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Gyarmati's Variational Principle of Dissipative Processes †

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Abstract: Like in mechanics and electrodynamics, the fundamental laws of the thermodynamics of dissipative processes can be compressed into Gyarmati's variational principle. This variational principle both in its differential (local) and in integral (global) forms was formulated by Gyarmati in 1965. The consistent application of both the local and the global forms of Gyarmati's principle provides all the advantages throughout explicating the theory of irreversible thermodynamics that are provided in the study of mechanics and electrodynamics by the corresponding classical variational principles, e.g., Gauss' differential principle of least constraint or Hamilton's integral principle.

Keywords: entropy production; second principle of thermodynamics; parabolic differential equation derived from variational principle; Gyarmati's principle; The Governing Principle of Dissipative Processes (GPDP)

1. Introduction

A number of efforts have been made to formulate variational principles for dissipative processes, namely those accounted by (“classical”) irreversible thermodynamics. The results seemed, and even seem, to contradict the known result in mathematics that says the parabolic equations of heat conduction, diffusion, *etc.*, cannot be obtained as Euler-Lagrange equations of a variational principle. The conditions of the mathematical theorem were not assumed (among which functions, the extremum was looked for), moreover, the derivation of a parabolic equation does not mean that it has to be the Euler-Lagrange

equation, e.g., the variational problem may result in biparabolic Euler-Lagrange equations with transversality conditions, and the first integration of them results in the parabolic equations [1]. Another procedure is based on some potential functions [2–4].

A brief and rather good survey can be found on Wikipedia [5] from the early ancestors to recent results; the works of Kelvin, Helmholtz, Rayleigh, Korteweg, Onsager, Prigogine, Casimir, Ziman, Ziegler, Gyarmati, Paltridge and others are mentioned. The survey is far from being complete; important results are missing from it; e.g., the works of Ziegler [6–12] and his influence [13–17], Biot [18,19] and Edelen [20–31] are omitted. A more skeptic website on the topics is The Azimuth Project [32].

In this paper, we put Gyarmati's variational principle into the limelight. This principle was applied to several fields of irreversible processes: first of all, by his colleagues (Verhás [33], Böröcz [34], Farkas [35,36], Sándor [37], Vincze [38–40] and Stark [41,42]); but also by many others (Singh [43,44], Bhattacharya [45,46], Dickel [47,48], *etc.*).

2. The Governing Principle of Dissipative Processes (GPDP)

Gyarmati's principle is based on the fact that the generalization of the dissipation functions that were introduced by Rayleigh and Onsager for special cases always exists locally in continua [3,4,49–52] in the linear theory with Onsager's reciprocal relations. These functions are defined as:

$$\Psi(X) = \frac{1}{2} \sum_{i,k} L_{ik} X_i X_k \quad (1)$$

and:

$$\Phi(J) = \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k. \quad (2)$$

The R_{ik} coefficients (general resistivities) are the components of the inverse of the conductivity matrix, (L_{ik}) .

The most important property of the dissipation function, $\Psi(X)$, is that it is a homogeneous quadratic function of the X_i forces in the strictly linear theory, while in the quasi-linear theory, it depends also on the state variables. In Gyarmati's terminology, the linear laws are "strictly linear" if the conductivity coefficients do not depend on anything and are "quasi-linear" if they do not depend on the forces, X_i , or fluxes, J_i , but on anything else; say, the heat conductivity depends on temperature, but does not depend on its gradient. The other fundamental property of Ψ is that its partial derivative with respect to X_k is equal to the current, J_k .

$$J_k = \frac{\partial \Psi}{\partial X_k} \quad (3)$$

Finally, the equality of the mixed second derivatives of Ψ with respect to the forces are equivalent to Onsager's reciprocal relations:

$$\frac{\partial^2 \Psi}{\partial X_i \partial X_k} = \frac{\partial J_i}{\partial X_k} = L_{ik} = L_{ki} = \frac{\partial J_k}{\partial X_i} = \frac{\partial^2 \Psi}{\partial X_k \partial X_i}. \quad (4)$$

Because of the above properties, the function, Ψ , is called a dissipation potential, more precisely: it is the flux potential (see Equation (3)).

The function, Φ , has similar properties. In the strictly linear theory the function, Φ , is a homogeneous quadratic function of the currents, J , while in the quasi-linear case, it depends also on the local state variables (through the coefficients). The partial derivative of the function, Φ , with respect to J_k equals X_k :

$$X_k = \frac{\partial \Phi}{\partial J_k} \quad (5)$$

Due to this relation, the function, Φ , is also a dissipation potential, more exactly: it is the force potential.

The equality of the mixed second derivatives of Φ with respect to the J s are equivalent to the Onsager relations, now expressed in terms of the R_{ik} resistances:

$$\frac{\partial^2 \Phi}{\partial J_i \partial J_k} = \frac{\partial X_i}{\partial J_k} = R_{ik} = R_{ki} = \frac{\partial X_k}{\partial J_i} = \frac{\partial^2 \Phi}{\partial J_k \partial J_i} \quad (6)$$

Hence, it can be seen that the necessary and sufficient condition of the existence of the dissipation potentials, Ψ and Φ , is the existence of Onsager's reciprocal relations.

