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THE WAVE EQUATIONS FOR SIMULTANEOUS HEAT AND MASS TRANSFER IN MOVING MEDIA—STRUCTURE TESTING, TIME–SPACE TRANSFORMATIONS AND VARIATIONAL APPROACH

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Abstract—The functionals leading to the linear wave equations that govern heat conduction as well as simultaneous heat and mass transfer in moving media (in Eulerian representation) are obtained. These functionals are found simply by substituting equations of the time–space transformations into the functional of a quiescent medium which, in the general case, contains some matrix function as an important term. This function is associated with the matrix of the relaxation coefficients that appear in a general flux-force relationship, equation (41), which generalizes the Cattaneo equation [1] for a multi-potential case and which evolves into the classical Onsager [2] expression when the relaxation effects are neglected. A synthesis of the linear wave equations and corresponding variational principles is obtained together with many new results. The logically self-consistent mathematical theory of simultaneous heat and mass transfer involving relaxation effects is developed and its direct application to thermal diffusion in a two-component fluid is given. This theory shows, in matrix notation, an important and remarkable analogy to the theory of pure heat conduction with non-Fourier heat flux.

NOMENCLATURE

a,	heat diffusivity;
a_{ik},	element of matrix of scalar derivative transformation, e.g. temperature derivatives;
$\mathbf{B}$,	matrix function in equation (93);
C_p,	heat capacity;
$\mathbf{C}$,	thermostatic matrix of capacities;
c,	speed of light in vacuum;
c_0,	constant speed of propagation of second sound wave;
c_h,	$\equiv -C_p(T^0)^2$, thermal capacity;
c_{ik},	capacities of the medium, equations (48) and (49);
D, D_T,	diffusion and thermal diffusion coefficients, respectively;
$\mathbf{E}$,	unit matrix;
G,	modulus of shear rigidity;
h,	enthalpy of mass unit;
$i, j, k, 1$,	indices of coordinates;
h_1, h_2,	partial enthalpies of components 1 and 2;
$\mathbf{J}_h, \mathbf{J}_q$,	vector of density of pure heat flux and irreversible energy flux, respectively;
$\mathbf{J}_q^*$,	heat flux in binary system;
$\mathbf{J}_1, \ldots, \mathbf{J}_{n-1}$,	vectors of densities of diffusive mass fluxes (components $1, \ldots, n-1$);
$\mathbf{J}$,	$= \text{col}\,(\mathbf{J}_1, \mathbf{J}_2, \ldots, \mathbf{J}_{n-1}, \mathbf{J}_n = \mathbf{J}_q)$, column matrix of all independent fluxes;
$\mathbf{K}(t-t')$,	matrix describing relaxation nucleus, equation (35);
$\mathbf{L}$,	Onsager's matrix with elements L_{ik};
$\mathbf{l}$,	$= \text{col}\,(t, x_1, x_2, x_3)$, column matrix of time–space coordinates;
L_h,	$= \lambda(T^0)^2$, Onsager's coefficient for pure heat transfer;
M_1, M_2,	molar mass of components 1 and 2;
$\mathbf{r}$,	$= (x, y, z)$, radius vector;
S,	action functional;
s,	entropy of mass unit;
T,	temperature;
T^0,	reference temperature at which coefficients of linear differential equations are evaluated;
t,	time;
$\mathbf{u}$,	$= \text{col}\left(\dfrac{\mu_n-\mu_1}{T}, \ldots, \dfrac{\mu_n-\mu_{n-1}}{T}, \dfrac{1}{T}\right)$, column matrix of transfer potentials;
$\mathbf{v}$,	$= (v_x, v_y, v_z)$, constant Cartesian velocity of medium investigated;
V,	volume;
$\mathbf{X}_k$,	thermodynamic force, equation (34), $k = 1, 2, \ldots, n$;
$\mathbf{X}$,	$= \text{col}\,(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_{n-1}, \mathbf{X}_n = \mathbf{X}_q)$, column matrix of thermodynamic forces;
x, y, z,	Cartesian coordinates;
x_1, x_2, x_3,	arbitrary orthogonal coordinates considered;
y_j,	mass fraction of jth component;
y_j^0,	reference mass fraction of jth component at which coefficients of linear differential equations are evaluated;
$\mathbf{z}$,	$= \text{col}\,(y_1, y_2, \ldots, y_{n-1}, h)$, column matrix of thermodynamic state of mixture;
∇^2,	Laplace operator;
Δ,	increment, excess with respect to reference state;

$\Box$,	d'Alembert's operator, $\Box = \nabla^2 - \frac{\partial^2}{c^2 \partial t^2}$;
$\Box_0$,	d'Alembert's operator based on second sound speed.

Greek symbols

γ,	$= (1 - v^2/c^2)^{-1/2}$
γ_0,	$= (1 - v^2/c_0^2)^{-1/2}$, coefficients in equations of transformations II and III, resp.;
δ,	variational symbol;
ρ,	mass density;
τ,	matrix of relaxation coefficients;
τ_d, τ_h, τ_T,	relaxation times for diffusion, heat and thermal diffusion, respectively;
μ_m,	chemical potential of component m;
$\bar{\Lambda}$,	Lagrangian;
λ,	heat conductivity;
$\lambda_1, \ldots, \lambda_n$,	eigenvalues of matrix $\mathbf{A}$.

Superscripts

$'$,	proper frame, in which medium rests;
0,	reference state at which coefficients are computed;
T,	transpose matrix;
$*$,	new fluxes, forces and capacities.

Subscripts

h,	heat;
0,	related to speed c_0;
p,	pressure;
q,	energy in coupled process.

1. INTRODUCTION

THE PRESENCE of relaxation terms in the non-Fourier type phenomenological equations, which link together the fluxes and gradients of the transfer potentials, leads to wave (hyperbolic) partial differential equations of change. The basic feature of the wave equations is that the local disturbance of any transfer potential in any originally homogeneous medium propagates with a finite speed c_0. Thanks to this fact, there exist two regions in this medium, at a definite instant of time, namely, the disturbed region, in which physical changes are already observed, and the undisturbed region, in which the medium is not altered. This explains the physical paradox of an infinite speed of disturbances resulting from standard parabolic equations, which has been noted by Luikov [3,4], Cattaneo [1], Vernotte [5], Kaliski [6] and others. A thoughtful discussion of the qualitative properties of the heat equations with finite propagation of disturbances is provided by Hamil and Baumeister [7] as well as by Berkovsky and Bashtovoi [8]. Solutions, which describe the mass transfer, have been given, among others, by Luikov, Bubnov and Soloviej [4,9]. A number of other contributors are listed in the earlier work of the present author [10], which the reader is referred to before reading this paper.†

For the case of pure heat conduction in quiescent media, the form of the wave equations quoted in literature is well defined, cf. [4,6]. However, as regards heat conduction in moving media, the form of the wave equations is not determined definitely; as we shall see later, equations given in various papers differ from one another. As far as coupled transport processes are concerned, i.e. when there is a simultaneous heat and mass transfer, the differences in the form of the wave equations are observed for both the moving and quiescent media.

Therefore, the objective of the present paper is to provide a unified and systematic method which will explain the differences in the basic forms of the linear wave equations for moving media and also will facilitate the derivation of wave equations of the coupled heat and mass transfer (in quiescent and moving systems) in a uniform way. This method will exploit a variational approach and it will also apply, in a moving medium case, the equations which describe the time and space variable transformations (linking these variables in stationary and moving frames) into the functionals describing a physical system in its proper frame. The operator description used will allow direct application of the present results to the case when the arbitrary orthogonal curvolinear coordinates are employed.

The solids and fluids are considered which are characterized by a single mechanism of an isobaric transport of energy and mass moving with a constant velocity. The constancy of the internal and transport properties (e.g. densities, capacities, diffusivities, Onsager coefficients, relaxation times, etc.) is assumed and viscous dissipation is neglected.† This constancy indicates that the assumptions typical of a linear description are accepted. Consequently, it will be assumed that every coefficient of the wave equation investigated is evaluated in some reference state (T^0, y_i^0) defined within the region considered. It will be shown that under this assumption, the wave equations based on various transfer potentials (e.g. on temperature T and the temperature reciprocal T^{-1}) can be precisely transformed analytically into one another, if the usual irreversible thermodynamics requirement of not too large gradients is satisfied for both space and time derivatives.

In most cases the differences between various forms of the linear wave equations are observed mainly in those equations that concern the moving

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†In [10] the variational principles for uncoupled transfer processes are discussed and, therefore, it will serve as an excellent introduction to the more advanced treatment performed here, which includes both the analysis of the coupled processes and some invariancy tests.

†In [10], the method of taking into account some velocity distribution with the help of a linearized equation of motion is discussed. It is omitted here since the assumption of constancy of v does not influence the form of wave equations obtained for heat and mass transfer.

media. These differences constitute the first principal object of our interest in the present work.

However, in the case of a simultaneous heat and mass transfer, the rigorous self-consistent mathematical theory of wave equations has not been developed as yet even for a resting medium. Therefore, the formulation of such a theory for a quiescent multicomponent fluid, and its extension to moving media, is the second basic object of this work.

The three kinds of generalization of the most popular linear hyperbolic heat equation [see equation (2) in Section 2 for heat conduction in a quiescent solid] are available in literature, these generalizations being concerned with moving medium. These are presented below in an abbreviated form with the use of the first and second substantial derivative operators.†

The first of the generalized equations is

$$\frac{1}{a}\frac{\mathrm{d}T}{\mathrm{d}t}-\nabla^2 T+\frac{1}{c_0^2}\frac{\mathrm{d}^2T}{\mathrm{d}t^2}=0, \tag{A}$$

see [11]. The second has the form:

$$\begin{gathered}\frac{1}{a}\frac{\mathrm{d}T}{\mathrm{d}t}-\Box T+\left(\frac{1}{c_0^2}-\frac{1}{c^2}\right)\gamma^2\frac{\mathrm{d}^2T}{\mathrm{d}t^2}=0\\ \gamma\equiv(1-v^2/c^2)^{-1/2},\end{gathered} \tag{B}$$

see Kranys' work [12]. The latter equation is a relativistic one, so it deals with the two characteristic speed values: the speed of light in vacuum, c, and the speed of heat wave propagation, c_0, measured in a quiescent medium (proper frame). The last, third, equation is as follows:

$$\frac{1}{a}\frac{\mathrm{d}T}{\mathrm{d}t}-\nabla^2 T+\frac{\partial^2 T}{c_0^2\partial t^2}=0; \tag{C}$$

cf. [10] as well as the mathematical analogs of this equation given by Kar [13] for velocity potential.

Equations (A)–(C) were obtained by different methods and in each case under different physical assumptions. Equation (A) was derived by Bubnov [11] as a result of the statistical analysis of a monoatomic gas. Equation (B), however, was found [12] after some reasoning which has led to the invariant form of the Cattaneo equation (cf. [1]) and the energy conservation equation in time–space x, y, z, ct, followed by their combination. Finally, equation (C) was derived by the author [10] as a result of the variational approach. It is quite clear that equations (A)–(C) are not equivalent, therefore it is advisable to examine the physical assumptions underlying each of them (of course apart from the already discussed assumption which refers to the constancy of thermal coefficients being common for all of the equations). Such an examination should reveal some generality in the method of obtaining the wave equations for moving media especially useful in a more difficult (and much less familiar) multipotential case when there is a coupled heat and mass transfer. Furthermore, such an examination should explain the present status of the theory investigated and adjust the material known so far.

