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Hamilton-Lagrange formalism of nonequilibrium thermodynamics

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The aim of this paper is to develop the field theory of nonequilibrium thermodynamics by the Hamiltonian formalism and to prepare an alternative foundation for the theory. We give the Lagrangian from which the field equations as Euler-Lagrange differential equations can be derived. We point to the canonically conjugated quantities and then we give the Hamiltonian. We deduce the canonical field equations and we explain the Poisson-bracket expressions. From the Poisson-bracket expression of the entropy density and the Hamiltonian we find that the entropy density is a bilinear expression of the current densities and the thermodynamic forces. At the end of this paper we deal with the invariance properties of irreversible thermodynamics. We show that geometrical transformations do not lead to new conserved quantities. Finally we give a dynamical transformation by which the Lagrangian is invariant and we see that the reciprocity relations are the consequences of this inner symmetry. We think that this Hamilton-Lagrange formalism of thermodynamics may be interesting and important not only for thermodynamics.

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I. INTRODUCTION

The Lagrange-Hamilton formalism is one of the most effective and widely applied deductive methods in different disciplines of physics [1-7]. The great number of publications [8-21] show that this formalism should be the required basis of nonequilibrium thermodynamics to exploit its well-developed mathematical method.

Particularly we would like to mention Sieniutycz and Berry's [8–10] and Anthony's [11] results in this field. Sieniutycz and Berry endeavor to describe the most general processes and they apply the reverse mathematical method of the Hamiltonian formalism because of the mathematical difficulties. Starting from the conserved quantities through Noether's theorem and the general structure of the energy-momentum (canonical) tensor they obtain the Lagrangian, the canonical equations, and the Poisson-bracket formalism. Their Lagrangian is a function of those physical quantities which describe the thermodynamic field. The extremum of the action is formulated as a restricted variational principle.

Another possible way is Anthony's method. Intoducing new field quantities, he surmounts those difficulties which appear in the case *of the deduction* of parabolic type differential equations. He introduces a complex-valued mathematical field, the so-called "field of thermal excitation." This function is an example to show how to introduce to the theories a new field which has a formal similarity to the quantum mechanical wave function.

We follow the usual way to develop the complete Hamilton-Lagrange formalism of nonequilibrium thermodynamics. However, for the sake of simplicity we restrict ourselves to convection- and source-free cases and we examine only parabolic type equations of motion. But this does not mean that we are not able to solve more complicated processes because the theory can be generalized [32,39]. Nevertheless it is of fundamental importance that the Hamiltonian formalism can be prepared in an essentially complete form at all.

II. LAGRANGIAN OF NONEQUILIBRIUM THERMODYNAMICS

In the development of the Hamilton-Lagrange formalism the first step is to find the Lagrangian of the physical processes. In field theories the dynamics of a system can be expressed by the Lagrangian which is generally a function of time and space and a function of the first or higher order derivatives of the field quantities with respect to time and space:

$$L = L(G(\mathbf{r},t), \partial G(\mathbf{r},t), ..., \mathbf{r}, t)). \tag{1}$$

As a description of the dynamics of fields we accept Hamilton's principle as a basic axiom:

$$\delta S = \int_{t_1}^{t_2} \int_V L dV dt = 0, \tag{2}$$

i.e., the variation of the action becomes zero for those field quantities which belong to the real motion of the system if the state of the system is described by given field quantities at t_1 and t_2. In thermodynamics those systems which can be described by equilibrium variables outside the equilibrium are called local equilibrium systems. The equilibrium states differ in the spatial distribution of the state variables.

