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Hamilton's principle in thermodynamics

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A SURVEY OF ATTEMPTS to describe dissipative processes by means of the Hamilton's variational principle is given. The most general and promising approach is that proposed by Anthony, where the full power of the Lagrange formalism is applied. Anthony's theory can be classified as the doubling of fields variational principle. Alternative sound interpretation of the additional variable $\varphi(t, x)$ introduced by Anthony on the example of the diffusion equation is given and discussed.

1. Introduction

ONE OF THE MOST striking features of the modern physics is its tendency towards the unification, i.e. to describe as many facts as possible by the smallest number of theories. This is a natural consequence of the historical development of the science stemming from our realization that if one attempts to describe theoretically a certain part of the real world then one is confronted by a very large number of objects and with a very complicated network of interrelations. To be able to grasp a problem, it is thus necessary to construct dramatically simplified models of reality which then can be usually divided into classes. Each class of models describes one set of phenomena while simultaneously neglecting another set. For example, in physics one has models for dissipative and non-dissipative processes. However, in nature most processes are dissipative. It is usually only the first step leading to understanding of such processes that one models them as non-dissipative; this is done when the dissipation can be regarded as negligible. Nevertheless, there remain two worlds in science, two kinds of physical theories: those which describe dissipative processes and those which describe non-dissipative ones, each with its own methodology and history.

It can be very fruitful, both from the practical and the methodological point of view, to apply in one's own area of interest the methods proved to be productive in other branches of science. From this approach new perspectives and new directions of studies can emerge. One example is the application of rather abstract mathematical constructions in nearly all branches of science. Another example is the new trend of applying ideas from physics to the social sciences. But, so far, the application of the unified field-theoretic method for treating both the dissipative and non-dissipative processes has not been encountered in the literature.

A very powerful and elegant tool used both in the dissipative and non-dissipative physics is the variational calculus. There exist many variational principles applied to the particular problems but one of them, the Hamilton's principle, is distinguished by its very physical significance because it needs the minimum number of fields to describe the physical system. Hamilton's variational principle is just the first part of the Lagrange formalism, i.e. it allows to obtain the Euler-Lagrange equations (equations of motion or field equations) and the boundary conditions on the basis of a given Lagrangian. The second part relies on obtaining the constitutive relations and conservation laws by applying the Noether theorem and on studying the stability conditions of the system by making use

of the accessory variational problem. The application of the Lagrange formalism to the dissipative phenomena is not well established as yet but the research is in progress.

2. Classification of variational principles and the Lagrange formalism

The classification of variational principles in thermodynamics was made by MUSCHIK and TROSTEL [8], where the references to literature were also given. They were interested in *global* principles which were characterized by a Lagrangian. The local principles like the minimum entropy production were not classified. The global variational principles were divided into *strict* and *non-strict* principles, and the strict ones were characterized as parameter Lagrangian or variational self-adjointness or doubling of fields.

Let us consider a candidate to be a Lagrangian to describe the heat conduction process

$$\mathcal{L} = \mathcal{L}(T, \partial T), \tag{2.1}$$

which depends on the one field only (temperature) and its first derivatives. It is seen [1] that the energy flux

$$\mathbf{j}_{(u)} = \frac{\partial \mathcal{L}}{\partial(\nabla T)} \partial_t T \tag{2.2}$$

vanishes in the stationary case, what contradicts the experiment. The situation can be improved by adding to the Lagrangian one extra field changing in time, e.g. $\varphi(t, x)$, while $T = T(x)$, because in this case

$$\mathbf{j}_{(u)} = \frac{\partial \mathcal{L}}{\partial(\nabla T)} \partial_t T + \frac{\partial \mathcal{L}}{\partial(\nabla \varphi)} \partial_t \varphi. \tag{2.3}$$

We conclude that the method of doubling of fields can be suitable to describe phenomena of this type. In what follows we restrict ourselves to this type of the variational principle only.