A complicated form of the heat- and mass-transfer equations (either of a parabolic or of a hyperbolic type) makes these equations difficult to solve. Therefore, it is worthwhile to consider simultaneously the variational principles leading to the wave equations. By obtaining the appropriate functionals, approximate fields of the transfer potentials can be found with the use of the direct variational methods [14, 15]. It is essential to note that for conventional (parabolic) equations of the non-stationary transport processes no classically defined functionals have been found although there are many non-classic variational methods such as the local potential method [16]. On the other hand, the classical principles of non-stationary wave transport equations do exist as it has been shown in [17, 18] and [10] for the uncoupled transfer processes.

In the present paper the hitherto existing considerations leading to such principles will be generalized. This will permit the derivation of many new variational principles. They will describe the coupled heat and mass transport processes in moving media. The way of deriving them is to employ equations describing transformations of the time and space coordinates in the functionals characterizing quiescent media.

The important fact, which will be used below, is the invariancy of the variational principle, $\delta S = 0$, with respect to the transformations of independent variables x, y, z, t [19]. Hence, in order to obtain the functional of the moving medium it is sufficient to know the adequate functional for a quiescent medium and then to express its space and time variables in space and time variables for a moving medium. This is in essence an approach resulting directly from the special relativity principle [20, 21]. The functional S obtained in such a way leads to partial equations of heat and mass transfer in moving media, which can be easily checked by writing down the appropriate Euler equations.

2. TIME–SPACE TRANSFORMATIONS AND VARIATIONAL PRINCIPLES FOR HEAT CONDUCTION

The method in question will be illustrated first for the simplest case of heat conduction in a moving solid body. To do this, we shall employ the known [17, 10] functional which describes the non-stationary heat conduction in the coordinate frame in which the solid body rests. It is the so-called proper frame denoted here by primed symbols. In the case of a constant temperature on the boundaries of the system, the functional of heat conduction in the proper frame has the form:

$$S'=\frac{1}{2}\iiiint\left[\left(\frac{\partial T}{\partial t'}\right)^2\frac{1}{c_0^2}-(\mathrm{grad}'\,T)^2\right]\times\exp\left(\frac{c_0^2t'}{a}\right)\mathrm{d}V'\,\mathrm{d}t', \tag{1}$$

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†These operators are defined by equations (13) and (16) of the present paper.

while its stationarity condition (Euler equation) is the following equation of heat conduction in a resting solid:

$$\frac{1}{a}\frac{\partial T}{\partial t'} - \nabla^2 T + \frac{\partial^2 T}{c_0^2 \partial t'^2} = 0. \tag{2}$$

The constants c_0 (thermal wave propagation velocity) and a (heat diffusivity) as well as the temperature $T' = T$ will always be understood as measured in the system in which a solid rests (the proper frame). Hence, they will not vary during transformations of the space coordinates, so primes will not be important for them.

The three kinds of time–space transformations will be employed. They express relations between the coordinates and time in the proper frame moving together with the solid (primed symbols) and the frame which is fixed in respect to the laboratory (non-primed symbols).

The first of the transformations (I) are the well-known Galillean transformations [20] having the following form:

$$\left.\begin{aligned} t &= t' && (3)\\ \mathbf{r} &= \mathbf{r}' + \mathbf{v}t' && (4)\end{aligned}\right\} \mathrm{I}$$

where $\mathbf{r} = (x, y, z)$ is the radius vector.

The next (II) are the relativistic generalized† Lorentz transformations (c.f. [20, 21])

$$\left.\begin{aligned} t &= \gamma\left(t' + \frac{\mathbf{rv}}{c^2}\right) && (5)\\ \mathbf{r} &= \mathbf{r}' - \mathbf{v}\left[\frac{\mathbf{r'v}(1-\gamma)}{v^2} - \gamma t\right] && (6)\\ &\text{where}\\ \gamma &= (1 - v^2/c^2)^{-1/2} && (7)\end{aligned}\right\} \mathrm{II}$$

and c is the speed of light in vacuum. Although such exact transformations are not needed in engineering practice, we shall consider them though for the theoretical and methodological reasons.

Transformations inverse to (5) and (6) will also be used. They have the form [20]

$$t' = \gamma\left(t - \frac{\mathbf{rv}}{c^2}\right) \tag{8}$$

$$\mathbf{r}' = \mathbf{r} + \mathbf{v}\left[\frac{\mathbf{rv}(\gamma - 1)}{v^2} - \gamma t\right]. \tag{9}$$

The third type of transformations (III) is constituted by those which are based on Kar's concepts [13], i.e. the "acoustic" transformations. They have the forms that are analogous to (5)–(9) but the basic speed is c_0 which is the speed of heat wave propagation instead of c [the factor $\gamma_0 = (1 - v^2/c_0^2)^{-1/2}$ is then used].

It should be emphasized that only transformations II yield a precise physical description. Transformations I, as is well known, are precise enough only if $v \ll c$. Similarly, transformations III are sufficiently precise only in the case when $v \ll c_0$ (since c_0 is of the order of sound velocity, transformations III are practically applicable only to subsonic flows). Because all of these inequalities are fulfilled in the majority of practical cases and the non-relativistic equations are always more simple, it is useful to discuss the heat-transfer equations derived on the basis of all the three kinds of transformations.

The first (time or space coordinate) partial derivatives of any scalar, particularly of temperature T, are transformed according to the following rule:

$$\frac{\partial T}{\partial l'_i} = \sum_{k=0}^{3} a_{ik}\frac{\partial T}{\partial l_k}, \tag{10}$$

for $i = 0, 1, 2, 3$ where l_i are the elements of the column matrix

$$\mathbf{l} = \mathrm{col}\,(t, x_1, x_2, x_3), \tag{11}$$

while $a_{ik} = \partial l_k/\partial l'_i$ are the elements of the Jacobi matrix corresponding respectively to transformations I, II or III. For the second partial derivatives of any scalar the following rule holds:

$$\frac{\partial^2 T}{\partial l'_i \partial l'_k} = \sum_{m=0}^{3}\sum_{j=0}^{3} a_{im}a_{kj}\frac{\partial^2 T}{\partial l_m \partial l_j}, \tag{12}$$

where $a_{im} = \partial l_m/\partial l'_i$ and $a_{kj} = \partial l_j/\partial l'_k$.

By substituting equations (3) and (4) into (10)–(12) it may be proved that when coming to a reference system in which the solid is in motion (non-primed) the following relations (transformations rules) are valid for transformations I:

$$\frac{\partial T}{\partial t'} = \frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T \equiv \frac{\mathrm{d}T}{\mathrm{d}t} \tag{13}$$

$$\mathrm{grad}'\,T = \mathrm{grad}\,T \tag{14}$$

$$(\nabla^2 T)' = \nabla^2 T \tag{15}$$

$$\frac{\partial^2 T}{\partial t'^2} = \frac{\partial^2 T}{\partial t^2} + 2\mathbf{v}\,\mathrm{grad}\left(\frac{\partial T}{\partial t}\right) + \mathbf{v}\,\mathrm{grad}(\mathbf{v}\,\mathrm{grad}\,T) \tag{16}$$

$$\mathrm{d}V' = \mathrm{d}V;\quad \mathrm{d}t' = \mathrm{d}t. \tag{17}$$

Formulas (13) and (16) mean that the first and second partial derivatives of a scalar are converted in the laboratory (non-primed) frame, respectively, into the first and second substantial derivative. Calculating $\mathrm{d}^2T/\mathrm{d}t^2$ as

$$\begin{aligned}\frac{\mathrm{d}^2T}{\mathrm{d}t^2} &= \left(\frac{\partial}{\partial t} + \mathbf{v}\,\mathrm{grad}\right)\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right)\\ &= \frac{\partial^2 T}{\partial t^2} + 2\mathbf{v}\,\mathrm{grad}\,\frac{\partial T}{\partial t}\\ &\qquad + \mathbf{v}\,\mathrm{grad}\,(\mathbf{v}\,\mathrm{grad}\,T) + \frac{\partial \mathbf{v}}{\partial t}\,\mathrm{grad}\,T,\end{aligned} \tag{16a}$$

the reader can check that the central expression of (16) describes the expanded form of the second substantial derivative when $\mathbf{v} = \text{constant}$ (inertial frame).

For transformations II the following rules are

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†The velocity $\mathbf{v}$ is not, in general, parallel to the one of the space axes.

obtained with the help of equations (5)–(7) and (10)–(12):†

$$\frac{\partial T}{\partial t'} = \gamma\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right) \equiv \gamma\frac{\mathrm{d}T}{\mathrm{d}t} \qquad (18)$$

$$(\mathrm{grad}'\,T)^2 - \frac{1}{c^2}\left(\frac{\partial T}{\partial t'}\right)^2 = (\mathrm{grad}\,T)^2 - \frac{1}{c^2}\left(\frac{\partial T}{\partial t}\right)^2 \qquad (19)$$

$$\Box' T = \Box T \qquad (20)$$

$$\frac{\partial^2 T}{\partial t'^2} = \gamma^2\left[\frac{\partial^2 T}{\partial t^2} + 2\mathbf{v}\,\mathrm{grad}\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}(\mathbf{v}\,\mathrm{grad}\,T)\right] = \gamma^2\frac{\mathrm{d}^2 T}{\mathrm{d}t^2} \qquad (21)$$

$$\mathrm{d}V'\mathrm{d}t' = \mathrm{d}V\mathrm{d}t. \qquad (22)$$

In the case of transformations III, the formulas analogous to (18)–(22) are valid, in which γ_0 replaces γ, c_0 replaces c and the d'Alembert operator is defined as $\Box_0 T$, i.e. it is based on the heat wave propagation velocity c_0. Because of this close resemblance, the writing of appropriate formulas is left to the reader.

By employing formulas (3)–(4) and (13)–(17) in functional (1), the following functional for heat conduction in a moving solid can be found:

$$S = \frac{1}{2}\iiiint\left[\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right)^2\frac{1}{c_0^2} - (\mathrm{grad}\,T)^2\right]\exp\left(\frac{c_0^2 t}{a}\right)\mathrm{d}V\mathrm{d}t, \qquad (23)$$

which is invariant with respect to any Galillean transformation describing the transition from one inertial system to another (both systems may be in motion relative to the observer). The condition of stationarity for the functional (23) (Euler equation) is the following wave equation of heat conduction in a moving solid:

$$\frac{1}{a}\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right) - \nabla^2 T + \frac{1}{c_0^2}\left[\frac{\partial^2 T}{\partial t^2} + 2\mathbf{v}\,\mathrm{grad}\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}(\mathbf{v}\,\mathrm{grad}\,T)\right] = 0. \qquad (24)$$

