

Examination of phenomenological coefficient matrices within the canonical model of field theory of thermodynamics

Katalin Gambár,¹ Katalin Martinás,² and Ferenc Márkus³

¹*Institute of Physics, Roland Eötvös University, Puskin utca 5-7, H-1088 Budapest, Hungary*

²*Department of Atomic Physics, Roland Eötvös University, Puskin utca 5-7, H-1088 Budapest, Hungary*

³*Institute of Physics, Technical University of Budapest, Budafoki út 8, H-1521 Budapest, Hungary*

(Received 3 July 1996; revised manuscript received 12 December 1996)

The field equations of linear irreversible thermodynamics have been deduced from Hamilton's principle. The Hamiltonian formalism has been considered as a theory of conservative systems without dissipative processes. In this paper, we present the field equations of linear irreversible thermodynamics that are deduced from a Hamiltonian principle. First, we present the canonical mathematical model for purely dissipative transport processes. Then introducing a Lie algebra of the potentials with the help of an algebraic-type transformation, we examine the physical processes in this algebra. We expect that two kinds of descriptions of the same physical situation develop into two such descriptions in time, which describe the same physical situations as well. Since the given transformation is a dynamical transformation (it leaves the Lagrangian invariant) in the sense of the above-mentioned expectation, we expect that the entropy density function and the entropy production density function (which pertains to the same physical situation) have to be invariant under that transformation which leaves the Lagrangian invariant. It is shown that these are satisfied if the phenomenological coefficient matrices are symmetric. [S1063-651X(97)08305-0]

PACS number(s): 44.60.+k

I. INTRODUCTION

In the field theory of irreversible thermodynamics [1–15] we regard the local specific entropy s as a fundamental state variable. In the case of local equilibrium systems it is the function of specific extensive quantities, which are continuously differentiable functions of space and time,

$$s = s(g_1(\mathbf{r}, t), \dots, g_f(\mathbf{r}, t)) = s(\mathbf{r}, t). \quad (1)$$

The specific extensive quantities satisfy the balance equations

$$\rho \frac{\partial g_i}{\partial t} + \nabla \cdot \mathbf{J}_i = \sigma_i, \quad (2)$$

where $\mathbf{J}_i(\mathbf{r}, t)$ is the conductive current density, ρ is the mass density, and ∇ means the nabla operator. There are two kind of constitutive equations

$$\frac{\partial g_i}{\partial t} = S_{ik}^{-1} \frac{\partial \Gamma_k}{\partial t} \quad (3)$$

and

$$\mathbf{J}_i = L_{ik} \nabla \Gamma_k, \quad (4)$$

where $\Gamma_i(\mathbf{r}, t)$ is an intensive quantity, e.g., $1/T, p/T$. If we substitute Eqs. (3) and (4) into the balance equations (2), we get the field equations (transport equations)

$$\rho S_{ik}^{-1} \frac{\partial \Gamma_k}{\partial t} + \nabla \cdot (L_{ik} \nabla \Gamma_k) = \sigma_i, \quad (5)$$

which are the equations of motion. S_{ik}^{-1}, L_{ik} are the phenomenological coefficient matrices, and these are supposed to be symmetric:

$$S_{ik}^{-1} = S_{ki}^{-1}, \quad (6)$$

$$L_{ik} = L_{ki}. \quad (7)$$

S_{ik}^{-1} is the matrix of generalized specific capacities, which is negative definite and related to the existence and stability of the local equilibrium [8,16,17]. The second equation is called Onsager's reciprocity relation [3,18,19] in field theory. This relation ranks among one of the most important statements of irreversible thermodynamics. There are numerous articles [18–47] that deal with the proof, generalization, and extension of it. They use statistical or/and phenomenological methods and different assumptions for the examinations of the relation. Since Miller's experimental results [48,49] most scientists have accepted the relation and taken advantage of it in various special cases. Onsager relations are of help in solving the set of differential equations because these reduce the number of independent quantities. Here we mention that fluxes and thermodynamical forces of different tensorial character do not couple (Curie's theorem), i.e., the number of independent quantities is decreased in this way too. This results from the invariance of the phenomenological equations (constitutive equations) under special orthogonal transformations.