The above equations were obtained using the Noether theorem. Let us recollect shortly the fundamentals of the Lagrange formalism. If Lagrangian $\mathcal{L}$ depends on the N functions $\psi_i(t, x)$ and their first time and space derivatives, i.e. $\mathcal{L} = \mathcal{L}(\psi_i, \partial_t \psi_i, \partial_x \psi_i)$, then equations of motion (Euler–Lagrange equations) are as follows:

$$\partial_t \frac{\partial \mathcal{L}}{\partial(\partial_t \psi_i)} + \nabla \cdot \frac{\partial \mathcal{L}}{\partial(\nabla \psi_i)} - \frac{\partial \mathcal{L}}{\partial \psi_i} = 0. \tag{2.4}$$

By applying the Noether theorem one obtains the conservation laws and the constitutive relations for the following quantities ($\otimes$ means tensor product, $\alpha = 0, \ldots, 3$; $i, j = 1, \ldots, N$; and the summation convention is assumed):

1) *energy* (invariance with respect to time translations $t \to t + \Delta t$)

(a) energy density

$$u = \frac{\partial \mathcal{L}}{\partial(\partial_t \psi_i)} \partial_t \psi_i - \mathcal{L}, \tag{2.5}$$

(b) energy flux density

$$\mathbf{j}_{(u)} = \frac{\partial \mathcal{L}}{\partial(\nabla \psi_i)} \partial_t \psi_i, \tag{2.6}$$

(c) conservation law

$$\partial_t u + \operatorname{div} \mathbf{j}_{(u)} = 0. \tag{2.7}$$

2) *momentum* (invariance with respect to space translations $x \to x + \Delta x$)

(a) density of linear momentum

$$\mathbf{p} = \frac{\partial \mathcal{L}}{\partial(\partial_t \psi_i)} \nabla \psi_i, \tag{2.8}$$

(b) linear momentum flux density

$$\hat{\sigma} = \frac{\partial \mathcal{L}}{\partial(\nabla \psi_i)} \otimes \nabla \psi_i - \hat{1} \cdot \mathcal{L}, \tag{2.9}$$

(c) conservation of linear momentum

$$\partial_t \mathbf{p} + \operatorname{div} \hat{\sigma} = 0. \tag{2.10}$$

3) *mass-like quantity* (invariance with respect to gauge transformation $\psi \to \psi \exp(i\Lambda\epsilon)$)

(a) mass-like density function

$$w = i\Lambda\left(\frac{\partial \mathcal{L}}{\partial(\partial_t \psi)}\psi - \frac{\partial \mathcal{L}}{\partial(\partial_t \psi^*)}\psi^*\right), \tag{2.11}$$

(b) mass-like flux density

$$\mathbf{j}_{(w)} = i\Lambda\left(\frac{\partial \mathcal{L}}{\partial(\nabla \psi)}\psi - \frac{\partial \mathcal{L}}{\partial(\nabla \psi^*)}\psi^*\right), \tag{2.12}$$

(c) mass-like balance equation

$$\partial_t w + \operatorname{div} \mathbf{j}_{(w)} = 0. \tag{2.13}$$

The stability of the system can be studied with the help of the accessory extremal problem [2, 5]. Let us consider the one-parameter group of process transformations

$$\overline{\psi}_i(t, x, \epsilon) = \mathcal{T}_\epsilon \psi_i(t, x), \tag{2.14}$$

within the one-parameter class of real processes satisfying the Euler–Lagrange equations.

$$\eta_i(t, x) = \left.\frac{\partial \psi_i(t, x, \epsilon)}{\partial \epsilon}\right|_{\epsilon=0}, \tag{2.15}$$

defines real variations of the process $\psi_i(x, t)$ with respect to the parameter ϵ

$$\delta\psi_i = \eta_i \delta\epsilon. \tag{2.16}$$

It is known from the ordinary theory of maxima and minima that the necessary condition for the functional $\mathcal{J}$ to have an extremum is vanishing of its first variation (what is ensured by the Euler–Lagrange equations), and that its second variation for the solutions of the Euler–Lagrange equations should satisfy the conditions

$$\delta^2 \mathcal{J} = \begin{cases} > 0 & \text{for the minimum,} \\ < 0 & \text{for the maximum.} \end{cases} \tag{2.17}$$