A concise form of equation (24) is obtained by using the operators of the first and the second substantial derivatives [see the RHS's of equations (13) and (16)] as well as the Laplace operator which gives:

$$\frac{1}{a}\frac{\mathrm{d}T}{\mathrm{d}t} - \nabla^2 T + \frac{1}{c_0^2}\frac{\mathrm{d}^2 T}{\mathrm{d}t^2} = 0, \qquad (25)$$

i.e. equation (A) in the Introduction. Although equation (25) is natural and simple generalization of equation (2), the functional (23), which leads to this generalization, is not known in the hitherto-published papers (the functionals known so far are not Galillean but, as we shall see later, they correspond to transformation III). Similarly, the functional which generalizes equation (1) in the relativistic case (transformation II) is not known either. Based on the above-given results, this functional is, however, easy to obtain. It is enough to note that equation (1) can be rewritten in the form:

$$S' = \frac{1}{2}\iiiint\left\{\left(\frac{\partial T}{\partial t'}\right)^2\left(\frac{1}{c_0^2} - \frac{1}{c^2}\right) - \left[(\mathrm{grad}'\,T)^2 - \frac{1}{c^2}\left(\frac{\partial T}{\partial t'}\right)^2\right]\right\} \times \exp\left(\frac{c_0^2 t'}{a}\right)\mathrm{d}V'\mathrm{d}t', \qquad (26)$$

for which the invariant structure of equation (19) is easily exploited. Using in addition formulas (8) and (22) in equation (26) results in the following functional for heat conduction in a moving solid:

$$S = \frac{1}{2}\iiiint\left[\gamma^2\left(\frac{1}{c_0^2} - \frac{1}{c^2}\right)\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right)^2 - (\mathrm{grad}\,T)^2 + \frac{1}{c^2}\left(\frac{\partial T}{\partial t}\right)^2\right] \times \exp\left[\left(\frac{c_0^2\gamma}{a}\right)\left(t - \frac{\mathbf{v}\mathbf{r}}{c^2}\right)\right]\mathrm{d}V\mathrm{d}t. \qquad (27)$$

The functional (27) is invariant with respect to transformations II used for any two inertial systems (with regard to the rule of velocity addition corresponding to this transformation). The condition of stationarity of the functional (27) is the following Euler equation:

$$\frac{\gamma}{a}\left(\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}\,T\right) - \left(\nabla^2 T - \frac{\partial^2 T}{c^2\partial t^2}\right) + \left(\frac{1}{c_0^2} - \frac{1}{c^2}\right)\gamma^2\left[\frac{\partial^2 T}{\partial t^2} + 2\mathbf{v}\,\mathrm{grad}\frac{\partial T}{\partial t} + \mathbf{v}\,\mathrm{grad}(\mathbf{v}\,\mathrm{grad}\,T)\right] = 0 \qquad (28)$$

or, after introducing operators of the first and second substantial derivatives and the d'Alembert operator:

$$\frac{\gamma}{a}\frac{\mathrm{d}T}{\mathrm{d}t} - \Box T + \left(\frac{1}{c_0^2} - \frac{1}{c^2}\right)\gamma^2\frac{\mathrm{d}^2 T}{\mathrm{d}t^2} = 0, \qquad (29)$$

i.e. equation (B). Equation (29) is known from literature. It has been obtained by Kranys [12] who used a different method in which an invariant form of the Cattaneo–Vernotte equation [see equation (72)] in a time-space ct, x_1, x_2, x_3 was combined with the energy conservation law. However, the variational principle [functional (27)] has not yet been known. It leads to equation (29). As is seen, the form of the functional (27) is somewhat complicated and it is only the systematic approach used which

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†Many of the formulas given here are imparted with the properties of three- or four-dimensional geometry corresponding to transformations I, II or III. The method described in this paper may turn out to be not always the most effective one but it is the most elementary since it does not require the knowledge of these geometries or the tensor calculus.

makes the finding of the functional possible. Note that if it is assumed that $c \to \infty$, then equations (27) and (28) are, as is expected, simplified respectively into equations (23) and (24).

The simplest functional and the corresponding wave equations are obtained in the case when transformation III is used (this is the only reason for employing this transformation at all). Since it is based on the heat propagation velocity c_0, the factor in brackets before the exponential term of equation (1) is transformed invariantly. The exponential term itself has the form (30) [according to equation (8) for $\gamma = \gamma_0$ and $c = c_0$]:

$$\exp\left[\frac{c_0^2\gamma_0}{a}\left(t - \frac{\mathbf{vr}}{c_0^2}\right)\right] = \exp\left[\frac{\gamma_0(c_0^2 t - \mathbf{vr})}{a}\right]. \quad (30)$$

Finally, equation (1), upon using transformation III, is transformed into the following form:

$$S = \iiiint \left[\left(\frac{\partial T}{\partial t}\right)^2 \frac{1}{c_0^2} - (\operatorname{grad} T)^2\right] \times \exp\left(\frac{c_0^2 t - \mathbf{vr}}{\gamma_0^{-1} a}\right) \mathrm{d}V \,\mathrm{d}t. \quad (31)$$

The Euler equation for the above functional is

$$\frac{\gamma_0}{a}\left(\frac{\partial T}{\partial t} + \mathbf{v} \operatorname{grad} T\right) - \left(\nabla^2 T - \frac{\partial^2 T}{c_0^2 \partial t^2}\right) = 0. \quad (32)$$

Considering that the use of transformation III has physical meaning only for small velocities ($v \ll c_0$), it can be assumed that in equations (31) and (32) $\gamma_0 \equiv (1 - v^2/c_0^2)^{-1/2} \cong 1$. Equations (31) and (32), simplified in such a manner, are known in literature [10, 17], see also equation (C).

The present approach helps to understand the fulfillment of the requirements of the special relativity principle [21] by the original equations given in [10]. Namely, they are invariant with respect to transformation III in the physically admissible case of small velocities ($v \ll c_0$). However, for velocities v comparable with the heat propagation speed, c_0, the mentioned equations, as well as equations (31) and (32), become meaningless. This limitation should be kept in mind despite the fact that the condition $v \ll c_0$ is fulfilled in the majority of practical cases.

For $v \ll c_0$, i.e. when $\gamma_0 \to 1$, equations (31) and (32) yield the simplest possible description of heat conduction in a moving solid, which ensures the consideration of the limited heat propagation speed c_0. In these, rather rare, cases where the velocities v are comparable with c_0, the more complex equations (23) and (24) are rather precise. They have wider range of applicability and become meaningless only for the velocities v comparable with the light speed c. For v close to c, the relativistic effects appear which are taken into account in equations (28) and (29).

Summarising the above, we conclude that the available linear hyperbolic equations have the form invariant with respect to one of the transformations, I, II or III. Thus, the unified approach presented here ascertains, classifies and explains some basic theoretical aspects. It will also be shown that this approach allows a number of unknown results to be obtained in the multipotential case involving the coupled heat and mass transfer in flowing fluids.

3. A DESCRIPTION OF COUPLED HEAT AND MASS TRANSFER FREE FROM THE PARADOX OF THE INFINITELY FAST DISTURBANCE PROPAGATION

For coupled processes it is necessary first to define the basic structures of the hyperbolic equations in a system at rest. Processes in a resting n-component mixture with mechanical equilibrium conditions (P = const) are now considered. In the present paper, we shall restrict ourselves to the wave equations consistent with such a form of the phenomenological equations (which link together the thermodynamic fluxes and forces) which are based on our generalization of the equation obtained by Shter [22] who modified Onsager's [2] classical relationships.

The Shter modification takes into account the relaxation phenomena and has the following form:

$$\mathbf{J}_i = \sum_{k=1}^{n} L_{ik} \int_0^t \mathbf{X}_k(t^0) K(t - t^0) \,\mathrm{d}t^0, \quad (33)$$

where $\mathbf{J}_i (i = 1, \ldots, n-1)$ is the density of the ith component flux, while $\mathbf{J}_n \equiv \mathbf{J}_q$ is the density of the irreversible energy flux. $\mathbf{X}_k$'s are the thermodynamic forces defined as:

$$\mathbf{X}_1 = \operatorname{grad}\left(\frac{\mu_n - \mu_1}{\mathrm{T}}\right), \ldots, \mathbf{X}_{n-1} = \operatorname{grad}\left(\frac{\mu_n - \mu_{n-1}}{\mathrm{T}}\right),$$

$$\mathbf{X}_n \equiv \mathbf{X}_q = \operatorname{grad}\left(\frac{1}{T}\right), \quad (34)$$

where μ_k is a chemical potential of the kth component. The function $K(t - t^0)$ denotes the so-called relaxation nucleus and it is the scalar function in Shter's original formulation [22]. It leads to a most approximate conclusion about a single relaxation time being common for all the fluxes.

In the present paper Shter's equation is generalized in the supposition that the relaxation nucleus is some matrix function $K(t - t^0)$, defined below, and it was shown that this concept leads to a more proper conclusion about the matrix of the relaxation coefficients.† The generalized equation (33) has the following matrix form:

$$\mathbf{J} = \int_0^t \mathbf{K}(t - t^0) \mathbf{L} \mathbf{X} \,\mathrm{d}t^0 \quad (\mathbf{L} = \text{constant}), \quad (35)$$

where

$$\mathbf{J} = \operatorname{col}(\mathbf{J}_1, \mathbf{J}_2, \ldots, \mathbf{J}_n \equiv \mathbf{J}_q)$$
$$\text{and} \quad \mathbf{X} \equiv \operatorname{col}(\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n \equiv \mathbf{X}_q) \quad (36)$$

(the matrix notation follows de Groot [2] description of the vector set $\mathbf{J}_1, \ldots, \mathbf{J}_q$ and $\mathbf{X}_1, \ldots, \mathbf{X}_q$).

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†The elements of this matrix can be computed with the help of equation (57) in this paper. They are generally called the relaxation coefficients, but not the relaxation times, since only diagonal elements have always the time dimension.

If it is assumed that the relaxation nucleus matrix, $\mathbf{K}(t-t^0)$, is equal to the product of the delta function and unit matrix $\mathbf{E}$, i.e. $\mathbf{K}(t-t^0) = \delta(t-t^0)\mathbf{E}$, then relations (35) evolve into the classical Onsager relations:

$$\mathbf{J} = \mathbf{L}\mathbf{X} \tag{37}$$

or

$$\mathbf{J}_i = \sum_{i=1}^{n} L_{ik}\mathbf{X}_k. \tag{38}$$

For an alternative form of the relaxation nucleus (containing the matrix exponential function,† $\exp[-\tau^{-1}(t-t^0)]$), i.e. for the form

$$\mathbf{K}(t-t^0) = \tau^{-1}\exp[-\tau^{-1}(t-t^0)], \tag{39}$$

relationship (35) can be written as

$$\exp[\tau^{-1}t]\tau\mathbf{J} = \int_0^t \exp(\tau^{-1}t^0)\mathbf{L}\mathbf{X}\,\mathrm{d}t^0. \tag{40}$$

Differentiating both sides of equation (40) with respect to t and simplifying the exponential term (the exponential matrix is non-singular) give the following matrix equation for a resting system:

$$\tau\frac{\partial \mathbf{J}}{\partial t} + \mathbf{J} = \mathbf{L}\mathbf{X} \tag{41}$$

or

$$\sum_{k=1}^{n} \tau_{ik}\frac{\partial \mathbf{J}_k}{\partial t} + \mathbf{J}_i = \sum_{k=1}^{n} L_{ik}\mathbf{X}_k$$

$$(i = 1,2,\ldots,n,\ \mathbf{J}_n \equiv \mathbf{J}_q,\ L_{ik} = L_{ki}). \tag{42}$$

Equation (42) represents generalization of the phenomenological Cattaneo–Vernotte relationship [see equation (72)] for a coupled multipotential process.

