THERMODYNAMICS OF COUPLED HEAT, MASS AND MOMENTUM TRANSPORT WITH FINITE WAVE SPEED II—EXAMPLES OF TRANSFORMATIONS OF FLUXES AND FORCES

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Abstract—Using the theory developed in Part I of this work [1], the linear transformations of thermodynamic fluxes and forces are comprehensively investigated for the coupled mass and energy transfer with the finite propagation speed c_0. The cases considered comprise transformations that are well known in the classical irreversible thermodynamics. Various non-Onsager phenomenological equations and a basic set of hyperbolic equations, equations (52) and (53), describing multi-component thermal diffusion are obtained. The generality of a thermodynamic approach based on the so-called relaxation entropy is shown and simplifications of the theory for the known special cases are discussed.

NOMENCLATURE

$a,$ $= \dfrac{\lambda}{\rho C_p}$, thermal diffusivity;

$C_p,$ specific heat;

$C_m,$ $= c_{ij}^m = \left[\dfrac{\partial y_i}{\partial (\mu_j T^{-1})} \right]_T$, matrix of mass capacities;

$C,$ $= c_{ik} = \dfrac{\partial \mathbf{z}}{\partial \mathbf{u}}$, thermostatic matrix of capacities;

$C^*,$ new matrix of capacities;

$c_0,$ $= \sqrt{(G/\rho)}$, constant speed of the second sound wave propagation;

$c_h,$ $= -C_p T^2$, thermal capacity $[\partial h/\partial T^{-1}]_{p,y}$;

$D^*,$ generalized diffusivity matrix, equation (45);

$D_m,$ matrix of mass diffusivities;

$\tilde{D}_T,$ column matrix of thermal diffusion coefficients;

$G,$ modulus of shear rigidity;

$h,$ specific enthalpy;

$h_i,$ partial specific enthalpy of ith component; $\tilde{h}_i = h_n - h_i$;

$\Delta h_y,$ increment of enthalpy h at $y = \text{const.}$;

$\Delta h,$ deviation of enthalpy; enthalpy increment on wave front;

$\mathbf{J}_q, \mathbf{J}_h,$ vector of density of diffusive energy flux and pure heat flux, respectively;

$\mathbf{J}_q^*,$ new energy flux, heat flux $\mathbf{J}_q^* = \mathbf{J}_h$, in particular;

$\mathbf{J}_s, \mathbf{J}_{sh},$ entropy fluxes defined by equations (54) and (56), respectively;

$\mathbf{J}_i,$ vectors of densities of diffusive mass fluxes, $1 \leqslant i \leqslant n-1$;

$\mathbf{J},$ $= \text{col}(\mathbf{J}_1, \mathbf{J}_2 \dots \mathbf{J}_{n-1}, \mathbf{J}_q)$, column matrix containing all independent fluxes;

$\mathbf{J}^*,$ new matrix of fluxes as a result of transformation of vector $\mathbf{J}$, equation (6);

$\mathbf{J}_m,$ $= \text{col}(\mathbf{J}_1, \mathbf{J}_2 \dots \mathbf{J}_{n-1})$, column matrix containing $n-1$ independent mass fluxes;

$\mathbf{L}, \mathbf{L}^*,$ Onsager matrix and new Onsager matrix, respectively;

$\mathbf{L}_m, \mathbf{L}_T,$ submatrices of matrix $\mathbf{L}^*$ connected with isothermal diffusion and thermal diffusion, respectively;

$L_h,$ $= \lambda T^2$, Onsager coefficient for heat conduction;

$M,$ molar mass;

$\mathbf{n},$ unit normal vector;

$s, s',$ specific static entropy and total entropy, respectively;

$s_i,$ partial specific entropy of ith component, $\tilde{s}_i = s_n - s_i$;

$\Delta s_y,$ entropy increment at $\mathbf{y} = \text{const.}$;

$\Delta s_r,$ relaxation entropy of unit volume;

$\mathbf{P}, \mathbf{Q},$ matrices of transformations (6) and (7);

$p,$ pressure;

$T,$ temperature;

$t,$ time;

$\mathbf{u},$ $= \text{col}\left(\dfrac{\mu_n - \mu_1}{T} \dots \dfrac{\mu_n - \mu_{n-1}}{T}, \dfrac{1}{T} \right)$, column matrix of original transfer potentials;

$\mathbf{u}^*$, $= \mathrm{col}\left(\dfrac{\tilde{\mu}_{T1}}{T}, \dfrac{\tilde{\mu}_{T2}}{T} \dots \dfrac{\tilde{\mu}_{Tn-1}}{T}, \dfrac{1}{T}\right)$, column matrix of new transfer potentials;

V, $= \rho^{-1}$, specific volume of the medium investigated;

$\mathbf{w}$, barycentric velocity;

$\mathbf{X}$, $= \mathrm{col}\left(\mathrm{grad}\,\dfrac{\mu_n - \mu_1}{T} \dots,\right.$

$\left. \mathrm{grad}\,\dfrac{\mu_n - \mu_{n-1}}{T}, \mathrm{grad}\,\dfrac{1}{T}\right)$,

column matrix of classical thermodynamic forces;

$\mathbf{X}^*$, new column matrix of classical thermodynamic forces;

y_i, mass fraction of ith component;

$\mathbf{y}$, $= \mathrm{col}\,(y_1, y_2 \dots y_{n-1})$, column matrix of independent mass fractions;

$\mathbf{z}$, $= \mathrm{col}\,(y_1, y_2 \dots y_{n-1}, h)$ column matrix of thermodynamic state of mixture at p $= \mathrm{const.}$;

$\mathbf{z}^*$, transformed state $\mathbf{z}$;

∇^2, Laplace operator;

Δ, deviation, increment;

σ, entropy source;

η, dynamic viscosity;

ρ, mass density;

τ, τ^*, ordinary and transformed matrix of relaxation coefficients, respectively;

π, diffusional part of pressure tensor;

μ_i, chemical potential of component i, $\tilde{\mu}_i = \mu_n - \mu_i$;

λ, thermal conductivity.