If we assume that the action functional is twice differentiable, we can write

$$\delta \mathcal{J} = \delta^1 \mathcal{J} + \delta^2 \mathcal{J} + \beta(\delta\psi)^2, \tag{2.18}$$

where

$$\mathcal{J} = \mathcal{J}(\psi, \partial\psi, \delta\psi, \delta\partial\psi), \tag{2.19}$$

and

$$\lim_{\delta\psi\to 0} \beta = 0, \tag{2.20}$$

$$\delta^1\mathcal{J} = \delta\epsilon \left.\frac{d\mathcal{J}}{d\epsilon}\right|_{\epsilon=0} = \int_{\mathcal{P}} d^4x \left(\frac{\partial\mathcal{L}}{\partial\psi_i}\delta\psi_i + \frac{\partial\mathcal{L}}{\partial(\partial_\alpha\psi_i)}\delta(\partial_\alpha\psi_i)\right), \tag{2.21}$$

$$\delta^2\mathcal{J} = \frac{1}{2}\delta^2\epsilon \left.\frac{d^2\mathcal{J}}{d\epsilon^2}\right|_{\epsilon=0} = \frac{1}{2}\int_{\mathcal{P}} d^4x \left(\frac{\partial^2\mathcal{L}}{\partial\psi_i\partial\psi_j}\delta\psi_i\delta\psi_j + 2\frac{\partial^2\mathcal{L}}{\partial\psi_i\partial(\partial_\alpha\psi_j)}\delta\psi_i\delta(\partial_\alpha\psi_j) + \frac{\partial^2\mathcal{L}}{\partial(\partial_\alpha\psi_i)\partial(\partial_\beta\psi_j)}\delta(\partial_\alpha\psi_i)\delta(\partial_\beta\psi_j)\right). \tag{2.22}$$

It is known from the calculus of variations [9] that to every differential equation its variational equation can be attached. The variational equations of the Euler–Lagrange equations

$$\mathcal{L}_i = d_\alpha \frac{\partial\mathcal{L}}{\partial(\partial_\alpha\psi_i)} - \frac{\partial\mathcal{L}}{\partial\psi_i} = 0, \tag{2.23}$$

are the Jacobi equations

$$\Omega_i = d_\alpha \frac{\partial\Omega}{\partial(\partial_\alpha\psi_i)} - \frac{\partial\Omega}{\partial\psi_i} = 0. \tag{2.24}$$

The kernel Ω has the form

$$2\Omega(\psi, \partial\psi, \eta, \partial\eta) = \frac{\partial^2\mathcal{L}}{\partial\psi_i\partial\psi_j}\eta_i\eta_j + 2\frac{\partial^2\mathcal{L}}{\partial\psi_i\partial(\partial_\alpha\psi_j)}\eta_i\partial_\alpha\eta_j + \frac{\partial^2\mathcal{L}}{\partial(\partial_\alpha\psi_i)\partial(\partial_\beta\psi_j)}\partial_\alpha\eta_i\partial_\beta\eta_j)), \tag{2.25}$$

and variations $\eta_i(t, x)$ are the solutions of the Jacobi equations. Making use of the Euler formula for the homogeneous function of the second degree (here the quadratic form $\Omega(\psi, \partial\psi, \eta, \partial\eta)$) and of the Jacobi equations (2.24) one can obtain the following expression

(a) non-homogeneous conservation law (balance equation)

$$\partial_t s + \operatorname{div}\mathbf{j}_{(s)} = \sigma_{(s)}, \tag{2.26}$$

(b) density function

$$s = \frac{\partial\Omega}{\partial(\partial_t\eta_i)}\eta_i, \tag{2.27}$$

(c) flux density vector

$$\mathbf{j}_{(s)} = \frac{\partial\Omega}{\partial(\nabla\eta_i)}\eta_i, \tag{2.28}$$

(d) density of the production rate

$$\sigma_{(s)} = 2\Omega. \tag{2.29}$$

The set of equations (2.25)–(2.29) associated with the group of process transformations (2.14) defines observables of the second kind.

3. Morse and Feshbach approach

In their famous book [7] MORSE and FESHBACH gave some examples how to obtain, by means of the Hamilton's principle and by applying the Bateman's embedding process, the equations describing the dissipative systems, i.e. such in which the energy losses are not negligible. To be able to treat the dissipative physical system as the conservative one, they propose to consider simultaneously with the starting equation its *mirror-image*. Let the one-dimensional oscillator with friction be described by the equation

$$m\ddot{x} + R\dot{x} + Kx = 0. \tag{3.1}$$

They propose the purely formal Lagrangian

$$\mathcal{L} = m(\dot{x}\dot{x}^*) - \frac{1}{2}R(x^*\dot{x} - x\dot{x}^*) - Kxx^*, \tag{3.2}$$

where x^* represents the *mirror-image* oscillator with negative friction. It can be obtained from the Hamilton's principle that the equations of motion (they call them Lagrange equations) have the following proper form

$$m\ddot{x}^* - R\dot{x}^* + Kx^* = 0, \quad m\ddot{x} + R\dot{x} + Kx = 0. \tag{3.3}$$