Taking the divergence operator for (42) and employing the mass and energy conservation equations, i.e.

$$\rho\frac{\partial y_i}{\partial t} = -\mathrm{div}\,\mathbf{J}_j \quad (j = 1,2,\ldots,n-1) \tag{43}$$

$$\rho\frac{\partial h}{\partial t} = -\mathrm{div}\,\mathbf{J}_q, \tag{44}$$

where y_i is the mass fraction of a component, h the enthalpy of mass unit yield the following system of wave equations for mass and energy transfer in a quiescent medium:

$$\sum_{m=1}^{n-1} \rho\tau_{jm}\frac{\partial^2 y_m}{\partial t^2} + \rho\tau_{jq}\frac{\partial^2 h}{\partial t^2} + \rho\frac{\partial y_j}{\partial t} + \sum_{m=1}^{n-1} L_{jm}\nabla^2\left(\frac{\mu_n-\mu_m}{T}\right) + L_{jq}\nabla^2\left(\frac{1}{T}\right) = 0 \tag{45}$$

$$\sum_{m=1}^{n-1} \rho\tau_{qm}\frac{\partial^2 y_m}{\partial t^2} + \rho\tau_{qq}\frac{\partial^2 h}{\partial t^2} + \rho\frac{\partial h}{\partial t} + \sum_{m=1}^{n-1} L_{qm}\nabla^2\left(\frac{\mu_n-\mu_m}{T}\right) + L_{qq}\nabla^2\left(\frac{1}{T}\right) = 0. \tag{46}$$

An equivalent matrix form of equations (45) and (46) is

$$\rho\boldsymbol{\tau}\frac{\partial^2 \mathbf{z}}{\partial t^2} + \rho\frac{\partial \mathbf{z}}{\partial t} + \mathbf{L}\nabla^2\mathbf{u} = 0 \tag{47}$$

where

$$\mathbf{z} \equiv \mathrm{col}(y_1, y_2, \ldots, y_{n-1}, h);$$

$$\mathbf{u} \equiv \mathrm{col}\left(\frac{\mu_n-\mu_1}{T}, \frac{\mu_n-\mu_2}{T}, \ldots, \frac{\mu_n-\mu_{n-1}}{T}, \frac{1}{T}\right). \tag{47a}$$

The coefficients of equations (45) and (46) are linked with the coefficients of equation (42) as:

$$L_{jq} \equiv L_{jn} \text{ for } j \equiv 1,2,\ldots,n-1 \text{ and } L_{qq} = L_{nn}.$$

In the general equation (47), there are no assumptions regarding the matrix of the relaxation coefficients τ_{ik}.

In equations (45) and (46) the mass fractions y_i and the enthalpy h are functions of the transfer potentials $(\mu_n-\mu_m)/T$ $(m = 1,\ldots,n-1)$ and $1/T$. Thus, in order to go over to the group of independent variables, the first of the variables (y_i, h) are expressed in terms of the other. The differentials $\mathrm{d}y_j$ and $\mathrm{d}h$ are described by the equations:

$$\mathrm{d}y_j = \sum_{m=1}^{n-1} c_{jm}\,\mathrm{d}\left(\frac{\mu_n-\mu_m}{T}\right) + c_{jq}\,\mathrm{d}\left(\frac{1}{T}\right) \tag{48}$$

$$\mathrm{d}h = \sum_{m=1}^{n-1} c_{qm}\,\mathrm{d}\left(\frac{\mu_n-\mu_m}{T}\right) + c_{qq}\,\mathrm{d}\left(\frac{1}{T}\right), \tag{49}$$

where the coefficients c_{ik} are the so-called capacities, i.e. the first-order derivatives of y_j and the enthalpy h in relation to the transfer potentials. As for the constant pressure, the following thermodynamical relation is valid:

$$\mathrm{d}\left(\frac{\mu_n}{T}\right) = h\,\mathrm{d}(1/T) + \sum_{m=1}^{n-1} y_m\,\mathrm{d}\left(\frac{\mu_n-\mu_m}{T}\right), \tag{50}$$

then the capacities are the second-order partial derivatives of the function μ_n/T with respect to variables $(\mu_n-\mu_m)/T$ $(m = 1,2,\ldots,n-1)$ and $1/T$. This means that they fulfill the symmetry relations $c_{ik} = c_{ki}$, $(i,k = 1,2,\ldots,n)$, similar to the Onsager symmetry relations $L_{ik} = L_{ki}$. The matrix form of equations (48) and (49) is:

$$\mathrm{d}\mathbf{z} = \mathbf{C}\,\mathrm{d}\mathbf{u}. \tag{51}$$

Substituting equation (51) into equation (47) and assuming that the coefficients c_{ik} and Onsager's coefficients L_{ik} are constants which are evaluated at the same reference state $(T^0, y_1^0, \ldots, y_{n-1}^0)$ defined within the region considered (the assumption typical of the linear thermodynamics), the following linear matrix equation is obtained:

$$\rho\tau\mathbf{C}\frac{\partial^2 \mathbf{u}}{\partial t^2} + \rho\mathbf{C}\frac{\partial \mathbf{u}}{\partial t} + \mathbf{L}\nabla^2\mathbf{u} = 0. \tag{52}$$

The two symmetrical matrices are linked with this equation, namely: the positively-determined kinetic

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†The basic properties of functions of this kind are given in the Appendix.

Onsager matrix, $\mathbf{L} = [L_{ik}]$, and "thermostatic" matrix of capacities, $\mathbf{C} = [c_{ik}]$. It is meaningful that the matrix $\mathbf{C}$ is negatively determined, because it is that very matrix which appears in the fluctuation theory for a square approximation of entropy deficiency of closed system caused by the lack of thermodynamical equilibrium in the system,† see [2, 16].

4. COMPUTATION OF THE RELAXATION COEFFICIENTS τ_{ik}

The phenomenological equation (41) or (42) and also the wave equation (47) or (52) are equally well applicable when the matrix of the relaxation coefficients τ is given independently of the matrices $\mathbf{L}$ and $\mathbf{C}$ as well as when there is some relationship between the elements of these three matrices.

For ideal gases, this relationship is a consequence of the fact that the speed of propagation of thermal and mass waves (and also of a momentum wave) are identical, i.e. that the propagation speed, c_0, has a scalar nature. This identity is a result of the kinetic theory, see [24, 26, 27, 10], and holds for the molecular transport of heat, mass and momentum. It appears [23, 27] that the propagation speed is of the order of sound speed under the given conditions.

For liquids and solids, the assumption about the scalar nature of the propagation speed is a hypothesis, which might be partially supported by comparing the relaxation times data for heat transfer τ_h given in [28]‡ with those for momentum transfer τ_m, evaluated in [29]. It turns out that ratios τ_m/τ_h are of the order of Prandtl number in accordance with the hypothesis. However, it is clear that such a hypothesis can be valid only in the case of the same mechanism of heat and mass transport (as assumed in Section 1 of the present paper). Consequently, it is expected that the hypothesis will apply in homogeneous fluids (with thermal diffusion occurring as a cross-effect) and that it may not be true, for example, for the drying processes where a multiple mechanism of transport can occur. In this last case, the overall mechanism should be deduced from the partial mechanism to which our theory can apply.

Let us consider which of the restrictions on the matrices τ, $\mathbf{L}$ and $\mathbf{C}$ results from the condition of a scalar nature of c_0. That this could be accomplished, it must be remembered that such a restriction should also be valid for the case of pure heat transfer in a one-component fluid. In such a case the definitions of the thermal capacity coefficient, c_h, equation (49), and also the thermal conductivity λ lead to relations

$$c_h = -C_p(T^0)^2 \qquad (53)$$

$$L_h = \lambda(T^0)^2 = \rho C_p a (T^0)^2 = -\rho c_h a \qquad (54)$$

where a is the thermal diffusivity and C_p the well-known heat capacity.

In the case considered, the relaxation time for heat transfer, τ_h is a scalar related to the thermal diffusivity $a \equiv D_h$ by the known equation [4]:

$$\tau_h = \frac{a}{c_0^2}. \qquad (55)$$

Hence, substituting (54) into (55) yields

$$\tau_h = \frac{-L_h c_h^{-1}}{\rho c_0^2}. \qquad (56)$$

The above equation defines the thermal relaxation time, τ_h, in terms of the parameters we are interested in, i.e. L_h and c_h. The general matrix relationship sought (which links τ, $\mathbf{L}$ and $\mathbf{C}$) should also reduce to equation (56) when the fluid becomes one-component. For a scalar nature of the propagation speed, such a condition is fulfilled by the matrix relationship:

$$\tau = \frac{-\mathbf{L}\mathbf{C}^{-1}}{\rho c_0^2}. \qquad (57)$$

This enables one to compute the relaxation coefficients τ_{ik} on the basis§ of the capacities c_{ik}, equations (48) and (49), and the Onsager coefficients L_{ik}. The propagation speed appearing in equation (57) can be computed from the known formula [4]

$$c_0 = (G/\rho)^{1/2}, \qquad (58)$$

where G is the modulus of shear rigidity that can be found theoretically or experimentally [28, 29]. For ideal gases $G = P$, i.e. the modulus of shear rigidity is just a pressure [24] and hence $c_0 = (P/\rho)^{1/2}$ [26]. These results hold for the isobaric case (see [27] for some alternative consideration). In an isohoric process, C_v should rather appear instead of C_p in the energy equation and then, as shown in [23], the more proper result should be $c_0 = [(C_pP)/C_v\rho]^{1/2}$, the speed of sound. The sound speed is also suggested to be taken as a first approximation of c_0 in the case of liquids [28], where C_p is close to C_v, especially as an ultrasonic velocity at low frequencies (see example below).

Based on equation (51) and the data for Onsager's coefficient from [30], the data of capacities and relaxation times were found for an isothermal $Na_2SO_4/H_2SO_4/H_2O$ system in Michalski's MsD thesis [31] supervised by the present author. A sample of these data, based on the sound speed c_0 is given in Table 1 below.

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†It appears that in our (isobaric) case

$$\Delta S_{\text{closed}} \cong \frac{1}{2}\left\{\Delta\frac{1}{T}\,\Delta h + \sum_{k=1}^{n-1}\Delta\left(\frac{\mu_n - \mu_k}{T}\right)\Delta y_k\right\}$$

$$= \frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n} c_{ik}\Delta u_i \Delta u_k = \frac{1}{2}\delta^2 s$$

where $\delta^2 s$ is the second derivative of entropy which is always negative, c.f. [16] for more information.

‡The shear relaxation times given in [28] are overestimated and should not be considered.

§Note that $-\mathbf{L}\mathbf{C}^{-1}/\rho = \mathbf{D}$. Here $\mathbf{D}$ is the diffusivity matrix, in agreement with definition of $\mathbf{D}$ in [2]. Hence $\tau_{ik} = D_{ik}/c_0^2$, as in the case of pure heat transfer where $\tau_h = a/c_0^2$.

