

GYARMATI'S VARIATIONAL PRINCIPLE OF DISSIPATIVE PROCESSES.

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ABSTRACT

Like mechanics and electrodynamics, the fundamental laws of the thermodynamics of dissipative processes can be compressed into a variational principle. This variational principle both in its differential (local) and in integral (global) forms was formulated by Gyarmati helped by the present author in 1965. This principle was applied to several fields of irreversible processes: first of all, his colleagues (Verhás [1], Böröcz [2], Farkas [3,4], Sándor [5], Vincze [6–8], Stark [9,10]); but also many others (Singh [11,12], Bhattacharya [13,14], Dickel [15,16] etc.). 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.

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 exist locally in continua [17–22]. In linear theory 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 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. The other fundamental property of Ψ is that its partial derivative with respect to X_k is equal to the current J_k conjugate to the force X_k in the entropy production density:

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

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 (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 the Onsager 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. The general theory of the "pictures" was worked out and applied by Gyarmati [23] and Farkas [3] (see also [5, 13, 14, 24–27]). 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 the Onsager-Casimir reciprocal relations. By choosing various functions for G , various pictures for the description of dissipative processes are obtained [3, 28, 29].

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.

THE LOCAL FORMS OF GYARMATI'S PRINCIPLE

Gyarmati's variational principle of non-equilibrium thermodynamics can be derived from the properties (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 (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 all the 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. It 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 [30].

The force representation of Gyarmati's principle is obtained by putting the relation (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 (13) and (15) can be put in the same form, as the subtraction of function 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:

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

by which the extremum properties (12) and (14) can be expressed universally.

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 (16) is stationary. This is a necessary and sufficient condition for the set of the currents and forces 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 (1) and (2). The matrices of the conductivities L_{ik} and resistivities R_{ik} are reciprocal matrices:

$$\sum_r L_{ir} R_{rk} = \delta_{ik}. \quad (17)$$

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

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

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

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

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

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

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. So the parameters Γ can also be varied independently.

This theorem is Gyarmati's supplementary theorem [31], 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

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

Executing the multiplications the form (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 are the coefficients of a positive definite quadratic form 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 (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 (Verhás [32], Gyarmati [29], Dickel [15]).

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 frame-work 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 got from Φ in the same way, ([30,31]).

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 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 be subjected to the Gyarmati-Li generalized reciprocal relations. It is rather inconvenient that no general physical law, or exact proof based on such laws, is known which would guarantee the fulfillment of the Gyarmati-Li generalized reciprocal relations, or of other equivalent conditions, for all possible constitutive equations. If, however, the reciprocal relations (11) hold in a particular case or approximation, then the dissipation potentials can be given and the Gyarmati principle can be applied. Dissipation potentials for non-linear cases were given first (and independently) by Verhás [33], Edele [34–37] and Presnov [38].

The function Ψ can be obtained from the bilinear form of the entropy production with 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.

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 [31].

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

$$\delta \int_V (\sigma_s - \Psi - \Phi) dV = 0, \quad (25)$$

and

$$\delta \int_{t_1}^{t_2} \int_V (\sigma_s - \Psi - \Phi) dV dt = 0. \quad (26)$$

The governing principle of dissipative processes given by Gyarmati can be regarded 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 (23) and (24) due to the validity of the generalized reciprocal relations (11), [3, 5, 7, 9, 10, 26–29, 34, 35, 39].

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 (25) and (26) 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 (25) arises from the fact that the Euler-Lagrange equations are identical to the parabolic transport equations. 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 [29].

The situation with the time integrated form in equation (26) 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 [40]. The other method introduces some potential functions the Euler-Lagrange equations concern to and the customary transport equations results after eliminating them [18, 19, 41, 42].

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 as the absolute maximum be 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 also valid:

$$\delta \int_V (\sigma_s - \Psi) dV = 0, \quad \delta J = 0, \quad (27)$$

and

$$\delta \int_V (\sigma_s - \Phi) dV = 0, \quad \delta X = 0. \quad (28)$$

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. [9–11, 26, 27, 43]. 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 [44], while the flux representation is the equivalent of the variational methods of Biot [45, 46]. (For details see references [11, 12, 31, 47–52].)

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 the different approaches is a permanent task. I mention only some works of P. Ván here [53–57].

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NOMENCLATURE

G	Any positive state function [variant]
i, j, k, r, s	Runing indices [integer, no unite]
J_i	the j -th of the generalized currents [variant]
J	any of the generalized currents [variant]
J_i^G	the j -th of the generalized currents in "G" picture [variant]
J^G	any of the generalized currents in "G" picture [variant]
L_{ik}	a conductivity coefficient [variant]
L	any of the conductivity coefficients [variant]
L_{ik}^G	a conductivity coefficient in "G" picture [variant]
L^G	any of the conductivity coefficient in "G" picture [variant]
R_{ik}	a resistivity coefficient [variant]
R	any of the resistivity coefficient [variant]
R_{ik}^G	a resistivity coefficient in "G" picture [variant]
R^G	any of the resistivity coefficient in "G" picture [variant]
t	runing integration variable [real number, no unite]
X_i	the i -th thermodynamic force [variant]
X	any of the thermodynamic forces [variant]
X_i^G	the i -th thermodynamic force in "G" picture [variant]
X^G	any of the thermodynamic force in "G" picture [variant]
$\mathcal{L}, \mathcal{L}_J, \mathcal{L}_X$	Lagrangian [W/K m ³]
Γ	a state variable [variant]
σ_s	entropy production density [W/K m ³]
Φ	force-potential [W/K m ³]
Φ^G	force-potential [variant]
Ψ	flux-potential [W/K m ³]
Ψ^G	flux-potential [variant]

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