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# THE VARIATIONAL PRINCIPLES OF CLASSICAL TYPE FOR NON-COUPLED NON-STATIONARY IRREVERSIBLE TRANSPORT PROCESSES WITH CONVECTIVE MOTION AND RELAXATION

STANISLAW SIENIUTYCZ
Institute of Chemical Engineering at the Warsaw Technical University,
00-645 Warsaw, Waryńskiego 1, Poland

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**Abstract**—A unified method is presented that leads to the new functionals of classical type for which the necessary stationarity conditions are linear hyperbolic differential equations of change describing uncoupled heat, mass and momentum transport in incompressible media. Attention is directed toward the significance of functionals found for a variational description of irreversible transport processes, especially those involving relaxation effects. The applicability of direct variational methods for finding nonstationary fields of temperature, concentration, pressure and velocities is emphasized.

## NOMENCLATURE

| | |
|---|---|
| $A$, | surface; |
| $\tilde{A}, \tilde{B}, \tilde{C}$, | constant multipliers in equation (41), see text; |
| $a$, | heat diffusivity; |
| $b_i, e, m$, | coefficients in equations (6) and (9); |
| C.V.P., | variational principle of classical (stationary action) type; |
| $C_p$, | specific heat capacity; |
| $c_h, c_d, c_m$, | velocities of wave propagation for heat transfer, diffusion and momentum transfer, respectively; |
| $D$, | mass diffusivity; |
| $F$, | external force per mass unit; |
| $I_s$, | internal source of heat; |
| $J_\mu$, | four-dimensional vector describing density of energy flux; |
| $\mathbf{J}$, | three-dimensional vector describing density of energy flux; |
| $j_\mu$, | four-dimensional vector of mass velocity; |
| $k$, | reaction rate constant; |
| $M_1$, | molar mass of component 1; |
| $\mathbf{n}$, | unit normal vector $(n_x, n_y, n_z)$; $n_\mu \equiv (\mathbf{n}, n_t)$ in space $x, y, z, c_n t$; |
| P, | overall pressure; |
| q, | dependent variable in functional (1); |
| $\mathbf{q}_h$, | irreversible heat flux vector, with components $q_{hi}$; |
| R, | universal gas constant; |
| $\mathbf{r}$, | radius vector with coordinates $x_i\,(x, y, z)$; |
| $\tilde{S}_h, \tilde{S}_d, \tilde{S}_m$, | action functionals for heat transfer, diffusion and momentum transfer, respectively; |
| $\tilde{S}$, | general action functional, equation (41); |
| $T, T_0$, | local temperature and reference temperature, respectively; |
| $T_e$, | temperature of external medium; |
| $t$, | time; |
| $V$, | volume; |
| $\mathbf{v}\,(v_x, v_y, v_z)$, | constant velocity (velocity of medium in infinity); $\lvert\mathbf{v}\rvert \ll c$; |
| $\mathbf{w}\,(w_x, w_y, w_z)$, | vector describing the fluid velocity field; $\lvert w\rvert \ll c$; |
| $X$, | half-thickness of the plate; |
| $x_i\,(x, y, z)$, | cartesian coordinates; |
| $x\,(x, y, z, c_h t)$, | coordinates of four-dimensional time-space; |
| $\tilde{y}$, $\tilde{Y}$, | mass concentration (weight fraction) and solid moisture content, respectively; |
| $Z$, | mass source. |

Greek symbols

| | |
|---|---|
| $\alpha$, | heat exchange coefficient; |
| $\delta$, | variational symbol ($\delta T = \varepsilon\psi$); |
| $\varepsilon$, | parameter of variation; $\delta T = \varepsilon\psi$; |
| $\tilde{\Lambda}$, $\Lambda$, | Lagrangian of functional (1) and its autonomous part, respectively; |
| $\lambda$, | heat conductivity; |
| $\lambda_{ik}$, | heat conductivity tensor; |
| $\mu_1, \mu_2$, | chemical potentials of components 1 and 2, respectively; |
| $\rho$, | mass density; |
| $\tau_n, \tau_d, \tau_m$, | relaxation times for heat transfer, diffusion and momentum transfer, respectively; |
| $\phi$, | function investigated in equations (2) and (6); |
| $\Omega_h$, | four-dimensional volume; |
| $\nabla$, | vector operator; |
| $\nabla^2$, | Laplace operator. |

Subscripts

| | |
|---|---|
| $h$, | heat transfer; |
| $d$, | diffusion; |
| $f$, | final time; |
| $m$, | momentum transfer; |
| 0, | reference state, e.g. stage at infinity; |
| 1, 2, | components 1 and 2, respectively. |

Remarks concerning index notation

| | |
|---|---|
| $i, k$, | indices in three-dimensional space; |
| $t$, | time coordinate; |
| $\mu, \varepsilon$, | indices in four-dimensional space. |

## 1. INTRODUCTION

THE VARIATIONAL principles that lead to the equations of mathematical physics have long been the subject of interest for numerous investigators. One of the reasons for that is that these principles are of theoretical significance for a systematic and exact derivation of the process equations and conservation laws. Their usefulness, in providing an alternative method of solution of such equations by minimizing the functional using any of the direct approaches, has also been recognised (Elsgolc [1]). Since no variational principles of classical type have been hitherto found for macroscopic processes in which dissipative phenomena are accompanied by nondissipative ones a consensus generally prevails that merely the elementary phenomena that occur in the microworld can be described by the principle of extremizing suitable functionals, and that this is due to reversibility of these phenomena on account of the changed direction of time in the Lagrange equations (see for instance Yourgrau and Mandelstam [2]). The "non-classical" variational principles, such as, e.g. the local potential method by Glansdorff and Prigogine [3] and a number of related methods based on limited variations, c.f. [4] are not contradictory to the above statement, as they in fact do not involve the minimizing of the classical functional. This has been clearly pointed out by Finlayson and Scriven [4] in their valuable critical review of the available variational principles, to which the reader is referred.

Our present goal is to construct the classical variational principle (C.V.P.) that will join both nondissipative and dissipative effects and result under definite assumptions* in basic equations of chemical engineering, i.e. in equations of change† for heat, mass and momentum transport in incompressible media. Consequently, the fact of existing such C.V.P.'s that describe either nondissipative or purely dissipative phenomena exclusively is not enough for us. These C.V.P. include among others variational principles of elementary particle dynamics [2] together with the ones of ideal fluid mechanics [6] as well as with many principles of elasticity theory [7, 8] where dissipation effects are neglected. On the other hand these C.V.P.'s comprise also of well-known principle of minimum entropy production [9] which deals with purely dissipative processes, c.f. [3].

All such principles are not, however, relevant to the matter at hand as they do not describe interdependences between dissipative and nondissipative effects occurring in our real macroscopic world.

Therefore, the new variational principle of the classical type will be reported in this paper. This principle will lead to the time—unsymmetrical and position—unsymmetrical Lagrange equations, and for that reason it will be extremely useful for the description of many processes in which the dissipative effects are accompanied by nondissipative ones. Subsequently, examples of application of the principle will be discussed in the variational derivation of linear equations of change for non-coupled processes of heat mass and momentum transfer, characterized physically in Section 3.