Table 1. Data of L_{ik}, c_{ik} and τ_{ik} for an isothermal $Na_2SO_4/H_2SO_4/H_2O$ system evaluated under the conditions $T = 298.3\,K$, $P = 10^5\,N\,m^{-2}$, $\rho = 1163\,kg\,m^{-3}$, $c_0 = 1387\,m\,s^{-1}$ and for molal concentrations $m_{Na_2SO_4} = m_{H_2SO_4} = 1.0832\,mol\,kg^{-1}_{H_2O}$ (the coefficients L_{12} and L_{21} were taken from experiments of [30]; hence there is some difference between L_{12} and L_{21})

$L_{ik}(kg^2\,KJ^{-1}\,m^{-1}\,s^{-1})$	$c_{ik}(kg\,KJ^{-1})$	$\tau_{ik}(s)$
$L_{11} = 9.9695 \times 10^{-10}$	$c_{11} = -6.3089 \times 10^{-4}$	$\tau_{11} = 0.6763 \times 10^{-15}$
$L_{12} = -3.4992 \times 10^{-10}$	$c_{12} = 0.3876 \times 10^{-4}$	$\tau_{12} = -0.4852 \times 10^{-15}$
$L_{21} = -3.1376 \times 10^{-10}$	$c_{21} = 0.3876 \times 10^{-4}$	$\tau_{21} = -0.1558 \times 10^{-15}$
$L_{22} = 8.0049 \times 10^{-10}$	$c_{22} = -2.3494 \times 10^{-4}$	$\tau_{22} = 1.4967 \times 10^{-15}$

It may be verified that the values of the diagonal relaxation coefficients equal by the order of magnitude those for isothermal binary systems Na_2SO_4/H_2O and H_2SO_4/H_2O, the latter being computed with the help of common definition $\tau_i = D_i c_0^{-2}$. It was found: $\tau_1 = 0.3535 \times 10^{-15}$ s, $\tau_2 = 0.9527 \times 10^{-15}$ s, respectively. Under the assumptions of the present work, heat relaxation time is $\tau_h = 0.663 \times 10^{-13}$ s.†

5. BASIC EQUATIONS OF COUPLED PROCESSES IN THE PRESENCE OF RELAXATION EFFECTS

Substituting expression (57) into the phenomenological equation (41) and into the wave equation (52) gives respectively the following matrix relationships

$$\mathbf{J} = \mathbf{L}\,\mathrm{grad}\,\mathbf{u} + \frac{\mathbf{L}\mathbf{C}^{-1}}{c_0^2}\partial\mathbf{J}/\partial t, \tag{59}$$

since $\mathbf{X} = \mathrm{grad}\,\mathbf{u}$, [see (34) and (47a)] and

$$\rho\mathbf{C}\frac{\partial\mathbf{u}}{\partial t} + \mathbf{L}\left(\nabla^2\mathbf{u} - \frac{\partial^2\mathbf{u}}{c_0^2\partial t^2}\right) = 0. \tag{60}$$

Equations (59) and (60) together with the following matrix equation [resulting from (43), (44) and (51)] describing conservation laws

$$\rho\mathbf{C}\frac{\partial\mathbf{u}}{\partial t} = -\nabla\mathbf{J}, \tag{61}$$

constitute the basic equations which characterize the coupled heat and mass transfer in the presence of relaxation effects. It can be readily seen that taking divergence of both sides of equation (59) and using the conservation law (61), the wave equation (60) is obtained.

In applications, the wave equation (60) is most important. Its solution at the pertinent boundary conditions for example

$$\mathbf{u}(x, y, z, 0) = \mathbf{u}_0(x, y, z) \tag{62}$$

$$\mathbf{u}(x_s, y_s, z_s, t) = \mathbf{u}_s(t) \quad (x_s, y_s, z_s) \in S \tag{63}$$

$$\frac{\partial\mathbf{u}(x, y, z, 0)}{\partial t} = \mathbf{0} \quad (j = 1, 2, 3) \tag{64}$$

allows determination of the fields of transfer potentials $\mathbf{u}(x, y, z, t)$.

An equivalent notation of relationships (60) is given below in the form of a set of the scalar wave equations

$$\sum_{m=1}^{n-1} \rho c_{jm}\frac{\partial}{\partial t}\left(\frac{\mu_n - \mu_m}{T}\right) + \rho c_{jq}\frac{\partial}{\partial t}\left(\frac{1}{T}\right) = \rho\frac{\partial y_j}{\partial t}$$
$$= -\left\{\sum_{m=1}^{n-1} L_{jm}\left[\nabla^2\left(\frac{\mu_n - \mu_m}{T}\right) - \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2}\left(\frac{\mu_n - \mu_m}{T}\right)\right]\right.$$
$$\left. + L_{jq}\left[\nabla^2\left(\frac{1}{T}\right) - \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2}\left(\frac{1}{T}\right)\right]\right\} = 0 \tag{65}$$

$$\sum_{m=1}^{n-1} \rho c_{qm}\frac{\partial}{\partial t}\left(\frac{\mu_n - \mu_m}{T}\right) + \rho c_{qq}\frac{\partial}{\partial t}\left(\frac{1}{T}\right) = \rho\frac{\partial h}{\partial t}$$
$$= -\left\{\sum_{m=1}^{n-1} L_{qm}\left[\nabla^2\left(\frac{\mu_n - \mu_m}{T}\right) - \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2}\left(\frac{\mu_n - \mu_m}{T}\right)\right.\right.$$
$$\left.\left. + L_{qq}\left[\nabla^2\left(\frac{1}{T}\right) - \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2}\left(\frac{1}{T}\right)\right]\right]\right\} = 0 \tag{66}$$

Just as in the case of pure heat transfer, equation (2), equations (65) and (66) contain d'Alembert's operators that replace more common Laplacians, since relaxation effects have been taken into account.

Equations (59) through (66) operate with the absolute temperature reciprocal $1/T$ as an energy transfer potential and not with the temperature T itself as it is usually done in the special case of pure heat transfer. Therefore it is of interest to see how the equations mentioned evolve into the known non-Fourier equations in the special case mentioned. For pure heat transfer, equations (59) and (60) take the form

$$\mathbf{J}_h = L_h\,\mathrm{grad}\frac{1}{T} + \frac{L_h c_h^{-1}}{c_0^2}\frac{\partial\mathbf{J}_h}{\partial t} = 0 \tag{67}$$

$$\rho c_h\frac{\partial}{\partial t}\left(\frac{1}{T}\right) + L_h\left[\nabla^2\left(\frac{1}{T}\right) - \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2}\left(\frac{1}{T}\right)\right] = 0. \tag{68}$$

Substituting equations (53), (54) and (56) into equations (67) and (68) and using relationships:†

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†The order of magnitude of τ_h agrees with evaluations in [28] for liquids.

†Approximations (70) and (71) require stronger assumptions than (69) since they result from identity:

$$\frac{\partial^2 T}{\partial x_j^2} = \frac{2}{T}\left(\frac{\partial T}{\partial x_j}\right)^2 - T^2\frac{\partial^2}{\partial x_j^2}\left(\frac{1}{T}\right)$$

in which the term containing the square of small value of $\partial T/\partial x_j$ was neglected.

$$\frac{\partial T}{\partial t} \cong -(T^0)^2 \frac{\partial}{\partial t}\left(\frac{1}{T}\right) \tag{69}$$

$$\frac{\partial^2 T}{\partial t^2} \cong -(T^0) \frac{\partial^2}{\partial t^2}\left(\frac{1}{T}\right) \tag{70}$$

$$\frac{\partial^2 T}{\partial x_i^2} \cong -(T^0)^2 \frac{\partial^2}{\partial x_i^2}\left(\frac{1}{T}\right), \tag{71}$$

gives the known Cattaneo–Vernotte equations (cf. [1, 4, 5]):

$$\mathbf{J}_h = -\lambda \operatorname{grad} T - \tau_h \frac{\partial \mathbf{J}_h}{\partial t} \tag{72}$$

$$\rho C_p \frac{\partial T}{\partial t} = \lambda\left(\nabla^2 T - \frac{1}{c_0^2}\frac{\partial^2 T}{\partial t^2}\right). \tag{73}$$

Thus, we have shown, on the simplest example, that under the linear theory assumptions the wave equations based on various transfer potentials (e.g. on T and $1/T$) can be transformed analytically, one into another, if a conventional requirement of the irreversible thermodynamics that the gradients should not be too large is met here for both space and time derivatives. It can be also shown that our conclusion is valid for various transfer potentials $(u_1, u_2, \ldots, u_n)$ in a general coupled case. The analysis below provides some example which focuses this question in a nontrivial way.

6. TRANSFORMATION OF FLUXES AND FORCES AND CONSTITUTIVE EQUATIONS FOR BINARY THERMODIFFUSION

In the case when the definitions of the thermodynamic fluxes and forces are changed according to the known rules of the Onsager irreversible thermodynamics, see [2], it can be shown that all of the general formulas derived previously, will remain valid for the new fluxes, forces and capacities. We shall discuss this important problem more extensively in another paper. Here we shall restrict our attention to the most simple example of isobaric binary system.

It is well-known, see e.g. [2], that for the heat flux of two-component mixture, defined as

$$\mathbf{J}_q^* = \mathbf{J}_q - (h_1 - h_2)\mathbf{J}_1, \tag{74}$$

provided that the mass flux is unchanged, i.e. for $\mathbf{J}_m^* = \mathbf{J}_m$, the thermodynamic forces resulting from invariancy of entropy production are:

$$\mathbf{X}_1^* = \operatorname{grad}\left(\frac{\mu_2 - \mu_1}{T}\right)_{T,P} = -\frac{1}{y_2 T}\left(\frac{\partial \mu_1}{\partial y_1}\right)_{T,P} \operatorname{grad} y_1 \tag{75}$$

$$\mathbf{X}_2^* = \mathbf{X}_2 = \operatorname{grad}\left(\frac{1}{T}\right) = \frac{-1}{T^2}\operatorname{grad} T$$

[the Gibbs–Duhem equation was used in the first of equations (75)]. Our new capacities should now be consequently defined so that the following equations should hold for $P =$ constant:

$$\mathrm{d}y_1 = c_1^* \mathrm{d}\left(\frac{\mu_2 - \mu_1}{T}\right)_{T,P} + c_{1q}^* \mathrm{d}\left(\frac{1}{T}\right) \tag{76}$$

$$\mathrm{d}h - (h_1 - h_2)\mathrm{d}y_1 = c_{q1}^* \mathrm{d}\left(\frac{\mu_2 - \mu_1}{T}\right)_{T,P} + c_{qq}^* \mathrm{d}\left(\frac{1}{T}\right) = C_p \mathrm{d}T \tag{77}$$

[compare the RHS of equation (74) and the LHS of equation (77)]. Substituting the following thermodynamic formula (cf. [2]):

$$\mathrm{d}\left(\frac{\mu_2 - \mu_1}{T}\right)_P = (h_2 - h_1)\mathrm{d}\left(\frac{1}{T}\right) + \mathrm{d}\left(\frac{\mu_2 - \mu_1}{T}\right)_{T,P} \tag{78}$$

into equations (48) and (49), applied in the case when $n = 2$, and computing the differential expressions $\mathrm{d}y_1$ and $C_p \mathrm{d}T$, it can be shown that the new matrix of capacities is again symmetric. Furthermore, it results that this matrix is at the same time diagonal, i.e. it is of the form $\mathbf{C}^* = \operatorname{diag}(c_{11}^*, c_{qq}^*)$ where (after using the Gibbs–Duhem equation)

$$c_{11}^* = \frac{\partial y_1}{\partial\left(\frac{\mu_2 - \mu_1}{T}\right)_{T,P}} = -\frac{y_2 T}{(\partial \mu_1/\partial y_1)_{T,P}} \tag{79}$$

and

$$c_{qq}^* = -C_p T^2. \tag{80}$$

The Onsager matrix, expressed in terms of more popular coefficients, i.e. the diffusion coefficient D, thermal conductivity λ and thermal diffusion coefficient D_T, is

$$\mathbf{L}^* = \begin{bmatrix} L_{11}^* & L_{1q}^* \\ L_{21}^* & L_{qq}^* \end{bmatrix} = \begin{bmatrix} \dfrac{\rho y_2 T D}{(\partial \mu_1/\partial y_1)_{P,T}} & \rho y_1 y_2 D_T T^2 \\ \rho y_1 y_2 T^2 D_T & T^2 \lambda \end{bmatrix} \tag{81}$$

as it results from the definitions of D, and D_T given, e.g. in [2]. Hence, substituting equations (79), (80) and (81) into equation (57) makes it possible to directly compute the relaxation coefficient matrix as

$$\boldsymbol{\tau}^* = -\frac{\mathbf{L}^* \mathbf{C}^{*-1}}{\rho c_0^2} = \begin{bmatrix} \dfrac{D}{c_0^2} & \dfrac{y_1 y_2 D_T}{C_p c_0^2} \\ \dfrac{T D_T y_1}{c_0^2}\left(\dfrac{\partial \mu_1}{\partial y_1}\right)_{P,T} & \dfrac{\lambda}{\rho C_p c_0^2} \end{bmatrix}. \tag{82}$$