Nonequilibrium thermodynamics is mainly restricted to the study of linear phenomena and the balance equation for the entropy plays a central role. The local mathematical expression for the second law of thermodynamics is

$$\sigma = \mathbf{J}_i \cdot \nabla \Gamma_i = \mathbf{J}_i \cdot \mathbf{X}_i \geq 0, \quad (8)$$

where σ is the entropy production density.

II. THE MATHEMATICAL MODEL

In this section we give a canonical mathematical model for those kind of irreversible transport processes that can be described by source-free and convection-free transport equations with constant coefficients. This model is based on three postulates

Postulate I. Hamilton's principle is

$$\delta S = \int_{t_1}^{t_2} \int_V L \, dV \, dt = 0, \quad (9)$$

where L is the Lagrange density function, which is generally a function of time and space, and the function of the first- or higher-order derivatives of the field quantities with respect to time and space.

Postulate II. The Lagrange density function of the source-free and convection-free nonequilibrium systems is

$$L(\varphi_i, \varphi_{i;t}, \Delta \varphi_i) = \frac{1}{2} (\varrho S_{ji}^{-1} \varphi_{j;t} - L_{ji} \Delta \varphi_j)^2, \quad (10)$$

where the φ_i are four times differentiable field quantities (potentials) [50,51] and $\Delta = \nabla^2$. These give the measurable quantities $\Gamma_i(\mathbf{r}, t)$ as

$$\Gamma_i = \varrho S_{ji}^{-1} \frac{\partial \varphi_j}{\partial t} - L_{ji} \Delta \varphi_j. \quad (11)$$

S_{ji}^{-1}, L_{ji} are constant coefficients, ρ is the mass density, and Δ is the Laplace operator.

Postulate III. The entropy density function s is the quadratic form of the generalized canonical momentum density functions

$$s = \frac{1}{2} \rho^{-1} p_i S_{ij} p_j, \quad (12)$$

where p_i is defined by

$$p_i = \frac{\partial L}{\partial \varphi_{i;t}}. \quad (13)$$

From the first two postulates we obtain the Euler-Lagrange equations

$$\frac{\partial L}{\partial \varphi_i} - \frac{\partial}{\partial t} \frac{\partial L}{\partial \varphi_{i;t}} + \Delta \frac{\partial L}{\partial \Delta \varphi_i} = 0. \quad (14)$$

These are the equations of motion or field equations for φ_i , which are equivalent to

$$\varrho S_{ik}^{-1} \Gamma_{k;t} + L_{ik} \Delta \Gamma_k = 0. \quad (15)$$

These are the source-free and convection-free transport equations.

The total variation of the functional

$$S = \int_T L(\varphi_i, \varphi_{i;\mu}, \varphi_{i;\mu\nu}) d^4x \quad (16)$$

over the domain T is

$$\begin{aligned} \delta_i S &= \int_T L(\varphi_i + \delta \varphi_i, \varphi_{i;\mu} + \delta \varphi_{i;\mu}, \varphi_{i;\mu\nu} + \delta \varphi_{i;\mu\nu}) \\ &\quad - \int_T L(\varphi_i, \varphi_{i;\mu}, \varphi_{i;\mu\nu}) \\ &= \int_T \frac{\partial}{\partial x_\mu} (\Theta_{\mu\xi} \delta x_\xi + \Pi_{i\mu} \delta_t \varphi_i + \lambda_{i\mu\nu} \delta_t \varphi_{i;\nu}) d^4x, \end{aligned} \quad (17)$$

where $\mu, \xi = 1, 2, 3, 4$; $x_1 = x$; $x_2 = y$; $x_3 = z$; and $x_4 = t$. $\Pi_{i\mu}$ and $\lambda_{i\mu\nu}$ are the canonical coefficients. The canonical momentum density p_i of the field is

$$p_i = \Pi_{i\mu} N_\mu = \frac{\partial L}{\partial \varphi_{i;t}} = \rho S_{ij}^{-1} \Gamma_j, \quad (18)$$

where the normal vector can be written $N_\mu = (0, 0, 0, 1)$. The thermodynamic tensor $\Theta_{\mu\xi}$ is the canonical tensor of the field. $-\Theta_{44}$ yields the Hamilton density function [51,52] if we take and define the canonical momentum density function (18) by the formula

$$\begin{aligned} -\Theta_{44} &= H(p_i, \Delta \varphi_i) = \varphi_{i;t} \frac{\partial L}{\partial \varphi_{i;t}} - L \\ &= \frac{1}{2} (\rho^{-1} S_{ij} p_j)^2 + \rho^{-1} S_{ij} p_j L_{ki} \Delta \varphi_k. \end{aligned} \quad (19)$$