The equation for the variation of x^* is just the equation (3.1) and the equation for the variation of x involves a negative frictional term. According to the terminology from the classical particle mechanics, the quantity

$$p_r = \frac{\partial \mathcal{L}(q_r, \partial_x q_r, \partial_t q_r)}{\partial(\partial_t q_r)} \tag{3.4}$$

is called the canonical momentum for the r-th coordinate [7]. In this case one obtains two *momenta*

$$p = m\dot{x}^* - \frac{1}{2}Rx^*, \quad p^* = m\dot{x} + \frac{1}{2}Rx, \tag{3.5}$$

which have little to do with the actual momentum of the oscillator.

Diffusion equation and heat conduction equation, very similar in form, are the next examples of equations describing the dissipative systems. In this case Morse and Feshbach have proposed the following Lagrangian

$$\mathcal{L} = -(\operatorname{grad}\psi)\cdot(\operatorname{grad}\psi^*) - \frac{1}{2}a^2(\psi^*\partial_t\psi - \psi\partial_t\psi^*), \tag{3.6}$$

where ψ is the density of the diffusing matter or the temperature, ψ^* refers to the *mirror-image* system, and a^2 is the diffusion constant. Here and above superscript * does not mean the complex conjugate. The field equations (called Euler equations) for this Lagrange density are again the proper ones

$$\Delta\psi = a^2\partial_t\psi, \quad \Delta\psi^* = -a^2\partial_t\psi^*. \tag{3.7}$$

The equation for ψ is the starting equation, and the equation for ψ^* is for the *mirror-image* system, which gains as much energy as the first loses. The calculated canonical momentum densities

$$p = -\frac{1}{2}a^2\psi^*, \quad p^* = \frac{1}{2}a^2\psi, \tag{3.8}$$

also in this case have not much to do with the physical reality.

4. Djukic and Vujanovic approach

DJUKIC and VUJANOVIC [4, 12] proposed another method to obtain the requested equations of the irreversible thermodynamics by means of Hamilton's principle. They assume that the Lagrangian depends not only on the field variables (e.g. the absolute temperature $T = T(t, x)$) and their first derivatives but also on a certain set of arbitrary functions $\Psi_k(t, x, \lambda)$, $k = 1, 2, \ldots, N$ with the following properties:

$$\lim_{\lambda \to 0} \Psi_k(t, x, \lambda) = 0, \tag{4.1}$$

and

$$\lim_{\lambda \to 0} \partial_x \Psi_k = 1, \quad \lim_{\lambda \to 0} \partial_t \Psi_k = 1. \tag{4.2}$$

Let us show how their method works for the heat conduction equations. In [4] they propose the following Lagrangian

$$\mathcal{L} = \frac{k^2(T)}{2}(\partial_x T)^2 - \frac{\Psi(t, \lambda)}{2}\rho(T)\, c(T)\, k(T)\, (\partial_t T)^2. \tag{4.3}$$

Here $\rho(T)$ is the mass density, $k(T)$ is the thermal conductivity and $c(T)$ is the heat capacity. The function $\Psi(t, \lambda)$ is not a subject of variation and the Euler–Lagrange equation takes the form

$$\begin{aligned} \partial_x[k(T)\partial_x T] - \partial_t \Psi \rho(T)\, c(T)\, \partial_t T \\ = \frac{\Psi(t, \lambda)}{k(T)}\left[\partial_t(\rho(T)\, c(T)\, k(T)\, \partial_t T) - \frac{1}{2}\partial_T(\rho(T)\, c(T)\, k(T)\, (\partial_t T)^2)\right]. \end{aligned} \tag{4.4}$$

Using equations (4.1) and (4.2) with $\lambda \to 0$ one obtains the one-dimensional heat conduction equation with coefficients depending on the temperature

$$\rho(T)\, c(T)\, \partial_t T = \partial_x(k(T)\, \partial_x T). \tag{4.5}$$

If we now try to apply the Noether theorem to the Lagrangian (4.3), we obtain the results

(a) internal energy density

$$u = -\frac{k^2}{2}(\nabla T)^2, \tag{4.6}$$

(b) internal energy flux

$$j = k^2(T)\, \partial_x T \partial_t T, \tag{4.7}$$

(c) pressure

$$p = 0, \tag{4.8}$$

(d) stress

$$\sigma = k^2(\nabla T)^2, \tag{4.9}$$

and all these results contradict the known theories and experiments.