Some weighted potentials, Ψ^G and Φ^G , can be defined, too. They show all the essential properties of Ψ and Φ , but correspond to the weighted entropy production, $G\sigma_s$. (G is any always positive state function.) The dynamic laws can be formulated in different forms by the help of so-called representations and pictures, which give mathematically equivalent formulae; one of them is as good as the other from the theoretical point of view, but in particular applications, the suitable one can make life easier. We refer again to Gyarmati's terminology. Representation means the way that the quantities accounting for the rate of processes have been chosen from the possibilities, e.g., the heat flow or the entropy flow. Picture refers to the particular weight function, G , e.g., if $G = 1$, we speak of the "entropy picture", $G = T$ gives the "energy picture", $G = T^2$ leads to the "Fourier picture", etc. The general theory of the "pictures" was worked out and applied by Gyarmati [53] and Farkas [35] (see also [37,45,46,54–57]). Different pictures are obtained by multiplying both sides of the bilinear expression of the entropy production by an always positive state function, G , i.e.,

$$G\sigma_s = \sum_j J_j X_j G. \quad (7)$$

The quantity, $G\sigma_s$, is evidently non-negative, taking a zero value in equilibrium only. The coefficients of the current, J_j , namely,

$$X_j^G = X_j G \quad (8)$$

regarded as forces, and substituted into the original form, give the linear laws in the " G -picture":

$$J_i = \sum_k \frac{1}{G} L_{ik} X_k^G = \sum_k L_{ik}^G X_k^G. \quad (9)$$

The coefficients obey Onsager's reciprocal relations. By choosing various functions for G , various pictures for the description of dissipative processes are obtained [35,58,59]. Making use of Equations (8) and (9), we obtain the forms of the dissipation potentials in the general G -picture:

$$\Psi^G = G\Psi, \quad \Phi^G = G\Phi. \quad (10)$$

Finally, we note another essential property of the functions, Ψ and Φ ; namely, that they are invariant scalar quantities with respect to the linear transformations of the currents and forces.

3. The Local Forms of Gyarmati's Principle

Gyarmati's variational principle of non-equilibrium thermodynamics can be derived from the properties in Equations (3) and (5) of the functions, Ψ and Φ . We mention that this derivation does not make use of the homogeneous quadratic forms of the functions, Ψ and Φ , given in Equations (1) and (2); thus, the variational principle is applicable to strictly non-linear phenomena that cannot be described by the linear laws, yet the currents are uniquely determined by the forces and the local variables of state. This is the situation with any phenomena the Gyarmati-Li generalization:

$$\frac{\partial J_i}{\partial X_k} = \frac{\partial J_k}{\partial X_i} \quad (11)$$

of the Onsager relations corresponds to. These relations are necessary and sufficient conditions of the existence of dissipation potentials, obeying Equations (3) and (5).

Notice that Equation (5) can be written in the form:

$$\frac{\partial}{\partial J_k}(\sigma_s - \Phi) = 0, \quad (12)$$

where, in executing the partial differentiation, the currents must be regarded variables independent of the forces and local state variables. This means that the constitutive relations given by Equation (5) are equivalent to the following statement: those currents correspond to a given set of forces and state variables, at which the function:

$$\mathcal{L}_J = \sigma_s - \Phi \quad (13)$$

has a stationary point in the space of the currents. This form of the principle, which stands nearest to Onsager's principle for small fluctuations around an equilibrium in an adiabatically closed discontinuous system, is called the flux representation of Gyarmati's principle [60]. Ziegler's principle [7–9,11,12] is equivalent to Onsager's one in Equation (12), but with different aspects and presentation; it was applied to several problems [13–15].

The force representation of Gyarmati's principle is obtained by putting the relation in Equation (3) in the form:

$$\frac{\partial}{\partial X_k}(\sigma_s - \Psi) = 0. \quad (14)$$

During partial differentiation, the forces and the fluxes must be regarded again as independent variables. Thus, those forces correspond to a given set of currents and state variables at which the function:

$$\mathcal{L}_X = \sigma_s - \Psi \quad (15)$$

has a stationary point in the space of the forces.

It is easily seen that the functions, \mathcal{L}_J and \mathcal{L}_X , in Equations (13) and (15) can be put in the same form, as the subtraction of a function, $f(X_i)$, independent of the J s from \mathcal{L}_J has no influence on Equation (12). The function, Ψ , just fits the purpose. On the other hand, Φ can be subtracted from \mathcal{L}_X (due to the same reasons). Now, a universal Lagrange density of Gyarmati's principle has been obtained:

$$\mathcal{L} = \mathcal{L}_X - \Phi = \mathcal{L}_J - \Psi = \sigma_s - \Psi - \Phi, \quad (16)$$

by which the extremum properties in Equations (12) and (14) can be expressed universally. The partial forms have historical relevance. Onsager’s principle is equivalent to Equation (12). Moreover, in some practical calculations, they are easier.

It can be said, quite generally, that if a sufficient number of the currents and forces is known, that is either every force or every current, or even one part of the currents and the other part of the forces, then the remaining variables must be chosen, so that the universal Lagrangian in Equation (16) is stationary. This is a necessary and sufficient condition for the set of the currents and forces to describe a real process. In other words, the variation of the universal Lagrangian in Gyarmati’s principle is zero around the real forces and fluxes, with respect to the simultaneous variation of the currents and forces.