It will be shown that the resulting linear equations of change (obtained as Euler equations of pertinent functionals) are of hyperbolic type, i.e. that they take into account the finite speed of disturbances (c.f. Appendix) due to the presence of relaxation terms. Although some of hyperbolic equations of change (for heat, mass and momentum) were derived in recent years, either by macroscopic balance method (using more exact nonlinear laws between dissipative fluxes and forces) [10–14], or by statistical method [15, 13] (c.f. Appendix for a brief review and also the illustration of the former method) it is always, however, important to verify that the hyperbolic terms rather than parabolic ones appear when using a unified variational approach. This approach will confirm the Morse and Fehsbach statement [14] that the d'Alembert's operators ($\nabla^2 - \partial/c^2\partial t$) rather than the standard Laplace operators should appear in equations of change, to resolve physical paradox of infinite speed of disturbances, this paradox resulting from standard (parabolic) equations. Furthermore, this approach will provide natural variational formulation for well-known standard form of equations of change when relaxation terms (which are most often very small) will be finally taken equal to zero in all resulting Euler equations.

The project of our analysis is as follows. After describing the general structure of functionals used (Section 2), the detailed characterization of assumptions for physical problems investigated is given (Section 3). Then, the action functionals and resulting Euler equations are found for the problem of pure heat transfer in solid (Section 4).

Afterwards, following the unified variational procedure, the diffusion equation is obtained for isothermal binary fluid (Section 5) and linearized equation for momentum transfer in isothermal one-component fluid are found (Section 6). Furthermore (Section 7), the results obtained in previous sections are simply ex-

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*See Section 3 for detailed specification of assumptions used.

†The terminology used by Bird *et al.* [5], for partial differential equations resulting from balance of heat, mass and momentum.

tended to find a general functional with several unknowns $(T, P, \tilde{y}, w_i)$ that leads to the complete system of linear equations of change (for energy, mass and momentum) in non-reacting binary mixtures. Finally, the transition to parabolic description is discussed and exemplified (Section 8) and the importance of the results obtained in this paper is discussed (Section 9).

In Appendix some basic information concerning relaxation effects is quoted and appearance of hyperbolic terms in equations of change is reminded (see [10–13]) by macroscopic balance method.

## 2. GENERAL STRUCTURE OF THE ACTION FUNCTIONALS

Our fundamental assumption in finding suitable functionals will be, that if the equations of physical processes are autonomous by themselves (i.e. independent variables do not appear there explicity), an integrand of the action functional (Lagrangian) can exist which is non-autonomous. This fact has not so far been discussed in more detail in the classical variational calculus and in the optimization theories.

Let us consider a non-autonomous functional

$$\tilde{S} = \iiiint \tilde{\Lambda}\left(q, \frac{\partial q}{\partial x}, \frac{\partial q}{\partial y}, \frac{\partial q}{\partial z}, \frac{\partial q}{\partial t}, x, y, z, t\right) \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}t \qquad (1)$$

and examine which sufficient conditions must be met so that the Euler equations (resulting from the vanishing of variation $\tilde{S}$) should explicitly contain no independent variables $x, y, z, t$. We assume the following form of Lagrangian $\tilde{\Lambda}$

$$\tilde{\Lambda} = \Lambda\left(q, \frac{\partial q}{\partial x}, \frac{\partial q}{\partial y}, \frac{\partial q}{\partial z}, \frac{\partial q}{\partial t}\right) \cdot \phi(x, y, z, t) \quad (\phi \neq 0). \qquad (2)$$

Using formula (2) in the Euler equation of the functional (1) and assuming that $x = x_1, y = y_2, z = x_3$, we obtain

$$\frac{\partial}{\partial t}\left(\frac{\partial \tilde{\Lambda}}{\partial q'_t}\right) + \frac{\partial}{\partial x_1}\left(\frac{\partial \tilde{\Lambda}}{\partial q'_{x_1}}\right) + \frac{\partial}{\partial x^2}\left(\frac{\partial \tilde{\Lambda}}{\partial q'_{x_2}}\right) + \frac{\partial}{\partial x_3}\left(\frac{\partial \tilde{\Lambda}}{\partial q'_{x_3}}\right) = \frac{\partial \tilde{\Lambda}}{\partial q} \qquad (3)$$

where

$$q'_{x_i} = \frac{\partial q}{\partial x_i} (i = 1, 2, 3) \quad \text{and} \quad q'_t = \frac{\partial q}{\partial t}.$$

Substitution of (2) into (3) leads to relation

$$\phi \frac{\partial}{\partial t}\left(\frac{\partial \Lambda}{\partial q'_t}\right) + \frac{\partial \phi}{\partial t}\frac{\partial \Lambda'}{\partial q'_t} + \sum_{i=1}^{s}\left\{\phi \frac{\partial}{\partial x_i}\left(\frac{\partial \Lambda}{\partial q'_{x_i}}\right) + \frac{\partial \phi}{\partial x_i}\frac{\partial \Lambda}{\partial q'_{x_i}}\right\} = \phi \frac{\partial \Lambda}{\partial q} \qquad (4)$$

or, after dividing both members by $\phi$:

$$\frac{\partial}{\partial t}\left(\frac{\partial \Lambda}{\partial q'_t}\right) + \sum_{i=1}^{3} \frac{\partial}{\partial x_i}\left(\frac{\partial \Lambda}{\partial q'_{x_i}}\right) + \frac{\partial \ln \phi}{\partial t}\frac{\partial \Lambda}{\partial q'_t} + \sum_{i=1}^{3} \frac{\partial \ln \phi}{\partial x_i}\frac{\partial \Lambda}{\partial q'_{x_i}} = \frac{\partial \Lambda}{\partial q}. \qquad (5)$$

Equation (5) will not have explicity independent variables $x_i$, $t$ if function $\ln[\phi(x_i, t)]$ that appears therein will be linear, that is,

$$\phi = \exp\left(mt + \sum_{i=1}^{3} b_i x_i + e\right). \qquad (6)$$

Euler equation (5) will then assume the autonomus form of a general structure

$$\psi\left(q, \frac{\partial q}{\partial x_i}, \frac{\partial q}{\partial t}, \frac{\partial^2 q}{\partial x_i \partial x_j}, \frac{\partial^2 q}{\partial x_i \partial t}, \frac{\partial^2 q}{\partial t^2}\right) = 0. \qquad (7)$$

i.e. upon substituting (6) into (5)

$$\frac{\partial}{\partial t}\left(\frac{\partial \Lambda}{\partial q'_t}\right) + \sum_{i=1}^{3} \frac{\partial}{\partial x_i}\left(\frac{\partial \Lambda}{\partial q'_{x_i}}\right) + m\left(\frac{\partial \Lambda}{\partial q'_t}\right) + \sum_{i=1}^{3} b_i\left(\frac{\partial \Lambda}{\partial q'_{x_i}}\right) = \frac{\partial \Lambda}{\partial q}. \qquad (8)$$

Thus functional (1) is

$$\tilde{S} = \iiiint \Lambda\left(q, \frac{\partial q}{\partial t}, \frac{\partial q}{\partial x_i}\right) \exp\left(mt + \sum_{i=1}^{3} b_i x_i + e\right) \mathrm{d}V\,\mathrm{d}t. \qquad (9)$$

Functional (9) is useful in variational descriptions to result in equations of change for a variety of problems in theory of heat, mass and momentum transfer, especially those analysed in Sections 4–7.

Noteworthy is that the exponential member in equation (9) proves to be good in the applications for which our autonomicity condition need not be met for function $\Lambda$ of this equation. (Some examples of that type will be treated herein in the discussion of the diffusion with chemical reaction in the presence of a deactivating catalyst and with the heat processes with internal sources.)