In [12] the authors have obtained equation (4.5) and the equation taking into account the finite velocity of heat propagation from another Lagrangian,

$$\mathcal{L} = \left[\frac{k^2(T)}{2}(\partial_x T)^2 - \frac{\tau}{2}S(T)\,k(T)(\partial_t T)^2\right]e^{\frac{t}{\tau}}. \tag{4.10}$$

As a small parameter function they have introduced here the relaxation time τ. The Euler-Lagrange equation takes the form

$$\partial_x[k(T)\partial_x T] - S(T)\partial_t T = \frac{\tau}{k(T)}\left(\partial_t(S(T)\,k(T)\,\partial_t T) - \frac{1}{2}\partial_T[S(T)\,k(T)\,(\partial_t T)^2]\right). \tag{4.11}$$

Here $S(T)$ is the volumetric heat capacity (product of density and heat capacity at a constant pressure). They have obtained equation (4.5) (in three dimensions) as a limit case of equation (4.11) with $\tau \to 0$. The Noether constitutive relations are the same as before.

5. Anthony's approach

Anthony's approach, according to the classification given by MUSCHIK and TROSTEL [8], can be called as doubling of fields, but it differs significantly from all other approaches we have already mentioned. Morse and Feshbach, and Djukic and Vujanovic stopped their analysis on obtaining the Euler–Lagrange equations. They did not go further, they did not study the symmetries of the Langrangian. It means, they did not apply the Noether theorem to the proposed Lagrangians. Anthony's approach is more general. He attempts to use the full power of the Lagrange formalism: all information about the system is contained in the Lagrangian, the Euler–Lagrange equation of motion (field equations) one obtains from the Hamilton's variational principle, constitutive relations and conservation laws one obtains from the Noether theorem, and the stability of the system can be studied with the help of the variational accessory problem [9]. Anthony published his theory in the series of papers, and a relatively full bibliography can be found e.g. in [3]. We present here the main points of his theory only, in order to distinguish the differences between his approach and the former ones, on the basis of the heat conductivity problem.

The main and the new notion of Anthony's theory is the complex-valued *field of thermal excitation* $\psi(t,x)$ defined as follows:

$$\psi(t,x)\psi(t,x)^* = T(t,x) \geq 0. \tag{5.1}$$

Let us notice that, from the very beginning, the absolute temperature $T(t,x)$ is positive defined, what does not follow from the heat conduction equation and must be additionally assumed. This representation of a positive defined quantity is known in physics as the Born representation. It is seen that

$$\psi(t,x) = \sqrt{T(t,x)}e^{i\varphi(t,x)}, \tag{5.2}$$

where phase $\varphi(t,x)$ is a certain unknown function. The proposed Lagrangian in the (ψ,ψ^*) representation is much longer than in the (T,φ) representation, and we show

here its shorter form only,

$$\mathcal{L} = -cT - \frac{c}{\omega}\left(T\partial_t\varphi + \frac{1}{2}\frac{\ln\frac{T}{T_0}}{\frac{T}{T_0}}\partial_t T\right) + \frac{1}{\omega}\hat{\lambda}..\left(\nabla T \otimes \nabla\varphi + \frac{T_0}{2T^2}\nabla T \otimes \nabla T\right), \tag{5.3}$$

where ω is a constant with the dimension of frequency, c is the specific heat, $\hat{\lambda} = (\lambda^{\alpha\beta})$ is the heat conductivity tensor and T_0 is the reference temperature.