In the quasi-linear theory, the functions, Ψ and Φ , depend on the state variables through the conductivities, L_{ik} , and resistivities, R_{ik} , due to Equations (1) and (2). The matrices of the conductivities, L_{ik} , and, resistivities R_{ik} , are reciprocal matrices:

$$\sum_r L_{ir} R_{rk} = \delta_{ik}. \tag{17}$$

Let us calculate the partial derivative of the \mathcal{L} Lagrange density with respect to a local state variable denoted by Γ :

$$\frac{\partial \mathcal{L}}{\partial \Gamma} = -\frac{1}{2} \sum_{i,k} \frac{\partial L_{ik}}{\partial \Gamma} X_i X_k - \frac{1}{2} \sum_{i,k} \frac{\partial R_{ik}}{\partial \Gamma} J_i J_k. \tag{18}$$

The partial derivatives $\partial R_{ik}/\partial \Gamma$, making use of Equation (17), are expressed by the coefficients, R_{ik} , and the derivatives, $\partial L_{ik}/\partial \Gamma$, as:

$$\frac{\partial R_{ik}}{\partial \Gamma} = - \sum_{r,s} R_{ir} \frac{\partial L_{rs}}{\partial \Gamma} R_{sk}. \tag{19}$$

Substituting this in Equation (18) and applying the reciprocal relations, the form:

$$\frac{\partial \mathcal{L}}{\partial \Gamma} = -\frac{1}{2} \sum_{i,k} \frac{\partial L_{ik}}{\partial \Gamma} (X_i - \sum_s R_{is} J_s)(X_k + \sum_s R_{ks} J_s). \tag{20}$$

is obtained. Hence, it is seen that the partial derivatives of the universal Lagrangian with respect to the local state variables, at real processes, are zero. Therefore, the parameters, Γ , can also be varied independently.

This theorem is Gyarmati’s supplementary theorem [61], which guarantees the validity of the universal local form of the variational principle to the quasi-linear case, too.

The universal form of the local Gyarmati principle states, consistently with the supplementary theorem, that the Lagrangian $\mathcal{L} = \sigma_s - \Psi - \Phi$ has an extremum in all points that describe a real process in the unified space of forces, currents and state variables.

In examining the type of the extremum, instead of considering second variations, we had better use another form of the Lagrangian, which is advantageous in other respects, as well. This form is:

$$\mathcal{L} = -\frac{1}{2} \sum_{i,k} R_{ik} (J_i - \sum_s L_{is} X_s)(J_k - \sum_s L_{ks} X_s). \tag{21}$$

Executing the multiplications, the form in Equation (16) of the universal Lagrange density is obtained again. This very form, however, clearly shows that the extremum for real processes is always a

maximum, and the value of this maximum is zero if no constraint is maintained; in other cases, the Lagrangian is always negative, since the R_{ik} s can be replaced, without changing the whole expression, with the coefficients of a positive definite quadratic form—the elements of the symmetric part of the R_{ik} matrix—and the variables of this quadratic form are $(J_i - \sum_s L_{is} X_s)$. This form of the local principle is considerably similar to Gauss' principle of least constraint, so this form is often called the Gaussian form of Gyarmati's principle. As the value of Equation (21) is zero only in the absence of local constraints, while in other cases the value of this maximum depends on the constraints, the Gauss type local principle is an excellent tool for introducing the notion of thermodynamic constraint forces; consequently, it is of great help in discussing problems with local constraints, such as ambipolar diffusion, barycentric component flows, stoichiometric restrictions, *etc.* (Verhás [62], Gyarmati [59], Dickel [47]).

The local Gyarmati principle of irreversible thermodynamics is of universal validity, yet its primary importance is that it is the ground the integral principles are built on. Before the discussion of integral principles, however, the place of the local principle in the framework of the theory should be examined. To this end, the local principle is resumed more explicitly.

The essence of the local principle is that it replaces the set of linear laws by a single scalar function. If either the function, Ψ , or the function, Φ , is known, the constitutive equations can be obtained by the variational principle. Actually, it is sufficient to know only one of the dissipation potentials, Ψ or Φ , since the matrix of the coefficients can be read from one of them, and the other potential is determined by the elements of the reciprocal matrix. This calculation can be executed via a more elegant method. Let us regard, for example, the function, Ψ , as the given one. Then, the Legendre-transformation of the function, Ψ , leads to the function, $\Phi \left(\frac{\partial \Psi}{\partial X} \right)$. Putting J in the place of $\frac{\partial \Psi}{\partial X}$, the function, Φ , is obtained. The function, Ψ , is gotten from Φ in the same way [60,61]. The Legendre-transformation is meant in the multidimensional sense or as the sequence with respect to all independent variables, one by one.

The advantage of the method of Legendre transformation lies in the fact that its formulation and application is independent of the linear or quasi-linear character of the theory; thus, it is applicable to dissipation potentials of an entirely different character. From the fact that the dissipation potentials, Ψ and Φ , are the Legendre transforms of each other, it is also seen that the validity of Gyarmati's supplementary theorem is not restricted to the quasi-linear case, but holds to any strictly non-linear theory, subject to the Gyarmati-Li generalized reciprocal relations (and where the higher order coefficients also depend on the variables of state). This, at the same time, means that the Lagrangian $\mathcal{L} = \sigma_s - \Psi - \Phi$ must be stationary at every point of space in every instant of time in the case of any non-linear theory, provided that dissipation potentials exist at all.

The next question is how a dissipation potential can be constructed from the constitutive equations. The potential character of the functions, Ψ and Φ , is defined by Equations (3) and (5). The condition to the existence of such functions with potential character to a given (say, empirically proven) set of constitutive equations is that they have to obey the Gyarmati-Li generalized reciprocal relations. It is rather inconvenient that no general physical law, or exact proof based on such laws, is known that would guarantee the fulfillment of the Gyarmati-Li generalized reciprocal relations or of other equivalent conditions, for all possible constitutive equations; on the contrary, reaction kinetics in chemistry displays plenty of well-examined examples disobeying them beyond the linear approximation [63]. If, however,

the reciprocal relations in Equation (11) hold in a particular case or approximation, then the dissipation potentials can be given, and the Gyarmati principle can be applied.