Equation (9) will conveniently be used for applications in its alternative form. For transport processes with relaxation effects of advantage is the assumption $e = 0$, $m = 1/\tau$ (where $\tau$ is relaxation time), and $b_i = v_i/D$ where $v$ are components of definite velocity (constant for motion of the medium), and $D$ is a definite diffusivity. Then

$$\tilde{S} = \iiiint \Lambda\left(q, \frac{\partial q}{\partial t}, \frac{\partial q}{\partial x_i}\right) \exp\left(\frac{t}{\tau} - \frac{\mathbf{v}\mathbf{r}}{D}\right) \mathrm{d}V\,\mathrm{d}t \qquad (10)$$

where $r(x_1, x_2, x_3)$ is the radius vector. In the case when $\mathbf{v} = 0$ functional (10) is reduced to the form already studied in the literature by Vujanovic and Djukic [17, 18].

## 3. PHYSICAL CHARACTERIZATION OF ASSUMPTIONS

In this paper we investigate exclusively the uncoupled transport processes in incompressible media for which approximation $\rho = \text{const}$ is allowed (solids, liquids and subsonic gases). As in [16] it is assumed that these media move with the known constant velocity at infinity $\mathbf{v}$ and $|\mathbf{v}| \ll c$. The velocity $\mathbf{v}$ should be distinguished, in fluid case, from unknown velocity $\mathbf{w}(x, y, z, t)$—a variable characterizing local momentum changes—which is sought within the volume investigated. For solids only pure heat transfer is analyzed.

It is generally assumed that

$$\mathbf{w}(x, y, z, t) = \mathbf{v} + \Delta\mathbf{w}(x, y, z, t)$$

where $\Delta \mathbf{w}$ is a small quantity and, consequently, that velocity $\mathbf{w}$ (but not its derivatives) can be replaced by $\mathbf{v}$ in every expression for substantial derivative (i.e. that operator $\partial/\partial t + \mathbf{w}\,\mathrm{grad}$ can be approximated by operator $\partial/\partial t + \mathbf{v}\,\mathrm{grad}$). This is *classical Oseen's approach* [16] to obtain linearized equations of fluid mechanics, see e.g. equation (40) in this paper. It may be observed that such approach is more exact in the case of solid where $\mathbf{w}$ practically equals to $\mathbf{v}$.

It is always possible to operate with specific heat under constant pressure, $C_p$, in all energy equations, c.f. [5]. This quantity is used particularly in description of heat transfer in solid, where $C_p \cong C_v$, replacing more proper quantity $C_v$ in internal energy term, see [5]. The constancy of transport properties (thermal and mass diffusivities, fluid viscosity as relaxation times) is assumed.

It should be pointed out that the absence of coupling effects is assumed, in cases with several transfer potentials* (Section 7), and that this uncoupling assumption concerns both kinetic laws between fluxes and forces (e.g. vanishing of reciprocity Onsager's coefficients) and the internal and transport properties of equations of change as well. Our approximation $\mathbf{w} \cong \mathbf{v}$ in substantial derivatives results in relationship between temperature (or concentration) and velocity $\mathbf{v}$ rather than $\mathbf{w}$. Negligence of viscous dissipation term in energy equation is assumed (necessary for uncoupling of $T$ and $\mathbf{w}$).

A direct consequence of uncoupling is that the solution of conservation equation for any internal transfer potential (e.g. temperature) is independent of changes in solutions of remaining potentials (e.g. concentration). Therefore for our most general problem of non-isothermal incompressible non-reacting fluid (Section 7) the action functional with several unknown transfer potentials can be constructed as a linear combination of partial functionals, all describing separately heat transfer, diffusion and momentum transfer (additivity property). This is a consequence of uncoupling assumptions due to which either prescribing or varying of definite transfer potential field does not effect the changes in fields of other potentials (see especially Section 7).

## 4. HEAT PROCESSES IN MOVING SOLIDS

In order to bring out the efficiency of the variational formulations using functionals (9) and (10), suitable integrals will be provided for which condition: $\delta\tilde{S} = 0$ leads to hyperbolic equations of time-dependent heat conduction in the solid that move with a constant velocity $\mathbf{w} = \mathbf{v}$. The classical functionals describing the time-dependent heat processes which occur in the presence of a macroscopic motion have hitherto been unsuccessfully sought in the variational calculus, c.f. [4]. The local potential approach by Glansdorff and Prigogine [3] applied for such processes does not introduce the functional in the classical meaning. Hence comes the shortcoming of this approach, as the error cannot be easily determined when any direct method is taken (see Schechter [19]).

In setting up the functional that describes time-dependent heat conduction a mathematical analogy with the mechanics of elastic bodies can be advantageously employed, for which Hamilton's principle of stationary action holds. Then the Lagrangian contains the difference of the kinetic and potential energies. The analogue of kinetic energy in the heat-transfer theory may be the following expression that incorporates thermal relaxation time

$$\frac{1}{2}\iiint_V \rho C_p \tau_h \left(\frac{\partial T}{\partial t}\right) \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{11}$$

whereas that of the potential energy under a constant strain is the expression

$$\frac{1}{2}\iiint_V \lambda(\mathrm{grad}\,T)^2\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{12}$$

If $I_s(x, y, z, t)$ denotes the amount of energy released from a unit volume of the body in which an internal source of heat is present, the product $TI_s(x, y, z, t)$ constitutes a contribution to the Lagrange function which is due to the action of the sources.* As an action functional for the process of the heat conduction in a moving solid body of a given temperature of the surface and of constant parametres ($\rho, C_p, \tau_h$ and $a$) it was assumed

$$\tilde{S}_h = \frac{1}{2}\int_0^{t_f}\iiint_V \left\{\rho C_p \tau_h \left(\frac{\partial T}{\partial t}\right)^2 - \lambda(\mathrm{grad}\,T)^2 + 2TI_s(x, y, z, t)\right\}\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right)\mathrm{d}V\,\mathrm{d}t. \tag{13}$$

The use of known physical relations between the coefficients

$$a = \frac{\lambda}{\rho C_p} \tag{14}$$

$$\tau_h = a/c_h^2 \tag{15}$$

in the Euler equation (8) applied for functional (13) gives

$$\rho C_p\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right) = \lambda\left(\nabla^2 T - \frac{\partial^2 T}{c_h^2\,\partial t^2}\right) + I_s(x, y, z, t). \tag{16}$$

The result obtained is the time-dependent heat-conduction equation in its more exact (hyperbolic) form, c.f. [10–13], with an account of the velocity of heat wave propagation $C_h = (a/\tau_h)^{1/2}$. It simplifies to classical energy equation if $c_h \to \infty$.

It should be observed that equations (13) and (16) can be used not only for solids but also (approximately with assumption $\mathbf{v} \cong \mathbf{w}$) for incompressible fluids, even

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*We mean here temperature $T$, concentration $\tilde{y}$, and velocity $\mathbf{w}$ as transfer potentials of uncoupled processes. Additionally, variables $T$ and $\tilde{y}$ are called internal transfer potentials.

*The above analogies have no physical meaning but are of purely mnemonic character.

in the case of solutions, when Dufour's effect is neglected and $C_{p1} \cong C_{p2}$, c.f. Bird *et al.* [5] for classical version of equation (16).

This fact should be remembered since it will be exploited in Section 7 where a general functional is found that leads to the complete set of linearized fluid mechanics equations, including equation (16).

If the heat sources are absent and the body is at rest, equation (16) resolves itself to a simpler form

$$\frac{\partial T}{\partial t} = a\left[\nabla^2 T - \frac{\partial^2 T}{c_h^2 \partial t^2}\right]. \tag{17}$$

The functional leading to equation (17) is a particular case of functional (13) in which $\mathbf{v} = 0$ and $I_s = 0$ have been substituted. The latter particular case is described in the literature [5]. The well-known derivation of hyperbolic equation (17), c.f. [10–13], based on conservation law and constitutive heat equation (involving relaxation effects) is given in Appendix.