Application of the Lagrange formalism machinery yields the field equations

$$c\partial_t T - \hat{\lambda}..\nabla \otimes \nabla T = 0, \tag{5.4}$$

$$c\partial_t\varphi - \hat{\lambda}..\nabla \otimes \nabla\varphi = -c\omega - \hat{\lambda}..\left(\frac{T_0}{T^2}\nabla \otimes \nabla T - \frac{T_0}{T^3}\nabla T \otimes \nabla T\right), \tag{5.5}$$

(here .. denotes summation over two indices) and the boundary conditions

$$\frac{1}{\omega}\mathbf{n}(\hat{\lambda} \cdot \nabla T) = 0, \quad \frac{1}{\omega}\mathbf{n}(\hat{\lambda} \cdot \nabla\varphi) = 0. \tag{5.6}$$

If the solution of equation (5.4) is known, then the particular solution

$$\varphi(t, x) = -\omega t + \frac{T_0}{2T(t, x)}, \tag{5.7}$$

fulfils equation (5.5), and the thermal excitation field takes the form

$$\psi(t, x) = \sqrt{T(t, x)}\exp\left(-i\omega t + i\frac{T_0}{2T(t, x)}\right). \tag{5.8}$$

In our case the energy density and the energy flux density are as follows

$$u = cT - \frac{1}{\omega}\hat{\lambda}..\left(\nabla T \otimes \nabla\varphi + \frac{T_0}{2T^2}\nabla T \otimes \nabla T\right), \tag{5.9}$$

$$\mathbf{j}_{(u)} = \frac{1}{\omega}\hat{\lambda}..\left[\left(\nabla\varphi + \frac{T_0}{T^2}\nabla T\right)\partial_t T + \nabla T\partial_t\varphi\right]. \tag{5.10}$$

Putting into the above equations the particular solution (5.7) one obtains expressions for

(a) thermal (internal) energy

$$u = cT, \tag{5.11}$$

(b) heat flux

$$\mathbf{j}_{(u)} = -\hat{\lambda} \cdot \nabla T. \tag{5.12}$$

We do not show the expressions for the linear momentum because they cannot be compared with the experiment as yet. Let us remind that the present considerations are carried on for a rigid conductor and the mechanical degrees of freedom are not taken into account. Moreover, the identity established in this case is fulfilled for every temperature distribution and gives no new information about the system.

The mass-like quantities in our case have the forms

$$w = \Lambda cT, \quad \mathbf{j}_{(w)} = -\Lambda\hat{\lambda} \cdot \nabla T. \tag{5.13}$$

It should be mentioned that they are proportional to the energy quantities. For further details see [1].

Anthony calls entropy the observable of the second kind associated with the gauge transformation

$$\overline{\psi}(t,x) = \psi(t,x)e^{i\Lambda}. \tag{5.14}$$

In fact, he reproduces from his Lagrangian the fundamental equations of Onsager's theory, and namely:

(a) entropy density

$$s = -c \ln \frac{T}{T_0}, \tag{5.15}$$

(b) entropy flux density

$$\mathbf{j}_{(s)} = -\frac{\hat{\lambda} \cdot \nabla T}{T}, \tag{5.16}$$

(c) density of entropy production rate

$$\sigma_{(s)} = \frac{\nabla T \cdot \lambda \cdot \nabla T}{T^2}. \tag{5.17}$$

The second part of the second law of thermodynamics

$$\sigma_{(s)} > 0, \tag{5.18}$$

is reproduced too. It is related to Lyapunov's stability theory which is also a part of the Lagrange formalism [2].

6. Other proposal

It was shown in [6], that another sound interpretation can be given to $\varphi(x,t)$, the additional field variable from the Anthony's theory. As the starting point, the classical diffusion theory was assumed.

The fundamental expression to describe the diffusion process is the mass balance equation

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0. \tag{6.1}$$

The peculiar diffusion velocity $\mathbf{v}$ is a sum of the velocity of the chaotic motion $\mathbf{u}$

$$\mathbf{u} = -D\frac{\nabla \rho}{\rho}, \tag{6.2}$$

and the drift velocity $\mathbf{b}$ caused by external sources

$$\mathbf{v} = \mathbf{b} + \mathbf{u}. \tag{6.3}$$

Here D is the diffusion coefficient. In the classical diffusion theory it is assumed that the velocity $\mathbf{b}$ is proportional to the force acting on a particle (it is the so-called Stokes relation) [11]

$$\mathbf{b} = \frac{1}{\zeta}\mathbf{F}(x,t), \tag{6.4}$$

where $1/\zeta$ is the mobility of a particle.