The function, Ψ , can be obtained from the bilinear form of the entropy production by introducing Equations (3); we get:

$$\sigma_s = \sum_i X_i \frac{\partial \Psi}{\partial X_i} = \sum_i X_i J_i(X) = \sigma_s(X) \quad (22)$$

for the entropy production. This expression can be regarded as a quasi-linear inhomogeneous first order partial differential equation. Its only solution subject to the condition $\Psi(0) = 0$ is the function:

$$\Psi(X) = \int_0^1 \frac{1}{t} \sigma_s(tX) dt \quad (23)$$

A similar formula is obtained for $\Phi(J)$:

$$\Phi(J) = \int_0^1 \frac{1}{t} \sigma_s(tJ) dt \quad (24)$$

The knowledge of the function, Ψ or Φ , defined so, is equivalent to the knowledge of the original constitutive equations; nevertheless, to get them, it is enough to know the single function, $\sigma_s(X_i)$ or $\sigma_s(J_i)$, instead of the whole set of the constitutive equations.

Dissipation potentials for non-linear cases were given first (and independently) by Verhás [64], Edelen [20–25,29,30] and Presnov [65]. Edelen's works went on also to applications on non-local and non-linear mechanical problems [26–28].

3.1. The Derivation of von Mises' Equations of Plasticity

Here, for an example, we present a very simple application of the local principle to a typical non-linear case: we derive Mises' theory of plastic flow (Verhás [64]). Here, we mention that a number of variational principles and variational methods are known in the literature concerning plastic, elasto-plastic, visco-plastic or even visco-elasto-plastic flow, which works well on the field, but generalizing them to more complicated interactions is hindered by the very special presumptions, e.g., first order Euler homogeneous terms in the entropy production are assumed as core results in thermodynamic plasticity, but they are unusable if the plastic material is semitransparent and is exposed to thermal radiation or the material is a plastic material that is also electrically polarizable and is under the influence of an electromagnetic field. The theories applying "rational" methods, especially the Clausius-Duhem inequality (see, e.g., [66]) are questionable, because of the essential use of the the idea of temperature as well defined for equilibrium only* and being ambiguous, e.g., in the presence of dielectric relaxations, without which there is no "heat supply". See in [67] how to get rid of the difficulty. The theories motivated by statistical and kinetic considerations are bearing the load of Loschmidt's paradox having persisted for 140 years.

The existence of the function, Φ , is assumed.

Let us consider a homogeneous, isotropic, incompressible fluid continuum in local equilibrium and ignore heat conduction. The energy dissipation for this case reads:

$$T\sigma_s = \mathbf{t}_0 : \mathring{\mathbf{d}}, \quad (25)$$

where $\mathring{\mathbf{d}}$ stands for the symmetric part of the velocity gradient and \mathbf{t}_0 for the deviatoric part of Cauchy's stress, and T is the absolute temperature.

It is well known that the direct application of the linear laws to this expression leads to Newton's viscosity law [59,68]. Instead, a different procedure is chosen, assuming the constitutive relation between the single thermodynamic force and non-linear flux, but still deducible from a Φ dissipation potential. This dissipation potential is a scalar and isotropic function of $\mathring{\mathbf{d}}$, thus:

$$\Phi = \Phi(\text{tr } \mathring{\mathbf{d}}, \text{tr } \mathring{\mathbf{d}}^2, \text{tr } \mathring{\mathbf{d}}^3). \quad (26)$$

During isochoric motions, the trace of $\mathring{\mathbf{d}}$ is zero, so:

$$\Phi = \Phi(\text{tr } \mathring{\mathbf{d}}^2, \text{tr } \mathring{\mathbf{d}}^3). \quad (27)$$

If Φ is assumed to be a continuous function of its variables (remember that $\Phi = 0$ at $\mathring{\mathbf{d}} = 0$), then, for sufficiently slow flows, we can ignore the $\text{tr } \mathring{\mathbf{d}}^3$ variable, too, as its value is small relative to $\text{tr } \mathring{\mathbf{d}}^2$. The trace of $\mathring{\mathbf{d}}^3$ is strictly zero for viscometric flows. Thus, the form of the potential, Φ , for viscometric flows exactly and for nearly viscometric flows approximately is:

$$\Phi = \Phi(\text{tr } \mathring{\mathbf{d}}^2). \quad (28)$$

Since Φ is regarded as a function of $\mathring{\mathbf{d}}$, let us introduce (to simplify calculations) the notation:

$$\mathring{\mathbf{d}} = \lambda \mathbf{a}, \quad (29)$$

where λ is a scalar variable. The tensor, \mathbf{a} , can be arbitrarily normed, the norm of which is now:

$$\text{tr } \mathbf{a}^2 = 1. \quad (30)$$

Thus, instead of Equation (28), we can use the function:

$$\Phi = \Phi(\lambda^2) = g(\lambda). \quad (31)$$

It is obvious that the function, $g(\lambda)$, has a physical meaning, but only for the positive values of its variable; consequently, for negative λ , the function, $g(\lambda)$, can be defined at will. It is plausible to assume $g(\lambda)$ differentiable at $\lambda = 0$. Then, for a sufficiently small value of λ , $g(\lambda)$ can be approximated by its tangent, so the function:

$$g = \alpha \lambda \quad (32)$$

can be taken, where α is an unspecified number. Hence, with respect to Equations (29) and (30), the form:

$$\Phi = \alpha (\text{tr } \mathring{\mathbf{d}}^2)^{\frac{1}{2}} \quad (33)$$

is obtained, from which the constitutive relation for the deviatoric part of Cauchy's stress:

$$\mathbf{t}_0 = \frac{2\alpha}{(\text{tr } \mathring{\mathbf{d}}^2)^{\frac{1}{2}}} \mathring{\mathbf{d}} \quad (34)$$

follows. Introducing the notation:

$$\alpha\sqrt{2} = k, \quad (35)$$

the expression:

$$\mathbf{t}_0 = \frac{k\sqrt{2}}{(\text{tr } \mathring{\mathbf{d}}^2)^{\frac{1}{2}}} \mathring{\mathbf{d}} \quad (36)$$

is obtained for the stress, which is well known form for the ideal plastic body in von Mises' approximation.