Physical interpretation of the difference $(t/\tau_h - \mathbf{vr}/a)$ which appears in the exponential term of equation (13) is of interest. The use of equation (15) then yields

$$\phi(\mathbf{r}, t) = \exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right) = \exp\left[\frac{1}{\tau_h}\left(t - \frac{\mathbf{vr}}{c_h^2}\right)\right]. \tag{18}$$

Quantity $(t - \mathbf{vr}/c_h^2)$ has the dimension of time and will be referred to as the proper time of heat propagation. Thus the exponential term of functional (13) contains a dimensionless quotient of the proper time and relaxation time $\tau_h$.

It appears attractive to consider generalization of the problem over a case of more complex boundary conditions. Let us take a moving solid body that passes through a given fixed balance shield confined by surface $A$. It is further assumed that over a part of surface $A$, say, $A_1$, heat exchange takes place between the body and the medium of a temperature $T_e$, whereas part $A_2$ of the surface is kept at a constant temperature $T_2$. Similar problems are involved during the cooling or heating of moving solid blocks of material.

On account of the heat exchange between the body and the medium the Lagrangian should contain an additional term in the form of a suitable surface integral which describes the phenomena occurring on surface $A_1$. Accordingly, the following action functional has been taken

$$\begin{aligned}\tilde{S}_h = \tfrac{1}{2}\int_0^{t_f}\iiint_V \Bigg\{&\rho C_p \tau_h\left(\frac{\partial T}{\partial t}\right)^2 - \lambda(\operatorname{grad} T)^2 \\ &+ 2TI_s(x, y, z, t)\Bigg\}\exp\Bigg\{\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\Bigg)\mathrm{d}V\,\mathrm{d}t \\ &+ \tfrac{1}{2}\int_0^{t_k}\iint_{A_1}\alpha(T[A_1, t] - T_e)^2\exp\Bigg(\frac{t}{\tau_h} \\ &- \frac{\mathbf{vr}(A_1)}{a}\Bigg)\mathrm{d}A_1\,\mathrm{d}t.\end{aligned} \tag{19}$$

By substituting into the above formula the variation of temperature as $\delta T = \varepsilon\psi$ the following formula is obtained for variation $\delta\tilde{S}_h$:

$$\begin{aligned}\delta\tilde{S}_h = \varepsilon\int_0^{t_f}\iiint_V \mathrm{d}V\,\mathrm{d}t\Bigg\{&I_s\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right) \\ &+ \sum_{k=1}^{3}\frac{\partial}{\partial x_k}\left[\lambda\frac{\partial T}{\partial x_k}\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right)\right] \\ &- \frac{\partial}{\partial t}\left[\frac{\lambda\tau_h}{a}\frac{\partial T}{\partial t}\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right)\right]\Bigg\} \\ &+ \varepsilon\int_0^{t_f}\iiint_V\Bigg\{\frac{\partial}{\partial c_h t}\left[\frac{\psi\lambda}{c_h}\frac{\partial T}{\partial t}\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right)\right] \\ &- \sum_{k=1}^{3}\frac{\partial}{\partial x_k}\left[\psi\lambda\frac{\partial T}{\partial x_k}\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right)\right]\Bigg\}\mathrm{d}V\,\mathrm{d}t \\ &+ \varepsilon\int_0^{t_f}\iint_{A_1}\alpha(T[A_1, t] - T_e)\exp\Bigg(\frac{t}{\tau_h} \\ &- \frac{\mathbf{vr}(A_1)}{a}\Bigg)\psi\,\mathrm{d}A_1\,\mathrm{d}t.\end{aligned} \tag{20}$$

Evaluation of derivatives of the products in the first integral, application of the Green theorem in the second integral of the above formula, with the condition $T = \text{const}$ on surface $A_2$, lead to the relation:

$$\begin{aligned}\delta\tilde{S}_h = \varepsilon\int_0^{t_f}\iiint_V\Bigg\{&I_s + \lambda\left(\operatorname{div}\operatorname{grad} T - \frac{\tau_h}{a}\frac{\partial^2 T}{\partial t^2}\right) \\ &- \rho C_p\left(\frac{\partial T}{\partial t} + \mathbf{v}\operatorname{grad} T\right)\Bigg\}\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}}{a}\right)\psi\,\mathrm{d}V\,\mathrm{d}t \\ &+ \varepsilon\int_0^{t_f}\iint_{A_1}\Bigg\{\lambda\Bigg(n_t\frac{\partial T[A_1, t]}{c_h \partial t} \\ &- \mathbf{n}\operatorname{grad} T[A_1, t]\Bigg) + \alpha(T[A_1, t] - T_e)\Bigg\} \\ &\exp\left(\frac{t}{\tau_h} - \frac{\mathbf{vr}(A_1)}{a}\right)\psi\,\mathrm{d}A_1\,\mathrm{d}t\end{aligned} \tag{21}$$

from which it results for $\delta\tilde{S}_h = 0$ the heat-conduction equation of a moving solid body

$$\begin{aligned}\rho C_p\left(\frac{\partial T}{\partial t} + \mathbf{v}\operatorname{grad} T\right) = \lambda\left(\nabla^2 T - \frac{1}{c_h^2}\frac{\partial^2 T}{\partial t^2}\right) \\ + I_s(x, y, z, t)\end{aligned} \tag{22}$$

and the boundary condition that describes the heat exchange on surface $A_1$:

$$\lambda\left[n_t\frac{\partial T}{c_h \partial t} - \mathbf{n}\operatorname{grad} T(A_1, t)\right] = \alpha(T_e - T[A_1, t]). \tag{23}$$

Note that $n_t = 0$ if $\mathbf{v} = 0$; the classical boundary condition is thus recovered for solid at rest.

The reader may additionally visualise that for the case of a contact of two surfaces, action $\tilde{S}_h$ represents the sum of two integrals which constitute the first member of equation (19), and that then the boundary condition on the surface of contact has the form:

$$\sum_{j=1}^{2}\lambda_j\left(n_{tj}\frac{\partial T_j}{\partial(C_h t)} - \mathbf{n}_j\operatorname{grad} T_j\right) = 0 \qquad (j = 1, 2). \tag{24}$$

We can see that the boundary conditions for the hyperbolic equation may not be simply related to the constitutive equation of heat conduction involving relaxation. The dissimilarity of boundary conditions has been pointed out by, among others, Luikov [13] and Chernyshov [20].