On the basis of the above formulae, the non-homogeneous diffusion equation is easily obtained,

$$\partial_t \rho - D\Delta\rho = -\frac{1}{\zeta}\operatorname{div}(\rho \mathbf{F}). \tag{6.5}$$

The Stokes relation is valid for very short relaxation times only,

$$\tau \ll \tau^*, \tag{6.6}$$

where

$$\tau = \frac{m}{\zeta} \tag{6.7}$$

is the kinematical relaxation time, m is the mass of a particle, and

$$\tau^* = dt = t - t_0 > 0, \tag{6.8}$$

is the length of a *physically* infinitesimally small interval of time, defining the scale of the observation time of the diffusion process. The generalization of the classical diffusion theory is based on such a new formulation of the constitutive relation $\mathcal{R}(\tau)$ which allows for the Lagrangian description of the diffusion process and which reduces to the Stokes relation for the very short relaxation times, i.e. for $\tau \to 0$. Let us observe that the elastic force $\mathbf{F}_{el}$ acting on a diffusing particle

$$\mathbf{F}_{el} = -V_0 \nabla \sigma_{el}, \tag{6.9}$$

is *proportional* to the gradient of the elastic dilatation ϑ because

$$\sigma_{el} = 3K\vartheta, \tag{6.10}$$

where V_0 is the volume transported by the diffusing particle. It is assumed that the force $\mathbf{F}_{pl}$ responsible for the inertial effects, depends on a certain internal variable ϕ in a similar way as the elastic force does, namely

$$\mathbf{F}_{pl} = -V(\rho)\nabla\sigma_{pl}, \tag{6.11}$$

where

$$V(\rho) = \frac{\rho_0}{\rho}V_0, \quad \rho_0 = \frac{m}{V_0}, \quad \sigma_{pl} = \kappa\dot{\phi}. \tag{6.12}$$

The internal variable $\dot{\phi}$ is interpreted as the velocity of plastic dilatation. In this case we obtain the non-homogeneous diffusion equation (6.5) in the form

$$\partial_t \rho - D\Delta\rho = \kappa\tau\Delta\dot{\phi}. \tag{6.13}$$

The following Lagrangian is proposed

$$\mathcal{L} = \frac{1}{\omega}(\rho\partial_t\chi - \frac{\kappa}{2}(\nabla\chi)^2 - D\nabla\rho\cdot\nabla\chi). \tag{6.14}$$

This Lagrangian yields the expected Euler–Lagrange equations

$$\partial_t\rho - D\Delta\rho = \kappa\Delta\chi \quad \text{and} \quad \partial_t\chi + D\Delta\chi = 0. \tag{6.15}$$

Here $\chi = \tau\dot{\phi}$. It was found by comparison of (6.4) and (6.5) with (6.13) that

$$\mathbf{b} = -\frac{\kappa\tau}{\rho}\nabla\dot{\phi} = -\frac{V(\rho)}{l_0^3}\mathbf{B}, \tag{6.16}$$

where $\mathbf{B} = l_0^2\nabla\dot{\phi}$ and $l_0 = m/\kappa\tau$ is the characteristic length of a diffusion process.

Applying the Noether theorem to the Lagrangian $\mathcal{L}$ (6.14) the following constitutive relations were obtained:

Energy

$$\varepsilon = \frac{1}{2\omega}\nabla\chi \cdot (\kappa\nabla\chi + 2D\nabla\rho), \tag{6.17}$$

$$\mathbf{j}_\epsilon = -\frac{1}{\omega}[D\nabla\chi\partial_t\rho + (\kappa\nabla\chi + D\nabla\rho)\partial_t\chi]. \tag{6.18}$$

It is easy to express the above formulae by $\mathbf{u}$ and $\mathbf{v}$ making use of equations (6.2), (6.3), (6.15) and (6.16), namely

$$\varepsilon = \frac{1}{2}\frac{\rho^2}{\rho_0}(\mathbf{v}^2 - \mathbf{u}^2), \tag{6.19}$$

$$\mathbf{j}_\epsilon = \frac{\rho}{\rho_0}D[(\mathbf{v} - \mathbf{u})\partial_t\rho + \mathbf{v}\nabla(\rho(\mathbf{v} - \mathbf{u}))] = \frac{\rho}{\rho_0}D[\mathbf{u}\,\mathrm{div}(\rho\mathbf{v}) - \mathbf{v}\,\mathrm{div}(\rho\mathbf{u})]. \tag{6.20}$$

We put here $\omega\kappa = A\rho_0$, and since ω is arbitrary, we can assume $A = 1$.