The specific extensive field quantities are $g_i(\mathbf{r},t)$, the currents of the extensive quantities are $\mathbf{J}_i$, and σ_i are the source densities. Let $g_1 = s$ be the specific entropy and we denote by Γ_i the following partial derivatives ($i = 2, ..., n$):

$$\Gamma_i = \frac{\partial s}{\partial g_i}. \qquad (3)$$

The $T\Gamma_i$ quantities (T is the temperature) are the intensive quantities for g_i. Furthermore, let S_{ik} be the following symmetric coefficient matrix [19]:

$$S_{ik} = \frac{\partial^2 s}{\partial g_i \partial g_k}. \qquad (4)$$

Let φ_i be four times differentiable field quantities (potentials) which give the $\Gamma_i(\mathbf{r},t)$ in this way [9,10]:

$$\Gamma_i = \varrho S_{ji}^{-1}\frac{\partial \varphi_j}{\partial t} - L_{ji}\Delta\varphi_j, \qquad (5)$$

where S_{ji}^{-1},L_{ji} are constant coefficients, ϱ is the mass density, and Δ is the Laplace operator (we use the Einstein convection).

The Lagrangian of the nonequilibrium thermodynamic system is [22,23]

$$L(\varphi_i, \varphi_{i;t}, \varphi_{i;xx}, \varphi_{i;yy}, \varphi_{i;zz}) = \tfrac{1}{2}(\varrho S_{ji}^{-1}\varphi_{j;t} - L_{ji}\Delta\varphi_j)^2 + \sigma_i\varphi_i, \qquad (6)$$

where σ_i are given functions. (The semicolons in the subscripts mean partial derivatives with respect to t, x, y, z.

In the sense of the Hamilton's principle the Euler-Lagrange equations are:

$$\frac{\partial L}{\partial \varphi_i} - \frac{\partial}{\partial t}\frac{\partial L}{\partial \varphi_{i;t}} + \frac{\partial^2}{\partial x^2}\frac{\partial L}{\partial \varphi_{i;xx}} + \frac{\partial^2}{\partial y^2}\frac{\partial L}{\partial \varphi_{i;yy}} + \frac{\partial^2}{\partial z^2}\frac{\partial L}{\partial \varphi_{i;zz}} = 0 \qquad (7)$$

i.e.,

$$\begin{aligned}&\sigma_i - \varrho S_{ik}^{-1}(\varrho S_{jk}^{-1}\varphi_{j;tt} - L_{jk}\varphi_{j;xxt} - L_{jk}\varphi_{j;yyt} - L_{jk}\varphi_{j;zzt})\\ &\quad - L_{ik}(\varrho S_{jk}^{-1}\varphi_{j;txx} - L_{jk}\varphi_{j;xxxx} - L_{jk}\varphi_{j;yyxx} - L_{jk}\varphi_{j;zzxx})\\ &\quad - L_{ik}(\varrho S_{jk}^{-1}\varphi_{j;tyy} - L_{jk}\varphi_{j;xxyy} - L_{jk}\varphi_{j;yyyy} - L_{jk}\varphi_{j;zzyy})\\ &\quad - L_{ik}(\varrho S_{jk}^{-1}\varphi_{j;tzz} - L_{jk}\varphi_{j;xxzz} - L_{jk}\varphi_{j;yyzz} - L_{jk}\varphi_{j;zzzz}) = 0. \end{aligned} \qquad (8)$$

If we take into account (5) we get [22,23]

$$\varrho S_{ik}^{-1}\Gamma_{k;t} + L_{ik}\Delta\Gamma_k = \sigma_i, \qquad (9)$$

which are precisely the transport equations for the cases when the currents of the extensive quantities are

$$\mathbf{J}_i = L_{ik}\mathbf{X}_k. \qquad (10)$$

The

$$\mathbf{X}_k = \nabla\Gamma_k \qquad (11)$$

are thermodynamic forces. The constitutive equations (10) are called Onsager linear laws [24–31].