In general, if we have a Hamiltonian density function $H(\varphi_i, \varphi_{i;\mu}, \varphi_{i;\mu\nu}, p_i)$ (where $\mu, \nu = 1, 2, 3$), the differential of H leads to

$$dH = \frac{\partial H}{\partial \varphi_i} d\varphi_i + \frac{\partial H}{\partial \varphi_{i;\mu}} d\varphi_{i;\mu} + \frac{\partial H}{\partial \varphi_{i;\mu\nu}} d\varphi_{i;\mu\nu} + \frac{\partial H}{\partial p_i} dp_i. \quad (20)$$

With the use of the definition of H

$$-\Theta_{44} = H(\varphi_i, \varphi_{i;\mu}, \varphi_{i;\mu\nu}, p_i) = \varphi_{i;t} \frac{\partial L}{\partial \varphi_{i;t}} - L, \quad (21)$$

we obtain dH in the form

$$dH = -\frac{\partial L}{\partial \varphi_i} d\varphi_i - \frac{\partial L}{\partial \varphi_{i;\mu}} d\varphi_{i;\mu} - \frac{\partial L}{\partial \varphi_{i;\mu\nu}} d\varphi_{i;\mu\nu} + \varphi_{i;t} dp_i. \quad (22)$$

When Eqs. (13) and (14) are taken into account, a comparison of Eqs. (20) and (22) yields

$$\frac{\partial H}{\partial \varphi_i} = -\frac{\partial L}{\partial \varphi_i}, \quad (23)$$

$$\frac{\partial H}{\partial \varphi_{i;\mu}} = -\frac{\partial L}{\partial \varphi_{i;\mu}}, \quad (24)$$

$$\frac{\partial H}{\partial \varphi_{i;\mu\nu}} = -\frac{\partial L}{\partial \varphi_{i;\mu\nu}}, \quad (25)$$

$$\frac{\partial H}{\partial p_i} = \varphi_{i;t}. \quad (26)$$

Equation (26) is the first group of canonical equations. With the help of Eqs. (23)–(25) we obtain the second group of canonical equations if we take the derivatives of canonical momentum densities p_i with respect to t and use the Euler-Lagrange equations

$$p_{i;t} = \frac{\partial}{\partial t} \frac{\partial L}{\partial \varphi_{i;t}} = \frac{\partial L}{\partial \varphi_i} - \frac{\partial}{\partial x_\mu} \frac{\partial L}{\partial \varphi_{i;\mu}} + \frac{\partial^2}{\partial x_\mu \partial x_\nu} \frac{\partial L}{\partial \varphi_{i;\mu\nu}}, \quad (27)$$

$$p_{i;t} = - \frac{\partial H}{\partial \varphi_i} + \frac{\partial}{\partial x_\mu} \frac{\partial H}{\partial \varphi_{i;\mu}} - \frac{\partial^2}{\partial x_\mu \partial x_\nu} \frac{\partial H}{\partial \varphi_{i;\mu\nu}}. \quad (28)$$

In our case, when the Hamilton density function is $H(p_i, \Delta \varphi_i)$, we obtain for the second canonical equation

$$p_{i;t} = - \Delta \frac{\partial H}{\partial \Delta \varphi_i}. \quad (29)$$

It is very useful to introduce the Poisson bracket in a general form because the time derivative of a physical quantity can be given by a Poisson bracket of the Hamilton density function and the quantity itself

$$[p_i, H] = \frac{\delta p_i}{\delta \varphi_j} \frac{\delta H}{\delta p_j} - \frac{\delta H}{\delta \varphi_j} \frac{\delta p_i}{\delta p_j}, \quad (30)$$

where the functional derivatives mean, e.g., the Hamiltonian density function H with respect to φ_i ,

$$\frac{\delta H}{\delta \varphi_i} = \frac{\partial H}{\partial \varphi_i} - \frac{\partial}{\partial x_\mu} \frac{\partial H}{\partial \varphi_{i;\mu}} + \frac{\partial^2}{\partial x_\mu \partial x_\nu} \frac{\partial H}{\partial \varphi_{i;\mu\nu}}. \quad (31)$$

The Poisson bracket expressions of the canonical equations hold

$$\varphi_{i;t} = [\varphi_i, H], \quad (32)$$

$$p_{i;t} = [p_i, H]. \quad (33)$$

Since this Hamiltonian density pertains to purely dissipative convection-free transport processes without heat sources and chemical reactions, we expect to get the well-known bilinear form of the entropy production density in the formalism.