Momentum

$$\mathbf{p} = -\frac{\rho}{\omega}\nabla\chi, \tag{6.21}$$

$$\sigma_{ij} = \frac{1}{\omega}(\rho\partial_t\chi - \frac{\kappa}{2}(\nabla\chi)^2 - D\nabla\rho\cdot\nabla\chi)\delta_{ij} + \frac{1}{\omega}[\kappa\partial_i\chi\partial_j\chi + D(\partial_i\rho\partial_j\chi + \partial_i\chi\partial_j\rho)]. \tag{6.22}$$

It was established that in the $\mathbf{u}$, $\mathbf{v}$ representation linear momentum and stress have the following form:

$$\mathbf{p} = \frac{\rho^2}{\rho_0}(\mathbf{v} - \mathbf{u}), \tag{6.23}$$

$$\sigma_{ij} = \frac{\rho^2}{\rho_0}\left\{\left[\frac{D}{\rho}\,\mathrm{div}(\rho(\mathbf{v} - \mathbf{u})) - \frac{1}{2}(\mathbf{v}^2 - \mathbf{u}^2)\right]\delta_{ij} + v_iv_j - u_iu_j\right\}. \tag{6.24}$$

Mass

To derive the mass conservation equation we have to write the Lagrangian $\mathcal{L}$ in the ψ representation, i.e. we have to introduce a new complex-valued variable $\psi(t, x)$ which, by analogy with the Anthony's *thermal excitation field*, we call the *diffusion excitation field*

$$\psi(t, x) = \sqrt{\rho(t, x)}e^{i\chi(t,x)}, \tag{6.25}$$

so that

$$\rho = \rho_0\psi\psi^*, \tag{6.26}$$

$$\chi = -\frac{i}{2}\ln(\frac{\psi}{\psi^*}), \tag{6.27}$$

and

$$\overline{\mathcal{L}} = \frac{i\rho_0}{2\omega}\left[D\left(\frac{\psi^*}{\psi}(\nabla\psi)^2 - \frac{\psi}{\psi^*}(\nabla\psi^*)^2\right) + (\psi\partial_t\psi^* - \psi^*\partial_t\psi)\right] + \frac{\kappa}{8\omega}\left[\frac{1}{\psi^2}(\nabla\psi)^2 + \frac{2}{\psi\psi^*}\nabla\psi\nabla\psi^* + \frac{1}{\psi^{*2}}(\nabla\psi^*)^2\right]. \tag{6.28}$$

We obtain from Noether's theorem that

$$w = \frac{\Lambda\rho_0}{\omega}\psi\psi^*, \tag{6.29}$$

$$\mathbf{j}_w = \frac{\Lambda}{\omega}\left[\frac{i\kappa}{2}\left(\frac{1}{\psi}\nabla\psi - \frac{1}{\psi^*}\nabla\psi^*\right) - \rho_0 D(\psi\nabla\psi^* + \psi^*\nabla\psi)\right]. \tag{6.30}$$

These constitutive relations have the following forms in the original ρ, χ representation

$$w = \frac{\Lambda}{\omega}\rho, \tag{6.31}$$

$$\mathbf{j}_w = -\frac{\Lambda}{\omega}(D\nabla\rho + \kappa\nabla\chi). \tag{6.32}$$

It is seen that they fulfil the mass-like balance equation (2.13), because inserting (6.31) and (6.32) into it we obtain the diffusion equation (6.13) which, as it was shown at the beginning of this section, is equivalent to the mass balance equation (6.1).

7. Conclusions

In the paper various attempts to describe the dissipative phenomena by means of the Hamilton principle are discussed. The basic differences between them are to be noticed: while the methods proposed by Morse and Feshbach or by Djukic and Vujanovic are of a purely mathematical nature and allow quite formally to formulate, in the language of variations, the equations describing dissipative phenomena, then the approach of Anthony has a deep physical meaning because it describes the physical system in its full extent, starting from equations of motion through constitutive laws and balance and conservation laws, to the dynamical stability conditions [2]. The fundamental significance for the further development of the theory has the complex-valued function $\psi(t, x)$, called by Anthony in the heat transport theory the thermal excitation field. This function is an example to follow showing how to introduce new fields to the theories, in which the cross-effects are to be described. A formal similarity to the quantum mechanical wave function may be observed, but the thermal excitation function describes *classical* phenomena.

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