III. THE CANONICAL FORMALISM AND THE ENTROPY PRODUCTION DENSITY

We examine the total variation of the action if we restrict ourselves to source-free ($\sigma_i = 0$) and convection-free cases:

$$\delta_t S = \int_{T'} L(\varphi_i + \delta\varphi_i, \varphi_{i;\mu} + \delta\varphi_{i;\mu}, \varphi_{i;\mu\nu} + \delta\varphi_{i;\mu\nu})d^4x - \int_T L(\varphi_i, \varphi_{i;\mu}, \varphi_{i;\mu\nu})d^4x, \qquad (12)$$

where $d^4x = dxdydzdt = dx_1dx_2dx_3dx_4$, and $\mu, \nu = 1, 2, 3, 4$. From this general form we obtain

$$\delta_t S = \int_T \frac{\partial}{\partial x_\mu}(\Theta_{\mu\xi}\delta x_\xi + \pi_{i\mu}\delta_t\varphi_i + \lambda_{i\mu\nu}\delta_t\varphi_{i;\nu})d^4x, \qquad (13)$$

where

$$\begin{aligned}\delta_t\varphi_i &= \delta\varphi_i + \varphi_{i;\xi}\delta x_\xi,\\ \delta_t\varphi_{i;\nu} &= \delta\varphi_{i;\nu} + \varphi_{i;\xi\nu}\delta x_\xi,\end{aligned} \qquad (14)$$

and the volume T' arose from the volume T with an infinitesimal deformation [22,23]

$$x'_\xi = x_\xi + \delta x_\xi. \qquad (15)$$

$\Theta_{\mu\xi}$ is the canonical tensor of the field, and $\pi_{i\mu}$ and $\lambda_{i\mu\nu}$ are the canonical coefficients,

$$\Theta_{\mu\xi} = L\delta_{\mu\xi} - \varphi_{i;\xi}\frac{\partial L}{\partial \varphi_{i;\mu}} + \varphi_{i;\xi}\frac{\partial}{\partial x_\nu}\frac{\partial L}{\partial \varphi_{i;\nu\mu}} - \varphi_{i;\xi\nu}\frac{\partial L}{\partial \varphi_{i;\mu\nu}}, \qquad (16)$$

$$\pi_{i\mu} = \frac{\partial L}{\partial \varphi_{i;\mu}} - \frac{\partial}{\partial x_\nu}\frac{\partial L}{\partial \varphi_{i;\nu\mu}}, \qquad (17)$$

$$\lambda_{i\mu\nu} = \frac{\partial L}{\partial \varphi_{i;\mu\nu}}. \qquad (18)$$

On the basis of these using the total variation of the action (5) with the Lagrangian

$$L = \tfrac{1}{2}(\varrho S_{ji}^{-1}\varphi_{j;t} - L_{ji}\Delta\varphi_j)^2, \qquad (19)$$

we can obtain the canonically conjugated quantities to φ_i, i.e., the canonical momentum densities are [22,23,32,33]

$$p_i = \frac{\partial L}{\partial \varphi_{i;t}} = \varrho S_{ik}^{-1}\Gamma_k. \tag{20}$$

The Hamiltonian plays a very important role in the foundation of the field theory of thermodynamics and can be written

$$H(p_i, \Delta\varphi_i) = \tfrac{1}{2}(\varrho^{-1}S_{ij}p_j)^2 + \varrho^{-1}S_{ij}p_jL_{ki}\Delta\varphi_k. \tag{21}$$

If H is a function of $p_i, \varphi_i, \varphi_{i;\nu}, \varphi_{i;\mu\nu}$ $(\mu, \nu = 1, 2, 3)$ then the canonical equations are in general

$$\varphi_{i;t} = \frac{\partial H}{\partial p_i}, \tag{22}$$

$$p_{i;t} = -\frac{\partial H}{\partial \varphi_i} + \frac{\partial}{\partial x_\mu}\frac{\partial H}{\partial \varphi_{i;\mu}} - \frac{\partial^2}{\partial x_\mu \partial x_\nu}\frac{\partial H}{\partial \varphi_{i;\mu\nu}}. \tag{23}$$

If we take the given form of the Hamiltonian (21) we get

$$\varphi_{i;t} = \frac{\partial H}{\partial p_i}, \tag{24}$$

$$p_{i;t} = -\Delta\frac{\partial H}{\partial \Delta p_i}, \tag{25}$$

which are the canonical field equations of thermodynamics [32,33].