It is convenient to express the matrix (82) in terms of the diffusional and heat relaxation times, defined according to the known definitions [4, 25] as

$$\tau_d = \frac{D}{c_0^2}; \quad \tau_h = \frac{a}{c_0^2} = \frac{\lambda}{\rho C_p c_0^2}. \tag{83}$$

We must also introduce the following relaxation time for thermal diffusion

$$\tau_T = \frac{D_T T}{c_0^2}. \tag{84}$$

Thus the matrix of the relaxation coefficient (82) is†

$$\boldsymbol{\tau}^* = \begin{bmatrix} \tau_d & \dfrac{y_1 y_2 \tau_T}{C_p T} \\ \tau_T y_1 \left(\dfrac{\partial \mu_1}{\partial y_1}\right)_{P,T} & \tau_n \end{bmatrix} \tag{85}$$

Now using equations (81), (85) and (75) in the general phenomenological relationships (41), the following set of constitutive equations is obtained:

$$J_1 = -\rho D \operatorname{grad} y_1 - \rho y_1 y_2 D_T \operatorname{grad} T - \tau_d \frac{\partial \mathbf{J}_1}{\partial t} - \frac{y_1 y_2 \tau_T}{C_p T} \frac{\partial \mathbf{J}_q^*}{\partial t} \tag{86}$$

$$J_q^* = -\rho y_1 T D_T \left(\frac{\partial \mu_1}{\partial y_1}\right)_{T,P} \operatorname{grad} y_1 - \lambda \operatorname{grad} T - \left(\frac{\partial \mu_1}{\partial y_1}\right)_{P,T} \cdot y_1 \tau_T \frac{\partial \mathbf{J}_1}{\partial t} - \tau_n \left(\frac{\partial \mathbf{J}_q^*}{\partial t}\right), \tag{87}$$

which describes coupled heat and mass transfer in binary fluid in the presence of relaxation effects. This set is suggested to describe non-stationary thermal diffusion with finite wave speed.

Taking divergence of equations (86) and (87) and using conservation laws, equation (43) for $n = 2$, as well as the following equation,

$$\rho C_p \frac{\partial T}{\partial t} = -\operatorname{div} \mathbf{J}_q^*, \tag{88}$$

the following set of wave equations are obtained *in the constant coefficient case*:

$$\rho \frac{\partial y_1}{\partial t} = \rho D \Box_0 y_1 + \rho D^T y_1 y_2 \Box_0 T \tag{89}$$

$$\rho C_p \frac{\partial T}{\partial t} = \rho y_1 T D_T \left(\frac{\partial \mu_1}{\partial y_1}\right)_{P,T} \Box_0 y_1 + \lambda \Box_0 T \tag{90}$$

which operate with d'Alembert's operators based on the propagation speed. Thus, the d'Alembert's operators should, as a rule, appear in the equations of change to resolve the physical paradox of the finite speed of disturbances. If, however, this speed is taken to approach infinity, then equations (86) and (87) as well as (89) and (90) simplify to the known conventional form without the relaxation terms, see e.g. [2].

We see that we have found a self-consistent description of the coupled relaxation phenomena. It has the properties that lead to the classical description when the propagation speed is assumed to be infinite.

7. VARIATIONAL PRINCIPLE FOR THE WAVE EQUATIONS OF THE COUPLED PROCESSES IN THE RESTING SYSTEM

The matrix wave equation (60) or the scalar equations (65) and (66) were formulated for the case of a quiescent medium (proper frame). We shall try, first of all, to find a variational principle for this case. This will result in generalization of the functional (1) for the coupled transport processes, the generalization being unknown so far. Then, using the time–space transformations I–III in the quiescent medium functional, we shall find the functionals describing simultaneous mass and energy transfer in moving media. Their forms will of course depend on the type of transformation (I, II or III), but not for too large velocities, used in most practical cases, the results will be similar.

We shall begin our reasoning with construction of an alternative form of the functional describing a pure heat transfer in which the temperature reciprocity $1/T$ [and not the temperature T as in equation (1)], is the transfer potential. For such a form it will be easier to find the matrix generalization of this form for the multipotential case with coupled heat and mass transfer. Substituting equations (55), (56), (69), (70) and (71) into expression (1) yield the functional

$$S' = \iiiint \frac{1}{2} L_h \left[\left(\operatorname{grad}' \frac{1}{T}\right)^2 - \frac{1}{c_0^2}\left(\frac{\partial\, 1/T}{\partial t'}\right)^2\right] \times \exp(-L_h^{-1} c_h \rho c_0^2 t')\, \mathrm{d}V'\, \mathrm{d}t' \tag{91}$$

which is equivalent to the functional (1) with an accuracy to the constant multiplier (the primed symbols are again used for transformation purposes since the proper frame, moving together with the medium, is considered first). It may be easily verified that for the constant phenomenological coefficients L_h, c_h and c_0 (under the assumption typical of the linear theories) the stationarity condition for equation (91) is the wave equation (68).

To obtain the variational principle for a coupled heat and mass transport we shall investigate the stationarity conditions for the following matrix generalization of the functional (91):

$$S' = \iiiint \tilde{\Lambda}\, \mathrm{d}V'\, \mathrm{d}t'$$

$$= \iiiint \frac{1}{2}\left\{\operatorname{grad}' \mathbf{u}^T \exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L} \operatorname{grad}' \mathbf{u} - \frac{1}{c_0^2} \frac{\partial \mathbf{u}^T}{\partial t'} \exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L} \frac{\partial \mathbf{u}}{\partial t'}\right\} \mathrm{d}V'\, \mathrm{d}t' \tag{92}$$

with respect to all of the components of the transport potential vector

$$\mathbf{u} = \operatorname{col}\left(\frac{\mu_n - \mu_1}{T}, \ldots, \frac{\mu_n - \mu_{n-1}}{T}, \frac{1}{T}\right).$$

We shall show that these stationarity conditions lead to the wave equations (65) and (66), i.e. to the matrix equation (60). In the following proof it is important that the matrix function appearing in equation (92), i.e. the function

$$\mathbf{B} = \exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L} = \exp(\boldsymbol{\tau}^{-1} t')\mathbf{L} \tag{93}$$

has a property of symmetry†, i.e.

$$\mathbf{B} = \mathbf{B}^T, \tag{94}$$

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† In the case of an ideal system the derivative $(\partial \mu_1/\partial y_1)_{T,P}$ appearing in the equations derived equals

$$\frac{RT}{y_1[M_1 - y_1(M_1 - M_2)]}.$$

† Similarly to Onsager's matrix **L**, the generalization of which is, in some sense, the matrix **B**.

and that this is a consequence of the symmetry of matrices **L** and **C**. The proof of this property together with some basic information concerning the exponential matrix function $\exp(\mathbf{A}t)$, where in our case $\mathbf{A} = \tau^{-1}$, is given in Appendix.

In the orthogonal curvilinear coordinates and for the Lagrangian given by equation (92), the set of the Euler equations for the variables $u_1, u_2, \ldots, u_n$ has the following matrix form

$$\frac{\partial}{\partial t'}\left[\frac{\partial\tilde{\Lambda}}{\partial(\partial\mathbf{u}/\partial t')}\right]+\operatorname{div}\left(\frac{\partial\tilde{\Lambda}}{\partial\,\mathrm{grad}'\,\mathbf{u}}\right)-\frac{\partial\tilde{\Lambda}}{\partial\mathbf{u}}=\mathbf{0} \quad (95)$$

where in our case $\partial\tilde{\Lambda}/\partial\mathbf{u} = \mathbf{0}$.

Since the matrix **B** is symmetric, we obtain

$$-c_0\frac{\partial\tilde{\Lambda}}{\partial(\partial\mathbf{u}/\partial t')}=\exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L}\frac{\partial\mathbf{u}}{c_0\partial t'} \quad (96)$$

and

$$\frac{\partial\tilde{\Lambda}}{\partial\,\mathrm{grad}'\,\mathbf{u}}=\exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L}\,\mathrm{grad}'\,\mathbf{u}. \quad (97)$$

Substituting equations (96) and (97) into (95), applying the formula for the product derivative of the matrices **B** and $\partial\mathbf{u}/\partial t$ and employing the basic property of the matrix exponential function

$$\frac{\partial}{\partial t'}\exp(\mathbf{A}t')=\exp(\mathbf{A}t')\mathbf{A}, \quad (98)$$

(see Appendix) gives the relationship

$$\exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\times\left[\mathbf{L}\left(\nabla^2\mathbf{u}-\frac{\partial^2\mathbf{u}}{c_0^2\partial t'^2}\right)+\rho\mathbf{C}\frac{\partial\mathbf{u}}{\partial t'}\right]=\mathbf{0}, \quad (99)$$

from which the matrix wave equation (60) results, or, the set of the scalar equations (65) and (66). For a resting medium, we thus find the variational principle that leads to the coupled mass and energy equations. It is of interest that this principle replaces, in some sense, the principle of minimum entropy production valid only in a stationary case [2]. Indeed, in the time–space x, y, z, c_0t, introduced in [10], the functional (92) may be written in the form

$$S'=\frac{1}{2}\iiiint \mathbf{J}_\mu\cdot\nabla_\mu\mathbf{u}\,\mathrm{d}\Omega' \quad (\mathrm{d}\Omega'\equiv\mathrm{d}V'\,\mathrm{d}t), \quad (100)$$

where $\mathbf{J}_\mu = (\mathbf{J}_x, \mathbf{J}_y, \mathbf{J}_z, \mathbf{J}_t)$ is comprised of four vectors of the n substitutional fluxes with the coordinates defined by the RHS of equations (96) and (97). (Note that in the space considered the scalar-product $a_\mu b_\mu$ is defined as $a_t b_t - \mathbf{ab}$ and the vector operator is

$$\nabla_\mu\equiv\left[\frac{\partial}{\partial(c_0t)},\frac{-\partial}{\partial x_1},\frac{-\partial}{\partial x_2},\frac{-\partial}{\partial x_3}\right].$$

See [10] and [32] for more information about the space mentioned.)

The functionals (92) or (100) can be broken down into the product of the time increment by the functional of a half entropy source if the exponential term and the terms with time derivatives (stationary process) are ignored.

The functional (92) allows formulation of the variational principles for the moving medium, which are invariant in the sense of transformation I, II or III (see the following section).