From the above results, it is clear that Gyarmati's local principle furnished with various approximations for the potential, ϕ , leads to the various theories of viscous flow or plasticity.

3.2. The Generalized Reciprocal Relations and the Generalization of Gyarmati's Principle for Non-Linear Cases

The possibility of generalizing the reciprocal relations for non-linear constitutive equations has already been mentioned earlier when describing Gyarmati's variation principle. However, the practical value of the suggestions made there is doubtful. The reason for this is that neither the macroscopic reversibility principle proposed by Meixner [69] nor the generalized reciprocal relations by Gyarmati [70,71] and Li [72,73] could be proved satisfactorily up to now, either theoretically or experimentally. Moreover, it is well known that the dynamic equations equivalent to the Guldberg-Waage equations for chemical reactions, which are regarded as prototypes of non-linear constitutive equations, definitely violate the general reciprocal relations of Gyarmati and Li, as well as Meixner's macroscopic reversibility principle, at least in the case where we consider affinities as the real driving force of chemical reactions in the non-linear region far from equilibrium. We cannot deal here with this very important and persistent problem of non-linear thermodynamics, but the interested reader is referred to some papers on the subject [63,74–76].

Nevertheless, in the following, a generalization will be presented, which is proven by strict mathematics and whose validity is not restricted if we have twice continuously differentiable constitutive equations.

Start from the bilinear form of entropy production:

$$\sigma_s = \sum_i J_i X_i, \quad (37)$$

but let us drop our usual notation, *viz.* that J_i stands for "current" and X_i for "force" of the process rate. Let X_i be the independent variable from among the canonically conjugate force and current and J_i the other variable characteristic for the i -th process. The independent variables should be chosen, so that close to equilibrium, *i.e.*, in the range of validity of the linear laws, only Onsager's reciprocal relations should hold. We do not suppose the linearity of the constitutive equations, but they should be twice

continuously differentiable with respect to X_i s. The role of equilibrium state parameters is not restricted in the constitutive equations. For them, it may be written in a general way that:

$$J_i = J_i(X_1, X_2, \dots, \Gamma_1, \Gamma_2, \dots), \tag{38}$$

where X_1, X_2, \dots are the independent variables selected from the expression of entropy production. For brevity, let us now call them forces; $\Gamma_1, \Gamma_2, \dots$ are other local state parameters whose specification is not necessary at present. Let us then take function:

$$J_i = J_i(\lambda X_1, \lambda X_2, \dots) \tag{39}$$

depending on λ , expand it into a Taylor series with respect to the powers of λ and stop after the linear term. On writing also the Lagrange remainder, expression:

$$J_i = \sum_k \left. \frac{\partial J_i}{\partial X_k} \right|_0 X_k \lambda + \frac{1}{2} \sum_{k,j} \left. \frac{\partial^2 J_i}{\partial X_k \partial X_j} \right|_{\xi X_1, \xi X_2, \dots} X_k X_j \lambda^2 \tag{40}$$

results, which at $\lambda = 1$, gives, again, constitutive Equation (38). If the remainder is negligible, Equation (40) is identical with Onsager’s linear laws, and the derivatives included in it may be identified with the Onsager coefficients:

$$\left. \frac{\partial J_i}{\partial X_k} \right|_0 = L_{ik}^0 = L_{ki}^0 = \left. \frac{\partial J_k}{\partial X_i} \right|_0. \tag{41}$$

We note that reciprocal relations do not follow from the expression; their validity has been taken from the linear theory. Now, for brevity, we introduce coefficients:

$$l_{ijk} = \left. \frac{1}{2} \frac{\partial^2 J_i}{\partial X_k \partial X_j} \right|_{\xi X_1, \xi X_2, \dots}. \tag{42}$$

Following from the nature of the Taylor series, derivatives should be taken at $\xi X_1, \xi X_2, \dots$, where ξ lies between zero and one and whose actual value is determined by the structure of constitutive Equation (38) and the actual values of the independent variables. (If more than one ξ is possible, the smallest should be chosen.) Now, the constitutive equations may be written in form:

$$J_i = \sum_k L_{ik}^0 X_k + \sum_{j,k} l_{ijk}(X_1, X_2, \dots) X_j X_k \tag{43}$$

where coefficients l_{ijk} may also depend on X ; but on the basis of Equation (42), correlations:

$$l_{ijk} = l_{ikj} \tag{44}$$

hold between them. Let us now introduce coefficients:

$$L_{ik} = L_{ik}^0 + \sum_j (l_{ijk} + l_{kji} - l_{jik}) X_j \tag{45}$$

for which, on the one hand, Onsager’s reciprocal relations of the linear theory are valid and, on the other hand, as a consequence of Equation (44), generalized reciprocal relations:

$$L_{ik} = L_{ki} \tag{46}$$

hold. By using them, the constitutive equations may be written as:

$$J_i = \sum_k L_{ik} X_k = \sum_k L_{ik}^0 X_k + \sum_{j,k} l_{ijk} X_j X_k + \sum_{j,k} (l_{kji} - l_{jik}) X_j X_k \tag{47}$$

Since the last term on the right-hand side is zero, Equations (43) are obtained again.