Noteworthy is also the following simple manner of interpretation of hyperbolic equation (22). Much like as Feynman did [21] in his interpretation of relativistic effects, but with $c_h$ understood here as the velocity of propagation of thermal wave, the time-space with coordinates $(x, y, z, c_h t)$ can be considered.* In this time-space a four-dimensional mass flux density $j_\mu(\rho v_1, \rho v_2, \rho v_3, \rho c_h)$ and a four-dimensional vector operator

$$\nabla_\mu\left(\frac{\partial}{\partial c_h t}, \frac{-\partial}{\partial x}, \frac{-\partial}{\partial y}, \frac{-\partial}{\partial z}\right)$$

are defined. The following expression is attained which describes the four-dimensional vector of the overall energy density $J_\mu(J_x, J_y, J_z, J_t)$

$$J_\mu = \lambda \nabla_\mu T + \rho v_\mu C_p T \qquad (v_\mu = \mathbf{v}, c_h). \tag{25}$$

In the space under consideration the scalar product of vectors $a_\mu \cdot b_\mu$ equals $a_t b_t - a_x b_x - a_y b_y - a_z b_z$. Hence it follows that the four-dimensional divergence as the scalar product $\nabla_\mu J_\mu$ is

$$\nabla_\mu J_\mu = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} + \frac{\partial J_t}{\partial(c_h t)}.$$

Calculating this divergence using formula (25) and comparing the result with the hyperbolic equation (22) it may be inferred that this equation can be written in the form

$$\nabla_\mu J_\mu = I_s(x, y, z, c_h t). \tag{26}$$

This is equivalent to the corollary that the four-dimensional vector of the energy flux density equals the density of the sources of heat $I_s$. For that reason the presence of hyperbolic members in the heat-conduction equation may be looked upon as a consequence of the appearance of the time component of the four-dimensional vector of heat flux which contains the irreversible relaxation term $\lambda(\partial T/\partial(c_h t))$, in addition to the reversible term which is the product of the propagation velocity of the heat wave, $c_h$, and the energy flux density, $\rho C_p T$. Equation (26) may be derived from the variational principle $\delta \tilde{S} = 0$, where

$$\tilde{S} = \tfrac{1}{2} \iiiint_\Omega \{\lambda(\nabla_\mu T)^2 + 2T I_s(x_\mu)\} \exp\left(\frac{x_\mu j_\mu}{a}\right) \mathrm{d}\Omega_h \tag{27}$$

in the case of constant temperatures at the boundary of the system and for given initial and final times. Equation (27) actually represents the four-dimensional notation of equation (13).

The results obtained till now can be easily generalized over the case of a moving anisotropic body with unsteady temperature for which the classical variational formulation leading to a differential equation describing energy conservation is not known, either.†

For the anisotropic case merely the scalar $\lambda$ should be changed into the three-dimensional heat conduction tensor $\lambda_{ik}$ in the action integral. On the other hand the exponential member of the action should contain in place of thermal diffusivity a matrix $a_{jk}^{-1} = \rho C_p \lambda_{jk}^{-1}$ whose elements are the components of the heat resistance tensor $\lambda_{jk}^{-1}$* multiplied by the scalar factor $\rho C_p$. The action integral in the case of a constant temperature of the boundaries has the following form:

$$\tilde{S}_h = \tfrac{1}{2} \iiiint_\Omega \left\{\lambda_{tt}\left(\frac{\partial T}{\partial(c_h t)}\right) - \lambda_{rs} \frac{\partial T}{\partial x_r}\frac{\partial T}{\partial x_s} + 2T I_s(x_i, t)\right\} \exp\left(\frac{t}{\tau_h} - x_i a_{ik}^{-1} v_k\right) \mathrm{d}\Omega_h \tag{28}$$

whereas the Euler equation for $\delta \tilde{S}_h = 0$ is

$$\rho C_p\left(\frac{\partial T}{\partial t} + v_i \frac{\partial T_i}{\partial x}\right) = \lambda_{ik} \frac{\partial^2 T}{\partial x_i \partial x_k} - \lambda_{tt} \frac{\partial^2 T}{\partial(c_h t)^2} + I_s(x_i, t) \tag{29}$$

as $\lambda_{ir} a_{ik}^{-1} = \rho C_p \delta_{rk}$, where $\delta_{rk}$ is unit tensor. The above equation can formally be derived from the requirement that source $I_s$ should be equal to the four-dimensional divergence of the following vector of the overall energy flux density

$$J_{\mu\varepsilon} = \begin{bmatrix} J_i \\ J_t \end{bmatrix} = \begin{bmatrix} -\lambda_{ik} \dfrac{\partial T}{\partial x_k} + \rho v_i C_p T \\ \lambda_{tt} \dfrac{\partial T}{\partial(c_h t)} + \rho c_h C_p T \end{bmatrix} \quad \begin{pmatrix} i, k = 1, 2, 3 \\ \mu, \varepsilon = 1, 2, 3, 4 \end{pmatrix}. \tag{30}$$

### 5. TWO-COMPONENT DIFFUSION WITH A CHEMICAL REACTION

As a matter of course, the analogous approach can be used in the description of the diffusion in solids and fluids without crossing effects in view of a close resemblance between the heat transfer and the mass-transfer equations. The subsequent discussion is merely restricted to the formulation of the variational principle for isobaric and isothermal diffusion in a two-component isotropic fluid with a single chemical reaction on the assumptions of a constant concentration at the boundaries of the system and small $\Delta \mathbf{w}$ ($\mathbf{w} \cong \mathbf{v}$). For non-isobaric and non-isothermal diffusion the results in this section can be simply exploited (under uncoupling assumption) as shown in Section 7. If the reaction rate is defined by equation

$$\tilde{r} = k\tilde{y}^n \qquad (k = \mathrm{const}(\tilde{y})) \tag{31}$$

the relevant action integral has the form

$$\tilde{S}_d = \int_0^{t_f} \iiint_V \left\{\tfrac{1}{2}\rho D\left[\left(\frac{\partial \tilde{y}}{\partial(C_d t)}\right) - (\operatorname{grad} y)^2\right] + \frac{k\tilde{y}^{n+1}}{n+1}\right\} \exp\left(\frac{t}{\tau_d} - \frac{\mathbf{vr}}{D}\right) \mathrm{d}V\, \mathrm{d}t \tag{32}$$

Condition $\delta S = 0$ and relation $\tau_d = D/c_d^2$ result in diffusion equation

$$\rho\left(\frac{\partial \tilde{y}}{\partial t} + \mathbf{v} \operatorname{grad} \tilde{y}\right) = \rho D\left(\nabla^2 \tilde{y} - \frac{1}{c_d^2}\frac{\partial^2 y}{\partial t^2}\right) + k\tilde{y}^n \tag{33}$$

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* Several remarks on four-dimensional interpretation of heat conduction can be found in [22] without, however, any reference to variational principles.

† A related problem of variational formulation for constitutive Fourier equation describing flux–force relationship in anisotropic case is critically reviewed by Finlayson and Scriven [4].

* Tensor $\lambda_{ik}$ obeys the Onsager symmetry relation $\lambda_{ik} = \lambda_{ki}$.

that simplifies to its classical counterpart for $c_d \to \infty$. The hyperbolic diffusion equation with sources was obtained in case $\mathbf{v} = 0$ by Goldstein [15] who used statistical method. Phenomenological method using macroscopic balance was also applied by Luikov [13], following analogous technique for heat equation, c.f. Appendix.

Formula (32) can be easily generalized over the case when the reaction rate is described by a function of the form

$$\tilde{r} = kf(\tilde{y}) \qquad k = \text{const}\,(\tilde{y}). \tag{34}$$

Here the source member that appears in the action integral (32) has the form

$$Z(\tilde{y}) = k\int_0^{\tilde{y}} f(\xi)\,\mathrm{d}\xi. \tag{35}$$

The most general form of the source member, for which still holds action integral of type (32), is

$$Z(\tilde{y}, x_i, t) = k(x_i, t)\int_0^{\tilde{y}} f(\xi, x_i, t)\,\mathrm{d}\xi. \tag{36}$$

Replacement of member $k\tilde{y}^{n+1}/n+1$ in integral (32) by the RHS term of formula (36) leads, with the condition $\delta\tilde{S}_d = 0$, to equation

$$\rho\frac{\mathrm{d}\tilde{y}}{\mathrm{d}t} = \rho D\left(\nabla^2 y - \frac{1}{c_d^2}\frac{\partial^2 y}{\partial t^2}\right) + k(x_i, t)f(y, x_i, t). \tag{37}$$

The latter result indicates that a variational formulation can be found which leads to the diffusion equation in which the source terms may be entered as an explicit function of concentration, time, and space coordinates. This is of significance for the description of the processes with a chemical reaction, in which the kinetic equation coefficient vary with space and time because of deactivation of the catalyst.