Let us derive the balance equations of the entropy density. If we calculate the Poisson bracket of specific entropy density s (postulate III) and the Hamiltonian density function H [Eq. (19)], we get the time evolution of entropy density s

$$\frac{\partial s}{\partial t} = [s, H]. \quad (34)$$

We calculate this Poisson bracket expression

$$\begin{aligned} [s, H] &= \left(\frac{\delta s(p_i)}{\delta \varphi_j} \frac{\delta H}{\delta p_j} - \frac{\delta H}{\delta \varphi_j} \frac{\delta s(p_i)}{\delta p_j} \right) \\ &= -\rho^{-1} S_{ij} p_j L_{ig} \Delta \rho^{-1} S_{gk} p_k \\ &= -\nabla \cdot [\rho^{-1} S_{ij} p_j L_{ig} \cdot \nabla (\rho^{-1} S_{gk} p_k)] \\ &\quad + \nabla (\rho^{-1} S_{ij} p_j) L_{ig} \cdot \nabla (\rho^{-1} S_{gk} p_k) \\ &= -\rho^{-2} S_{ij} L_{ig} S_{gk} \nabla \cdot (p_j \nabla p_k) \\ &\quad + \rho^{-2} S_{ij} L_{ig} S_{gk} \nabla p_j \cdot \nabla p_k. \end{aligned} \quad (35)$$

Thus we obtain the entropy balance equation

$$\frac{\partial s}{\partial t} + \rho^{-2} S_{ij} L_{ig} S_{gk} \nabla \cdot (p_j \nabla p_k) = \rho^{-2} S_{ij} L_{ig} S_{gk} \nabla p_j \cdot \nabla p_k, \quad (36)$$

where

$$\mathbf{J}_s = \rho^{-2} S_{ij} L_{ig} S_{gk} p_j \nabla p_k \quad (37)$$

is the entropy current density and

$$\sigma = \rho^{-2} S_{ij} L_{ig} S_{gk} \nabla p_j \cdot \nabla p_k = \rho^{-1} S_{ij} \nabla p_j \cdot L_{ig} \rho^{-1} S_{gk} \nabla p_k \quad (38)$$

is the entropy production density. This can be simply written [taking into account Eqs. (4), (8), and (18)]

$$\sigma = \mathbf{X}_i \cdot \mathbf{J}_i. \quad (39)$$

On the basis of Eq. (39) we can express the entropy production density with the potentials φ_i ,

$$\begin{aligned} \sigma(\varphi) &= \nabla \cdot (\rho S_{ji}^{-1} \varphi_{j;t} - L_{ji} \Delta \varphi_j) \cdot L_{ik} \nabla \\ &\quad \times (\rho S_{mk}^{-1} \varphi_{m;t} - L_{mk} \Delta \varphi_m) \\ &= \rho S_{ji}^{-1} L_{ik} S_{mk}^{-1} \nabla \varphi_{j;t} \cdot \nabla \varphi_{m;t} \\ &\quad - L_{ji} L_{ik} \rho S_{mk}^{-1} \nabla \Delta \varphi_j \cdot \nabla \varphi_{m;t} \\ &\quad - \rho S_{ji}^{-1} L_{ik} L_{mk} \nabla \varphi_{j;t} \cdot \nabla \Delta \varphi_m + L_{ji} L_{ik} L_{mk} \nabla \Delta \varphi_j \\ &\quad \cdot \nabla \Delta \varphi_m. \end{aligned} \quad (40)$$

III. LIE ALGEBRA

$\varphi_1(\mathbf{r}, t), \varphi_2(\mathbf{r}, t), \dots, \varphi_K(\mathbf{r}, t)$ are scalar-vector functions, which are four times differentiable and linearly independent. Let us consider a linear vector space ϕ_K over the field of real numbers; the basis vectors are $\varphi_1, \varphi_2, \dots, \varphi_K$. Any vector ξ can be expanded in terms of the basis $\{\varphi_i\}$. If we introduce multiplication among the elements of ϕ_K , which means the multiplication of scalar-vector functions, then we obtain a linear associative and commutative algebra A_K .

