 Appendix

Let A, B and C be arbitrary sets, $a \in A$, $b \in B$ and denote the functions mapping the elements of B into C by Fun(B, C).

Definition 6.1 The function \tilde{f} is called the **a-parametric form of** f, if $f: A \times B \to C$, $(a,b) \mapsto f(a,b)$ and $\tilde{f}: A \to Fun(B,C)$, $a \mapsto \tilde{f}(a)$, where $\tilde{f}(a): B \to C, b \mapsto f(a,b)$. Sometimes we denote $\tilde{f}(a)$, the value of \tilde{f} at the point a, by f(a,).

In case of parametric functions we should be careful with the meaning of the differentiation. For example, if $A, B, C \subset \mathbb{R}$ and there is a norm on the set Fun(B, C) then

$$D\tilde{f}(a) = \frac{d\tilde{f}}{da}(a) \not\equiv \frac{\partial \tilde{f}}{\partial a}(a) = \frac{\partial f}{\partial a}(a, ...),$$

the derivative of the a-parametric form of f does not equal the a-parametric form of the partial derivative of f with respect to a. The usual notation does not distinguish f from \tilde{f} , which can lead to confusion.

Example

Let us suppose that $[t_1, t_2] \subset \mathbb{R}, U \subset \mathbb{R}^3$ is compact and

$$X^{1,3}(U,g,g_i) := \left\{ \varphi \in C^2 \left([t_1, t_2] \times U, \mathbb{R} \right) \, \big| \, \varphi \, |_U \, \in X^3(U,g); \varphi |_{t_1} = g_i \, \right\},$$

where g_i is the initial, g is the boundary condition. $X^{1,3}(U, g, g_i)$ is a proper function space to formulate some initial-boundary value problems for parabolic partial differential equations in the classical space-time. In this case the $\tilde{\varphi}$, the t-parametric form of $\varphi \in X^{1,3}(U, g, g_i)$ maps to every time point of the given interval a space configuration:

$$\tilde{\varphi}: [t_1, t_2] \to X^3(U, g), t \mapsto \tilde{\varphi}(t) \text{ where } \tilde{\varphi}(t) \in X^3(u, g), x \mapsto \varphi(t, x).$$

and

$$X^{3}(U,g) = \left\{ \varphi \in C^{2}(U,\mathbb{R}) \cap C^{0}(\overline{U},\mathbb{R}) \, | \varphi |_{\partial U} = g \right\}$$

is a field satisfying the given boundary conditions.

As an example to the usage of $\tilde{\varphi}$ let us see the construction of a restricted variational potential for the full heat conduction equation of Fourier with a constant heat conduction coefficient:

$$\frac{\partial \varphi}{\partial t} - \nabla \cdot (\lambda_0 \nabla \varphi) = \frac{\partial \varphi}{\partial t} - \lambda_0 \Delta \varphi = 0$$

The $\lambda_0 \in \mathbb{R}^+$ heat conduction coefficient is generally not a constant function, it can depend on the temperature. In this case the differential equation is a quasilinear one, only the left hand side form is valid.

It is well known that the second term of the left hand side is a potent operator but it is easy to prove that there exist no variational potential for the time derivative.

Rosen [44] proposed a variational potential for the whole equation with the prescription "the time derivative must be held fixed during the variation". This specification can be interpreted that we restrict our $X^{1,3}(U, g, g_i)$ function space

onto $X^{3}(U,g)$. With the notations introduced above a possible variational potential can be written as

$$S(\tilde{\varphi}(t)) = \int_{U} \left(\tilde{\varphi}(t) \frac{\partial \tilde{\varphi}(t)}{\partial t} - \frac{\lambda}{2} \left(\nabla \tilde{\varphi}(t) \right)^{2} \right) dV$$

where $\tilde{\varphi}$ is not the original function but its t-parametric form.