8. VARIATIONAL PRINCIPLES FOR WAVE EQUATIONS OF COUPLED HEAT AND MASS TRANSFER IN MOVING MEDIA

Now, with formula (92) available, we can easily write the expressions for the action functional in the case when the medium moves with a constant velocity **v**. It is sufficient to make transformations I, II or III (Section 2) in the functional (92), as it was done previously in the case of pure heat transfer. In this manner the Galilean functional is obtained for transformation I:

$$\begin{aligned}S=\iiiint\frac{1}{2}\Bigg[&\mathrm{grad}\,\mathbf{u}^T\exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t)\mathbf{L}\,\mathrm{grad}\,\mathbf{u}\\&-\frac{1}{c_0^2}\left(\frac{\partial\mathbf{u}}{\partial t}+\mathbf{v}\,\mathrm{grad}\,\mathbf{u}\right)^T\exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t)\mathbf{L}\\&\times\left(\frac{\partial\mathbf{u}}{\partial t}+\mathbf{v}\,\mathrm{grad}\,\mathbf{u}\right)\Bigg]\mathrm{d}V\,\mathrm{d}t. \quad (101)\end{aligned}$$

After analyzing the structure of (27) and substituting equations (8) and (18)–(22) into the functional (92), the following functional is found for transformation II

$$\begin{aligned}S=\iiiint\frac{1}{2}\Bigg\{&\mathrm{grad}\,\mathbf{u}^T\exp\left[-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2\gamma\left(t-\frac{\mathbf{vr}}{c^2}\right)\right]\\&\times\mathbf{L}\,\mathrm{grad}\,\mathbf{u}-\frac{1}{c^2}\frac{\partial\mathbf{u}^T}{\partial t}\exp\left[-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2\gamma\left(t-\frac{\mathbf{vr}}{c^2}\right)\right]\\&\times\mathbf{L}\frac{\partial\mathbf{u}}{\partial t}+\gamma^2\left(\frac{1}{c^2}-\frac{1}{c_0^2}\right)\left(\frac{\partial\mathbf{u}}{\partial t}+\mathbf{v}\,\mathrm{grad}\,\mathbf{u}\right)^T\\&\times\exp\left[-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2\gamma\left(t-\frac{\mathbf{vr}}{c^2}\right)\right]\\&\times\mathbf{L}\left(\frac{\partial\mathbf{u}}{\partial t}+\mathbf{v}\,\mathrm{grad}\,\mathbf{u}\right)\Bigg\}\mathrm{d}V\,\mathrm{d}t. \quad (102)\end{aligned}$$

For transformation III the fundamental velocity is c_0. Hence the functional (92) transforms into the simplest form

$$\begin{aligned}S=\iiiint\frac{1}{2}\Bigg\{&\mathrm{grad}\,\mathbf{u}^T\exp\Bigg[-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2\gamma_0\left(t-\frac{\mathbf{vr}}{c_0^2}\right)\Bigg]\\&\times\mathbf{L}\,\mathrm{grad}\,\mathbf{u}-\frac{1}{c_0^2}\frac{\partial\mathbf{u}^T}{\partial t}\exp\Bigg[-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2\gamma_0\\&\times\left(t-\frac{\mathbf{vr}}{c_0^2}\right)\Bigg]\mathbf{L}\frac{\partial\mathbf{u}}{\partial t}\Bigg\}\mathrm{d}V\,\mathrm{d}t. \quad (103)\end{aligned}$$

We shall write the stationary conditions (Euler equations) for the functionals (101)–(103). Taking the components of **u**, i.e. potentials

$$\frac{\mu_n-\mu_1}{T},\ldots,\frac{\mu_n-\mu_{n-1}}{T},\frac{1}{T},$$

as varied variables, the Euler equations are obtained that generalize the matrix equation (60) or the set of the scalar equations (65) and (66). For transformation I [functional (101)] this generalization has the following simple operator form:

$$\rho \mathbf{C}\frac{\mathrm{d}u}{\mathrm{d}t} + \mathbf{L}\nabla^2\mathbf{u} - \frac{\mathbf{L}}{c_0^2}\frac{\mathrm{d}^2\mathbf{u}}{\mathrm{d}t^2} = 0. \qquad (104)$$

The result obtained is in agreement with the alternative method in which the direct substitution of transformation relationships [equations (13)–(16)] into equation (60) is made. The direct substitution is, as a rule, simpler than the variational method, but it looses the option of obtaining the valuable functionals for moving media [equations (101)–(103)], these functionals giving additional possibility to solve particular wave equations with the use of direct variational methods. Since, however, we have just these functionals known, therefore, the direct substitution of the time–space relationships into equation (60) may be used for verification. This was also the method used in the present paper yielding the same result as the method based on the Euler equations.

For transformation I the already described equation (104) was obtained, while for transformation II [functional (102)]

$$\rho\gamma\mathbf{C}\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} + \left(\frac{1}{c^2} - \frac{1}{c_0^2}\right)\gamma^2\mathbf{L}\frac{\mathrm{d}^2\mathbf{u}}{\mathrm{d}t^2} + \mathbf{L}\Box\mathbf{u} = 0. \qquad (105)$$

This matrix relationship constitutes the generalization of Kranys' equation, c.f. [12], for the case of coupled mass and energy transfer. Taking into account that equations (53), (54), (69), (70) and (71) hold for pure heat transfer, one may indeed show equivalency of equations (105) and (29) in this special case.

For the functional (103), transformation III, the stationarity conditions take the simplest form

$$\rho\gamma_0\mathbf{C}\frac{\mathrm{d}u}{\mathrm{d}t} + \mathbf{L}\Box_0\mathbf{u} = \mathbf{0} \qquad (106)$$

where the coefficient γ_0 and the d'Alembercian $\Box_0$ are based on the propagation speed c_0. Since transformation III is acceptable for small velocities, $v \ll c_0$, the approximation $\gamma_0 \cong 1$ can be made in equation (103). Equation (106) with $\gamma_0 = 1$ is then obtained as a stationarity condition of the functional (103) simplified in this manner. This simplification gives the following set of the scalar wave equations:

$$\rho\frac{\mathrm{d}y_j}{\mathrm{d}t} + \sum_{m=1}^{n-1} L_{jm}\Box_0\left(\frac{\mu_n - \mu_m}{T}\right) + L_{jq}\Box_0\left(\frac{1}{T}\right) = 0 \qquad (107)$$

$$\rho\frac{\mathrm{d}h}{\mathrm{d}t} + \sum_{m=1}^{n-1} L_{qm}\Box_0\left(\frac{\mu_n - \mu_m}{T}\right) + L_{qq}\Box_0\left(\frac{1}{T}\right) = 0 \qquad (108)$$

which represent the set of the simplest possible equations allowing for a finite propagation speed. This set was suggested without proof by the present author in [34]. In case when $c_0 \to \infty$ the set simplifies to the set of the classical parabolic equations given by de Groot [2].

The knowledge of the action integrals equations (1), (23), (27), (31) and (101)–(103) provides us with the method of obtaining the functionals given by direct variational techniques as, for example, in the Ritz or Kantorovich method, c.f. [14, 15].

Numerical examples of such an approach to equation (1) are given by Vujanovic (non-stationary cases) in his series of articles, see e.g. [17] and [18], as well as by Kashkaha [33] (the Ritz solution in stationary, classical cases). The variational method of finding the transfer potential fields is usually characterized by a considerable accuracy, see e.g. author's simple example in [10]. It can be effectively used especially for the case of complex boundary conditions.

9. DISCUSSION OF RESULTS AND SIGNIFICANCE

Using systematically the time–space transformation equations in the functionals and wave equations for quiescent media, the appropriate functionals and equations were found for a medium moving with a constant velocity $\mathbf{v}$. The wave equations obtained in this manner are also valid for any element of a moving fluid in which the distribution of velocity $\mathbf{v}$ (x, y, z, t) occurs.

A logical self-consistent theory of the wave equations for the coupled processes with simultaneous heat and mass transfer was developed based on the phenomenological equation (41) of the non-Onsager type that simplifies to the classical Onsager relation in the case of an infinite speed of propagation, c_0. Such a simplification can especially result from the new important formula, equation (57), which describes the matrix of the relaxation coefficients τ as a function of the two basic matrices, the kinetic matrix of Onsager's $\mathbf{L}$ and the static matrix of capacities $\mathbf{C}$, which are well-known in the irreversible thermodynamics. It appears that all of the matrix relationships obtained for coupled heat and mass transfer generalize non-trivially the known relationships for pure heat transfer.

The role of the exponential matrix function should be especially pointed out which plays a crucial part in our generalization of Shter's expression [22] for the relaxation nucleus as well as in formulation of many new variational principles for coupled heat and mass transfer. This matrix function generalizes nontrivially the scalar exponential function $\exp(t/\tau)$ appearing in several variational principles formulated earlier [18, 10, 33] for pure heat transfer and other uncoupled cases.

Application of the time–space transformations in the functionals of resting media lead directly to the adequate functionals describing these media in motion. This simple systematic approach reveals some interesting feature of the hitherto existing variational principles [17, 10, 33, 34] applied to pure heat transfer or other uncoupled cases. Sometimes these principles contain velocity $\mathbf{v}$ (and not the speed of light c) in the exponential function and, as such, they are neither of the Gallilean nor of the relativistic type but rather of acoustic or "second sound" type [compare e.g. the functionals (23), (27) and (31) to reveal this conclusion]. Although it does not usually introduce considerable errors, it should be remembered that the principles quoted (and corresponding Ritz solutions) will become meaningless for the velocities v comparable with the sound speed whereas the Gallilean type variational principles will still be sufficiently accurate. The material contained in this paper allows one to perform such critical analysis and to make necessary adjustments.

REFERENCES

1. C. Cattaneo, Sur une forme de l'équation de la chaleur eliminant le paradoxe d'une propagation instantanée, *C.R. Hebd. Séanc. Acad. Sci., Paris* **247**, 431–433 (1958).
2. S. R. De Groot and P. Mazur, *Non-equilibrium Thermodynamics*. North Holland, Amsterdam (1962).
3. A. V. Luikov, *Analytical Heat Diffusion Theory*. Academic Press, New York (1969).
4. A. V. Luikov, Application of irreversible thermodynamics methods to investigation of heat and mass transfer, *Int. J. Heat Mass Transfer* **9**, 139–152 (1966).
5. P. Vernotte, Les paradoxes de la teorie continue de l'équation de la chaleur, *C.R. Hebd. Séanc. Acad. Sci., Paris* **246**, 3154–3155 (1958).
6. S. Kaliski, Wave equation of heat conduction, *Bull. Acad. Pol. Sci., Sér. Sci. Tech.* **13**, 211–219 (1965).
7. K. J. Baumeister and T. D. Hamil, Hyperbolic heat conduction equation—A solution for the semi-infinite body problem, *J. Heat Transfer* **91**, 543–548 (1969).
8. B. M. Berkovsky and V. G. Bashtovoi, The finite velocity of heat propagation from the view-point of the kinetic theory, *Int. J. Heat Mass Transfer* **20**, 621–627 (1977).
9. A. V. Luikov, V. A. Bubnov and I. A. Soloviev, On wave solutions of the heat conduction equation, *Int. J. Heat Mass Transfer* **19**, 245–249 (1976).
10. S. Sieniutycz, The variational principles of classical type for non-coupled non-stationary irreversible transport processes with convective motion and relaxation, *Int. J. Heat Mass Transfer* **20**, 1221–1231 (1977).
11. V. A. Bubnov, Wave concepts in the theory of heat, *Int. J. Heat Mass Transfer* **19**, 175–195 (1976).
12. M. Kranys, Relativistic hydrodynamics with irreversible thermodynamics without the paradox of infinite velocity of heat conduction, *Nuovo Cim.* **42B**, 1125–1194 (1966).
13. K. C. Kar, Relativity in acoustic world, *Indian J. Theor. Phys.* **18**, 1–12 (1970).
14. L. E. Elsgolc, *Calculus of Variations*. PWN, Warsaw (1960).
15. L. V. Kantorovich and V. I. Krylov, *Approximate Methods of Higher Analysis*. The Netherlands (1958).
16. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure Stability and Fluctuations*. John Wiley, New York (1971).
17. B. Vujanovic, An approach to linear and nonlinear heat transfer problem using a Lagrangian, *AIAA Jl* **9**, 131–134 (1971).
18. B. Vujanovich, D. Djukic and M. Pavlovich, A variational principle for the laminar boundary layer theory, *Bull. U.M.I.* **7**, 317–391 (1973).
19. I. M. Gelfand and S. W. Fomin, *Calculus of Variations*. PWN, Warsaw (1970).
20. G. Bialkowski, *Classical Mechanics*. PWN, Warsaw (1975).
21. D. Bohm, *The Special Theory of Relativity*. W. A. Benjamin, New York (1965).
22. I. M. Shter, The generalized Onsager principle and its application, *Inzh. Fiz. Zh.* **25**, 736–742 (1973).
23. A. D. Honkin, On hydrodynamic equations of intensive processes, *DAN SSSR* **210**, 1033–1039 (1973).
24. J. C. Maxwell, On the dynamical theory of gases, *Phil. Trans. R. Soc.* **157**, 49–88 (1967).
25. A. V. Luikov, Some current problems of heat and mass transfer theory, in *Problems in Heat and Mass Transfer*, pp. 9–81. Nauka i Tekhnika Press, Minsk (1966).
26. L. Natanson, Über die Gesetze nicht umkehrbarer Vorgange, *Z. Phys. Chem.* **21**, 193 (1896).
27. M. Carrasi and A. Moro, A modified Navier–Stokes equation and its effect on sound dispersion, *Nuovo Cim.* **9B**, 321–343 (1972).
28. R. E. Nettelton, Relaxation theory of thermal conduction in liquids, *Physics Fluids* **3**, 216–226 (1960).
29. K. E. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves*, p. 363. Academic Press, New York (1959).
30. R. P. Wendt, Studies of isothermal diffusion at 25° in the system $H_2O/Na_2SO_4/H_2SO_4$ and tests of Onsager relation, *J. Phys. Chem.* **66**, 1279–1288 (1962).
31. K. Michalski, Optimization approach to heat and mass transfer, MsD Thesis, Warsaw Techn. Univ. (1977).
32. R. P. Feynman, R. B. Leighton and M. Sands, The Feynman Lectures on Physics, Vol. 2, Chapter 25. Addison-Wesley, Reading, MA (1963).
33. V. E. Kashkaha, On Ritz method when investigating two-phase quasi-stationary problem of Stefan type, *Mathl Phys.* **17**, 128–137 (1975).
34. S. Sieniutycz, The variational principles for phenomenological equations of non-Fourier type, Inst. Chem. Engng, Warsaw (1977).
35. N. R. Amundson, *Mathematical Methods in Chemical Engineering, Matrices and their Application*. Prentice Hall, Englewood Cliffs, N.J. (1966).
36. B. P. Demidovich, Mathematical Theory of Stability. *WNT*, Warsaw (1972).
37. A. P. Mishina and F. V. Proscuriakov, *Higher Algebra*. PWN, Warsaw (1956).