If we have an arbitrary associative algebra, a Lie algebra can be constructed from it if we introduce a different multiplication

$$a \odot b = (ab - ba). \quad (41)$$

Thus we obtain a Lie algebra $L(A)$ from an associative algebra A on the same field.

Let us consider the following infinitesimal, linear, and bijective transformation, which transforms the basis vectors φ_i into the basis vectors φ'_i :

$$\varphi_i \mapsto \varphi'_i = \delta_{il} \varphi_l - \Theta T_{il} \hat{P} \varphi_l, \quad (42)$$

where the transformation $\hat{T}: \phi_K \rightarrow \phi'_K$ is an isomorphism, and ϕ'_K is the different vector field. The inverse of transformation \hat{T} is

$$\hat{T}^{-1}: \phi'_K \rightarrow \phi_K, \quad (43)$$

$$\varphi_j = \delta_{jl} \varphi'_l + \Theta T_{jl} \hat{P} \varphi'_l. \quad (44)$$

We emphasize that \hat{T} and \hat{T}^{-1} are infinitesimal linear transformations, i.e., the second-order terms are negligible. The δ_{il} is the Kronecker symbol, Θ is an infinitesimal constant, T_{il} is the mixing matrix in which the elements $T_{ii} = 0$, and \hat{P} is the ordering operator. The operator \hat{P} orders the indices of φ . There are three different cases: (I) $\hat{P} = +1$, in the case of $\varphi_{i_1} \varphi_{i_2}$ the ordering $i_1 i_2$ is even, i.e., the number of inversions is 0, so $i_1 > i_2$; (II) $\hat{P} = 0$, if there is no ordering, i.e., $i_1 = i_2$; (III) $\hat{P} = -1$, if the ordering $i_1 i_2$ is odd, i.e., the number of inversions is 1, $i_2 > i_1$. The effect of operator \hat{P} in the last case is that \hat{P} makes the ordering ($i_1 i_2 \rightarrow i_2 i_1$) inversion-free. Moreover, the operator \hat{P} commutes with all other operators because this acts only on the ordering.

We consider that case when $K=3$ and we take the products

$$\begin{aligned} \varphi'_2 \varphi'_3 &= (\varphi_2 - \Theta T_{21} \hat{P} \varphi_1 - \Theta T_{23} \hat{P} \varphi_3) \\ &\quad \times (\varphi_3 - \Theta T_{31} \hat{P} \varphi_1 - \Theta T_{32} \hat{P} \varphi_2) \\ &= \varphi_2 \varphi_3 - \Theta T_{21} \hat{P} \varphi_1 \varphi_3 - \Theta T_{23} \hat{P} \varphi_3 \varphi_3 \\ &\quad - \varphi_2 \Theta T_{31} \hat{P} \varphi_1 - \varphi_2 \Theta T_{32} \hat{P} \varphi_2 \\ &= \varphi_2 \varphi_3 - \Theta T_{21} \varphi_1 \varphi_3 + \Theta T_{31} \varphi_1 \varphi_2 \end{aligned} \quad (45)$$

and

$$\varphi'_3 \varphi'_2 = \varphi_3 \varphi_2 - \Theta T_{31} \varphi_1 \varphi_2 + \Theta T_{21} \varphi_1 \varphi_3. \quad (46)$$

We can calculate the difference of these products

$$\varphi'_2 \varphi'_3 - \varphi'_3 \varphi'_2 = 2\Theta (T_{31} \varphi_1 \varphi_2 - T_{21} \varphi_1 \varphi_3), \quad (47)$$

from which we can see that it is useful to introduce and define a different algebraic product among the elements of ϕ'_K

$$\varphi'_j \odot \varphi'_k = \varphi'_j \varphi'_k - \varphi'_k \varphi'_j = 2\Theta (T_{kl} \varphi_l \varphi_j - T_{jm} \varphi_m \varphi_k), \quad (48)$$

where $l, m \neq j, k$. In this way, it is easy to prove

$$\varphi'_j \odot \varphi'_k = -\varphi'_k \odot \varphi'_j. \quad (49)$$

We can conclude that $\hat{T}(\phi_K) = \phi'_K$ linear vector space with the above-defined algebraic multiplication is a Lie algebra [53,54].