It is usual to define the Poisson bracket in field theories as [2,5]

$$[f, g] = \left(\frac{\delta f}{\delta \varphi}\frac{\delta g}{\delta p} - \frac{\delta g}{\delta \varphi}\frac{\delta f}{\delta p}\right), \tag{26}$$

where

$$f(\varphi, \varphi_{;\mu}, \varphi_{;\mu\nu}, p, p_{;\mu}, p_{;\mu\nu}),$$
$$g(\varphi, \varphi_{;\mu}, \varphi_{;\mu\nu}, p, p_{;\mu}, p_{;\mu\nu}),$$
$$(\mu, \nu = 1, 2, 3),$$

and

$$\frac{\delta f}{\delta \varphi} = \frac{\partial f}{\partial \varphi} - \frac{\partial}{\partial x_\mu}\frac{\partial f}{\partial \varphi_{;\mu}} + \frac{\partial^2}{\partial x_\mu \partial x_\nu}\frac{\partial f}{\partial \varphi_{;\mu\nu}}. \tag{27}$$

The $\frac{\delta g}{\delta p}$, $\frac{\delta g}{\delta \varphi}$, and $\frac{\delta f}{\delta p}$ can be defined in the same way. Using these notations the canonical equations (24) and (25) are [32,33]

$$\varphi_{i;t} = [\varphi_i, H] = \frac{\delta H}{\delta p_i}, \tag{28}$$

$$p_{i;t} = [p_i, H] = -\frac{\delta H}{\delta \varphi_i}. \tag{29}$$

The time derivative of a physical quantity can be obtained as a Poisson-bracket expression of the Hamiltonian. Moreover, the entropy has a central role in the thermodynamics. That is why we pay attention to the entropy production in particular.

In the interest of this we examine the Poisson-bracket expression of

$$F(p) = \tfrac{1}{2}\varrho^{-1}p_iS_{ij}p_j \tag{30}$$

with the Hamiltonian. After a short calculation we get

$$\frac{\partial F}{\partial t} = \left(\frac{\delta F}{\delta \varphi_j}\frac{\delta H}{\delta p_j} - \frac{\delta H}{\delta \varphi_j}\frac{\delta F}{\delta p_j}\right) = -\nabla(\Gamma_iL_{ij}\nabla\Gamma_j) + \nabla\Gamma_iL_{ij}\nabla\Gamma_j, \tag{31}$$

i.e.,

$$\frac{\partial F}{\partial t} + \nabla(\Gamma_iL_{ij}\nabla\Gamma_j) = \nabla\Gamma_iL_{ij}\nabla\Gamma_j, \tag{32}$$

which is the entropy balance equation exactly. The expressions

$$s = \tfrac{1}{2}\varrho^{-1}p_iS_{ij}p_j, \tag{33}$$

$$\mathbf{J}_s = \Gamma_i\mathbf{J}_i, \tag{34}$$

$$\mathbf{J}_i = L_{ij}\nabla\Gamma_j, \tag{35}$$

are the entropy density, the entropy current, and the Onsager linear laws. So the entropy production is

$$\nabla\Gamma_iL_{ij}\nabla\Gamma_j = \mathbf{X}_i\mathbf{J}_i = \sigma_s. \tag{36}$$

We consider this result to be one of the most important consequences of our Hamilton-Lagrange formalism for thermodynamics [32,33].

IV. INVARIANCE PROPERTIES IN THE FIELD THEORY OF NONEQUILIBRIUM THERMODYNAMICS

Now we examine the invariance properties. If the equations of motion are invariant with respect to the transformations of $\mathbf{r}, t$ and certain transformations of field quantities $\varphi(\mathbf{r}, t)$, we speak about symmetry. We distinguish two kinds of symmetry, geometrical symmetry and dynamical symmetry.