Our results can be summarized as follows. The constitutive equations, also for non-linear cases, may be written in the form:

$$J_i = \sum_k L_{ik} X_k, \tag{48}$$

where coefficients, L_{ik} , may depend also on X , and between conductivity coefficients reciprocal relations:

$$L_{ik} = L_{ki} \tag{49}$$

hold if they are valid in the linear limiting case, *i.e.*, close enough to equilibrium. Keep in mind that the so-defined L_{ik} quantities are not uniquely determined by the constitutive equations. This form has been used by several authors, e.g., by Gurtin [77] or by Ván [78]

The selection of independent variables can be varied by a linear transformation of forces and currents, which is formally analogous to that applied in the linear theory. This means that in the equation with the changed independent variables, Casimir-type reciprocal relations also appear, similar to the linear theory. Of course, from the viewpoint of the validity of the generalized Onsager-Casimir reciprocal relations between coefficients L_{ik} , it is of no importance what the independent variables of the coefficients are. Since the determinant of the matrix constructed from coefficients L_{ik} is positive at equilibrium, the constitutive equations are twice continuously differentiable, and thus, the above determinant is a continuous function of the independent variables. From this, it follows that the matrix constructed from coefficients L_{ik} can be inverted in a wider range around equilibrium than the realm of linear laws. A similar consideration is applied for the principal minors of matrix L_{ik} ; hence, the homogeneous quadratic form using coefficients L_{ik} remains positive definite.

The above generalization of Onsager’s reciprocal relations permits the writing of the Lagrange function belonging to Gyarmati’s principle provided by Equation (21) in its usual form as:

$$\mathcal{L} = -\frac{1}{2} \sum_{i,k} R_{ik} \left(J_i - \sum_s L_{is} X_s \right) \left(J_k - \sum_s L_{ks} X_s \right) \tag{50}$$

where numbers R_{ik} again mean the elements of the reciprocal matrix. Since the homogeneous quadratic form constructed with coefficients L_{ik} is positive definite and, consequently, also that formed by coefficients R_{ik} , the Lagrange function, \mathcal{L} , is always negative if constitutive equations (48) are not satisfied. If they are satisfied, \mathcal{L} is zero. This means, at the same time, that in the case of X and J , values corresponding to the real process, \mathcal{L} , were maximum, even an absolute maximum.

The Lagrange function can be reduced to its well-known simpler form by removing the parentheses:

$$\mathcal{L} = \sum_i J_i X_i - \frac{1}{2} \sum_{i,k} L_{ik} X_i X_k - \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k = \sigma - \Psi - \Phi. \tag{51}$$

From this expression, dissipation potentials may be determined as:

$$\Psi = \frac{1}{2} \sum_{i,k} L_{ik}(X) X_i X_k, \quad \Phi = \frac{1}{2} \sum_{i,k} R_{ik}(X) J_i J_k. \tag{52}$$

It is very important and striking that relative to the linear theory, the only change is that dissipation potential, Ψ , is not a quadratic function of X s any more, and potential Φ also depends on X s. However, a significant difference is that although equality:

$$\frac{\partial \Phi}{\partial J_i} = \sum_k R_{ik}(X) J_k = X_i \tag{53}$$

holds also here, partial derivative:

$$\frac{\partial \Psi}{\partial X_i} = \sum_k L_{ik} X_k + \frac{1}{2} \sum_{i,k} \frac{\partial L_{jk}}{\partial X_i} X_j X_k \neq J_i \tag{54}$$

does not give the currents, since in this non-linear theory, Ψ cannot be regarded as a potential. It should also be noted that the problem of these derivatives becomes even more complicated if X s are not chosen as independent variables in the conduction coefficients, but this does not interfere with the validity of the variational principle.

The unchanged validity of the local form of Gyarmati’s principle in non-linear cases and the existence of an absolute maximum allows the integration of the local form with respect to time and space. Therefore, we can say that the validity of the Governing Principle of Dissipative Processes whose basis is the integrated form of Equation (51) with respect to space and time is not restricted to linear thermodynamics, but it is almost general, since the requirement of its being twice continuously differentiable is not a strong restriction from a physical point of view.

After the above results were reached, a new variational technique was proposed [2–4,49,79] that gives the transport equations as Euler-Lagrange equations for the potential functions introduced suitably. Nevertheless, this technique may be assumed as an entirely different variational principle; it is undeniably an offshoot. Nyíri [80–82] showed that a particular form of Gyarmati’s variational principle is valid even if the constitutive equations are non-linear and no symmetry relation holds even in the linear approximation.

3.3. Another Generalization for Non-Symmetric Equations

Up to now, the symmetry of the conductivity matrix was presumed. Nevertheless, the complete symmetry is frequent; it does not always hold. A magnetic field or Coriolis force in the rotating frame may result in the skew-symmetric part, even in the linear approximation. Getting rid of the skew-symmetric part is easy and always possible. Colman and Truesdell showed a good method [83].