IV. \hat{T} AS A DYNAMICAL TRANSFORMATION

If the equations of motion are invariant with respect to (i) the transformations of \mathbf{r}, t , we speak about geometrical transformations and geometrical symmetry, and (ii) the transformations of field quantities $\varphi(\mathbf{r}, t)$, we speak about dynamical transformations and dynamical symmetry. Since we have deduced the equations of motion from the variation of action S (Hamilton's principle), the sufficient condition for the equations of motion is the invariance of the action. If the action is invariant with respect to dynamical transformation, it means mathematically that [55–58]

$$\begin{aligned} L(\varphi_i(\mathbf{r}, t), \varphi_{i;\mu}(\mathbf{r}, t), \varphi_{i;\mu\nu}(\mathbf{r}, t)) \\ = L(\varphi'_i(\mathbf{r}, t), \varphi'_{i;\mu}(\mathbf{r}, t), \varphi'_{i;\mu\nu}(\mathbf{r}, t)), \end{aligned} \quad (50)$$

i.e., it is sufficient to examine the invariance of Lagrangian. Our aim is to discuss how the Lagrangian (10) behaves against the transformation \hat{T} . We can point out after a long but elementary calculation [43] that the Lagrangian is invariant with respect to \hat{T} , so this dynamical transformation pertains to the dynamical invariance of equations of motion of nonequilibrium thermodynamics.

Given this knowledge, the question arises how the specific entropy density s and the specific entropy production density σ behave under this dynamical transformation \hat{T} . First we write the entropy density s with the potential functions φ_i ,

$$\begin{aligned} s &= \frac{1}{2} \rho^{-1} [\rho S_{ik}^{-1} (\rho S_{fk} \varphi_{f;t} - L_{fk} \Delta \varphi_f) S_{ij} \rho S_{jl}^{-1} \\ &\quad \times (\rho S_{gl} \varphi_{g;t} - L_{gl} \Delta \varphi_g)] \\ &= \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} \varphi_{f;t} S_{ij} S_{jl}^{-1} S_{gl} \varphi_{g;t} \\ &\quad - \frac{1}{2} \rho^2 S_{ik}^{-1} L_{fk} \Delta \varphi_f S_{ij} S_{jl}^{-1} S_{gl} \varphi_{g;t} \\ &\quad - \frac{1}{2} \rho^2 S_{ik}^{-1} S_{fk} \varphi_{f;t} S_{ij} S_{jl}^{-1} L_{gl} \Delta \varphi_g \\ &\quad + \frac{1}{2} \rho S_{ik}^{-1} L_{fk} \Delta \varphi_f S_{ij} S_{jl}^{-1} L_{gl} \Delta \varphi_g. \end{aligned} \quad (51)$$

Now we transform the potential functions and get the transformed entropy density s' . We show the transformation for the first term of s , which is underlined in Eq. (51), and we can sign $[s]_1$. The transformed of this term is signed $[s']_1$, which is the first term of the transformed entropy density $s'(\varphi)$,

$$\begin{aligned}
[s']_1 &= \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} \varphi'_{f;t} S_{ij} S_{jl}^{-1} S_{gl} \varphi'_{g;t} \\
&= \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} (\delta_{fm} \varphi_{m;t} - \Theta T_{fm} \hat{P} \varphi_{m;t}) \\
&\quad \times (\delta_{gp} \varphi_{p;t} - \Theta T_{gp} \hat{P} \varphi_{p;t}) \\
&= \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} (\varphi_{f;t} \varphi_{g;t} - \Theta T_{fm} \hat{P} \varphi_{m;t} \varphi_{g;t} \\
&\quad - \varphi_{f;t} \Theta T_{gp} \hat{P} \varphi_{p;t}) = \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} \varphi_{f;t} \varphi_{g;t} \\
&\quad - \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} \Theta T_{fm} \hat{P} \varphi_{m;t} \varphi_{g;t} \\
&\quad - \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} \varphi_{f;t} \Theta T_{gp} \hat{P} \varphi_{p;t}. \quad (52)
\end{aligned}$$