While the geometrical invariances have a general validity for each law of nature — they are related to the symmetry properties of space and time —, the dynamical invariances have no general validity; they are based on special interactions and they are consequences of inner symmetry properties of the system. Since we have deduced the equations of motion from the variation of the action S, the sufficient condition for the equations of motion is invariance of the action.

In the discussion of the geometrical invariance of the equations of motion we have to examine the invariance of the action. If — in the sense of Noether's theorem — the total variation of the action $\delta_t S$ is zero or equals a total divergence then S is invariant and the first integrals of the Euler-Lagrange differential equations of the variational problem exist, i.e., we obtain conservation theorems.

After these we treat a geometrical invariance of the action S,

$$S = \int_T L(\varphi_i, \varphi_{i;\mu}, \varphi_{i;\mu\nu}) d^4x \tag{37}$$

($\mu, \nu = 1, 2, 3, 4$), specifically, the time displacement. So we take the following infinitesimal transformation:

$$\begin{aligned} \delta x_1 = \delta x_2 = \delta x_3 &= 0, \\ \delta x_4 = \delta t = \varepsilon &= \text{infinitesimal const}, \\ \delta\varphi_i &= 0, \\ \delta\varphi_{i;\mu} &= 0. \end{aligned} \tag{38}$$

Generally, in the sense of Noether's theorem, we take into account (13) and we expect that

$$\begin{aligned} &\frac{\partial}{\partial x_\mu}(\Theta_{\mu\xi}\delta x_\xi + \pi_{i\mu}\delta_t\varphi_i + \lambda_{i\mu\nu}\delta_t\varphi_{i;\nu}) \\ &\quad = \frac{\partial}{\partial x_\mu} K_\mu(\varphi_i, \varphi_{i;t}, \Delta\varphi_i, \delta x_\nu, \delta_t\varphi_i, \delta_t\varphi_{i;\nu}), \end{aligned} \tag{39}$$

if the transformation is a symmetry transformation of the equation of motion [1,6,32]. In the case of the transformation (38) the total variations of φ_i and $\varphi_{i;\nu}$ are

$$\begin{aligned} \delta_t\varphi_i &= \varphi_{i;t}\delta t, \\ \delta_t\varphi_{i;\nu} &= \varphi_{i;t\nu}\delta t. \end{aligned} \tag{40}$$

Let K_μ be the following:

$$\begin{aligned} &K_\mu(\varphi_i, \varphi_{i;t}, \Delta\varphi_i, \delta x_\nu, \delta_t\varphi_i, \delta_t\varphi_{i;\nu}) \\ &\quad = L(\varphi_i, \varphi_{i;t}, \Delta\varphi_i)\delta x_\mu, \end{aligned} \tag{41}$$

where L is our Lagrangian (19) [32]. It is easy to see that the action

$$S = \int_T L(\varphi_i, \varphi_{i;t}, \Delta\varphi_i) d^4x \tag{42}$$

is invariant with respect to the infinitesimal transformation (38), taking into consideration the divergence expression.

Now we turn our attention to the dynamical invariances. If the action is invariant with respect to a dynamical symmetry in consequence of inner symmetry that means mathematically that

$$\begin{aligned} &L(\varphi_i(\mathbf{r},t), \varphi_{i;\mu}(\mathbf{r},t), \varphi_{i;\mu\nu}(\mathbf{r},t)) \\ &\quad = L(\varphi_i'(\mathbf{r},t), \varphi_{i;\mu}'(\mathbf{r},t), \varphi_{i;\mu\nu}'(\mathbf{r},t)), \end{aligned} \tag{43}$$

i.e., it is sufficient to examine the invariance of Lagrangian.