## 6. THE MOMENTUM TRANSPORT PROCESSES IN ISOTHERMAL FLUID

The experience gained in the investigation of the previous problems is useful in an easy finding of a functional that leads to a linearized equation of motion of an incompressible isothermal viscous fluid. As pointed in Section 3 it is assumed that vector $\mathbf{v} = \text{const}$ in equation (10) describes the constant velocity of the fluid in infinity, whereas within the volume investigated (at the boundaries of which the pressure $P$ and the velocity are established) the velocity is described by the vector field $\mathbf{w}(x, y, z, t)$, and $\mathbf{w} = \mathbf{v} + \Delta\mathbf{w}$ where $\Delta\mathbf{w}$ is a small quantity. Action functional has the form ($\nu$ is a constant kinematic viscosity)

$$\tilde{S}_m = \iiiint\left\{\tfrac{1}{2}\rho\nu\left[\frac{\partial w_i}{\partial(c_m t)}\frac{\partial w_i}{\partial(c_m t)} - \frac{\partial w_i}{\partial x_j}\frac{\partial w_i}{\partial x_j}\right] + \frac{v_i v_i P}{\nu} - w_i\left(\frac{\partial P}{\partial x_i} - \rho F_i\right)\right\}\exp\left(\frac{t}{\tau_m} - \frac{v_i x_i}{\nu}\right)\mathrm{d}V\,\mathrm{d}t \tag{38}$$

and the necessary condition of stationarity of $\tilde{S}_m$ with respect to the pressure $P$ (the Euler equation) is approximately* for small $\Delta\mathbf{w}$

$$\frac{\partial w_j}{\partial x_j} = 0 \tag{39}$$

i.e. is the continuity equation for an incompressible fluid. The $\tilde{S}_m$ stationary conditions, with respect to the velocity components $w$, have the form of:

$$\rho\left(\frac{\partial w_i}{\partial t} + V_j\frac{\partial w_i}{\partial x_j}\right) = \rho\nu\left(\frac{\partial^2 w_i}{\partial x_j \partial x_j} - \frac{1}{c_m^2}\frac{\partial^2 w_i}{\partial t^2}\right) - \frac{\partial P}{\partial x_i} + \rho F_i \tag{40}$$

i.e. these have Oseen's linearized form, c.f. [16], of hyperbolic Navier–Stokes equations. The presence of second time derivative in equation (40) provides the finite speed of shear strain, c.f. [23], [13].

Note that due to the uncoupling assumption, functional (38) still can, be exploited to derive equations (39) and (40) in the case of non-isothermal two-component fluid. This notion is exploited with more details in the forthcoming section.

## 7. AN APPROACH FOR UNCOUPLED HEAT MASS AND MOMENTUM TRANSFER IN NON-ISOTHERMAL NON-REACTING BINARY FLUID

The previous section has shown that for the fluid flow problem, the functional just considered, with several unknown functions [$w_i(\mathbf{r}, t)$ and $P(\mathbf{r}, t)$] had to be sought. Now, one can generalize that problem considering non-isothermal binary fluid in the absence of chemical reaction† ($k = I_s = 0$) to obtain suitable functional [with the unknowns $T(\mathbf{r}, t)$, $\tilde{y}(\mathbf{r}, t)$, $P(\mathbf{r}, t)$ and $w_i(\mathbf{r}, t)$] giving rise to complete system of equations of change, i.e. equations (16), (33), (39) and (40) with $k = I_s = 0$. In order to accomplish such a variational formulation it is useful to note that under uncoupling assumptions (c.f. Section 3) the form and solution of momentum equation (40) and continuity equation (39) do not change whether or not temperature and concentration fields vary. Therefore, in the present case, the complete set of differential relationships [equations (16), (33), (39) and (40) with $k = I_s = 0$] can be obtained from a functional (41), the additive parts of which are—with accuracy to the constant multipliers—functionals $\tilde{S}_h$, $\tilde{S}_d$, and $\tilde{S}_m$ [equations (13), (32) and (38)] taken with $k = I_s = 0$. It means that our general action functional has the following additive form

$$\tilde{S} = \tilde{A}\tilde{S}_h + \tilde{B}\tilde{S}_d + \tilde{C}\tilde{S}_m \qquad (k = I_s = 0) \tag{41}$$

where all multipliers $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ can be arbitrary but non-zero constants.

The stationarity conditions for $\tilde{S}$, equation (41), with respect to variables $T$, $\tilde{y}$, $P$ and $w_i$ are equations (16), (33), (39) and (40) with $k = I_s = 0$. They are all linear because of the presence of velocity $\mathbf{v}$ instead of $\mathbf{w}$ in

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*The term $(v_i \Delta w_i)/\nu$ was neglected since it approaches zero when $\Delta w_i \to 0$.

† In the case of non-isothermal reacting mixture, heat and diffusion equations are necessarily coupled and their consideration is beyond the scope of this paper.

substantial derivative operators. Due to this approximation the range of the present theory, in its application to the non-reacting fluid mechanics problems is restricted to the case of small changes of fluid velocity **w**.

Some additional remarks can be made concerning multipliers (or weights) in equation (41). Although they can be arbitrary it seems to be reasonable to choose them in a definite manner allowing some physical interpretation. It may be verified that if one defines these multipliers as

$$\tilde{A} = -\frac{1}{T_0^2},\quad \tilde{B} = \left[\frac{\partial(\mu_1-\mu_2)_T}{\partial\tilde{y}}\right]_{\tilde{y}_0 P_0 T_0}$$
$$= -\frac{M_1 R}{\tilde{y}_0(1-\tilde{y}_0)(\tilde{y}_0 M_2/M_1+1-\tilde{y}_0)},\quad \tilde{C} = -\frac{1}{T_0} \tag{42a, b, c}$$

where subscript zero pertains to some reference state, e.g. state at infinity, then all components of Lagrangian of functional (41) will provide entropy source dimension. Furthermore, in the case of quiescent fluid ($\mathbf{w} = \mathbf{v} = 0$) and the absence of nonstationarities (e.g. relaxation effects) the exponential terms equal to unity and the total Lagrangian also approximates* (under uncoupling assumptions) this entropy source itself. This is of course not surprise, since, as is widely known [9], the minimum entropy production principle holds for stationary dissipative systems, this principle leading to the simplified *stationary* form of equations of change without convective terms, c.f. [9]. Thus our principle replaces the principle of minimum entropy production for non-stationary cases with convection which were just considered. For this reason equation (42) is recommended to define $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ in equation (41).

## 8. LIMITING PROCEDURE LEADING TO STANDARD DESCRIPTION

The compatibility of the hyperbolic differential equations and a well-known standard parabolic form of conservation equations is obvious as long as all relaxation times are finally taken equal to zero in all the Euler equations obtained here. Such limiting procedure can also be accomplished when any direct method, as e.g. Rayleigh–Ritz method or Kantorovich method, c.f. [1] is completed for extremizing the action functionals.

To illustrate briefly the latter method, where the coefficients of approximate solution are unknown functions of definite independent variable (e.g. time), consider simple example, the exact standard solution of which is known in series form in [24].