APPENDIX

Some basic information concerning matrix exponential function, exp(**A***t*)*, as well as a proof of the symmetry property of the matrix function* **B**

Let $\mathbf{A} = [a_{jk}]$ be a square matrix of order n (in the case of this work it can be the matrix $\mathbf{A} = \tau^{-1}$). The matrix function defined as [35, 36]:

$$\exp(\mathbf{A}t) = \sum_{p=0}^{\infty} \frac{\mathbf{A}^p t^p}{p!} \tag{A1}$$

is called the exponential function of the square matrix **A** with the parameter t. It is proved that the series (A1) is absolutely convergent for the arbitrary square matrix **A**.

Assume that the two matrices **A** and **D** are commutative, i.e. **AD** = **DA**. Then the fundamental property of the matrix exponential function is:

$$\exp(\mathbf{A}t)\exp(\mathbf{D}t) = \exp(\mathbf{A}+\mathbf{D})t. \tag{A2}$$

It results from (A1) that

$$[\exp(\mathbf{A}t)]^T = \exp(\mathbf{A}^T t) \tag{A3}$$

[compare equations (A6) below]. Furthermore, it can also be shown, see (A1), that

$$\frac{\mathrm{d}}{\mathrm{d}t}[\exp(\mathbf{A}t)] = \mathbf{A}\exp(\mathbf{A}t) = \exp(\mathbf{A}t)\mathbf{A} \tag{A4}$$

[compare equation (98) in the text].

Let $\mathbf{A}_1$ be the square matrix similar to the matrix **A**, e.g.

$$\mathbf{A}_1 = \mathbf{L}\mathbf{A}\mathbf{L}^{-1} \quad (\det \mathbf{L} \neq 0).$$

Then, exploiting the obvious properties of similar matrices

$$\mathbf{L}(\mathbf{A}+\mathbf{D})\mathbf{L}^{-1} = \mathbf{L}\mathbf{A}\mathbf{L}^{-1}+\mathbf{L}\mathbf{D}\mathbf{L}^{-1}$$

and

$$\mathbf{L}(\mathbf{A}\mathbf{D})\mathbf{L}^{-1} = \mathbf{L}\mathbf{A}\mathbf{L}^{-1}\mathbf{L}\mathbf{D}\mathbf{L}^{-1}$$

it results from equation (A1) that

$$\exp(\mathbf{L}\mathbf{A}\mathbf{L}^{-1}t) = \mathbf{L}\exp(\mathbf{A}t)\mathbf{L}^{-1} \tag{A5}$$

[consider equations (A6) and (A7) below].

The computation of the elements of the matrix exponential function is an important problem, well-established in algebra [37]. The following methods are used:

(a) transformation of $\exp(\mathbf{A}t)$ into a canonical form. Then $\exp(\mathbf{A}t)$ equals $\mathbf{M}\exp(\Lambda t)\mathbf{M}^{-1}$ where $\mathbf{M}$ is the modal matrix and $\Lambda = \mathrm{diag}(\lambda_1,\ldots,\lambda_n)$.

(b) summing up of the series (A1);

(c) use of the Laplace transformation;

(d) application of the Cayley–Hamilton theorem, see [37]. If the order of $\mathbf{A}$ is larger than $4 \div 5$, the use of computer is recommended.

We are now prepared to prove the symmetry of the matrix **B**, equation (93), in the text. Since

$$\mathbf{B} = \exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L} \tag{93}$$

and property (A3) holds, then taking into consideration that

$$\mathbf{L} = \mathbf{L}^T \quad \text{and} \quad \mathbf{C} = \mathbf{C}^T,$$

one has

$$\begin{aligned}\mathbf{B}^T &= \mathbf{L}\exp(-\mathbf{L}^{-1}\mathbf{C}\rho c_0^2 t') \\ &= \mathbf{L}\exp[-\mathbf{L}^{-1}(\mathbf{C}\mathbf{L}^{-1})\mathbf{L}\rho c_0^2 t'].\end{aligned} \tag{A6}$$

But from property (A5) it results that the above result equals

$$\mathbf{B}^T = \mathbf{L}\mathbf{L}^{-1}\exp(-\mathbf{C}\mathbf{L}^{-1}\rho c_0^2 t')\mathbf{L} = \mathbf{B} \tag{A7}$$

and the proof is completed.

LES EQUATIONS D'ONDE POUR LES TRANSFERTS SIMULTANES DE CHALEUR ET DE MASSE DANS LES MILIEUX MOBILES

Résumés—On obtient la solution fonctionnelle des équations d'onde linéaire qui gouvernent la conduction thermique aussi bien que les transferts simultanés de chaleur et de masse dans les milieux mobiles (dans la représentation d'Euler). Ces fonctionnelles sont trouvées simplement à partir des équations de substitution par transformation espace—temps en fonctionnelle d'un milieu immobile qui, dans le cas général, contient une fonction matricielle comme terme principal. Cette fonction est associée à la matrice des coefficients de relaxation qui apparaissent dans une relation générale flux-force, équation (41), qui généralise l'équation de Cattaneo [1] pour le cas multipotentiel et qui couvre l'expression classique d'Onsager [2] quand les effets de relaxation sont négligés. Une synthèse des équations linéaires d'onde et des principes variationnels correspondants est obtenue en même temps que de nouveaux résultats. La théorie mathématique des transferts simultanés de chaleur et de masse avec effets de relaxation, est développée et on donne son application directe à la diffusion thermique dans un fluide à deux composants. Cette théorie montre, en notation tensorielle, une importante et remarquable analogie avec la théorie de la conduction thermique basée sur un flux thermique autre que celui de Fourier.

DIE WELLENGLEICHUNGEN FÜR GLEICHZEITIGEN WÄRME- UND STOFFÜBERGANG IN BEWEGTEN MEDIEN—STRUKTURTEST, ZEIT-RAUM-TRANSFORMATION UND VARIATIONSRECHNUNG

Zusammenfassung—Es wurden die Funktionale hergeleitet, die auf die linearen Wellengleichungen führen, die sowohl die Wärmeleitung als auch den gleichzeitigen Wärme- und Stoffübergang in bewegten Medien beschreiben (in Eulerscher Darstellung). Diese Funktionale werden einfach ermittelt durch Einsetzen der Gleichungen der Zeit-Raum-Transformationen in das Funktional für ein ruhendes Medium, welches im allgemeinen Fall eine Matrixfunktion als wesentlichen Term enthält. Diese Funktion hängt mit der Matrix der Relaxationskoeffizienten zusammen, die in einer allgemeinen Strömungs-Energie-Beziehung vorkommen, Gleichung (41), welche die Cattaneo-Gleichung [1] für den Fall mehrerer Potentiale verallgemeinert und die bei Vernachlässigung der Relaxationseffekte auf den klassischen Onsager-Ansatz [2] führt. Neben vielen neuen Ergebnissen wurde eine Synthese der linearen Wellengleichungen und der zugehörigen Variationsprinzipien erreicht. Die logisch konsistente mathematische Theorie des gleichzeitigen Wärme- und Stoffübergangs mit Relaxationseffekten wurde entwickelt und ihre direkte Anwendung auf thermische Diffusion in einem Zwei-Komponenten-Fluid angegeben. Diese Theorie zeigt, in Matrizenschreibweise, eine wichtige und bemerkenswerte Analogie zur Theorie der reinen Wärmeleitung mit nicht-Fourierschem Wärmestrom.

ВОЛНОВЫЕ УРАВНЕНИЯ ДЛЯ ОДНОВРЕМЕННОГО ПЕРЕНОСА ТЕПЛА И МАССЫ В ДВИЖУЩИХСЯ СРЕДАХ — АНАЛИЗ СТРУКТУРЫ, ПРОСТРАНСТВЕННО-ВРЕМЕННЫЕ ПРЕОБРАЗОВАНИЯ И ВАРИАЦИОННЫЙ ПОДХОД

Аннотация — Получены функционалы, с помощью которых можно вывести линейные волновые уравнения, описывающие теплопроводность, а также одновременный тепло- и массоперенос в движущихся средах (в эйлеровом представлении). Данные функционалы получаются путем простой подстановки пространственно-временных соотношений в функционал для неподвижной среды, который в общем случае в качестве важного компонента содержит некоторую матричную функцию. Эта функция связана с матрицей релаксационных коэффициентов, которые появляются в общем соотношении для потоков и сил в уравнении (41), с помощью которого можно обобщить уравнение Каттанео [1] для многопотенциального случая и которое в пренебрежении релаксационными эффектами переходит в классическое выражение Онзагера [2]. Наряду с многими новыми результатами получен синтез линейных волновых уравнений с соответствующими вариационными принципами. Развита логически согласованная математическая теория одновременного тепло- и массопереноса, включающая релаксационные эффекты, и показано, как ее можно непосредственно применить к случаю диффузии тепла в двухкомпонентной жидкости. Важным является то, что в матричном представлении данная теория аналогична теории чистой теплопроводности, когда тепловой поток не подчиняется закону Фурье.