After the differentiation of S by $\tilde{\varphi}$ we can get the Euler-Lagrange equation:

$$\frac{\partial \tilde{\varphi}(t)}{\partial t} - \lambda_0 \nabla^2 \tilde{\varphi}(t) = 0,$$

because in this case $\tilde{\varphi}(t)$ and $\frac{\partial \tilde{\varphi}(t)}{\partial t}$ are independent functions of $X^3(U,g)$! Here we must not identify $\tilde{\varphi}(t)$ and φ , as Rosen did it, because so we would return from $X^3(U,g)$ to $X^{1,3}(U,g,g_i)$ and S is not a variational potential on $X^{1,3}(U,g,g_i)$. So we cannot get back the original heat conduction equation, we must remain on the restricted one! However this can result variational techniques for the *original* problem too [13].

References

- Ván P.: Dissipative Processes in Magnetohydrodynamics, PhD dissertation, Budapest, 1993.
- [2] Ván P., Muschik, W., The structure of variational principles in nonequilibrium thermodynamics, to be appear in Periodica Polytechnica.
- [3] Muschik, Trostel, R., Variational Principles in Thermodynamics (Survay), ZAMM 63, (1983), 190.
- [4] Havas, P., The range of application of the Lagrange formalism I., Nuovo Cimento, 1/3, (1957), 363.
- [5] Santilli, R. M., Necessary and sufficient conditions for the existence of a Lagrangian in field theory I., Annals of Physics, 103, (1977), 354.
- [6] Tonti, E., Variational formulation for every nonlinear formalism, Int. J. Eng. Sci., 22 (1984), 1343.
- [7] Vainberg, M. M., Variational Methods for the Study of Nonlinear Operators, Holden-Day, San Francisco, California, 1964.

- [8] Finlayson, B. A., Scriven, L. E., On the search for variational principles, Int. J. Heat Mass Transfer, 10 (1967), 799.
- [9] Finlayson, B. A., The Method of Weighted Residuals and Variational Principles (with application in fluid mechanics, heat and mass transfer) /Mathematics in science and engineering, Vol. 87/, Academic Press, New York -London, 1972.
- [10] Lebon, G., Variational principles in thermomechanics, in: *Recent Develop*ments in Thermomechanics of Solids, Eds. Lebon, G., Perzyna, P., pp. 221, Springer Verlag, Wien - New York, 1980.
- [11] Glansdorff, P., Prigogine, I., Thermodynamic Theory of Structure, Stability and Fluctuations, Wiley-Interscience, London-etc., 1971.
- [12] Schechter, R. S., The Variational Method in Engineering, McGraw-Hill, New York, 1967.
- [13] Stark A., Approximation methods for the solution of heat conduction problems using Gyarmati's principle, Ann. Physik, 31/7 (1974), 53.
- [14] Gyarmati I., On the "Governing Principle of Dissipative Processes" and its extension to non-linear problems, Ann. Physik, 23/7-8 (1969), 353.
- [15] Gyarmati I., Non-equilibrium Thermodynamics (Field theory and Variational Principles), Springer Verlag, Berlin, etc. 1970.
- [16] Verhás J., Deduction of transport equations from the integral principle of thermodynamics, Zeitschr. Physikal. Chemie, 234 (1967), 226.
- [17] Verhás J., On the Gyarmati principle and the canonical equations of thermodynamics, Ann. Physik, 20/1-2, 7. Folge (1967), 90.
- [18] Verhás J., The construction of dissipation potentials for non-linear problems and the application of Gyarmati's principle to plastic flow, Zeitschr. Physikal. Chemie, 249/1-2 (1972), 119.
- [19] Verhás J., On the thermodynamic theory of deformation and flow, *Period. Polytech. Chem. Eng.*, 21/4 (1977), 319.