If Onsager’s reciprocity does not hold, the constitutive equations have the form:

$$J_i = \sum_k (L_{ik}^+ + L_{ik}^-) X_k \tag{55}$$

with:

$$L_{ik}^+ = L_{ki}^+ \quad L_{ik}^- = -L_{ki}^- \tag{56}$$

Introducing new variables for the fluxes by:

$$J_i^* = J_i - \sum_k L_{ik}^- X_k, \quad (57)$$

we find that the bilinear form of the entropy production remain unchanged;

$$\sigma_s = \sum_i J_i^* X_i = \sum_i J_i X_i - \sum_{i,k} L_{ik}^- X_i X_k \quad (58)$$

as the last term in the right-hand side is zero.

The above train of thought is valid both for the linear and the non-linear approximation. This means that, even in the presence of a skew-symmetric part in the matrix of the conductivity (or the resistivity) coefficients, with changing the variables accounting on processes, the results of the previous subsection can be applied; nevertheless, the marvelous freedom of picking up the fluxes has been reduced.

4. The Governing Principle of Dissipative Processes

Though the local form of Gyarmati's principle is indispensable for the description of local constraints, an integral form of the principle is of much greater importance in practical calculations. The integral forms are obtained by the integration of the universal Lagrange density with respect to space or space and time coordinates. The universal (global) principle, obtained so, is called the "Governing Principle of Dissipative Processes" (GPDP) [61].

Since the universal Lagrange density is everywhere and always stationary, it is also true that:

$$\delta \int_V (\sigma_s - \Psi - \Phi) dV = 0, \quad (59)$$

and:

$$\delta \int_{t_1}^{t_2} \int_V (\sigma_s - \Psi - \Phi) dV dt = 0. \quad (60)$$

The Governing Principle of Dissipative Processes given by Gyarmati can be regarded as the most widely valid and the most widely applied integral principle of irreversible thermodynamics. From this principle, the parabolic transport equations of irreversible transport processes can be derived both in the linear and quasi-linear case, as well as in all those non-linear cases where dissipation potentials can be determined by Equations (23) and (24), due to the validity of the generalized reciprocal relations in Equation (11) [20,21,35,37,39,41,42,56–59,84].

The application of the governing principle can be understood through the properties of the local principle. The variational principle alone does not contain sufficient information about the system; the functional takes its absolute maximum in several points of the (Γ, X, J) space; but if the Γ and X values are given, then J can be determined. Obviously, not only the knowledge of Γ and X is suitable, but any other restrictive circumstance denoting an equivalent hypersurface in the (Γ, X, J) space. Such a restrictive condition is the ensemble of the balance equations and the definition of the forces together with the equation of state.

Hence, it follows that the variational principles in Equations (59) and (60) are to be understood with the above subsidiary conditions, and thus, the processes occurring in the system are uniquely described.

The extraordinary importance of the formula in Equation (59) arises from the fact that the Euler-Lagrange equations are identical to the parabolic transport equations. Observe that the set of functions, in which the maximum is looked for, concern a snapshot of the processes at an, otherwise arbitrary, moment; consequently, even though the Euler-Lagrange equations resemble parabolic ones, they are not, as the time is not an independent variable; they turn out to be parabolic ones when the time slices are assembled into a whole. Its use has the greatest advantage in the entropy picture, since the substitution of Γ with the entropy balance gives a particular form. The corresponding Euler-Lagrange equations have a separable subsystem of differential equations (*viz.* independently solvable) for the Γ parameters, and neither the consideration of the balance equations as subsidiary conditions nor the determination of the J currents is necessary [59].

The situation with the time integrated form in Equation (60) is a bit different. The Euler-Lagrange equations do not display the set of transport equations directly. The latter can be calculated from transversality conditions and is obtained after a first integration of the Euler-Lagrange equations [1]. The other method introduces some potential functions the Euler-Lagrange equations concern, and the customary transport equations result after eliminating them [2–4,79].

The Governing Principle of Dissipative Processes, like any other integral principle of physics, contains information on the boundary conditions, too. They have to be given, so that the absolute maximum is provided, *viz.* any further weakening of the proper boundary conditions may not increase the value of the maximum.

We mention that for strictly linear problems, there are two partial forms that are also valid:

$$\delta \int_V (\sigma_s - \Psi) dV = 0, \quad \delta J = 0, \quad (61)$$

and:

$$\delta \int_V (\sigma_s - \Phi) dV = 0, \quad \delta X = 0. \quad (62)$$

The first of these is called force, and the second is called flux representation. Both representations were widely applied to the solution of several practical problems [41–43,56,57,85]. It is also well known that the force representation of Gyarmati's governing principle is equivalent to the local potential method of Prigogine and Glansdorff [86], while the flux representation is the equivalent of the variational methods of Biot [18,19]. (For details, see [43,44,61,87–92].)

Here, a more or less “classical” framework of Gyarmati's variational principle has been surveyed, but life does not stop; new fields of applications and new aspects emerge. The unification of and relating the different approaches is a permanent task. I mention only some works of Sieniutycz [93], Anthony [94], Polizzotto [95], Ván [96–103], Merker and Krueger [104], Cimmelli [105], Jou, Cimmelli and Sellitto [106], Gerasev [107], Triani and Cimmelli [108], Villaluenga and Kjelstrup [109] and Hutter and Svendsen [110] etc.

Some of them (e.g., [105] and [106]) are loosely or not related to Gyarmati's variational principle, but concern systems that are worth studying if they can be inserted into Gyarmati's framework and if they can then know how to do it.

4.1. A Very Simple Illustration [1]

For those readers who are interested in how a parabolic equation can be derived from a variational principle, a very simple example is put forward here.