We neglected the second-order terms and now change the indices $m \rightarrow p$, $f \rightarrow g$, $g \rightarrow f$, $i \rightarrow j$, $j \rightarrow i$, $l \rightarrow k$, and $k \rightarrow l$ in those terms which contain m , underlined in Eq. (52); we obtain the result

$$\begin{aligned}
[s']_1 &= \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} \varphi_{f;t} \varphi_{g;t} \\
&\quad - \frac{1}{2} \rho^3 S_{jl}^{-1} S_{gl} S_{ji} S_{ik}^{-1} S_{fk} \Theta T_{gp} \varphi_{p;t} \varphi_{f;t} \\
&\quad + \frac{1}{2} \rho^3 S_{ik}^{-1} S_{fk} S_{ij} S_{jl}^{-1} S_{gl} \Theta T_{gp} \varphi_{p;t} \varphi_{f;t}. \quad (53)
\end{aligned}$$

We recognize, comparing the second and third terms of Eq. (53), that $[s]_1 = [s']_1$ if and only if

$$S_{ij} = S_{ji}, \quad (54)$$

i.e., the entropy density is invariant if and only if the matrix S_{ij} is symmetric. We can examine the invariance property of entropy production density in the same way [43,51] and we get

$$\sigma(\varphi) = \sigma(\varphi'). \quad (55)$$

This equality is true if and only if the Onsager reciprocity relations hold

$$L_{ik} = L_{ki}. \quad (56)$$

Consequently, if we demand the invariance of entropy density function and the entropy production density under the introduced transformation, which is a dynamical transformation since it leaves the Lagrangian invariantly, the phenomenological coefficient matrices are symmetric in linear cases.

V. CONCLUSION

The canonical model developed allows us to exploit the possibilities of the invariance principles. We have shown that the descriptions of the dissipative processes in the linear vector space generalized by φ_i and in the Lie algebra generalized by φ'_i are equivalent if the phenomenological coefficient matrices are symmetric. This is in line with our expectation from a suitable model, i.e., our canonical model can provide the existence of the reciprocity relations in the framework of the model.

ACKNOWLEDGMENT

The authors would like to thank the OTKA (Hungarian Scientific Research Fund) for Grants Nos. F7369/1993, T6837/1993, and F19017/1996.

-
- [1] C. Eckart, Phys. Rev. **58**, 267 (1940).
[2] C. Eckart, Phys. Rev. **58**, 269 (1940).
[3] S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland, Amsterdam, 1951).
[4] J. Meixner and H. G. Reik, in *Encyclopedia of Physics, Vol. III/2*, edited by S. Flügge (Springer, Berlin, 1959).
[5] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[6] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes* (Interscience, New York, 1969).
[7] I. Gyarmati, *Non-Equilibrium Thermodynamics* (Springer, Berlin, 1970).
[8] P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure Stability and Fluctuations* (Wiley, New York, 1971).
[9] G. Lebon, *Recent Developments in Thermomechanics of Solids* (Springer, New York, 1980).
[10] H. J. Kreuzer, *Nonequilibrium Thermodynamics and its Statistical Foundations* (Clarendon, Oxford, 1981).
[11] D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **51**, 1105 (1988).
[12] B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992).
[13] I. Müller and T. Ruggeri, *Extended Thermodynamics* (Springer, New York, 1993).
[14] D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics*, 2nd ed. (Springer, Berlin, 1996).
[15] S. Sieniutycz, *Conservation Laws in Variational Thermohydrodynamics* (Kluwer, Dordrecht, 1994).
[16] B. Lukács and K. Martinás, Phys. Lett. **114A**, 306 (1986).
[17] L. Diósi, K. Kulacsy, B. Lukács, and A. Rácz, J. Chem. Phys. **105**, 11 220 (1996).
[18] L. Onsager, Phys. Rev. **37**, 405 (1931).
[19] L. Onsager, Phys. Rev. **38**, 2265 (1931).
[20] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).
[21] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).
[22] E. P. Wigner, J. Chem. Phys. **22**, 1912 (1954).
[23] W. Muschik, Ph.D. dissertation, Technische Universität Berlin, 1966 (unpublished).
[24] C. Truesdell, *Rational Thermodynamics* (McGraw-Hill, New York, 1969).
[25] F. Sauer, in *Handbook of Physiology, Renal Physiology*, edited by J. Orloff and R. W. Berliner (American Physiological Society, Washington, DC 1973), Sec. 8, pp. 399–414.
[26] J. Meixner, Arc. Rat. Mech. Anal. **39**, 108 (1970).