- [20] Verhás J., Irreversible thermodynamics of nematic liquid crystals, Acta Phys. Hung., 55/1-4 (1984), 275.
- [21] Verhás J., Papenfuss, C., Muschik, W., A simplified thermodynamic theory for biaxial nematics using Gyarmati Principle, *Mol. Cryst. Liq. Cryst.*, 215 (1992), 313.
- [22] Verhás J., Termodinamika és reológia, Műszaki Könyvkiadó (Technical Publishers), Budapest, 1985. (in Hungarian)
- [23] Sándor J., The treatment of non-isothermal multicomponent diffusion in electrostatic fields on the basis of Gyarmati's variational principle, *Elec*trochim. Acta, **17** (1972), 673.
- [24] Dickel, G., Baelz, U., Pitesa, B., Investigations of electromechanical equilibrium in ionexchange membranes, *Journal of Chem. Soc. Faraday Trans.*, 77/2 (1981), 451.
- [25] Dickel, G., Electro-Mechanical Equilibrium in Membranes, Topics in Bioelectrochemistry and Bioenergetics, V.4., 271-342.
- [26] Heynmann, J., Fleischer, G., Jablonsky, G. S., Slinko, H. G., Lineare und nichtlineare thermodynamische Materialgleichungen (constitutive equations) chemischer Reaktionen und ihre variationtechnische Ableitung, *Zeitschr. Physikal. Chemie*, **259** (1978), 557.
- [27] Vincze Gy., On the treatment of thermo-electrodynamical processes, Ann. Physik, 30 (1973), 55.
- [28] Singh, P., Bhattacharya, D. K., Application of Gyarmati Principle to Boundary Layer Flow, Acta Mech., 30 (1978), 137.
- [29] Singh P., The application of the Governing Principle of Dissipative Processes to Bénard convection, Int. J. Heat Mass Transfer 19 (1976), 581.
- [30] Tung, N. H., An application of the Governing Principle of Dissipative Processes (GPDP) to a quasi-linear problem of hydro-thermodynamics, J. Non-Equilib. Thermodyn., 14 (1989), 61.
- [31] Lambermont, J., Lebon, G., A rather general variational principle for purely dissipative non-stationary processes, Ann. Physik, 28/1 (1972), 15.

- [32] Lavenda, B. H., Thermodynamics of Irreversible Processes, The McMillan Press Ltd., 1978.
- [33] Gyarmati I., Relations between the integral principle of thermodynamics and the Hamilton principle, Acta Chimica Hungarica, 47, (1966), 367.
- [34] Matolcsi T., On material frame-indifference, Arch. Ration. Mech. Anal., 91/2 (1986), 99.m
- [35] Matolcsi T., A Concept of Mathematical Physics, Models for Space-time, Akadémiai Kiadó, Budapest, 1984.
- [36] Matolcsi T., Spacetime without Reference Frames, Akadémiai Kiadó, Budapest, 1993.
- [37] Bhattacharya, D. K., On the problem of evolution criterion for thermodynamic waves, Acta Mech., 47 (1983), 87.
- [38] Farkas H., , Noszticzius Z., On the non-linear generalization of the Gyarmati principle and theorem, Ann. Physik, 7/26/4 (1971), 341.
- [39] Verhás J., An extension of the Governing Principle of Dissipative Processes to nonlinear constitutive equations, Ann. Physik, 40/4-5, 7. Folge (1983), 189.
- [40] Nyíri B., A nonlinear extension of the local form of Gyarmati's Governing Principle of Dissipative Processes, Acta Phys. Hung., 63/1-2 (1988), 13.
- [41] Nyíri B., On the extension of the Governing Principle of Dissipative Processes to nonlinear constitutive relations, *Acta Phys. Hung.*, 66/1-4 (1989), 19.
- [42] Muschik, W., Szer, J., On the formulation of variational principles of irreversible thermodynamics in presence of a magnetic field, J. Non-Equilib. Thermodyn., 1 (1976), 61.
- [43] Lebon, G. J., Lambermont, J. H., Generalization of Hamilton's principle to continuous dissipative systems, J. Chem. Phys., 59/6 (1973), 2929.
- [44] Rosen, P., On variational principles for irreversible processes, J. Chem. Phys., 21 (1953), 1220.

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