Assume that our task is to determine moisture content $\tilde{Y}(x,t)$ in a resting infinite plate the sides of which are maintained at a constant concentration, i.e. $\tilde{Y} = \tilde{Y}_e$, and the initial moisture content field $\tilde{Y}(x,0)$ is parabolic. Thus, the initial and boundary conditions pertain to onset of so called second drying period, i.e.

$$\tilde{Y} = \tilde{Y}_e + \tilde{Y}(0,0)[1-(x/X)^2] \quad \text{at} \quad t = 0 \quad \text{for} \quad -X \leqslant x \leqslant X \tag{43}$$

$$\tilde{Y} = \tilde{Y}_e \quad \text{at} \quad x = \pm X \quad \text{for} \quad t \geqslant 0 \quad \text{if} \quad Bi \to \infty. \tag{44}$$

For these conditions we want to determine an approximated solution of equation (33) in one-dimensional case and when $v = k = c_d^{-1} = 0$ with the help of direct variational method. Applying Kantorovich method to extremize the integral

$$\tilde{S}_d = \rho\frac{D}{2}\int_0^{t_f}\int_{-X}^{X}\left\{\frac{1}{c_d^2}\left(\frac{\partial\tilde{Y}}{\partial t}\right)^2 - \left(\frac{\partial\tilde{Y}}{\partial x}\right)^2\right\}\exp\left(\frac{t}{\tau_d}\right)\mathrm{d}x\,\mathrm{d}t \tag{45}$$

which is a truncated form of the action functional (32) in case considered, one may assume the following form of moisture content field

$$\tilde{Y}(x,t) = \tilde{Y}_e + \tilde{Y}(0,0)[1-(x/X)^2]h(t) \tag{46}$$

where $h(t)$ is an unknown function of time such that $h(0) = 1$. Applying equation (46) into equation (45) and integrating the result obtained with respect to $x$ one finds:

$$\tilde{S}_d = \frac{8\rho D\tilde{Y}^2(0,0)X}{15}\int_0^{t_f}\left\{c_d^{-2}\dot{h}^2(t) - 2.5 \times X^{-2}h^2(t)\right\}\exp\left(\frac{t}{\tau_d}\right)\mathrm{d}t. \tag{47}$$

The unknown function $h(t)$ must be chosen so that integral (47) becomes stationary. It means that one-dimensional Euler equation, describing $h(t)$, must be met for integrand of equation (47). Thus, one has

$$\tau_d\ddot{h} + \dot{h} = 2.5hDX^{-2}. \tag{48}$$

Realizing limiting procedure, $\tau_d = 0$ must be taken in equation (48) and the resulting equation, under condition $h(0) = 1$, must be integrated. Hence

$$h(t) = \exp\left(-\frac{2.5Dt}{X^2}\right) \tag{49}$$

and after substituting equation (49) into equation (46):

$$\tilde{Y} = \tilde{Y}_e + \tilde{Y}(0,0)[1-(x/X)^2]\exp(-2.5DtX^{-2}). \tag{50}$$

This approximation agrees with accuracy of 4% with exact analytical solution of parabolic equation presented graphically by Carslaw and Jaeger in Fig. 10(d) in [24].

The physical justification for the procedure just described lies in the fact that relaxation times are usually very small, e.g. for solids they are of order $10^{-12}$ s (it was a reason for neglecting the relaxation effects at all in the past, c.f. Appendix).

It should be, however, pointed out that the limiting procedure is not necessary, since in the light of many more recent investigations, e.g. [10–14] (see also Appendix) the hyperbolic equations represent more

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*An approximation $T \cong T_0$, $\tilde{y} \cong \tilde{y}_0$ should be made in *coefficients* of expression for entropy source. The Gibbs–Duhem relation has been used in equation (42b) as well as formula

$$\mu_{1T} = M_1 RT\ln\left[\frac{\tilde{y}/M_1}{\tilde{y}/M_1+(1-\tilde{y})/M_2}\right] + \text{const}(P,T).$$

correct form of conservation laws than parabolic ones as they are based on more exact constitutive relationships resolving paradox of infinite speeds of disturbances. Thus, one may omit the limiting procedure especially in cases where the significance of relaxation effects is to be expected, e.g. in viscoelastic fluids, rarefied gases, dispersed systems, in Helium II, etc. (see Appendix for information concerning computation of relaxation times.

## 9. FINAL REMARKS AND IMPORTANCE

It is a not rare opinion, see [4, 19, 2], that the irreversible processes can not be generally characterized by extremum principles such as classical variational principles (of stationary action type). The failure to construct such principles for standard (parabolic) form of well-known equations of change, is as a rule the principal criterion in testing the validity of the above opinion.

In this work it was, however, shown that the principles of the kind considered can be constructed for linear hyperbolic conservation equations which take into account relaxation effects in transport processes investigated. The principles obtained are the first in literature which can account for, with considerable generality, both dissipative and non-dissipative effects in heat, mass and momentum transfer processes. Their practical value consist in that that action functionals can be minimized by means of direct methods to find the time-dependent fields of transfer potentials, even for very involved boundary conditions, when the analytical solution of transport equations is unfeasible.

Effectiveness and novelty of the mathematical method, that was applied for construction of action functionals, is an additional important point of this work. It is seen that due to the presence of non-autonomous exponential terms of our Lagrangians, the resulting Euler equations contain both odd and even partial derivatives and as such, these equations have the following significant property: the change of time sign $(t \to -t)$ or spatial coordinate sign $(x_j \to -x_j)$ changes the resulting solution. This is clearly just an irreversibility property of our real macroscopic world—a property that was fit into our variational scheme. Possible adaptation of this scheme for finding the variational principles that lead to coupled transport equations involving Onsager's relations will be a subject of further effort along this line.

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## APPENDIX

### *Some Basic Information Concerning Relaxation Effects*

When describing heat, mass and momentum transfer it is customary to use Fourier's, Fick and Newton constitutive equations, respectively. If, e.g. heat conduction in solid is considered and Fourier's equation is applied into energy conservation formula, the well-known parabolic equation of chage is obtained with the Laplacian operator. This operator appears also in equations of change describing diffusion and momentum transfer. Consequently, all standard equations of change with parabolic terms) have an absurd property, [10–14]; a disturbance (thermal, concentrational etc.) at any point in the medium is felt instantly at every other point or, the velocity of propagation of disturbances is infinite.

This absurd has been pointed out by many people, and the dilemma was resolved, see e.g. [10–13] by noting that, e.g. Fourier's equation is an approximation to a more exact equation called Maxwell–Cattaneo equation:

$$q_h = -\lambda \operatorname{grad} T - \tau_h \frac{\partial \mathbf{q}_h}{\partial t} \qquad (v = 0) \tag{A.1}$$

which takes into account a relaxation of thermal flux.