Assume one-dimensional heat conduction with constant density, specific heat and heat conductivity in, e.g., a wall with constant thickness; moreover, use such units that both the heat capacity of the unit volume and the heat conductivity are one (and dimensionless). In this model, the conservation of energy is expressed by:

$$\frac{\partial T}{\partial t} + \frac{\partial J_q}{\partial x} = 0. \tag{63}$$

Here, T is the temperature, t is the time, J_q the heat flow and x is the coordinate perpendicular to the wall. In such a simple model, the local equilibrium makes the temperature well defined.

The entropy balance reads:

$$\rho \frac{\partial s}{\partial t} + \frac{\partial}{\partial x} \left(\frac{J_q}{T} \right) = \sigma_s = -\frac{1}{T^2} \frac{\partial T}{\partial x} J_q \geq 0. \tag{64}$$

In this simple case, the so-called Fourier picture is the most convenient one. The quantity:

$$T^2 \sigma_s = -\frac{\partial T}{\partial x} J_q = X J_q \geq 0 \tag{65}$$

is a comfortable starting point to write Onsager’s linear law, which reads:

$$J_q = -\frac{\partial T}{\partial x}. \tag{66}$$

Nevertheless, substituting this into Equation (63) is a straightforward way to Fourier’s equation; this time, not obtaining it is the main purpose, but it is deriving from a variational principle. The linear law is used to get the Φ and Ψ potentials only, and having got them, we pretend to have forgotten it. The mentioned potentials are:

$$\Phi = \frac{1}{2} J_q^2; \quad \Psi = \frac{1}{2} \left(\frac{\partial T}{\partial x} \right)^2 \tag{67}$$

and the Lagrangian in Equation (60) is:

$$\mathcal{L} = -\frac{\partial T}{\partial x} J_q - \frac{1}{2} \left(\frac{\partial T}{\partial x} \right)^2 - \frac{1}{2} J_q^2. \tag{68}$$

The two functions looked for are correlated by the conservation of the energy in Equation (63); we have two possibilities. The first is using the Lagrangian multiplier with the auxiliary Lagrangian:

$$\mathcal{L}^* = -\frac{\partial T}{\partial x} J_q - \frac{1}{2} \left(\frac{\partial T}{\partial x} \right)^2 - \frac{1}{2} J_q^2 + \mu \left(\frac{\partial T}{\partial x} + \frac{\partial J_q}{\partial t} \right), \tag{69}$$

or better, introducing a potential, φ , with the equations:

$$\frac{\partial \varphi}{\partial x} = T; \quad \frac{\partial \varphi}{\partial t} = -J_q, \tag{70}$$

with which the conservation of the energy automatically holds. Now, the form of the variational problem in Equation (60) takes:

$$\int_{t_1}^{t_2} \int_a^b \frac{\partial^2 \varphi}{\partial^2 x} \frac{\partial \varphi}{\partial t} - \frac{1}{2} \left(\frac{\partial^2 \varphi}{\partial^2 x} \right)^2 - \frac{1}{2} \left(\frac{\partial \varphi}{\partial t} \right)^2 dx dt = max. \tag{71}$$

The Euler-Lagrange equation reads:

$$-\frac{\partial}{\partial t} \left(\frac{\partial^2 \varphi}{\partial x^2} - \frac{\partial \varphi}{\partial t} \right) + \frac{\partial^2}{\partial x^2} \left(\frac{\partial \varphi}{\partial t} - \frac{\partial^2 \varphi}{\partial x^2} \right) = 0 \quad (72)$$

or:

$$\left(\frac{\partial}{\partial t} + \frac{\partial^2}{\partial x^2} \right) \left(\frac{\partial}{\partial t} - \frac{\partial^2}{\partial x^2} \right) \varphi = 0, \quad (73)$$

or

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{\partial^4 \varphi}{\partial x^4}. \quad (74)$$

The usual initial and boundary conditions prescribe the temperature; now, they prescribe the value of $\frac{\partial \varphi}{\partial x}$, *i.e.*, the value of φ is free on the boundary, and at t_2 , consequently, the transversality conditions:

$$\frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial \left(\frac{\partial^2 \varphi}{\partial x^2} \right)} \Big|_{a,b} = \frac{\partial}{\partial x} \left(\frac{\partial \varphi}{\partial t} - \frac{\partial^2 \varphi}{\partial x^2} \right) \Big|_{a,b} = 0; \quad \frac{\partial \mathcal{L}}{\partial \left(\frac{\partial \varphi}{\partial t} \right)} \Big|_{t_2} = \left(\frac{\partial^2 \varphi}{\partial x^2} - \frac{\partial \varphi}{\partial t} \right) \Big|_{t_2} = 0 \quad (75)$$

also hold. Introducing temporarily the:

$$u = \frac{\partial \varphi}{\partial t} - \frac{\partial^2 \varphi}{\partial x^2} \quad (76)$$

auxiliary variable, the equation turns into:

$$\frac{\partial u}{\partial t} + \frac{\partial^2 u}{\partial x^2} = 0 \quad (77)$$

with the initial (now final) and boundary conditions:

$$u|_{t_2} = 0; \quad \frac{\partial u}{\partial x} \Big|_{a,b} = 0. \quad (78)$$

The $t' = -t$ transformation results in the simple heat conduction problem of constant (zero) initial temperature and no heat flow on the boundary. We conclude that Equation (77) with the initial and boundary conditions is a well-posed Cauchy problem, the only solution of which is the trivial one $u = 0$. Now, Equation (76) turns into a parabolic equation, from which Fourier's equation results by evaluating the partial derivative of both sides with respect to x .

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Conflicts of Interest

The author declares no conflict of interest.

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