- [27] J. Keizer, *Statistical Thermodynamics of Nonequilibrium Thermodynamics Processes* (Springer, New York, 1977).
- [28] I. Gyarmati, *J. Non-Equilib. Thermodyn.* **2**, 233 (1977).
- [29] J. Hurley and C. Garrod, *Phys. Rev. Lett.* **48**, 1575 (1982).
- [30] L. S. Garcia-Colin, M. Lopez de Haro, R. F. Rodriguez, J. Casas-Vázquez, and D. Jou, *J. Stat. Phys.* **37**, 465 (1984).
- [31] R. F. Rodriguez, L. S. Garcia-Colin, and M. Lopez de Haro, *J. Chem. Phys.* **83**, 4099 (1985).
- [32] W. Muschik, in *Statistische Physik und Theorie Wärme*, edited by F. Reif (de Gruyter, Berlin, 1985), pp. 709–744.
- [33] B. Lukács, K. Martinás, and T. Pacher, *Astron. Nachr.* **307**, 171 (1986).
- [34] L. S. Garcia-Colin and R. F. Rodriguez, *J. Non-Equilib. Thermodyn.* **13**, 81 (1988).
- [35] B. Nyíri, *Acta Phys. Hung.* **66**, 19 (1989).
- [36] R. E. Nettleton and E. S. Friedkin, *Physica A* **158**, 672 (1989).
- [37] K. Oláh, J. Bódiss, and H. Farkas, *Acta Chim. Hung.* **127**, 783 (1990).
- [38] M. Grmela and D. Jou, *J. Phys. A* **24**, 741 (1991).
- [39] L. S. Garcia-Colin and R. M. Velasco, *Rev. Mex. Fis.* **38**, 92 (1992).
- [40] K. Martinás, *Atti Accad. Peloritana Pericolanti Cl. Sci. Fis. Mat. Nat.* **70**, 169 (1992).
- [41] R. E. Nettleton, in *Advances in Thermodynamics 7: Extended Thermodynamic Systems*, edited by S. Sieniutycz and P. Salamon (Taylor and Francis, New York, 1992).
- [42] F. Vázquez and J. A. del Río, *Phys. Rev. E* **47**, 178 (1993).
- [43] K. Gambár and F. Márkus, *J. Non-Equilib. Thermodyn.* **18**, 51 (1993).
- [44] R. M. Velasco and L. S. Garcia-Colin, *J. Non-Equilib. Thermodyn.* **18**, 157 (1993).
- [45] V. Ciancio and J. Verhás, *J. Non-Equilib. Thermodyn.* **19**, 184 (1994).
- [46] M. A. Olivares-Robles and L. S. Garcia-Colin, *Phys. Rev. E* **50**, 2451 (1994).
- [47] F. Vázquez, J. A. del Río, K. Gambár, and F. Márkus, *J. Non-Equilib. Thermodyn.* **21**, 357 (1996).
- [48] D. G. Miller, *Chem. Rev.* **60**, 15 (1960).
- [49] D. G. Miller, in *Foundations of Continuum Thermodynamics*, edited by J. J. Delgado Domingos, M. N. R. Nina, and J. H. Whitelaw (MacMillan, London, 1974).
- [50] F. Márkus and K. Gambár, *J. Non-Equilib. Thermodyn.* **16**, 27 (1991).
- [51] K. Gambár and F. Márkus, *Phys. Rev. E* **50**, 1227 (1994).
- [52] F. Márkus and K. Gambár, *J. Non-Equilib. Thermodyn.* **18**, 288 (1993).
- [53] R. Gilmore, *Lie Groups, Lie Algebras, and Some of their Applications* (Wiley, New York, 1974).
- [54] P. H. Sattinger and O. L. Weaver, *Lie Groups and Algebras with Applications to Physics, Geometry, and Mechanics* (Springer, New York, 1986).
- [55] E. L. Hill, *Rev. Mod. Phys.* **23**, 253 (1951).
- [56] E. Wigner, *Prog. Theor. Phys.* **11**, 437 (1954).
- [57] V. P. Vizgin, *Razvitie Vzaimosvazi Principov Invariantnosti s Zakonami Sahranenia v Klassicheskoi Fizike* (Nauka, Moscow, 1972).
- [58] P. H. Frampton, *Gauge Field Theories* (Benjamin/Cummings, Menlo Park, CA, 1987).