Let us consider our Lagrangian (19) where L_{ik} is independent of the space and time variables and the physical quantities. We can give the following infinitesimal transformation [32,34]:

$$\varphi_j' = A\varphi_l = [E - \Theta T_{jl} I(\,,\,)]\varphi_l, \tag{44}$$

where A is the matrix of the infinitesimal transformation, E is the unit matrix, Θ is an infinitesimal (constant) parameter, and T_{jl} is the mixing matrix where the diagonal elements are zero ($T_{11} = \cdots = T_{nn} = 0$). The operator I carries such a property of the transformed field φ_i' which becomes apparent in the products. The I has two variables which are the indices of the φ's. If we take, e.g., the product of $\varphi_j'(\varphi_l) = A\varphi_l$ and $\varphi_i'(\varphi_k) = A\varphi_k$,

$$\varphi_j'(\varphi_l)\varphi_i'(\varphi_k), \tag{45}$$

then l stands at the first and k in the second position in the arguments of I: $I(l,k)$. The operator I equals 1 for the starting sequence of (l,k). If we change the sequence (k,l) we get $I(k,l) = -1$. After a long but elementary calculation neglecting the second-order terms we obtain

$$\begin{aligned} L' &= \tfrac{1}{2}(\varrho S_{ji}^{-1}\varphi_{j;t}' - L_{ji}\Delta\varphi_j')^2 \\ &= \tfrac{1}{2}(\varrho S_{ji}^{-1}\varphi_{j;t} - L_{ji}\Delta\varphi_j)^2 = L. \end{aligned} \tag{46}$$

This shows that the Lagrangian is invariant with respect to the transformation (44), i.e., the equations of motion of nonequilibrium thermodynamics have dynamical invariances. The Lagrangian (19) belongs to those irreversible processes in which the entropy production density is a bilinear expression (36) of the currents and the thermodynamic forces,

$$\sigma_s = \mathbf{X}_i\mathbf{J}_i. \tag{47}$$

Since the entropy production density is the gauge of the irreversibility of the processes, we expect that σ_s (46) is invariant against the infinitesimal transformation (44).

We have to write the forces

$$\mathbf{X}_i = \boldsymbol{\nabla}\Gamma_i = \boldsymbol{\nabla}(\varrho S_{ji}^{-1}\varphi_{j;t} - L_{ji}\Delta\varphi_j) \tag{48}$$

and the currents

$$\mathbf{J}_i = L_{ik}\mathbf{X}_k = L_{ik}\boldsymbol{\nabla}(\varrho S_{jk}^{-1}\varphi_{j;t} - L_{jk}\Delta\varphi_j) \tag{49}$$

with the potentials. So the transformed entropy production density is

$$\begin{aligned} \sigma' = \nabla\{&\varrho S_{ji}^{-1}[\delta_{jl}\varphi_{l;t} - \Theta I(l,m)T_{jl}\varphi_{l;t}] \\ &- L_{ji}[\delta_{jl}\Delta\varphi_l - \Theta I(l,m)T_{jl}\Delta\varphi_l]\} \\ &\times L_{ig}\nabla\{\varrho S_{kg}^{-1}[\delta_{km}\varphi_{m;t} - \Theta I(l,m)T_{km}\varphi_{m;t}] \\ &- L_{kg}[\delta_{km}\Delta\varphi_m - \Theta I(l,m)T_{km}\Delta\varphi_m]\}. \end{aligned} \tag{50}$$

Neglecting the second order terms we can see that the entropy production is invariant if and only if Onsager's reciprocity relations hold [32,34].

After this we can say that the linear laws and reciprocity relations which have been proposed by Onsager for more than 60 years cope also with a consistent mathematically model of nonequilibrium thermodynamics. Using the above results we can make the generalization for nonlinear cases and for systems which are out of local equilibrium [31,32,35–40].

V. SUMMARY

On the basis of this paper we see that the statement that the parabolic differential equations cannot be derived from Hamilton's principle, i.e., the Hamilton formalism of irreversible theories cannot be developed, is completely incorrect. Our foundation of the theory presents a good possibility of finding connections and making comparisons with other field theories. The description of the irreversible and the reversible theories has become the same.

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