Neglecting Onsager's coupling the analogous equations for irreversible fluxes of mass $\mathbf{q}_d$ and momentum $\sigma_{ik}$ and have also been found with additional terms $-\tau_d(\partial \mathbf{q}_d)/(\partial t)$ and $-\tau_m(\partial \sigma_{ik})/(\partial t)$ appearing in Fick laws and Newton laws, see e.g. [13] as well as [25]. These terms were known already by Maxwell [26] who first introduced a relaxation time concept, rejecting, relaxation terms, however, in most cases as small. (He conserved these terms, e.g. for viscoelastic fluids.) The presence of relaxation terms in constitutive equations proves that flows do not start instantaneously but rather grow gradually with relaxation times $\tau_h$, $\tau_d$, and $\tau_m$. With the help of macroscopic balance method and corrected constitutive equations the hyperbolic equations of change are found. For instance, [10–13], substituting RHS of (A.1) into conservation formula for resting solid

$$\rho C_p \frac{\partial T}{\partial t} = -\sum_{1}^{3} \frac{\partial q_{hi}}{\partial x_i} \tag{A.2}$$

gives (for constant thermal conductivity) the expression

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + \tau_h \sum_{1}^{3} \frac{\partial^2 q_{hi}}{\partial t \partial x_i}. \tag{A.3}$$

Differentiating (A.2) by sides with respect to time leads to

$$\rho C_p \frac{\partial^2 T}{\partial t^2} = -\sum_{i=1}^{3} \frac{\partial^2 q_{hi}}{\partial t \partial x_i} \tag{A.4}$$

Hence, after eliminating the mixed derivative term from (A.3) and (A.4) the hyperbolic "telegraph" equation is obtained, i.e.:

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T - \tau_h \rho C_p \frac{\partial^2 T}{\partial t^2} \tag{A.5}$$

which is equation (17) in the text since $c_h = (a/\tau_h)^{\frac{1}{2}}$ and $a = \lambda/\rho C_p$. Its generalization for the case of moving solid with heat sources is equation (16) in the text.

Using macroscopic balance method [10–13] and statistical method [15] the hyperbolic equations of change have been also found in the case of diffusion, see [13] and [15].

The role of magnetic field effects was also investigated for wave equations of solids [27].

Hyperbolic equations predict a finite upper velocities for the propagation of disturbances [28, 14], called briefly the propagation velocities

$$c_h = (a/\tau_h)^{\frac{1}{2}} \quad c_d = (D/\tau_d)^{\frac{1}{2}} \quad c_m = (v/\tau_m)^{\frac{1}{2}} \tag{A.6}$$

due to the presence of d'Alembert's operators replacing standard Laplace operators.

The important question concerns the values of relaxation times $\tau_h$, $\tau_d$, $\tau_m$ [or related propagation velocities, equation (A.6)]. For ideal gases it is found, c.f. [29, 26], that

$$\tau_h = \frac{\rho a}{P} \qquad \tau_d = \frac{\rho D}{P} \qquad \tau_m = \frac{\rho v}{P}. \tag{A.7}$$

Consequently, it results from (A.6) and (A.7) that the propagation velocities are equal, i.e.

$$c_h = c_d = c_m = (P/\rho)^{\frac{1}{2}}. \tag{A.8}$$

For gases it is roughly $\tau_h \cong \tau_d \cong \tau_m \cong 10^{-8} - 10^{-10}$ s; and $c = 3.10^2$m/s close to normal conditions.

It is seen that, by their order, propagation velocities correspond to the velocity of sound under given conditions. This notion was extended by Chester [28] for dielectric solid where transport of heat occurs via phonon gas. It was found [28] that

$$c_h = s/\sqrt{3} \tag{A.9}$$

where $s$ is the sound velocity in solid. Equation (A.9) allows to evaluate $\tau_h$, too, since $\tau_h = a/c_h^2$. The results are of order $c_h = 5.10^3$m/s, $\tau_h = 10^{-11}$–$10^{-12}$ s.

For liquids, the relaxation time $\tau_m$ can be computed as [13]

$$\tau_m = \frac{\rho v}{G} \tag{A.10}$$

where $G$ is modulus of shear rigidity that can be found experimentally [30] or theoretically [31]. Thus propagation velocity for shear strain is

$$c_m = (G/\rho)^{\frac{1}{2}}. \tag{A.11}$$

Some data of $c_h$ for liquids can be found in [31] and $c_h$ computed. No information is available concerning values $c_d$. Since, however, the propagation velocities are expected to be of the same order of magnitude one can assume $c_h = c_d = c_m$. This concept leads us to evaluations: $\tau_h = \tau_m/Pr$ and $\tau_d = \tau_m/Sc$, where $Pr$ and $Sc$ are Prandtl and Schmidt numbers, respectively. For usual liquids where times $\tau_m$ change in the range of $10^{-10}$–$10^{-12}$ s one has the values: $Pr = 1$–$10^3$ [32] and $Sh = 10^2$–$2 \times 10^3$ [33] with notion that times $\tau_h$ and $\tau_d$ are often much shorter than $\tau_m$, c.f. [31]. Some data on *effective* relaxation times $\tau_d$ were given by Luikov [13] for colloidal capillary porous bodies, who found them to be of order of $10^{-4}$ s.

At present no general criterion is available concerning necessity of including relaxation terms in equations of change. Cases are usually cited [13, 23, 28, 34], when these terms should be significant: viscoelastic fluids, capillary porous bodies, dispersed systems, rarefied gases, helium II; especially for high-rate unsteady state processes. Experiments confirming wave nature of heat, equation (A.5), can be found in [34] and [35].

# PRINCIPES VARIATIONELS DE TYPE CLASSIQUE POUR LES MECANISMES DE TRANSPORT IRREVERSIBLES, NON COUPLES ET INSTATIONNAIRES, AVEC CONVECTION ET RELAXATION

**Résumé**—On présente une méthode unifiée qui conduit à de nouvelles fonctionnelles de type classique pour lesquelles les conditions nécessaires de stationnarité sont des équations hyperboliques linéaires, décrivant les transferts non couplés de quantité de mouvement, de chaleur et de masse dans un milieu incompressible. L'attention est portée sur la signification des fonctionnelles trouvées pour une description variationnelle des mécanismes de transfert irréversibles, spécialement celles qui concernent les effets de relaxation. On développe l'applicabilité des méthodes variationnelles directes pour trouver les champs instationnaires de température, de concentration, de mesure et de vitesse.

# DAS VARIATIONSPRINZIP DER KLASSISCHEN FORM FÜR NICHT GEKOPPELTE INSTATIONÄRE IRREVERSIBLE TRANSPORTVORGÄNGE MIT KONVEKTION UND RELAXATION

**Zusammenfassung**—Zur Beschreibung des nicht gekoppelten Wärme-, Stoff- und Impulsaustausches wird eine einheitliche Methode vorgestellt, welche zu neuen Funktionen des klassischen Typs führt und für welche die notwendigen stationären Bedingungen durch lineare hyperbolische Differentialgleichungen gegeben sind. Besondere Beachtung findet die Bedeutung der Funktionen für eine Variationsbeschreibung irreversibler Transportvorgänge, insbesondere solche mit Relaxationseffekten. Die Anwendung des direkten Variationsprinzips zur Ermittlung instationärer Temperatur-, Konzentrations-, Druck- und Geschwindigkeitsfelder wird hervorgehoben.

# ВАРИАЦИОННЫЕ ПРИНЦИПЫ КЛАССИЧЕСКОГО ТИПА В ПРИЛОЖЕНИИ К НЕВЗАИМОСВЯЗАННЫМ НЕСТАЦИОНАРНЫМ НЕОБРАТИМЫМ ПРОЦЕССАМ ПЕРЕНОСА ПРИ КОНВЕКТИВНОМ ДВИЖЕНИИ И РЕЛАКСАЦИИ

**Аннотация** — Рассматривается унифицированный метод, позволяющий получить новые функционалы классического типа, для которых необходимыми условиями стационарности являются гиперболические дифференциальные уравнения, описывающие невзаимосвязанные процессы переноса тепла, массы и количества движения в несжимаемых средах. Особое внимание обращается на значение полученных функционалов для вариационного описания необратимых процессов переноса, в частности процессов, включающих эффекты релаксации. Подчеркивается возможность применения прямых вариационных методов для определения нестационарных полей температуры, концентрации, давления и скоростей.