Subscripts

o, undisturbed state;

h, heat;

i, j, elements i and j of column matrix $\mathbf{J}$;

m, mass;

n, component in normal direction;

p, constant pressure;

q, energy in coupled process;

r, relaxation;

s, entropy;

T, temperature or thermal diffusion.

Superscripts

$'$, total entropy;

T, transpose matrix;

$*$, new fluxes, forces, capacities and Onsager matrices;

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† It should be kept in mind that an expanded (i.e. non-matrix) form of relaxation entropy is

$$(2G_1\rho_1)^{-1} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{\alpha=x,y,z} c_{jk} J_{j\alpha} J_{k\alpha}$$

in the Cartesian coordinates x, y, z. Note an analogous structure of similar bilinear expressions. Remember also that the multiple temperature relaxation is not considered in the present theory.

-1, reverse matrix;

o, deviatoric part of tensor.

INTRODUCTION

IN PART 1 of this work [1], the fundamental equations for the coupled heat, mass and momentum transport with a finite speed of propagation c_0 [1, 2] have been derived on the basis of the non-equilibrium thermodynamics. As a result of the analysis of coupled processes of isobaric mass and energy transport in the "second sound" shock wave front, the following equations have been obtained:

$$J_{in_0} = \rho_0 c_0 \Delta y_i, \tag{1}$$

$$J_{qn_0} = \rho_0 c_0 \Delta h. \tag{2}$$

($\Delta y_i = y_{i0} - y_{i1}$ etc., cf. Fig. 2 in [1])

These equations relate the diffusive fluxes of mass and energy to the increments of concentrations y_i and enthalpies h on the wave front. Using equations (1) and (2) in the well known thermodynamic formula for the entropy deficiency caused by non-equilibrium [3, 4], it was shown [1] that the total specific entropy of the disturbed side of the shock wave front s'_1 is related to the classical entropy $s_1(y_1, \dots y_{n-1}, h_1)$ as

$$s'_1 = s_1(y_{1,1}, \dots y_{n-1,1}, h_1) + \frac{\mathbf{J}^T \mathbf{C}^{-1} \mathbf{J}}{2\rho_1 G_1}, \tag{3}$$

where $\mathbf{J} = \mathrm{col}(\mathbf{J}_1, \mathbf{J}_2 \dots \mathbf{J}_{n-1}, \mathbf{J}_q)$ and $G_1 = \rho_1 c_0^2$ is the modulus of shear rigidity.

The term with the fluxes in equation (3) is called the relaxation entropy†. The matrix $\mathbf{C}^{-1}$—a reciprocal of the so-called capacity matrix [2]—is the same as the matrix of the second differential of entropy [4] expressed as the function of the variables y_i and h.

It was postulated [1] that equation (3) pertains also to a situation in the interior of the disturbed region and it was shown that this formula leads to a certain non-classical expression for entropy production, from which the following non-Onsager, phenomenological equation results

$$\mathbf{J} - \frac{\mathbf{L}\mathbf{C}^{-1}}{G} \frac{d\mathbf{J}}{dt} = \mathbf{L}\,\mathrm{grad}\,\mathbf{u}, \tag{4}$$

where

$$\mathrm{grad}\,\mathbf{u} = \mathrm{col}\left(\mathrm{grad}\,\frac{\mu_n - \mu_1}{T} \dots \mathrm{grad}\,\frac{\mu_n - \mu_{n-1}}{T}, \mathrm{grad}\,\frac{1}{T}\right)$$

and $\mathbf{L}$ is Onsager's matrix. The matrix

$$\tau = -\frac{\mathbf{L}\mathbf{C}^{-1}}{G}. \tag{5}$$

found in equation (4) is the matrix of the relaxation coefficients. For pure heat conduction a well known formula, $\tau_h = a/c_0^2$, is obtained from equation (5). Equation (4) holds in the region of validity of relation (3).

It was shown in [1] that for linear transformations of thermodynamic fluxes and forces

$$\mathbf{J^*} = \mathbf{PJ}, \tag{6}$$

$$\mathbf{X^*} = \mathbf{QX}, \quad \mathbf{X} = \text{grad } \mathbf{u}, \tag{7}$$

where $\mathbf{J^*}$ and $\mathbf{X^*}$ are new fluxes and forces, the following rules of transformations of the basic matrices $\mathbf{L}$, $\mathbf{C}$ and τ should be adhered to:

$$\mathbf{L^*} = \mathbf{PLP^T}, \tag{8}$$

$$\mathbf{C^*} = \mathbf{PCP^T}, \tag{9}$$

$$\tau^* = \mathbf{P\tau P^{-1}}. \tag{10}$$

These rules ensure the invariance of formulae expressing, among other things, the relaxation entropy of unit volume, i.e. entropy of diffusive fluxes

$$\Delta s_r = \frac{\mathbf{J^T C^{-1} J}}{2G}, \tag{11}$$

and the contribution of the relaxation entropy to the classical entropy source

$$\Delta \dot{s}_r = \frac{\mathbf{J^T C^{-1}}}{G} \frac{d\mathbf{J}}{dt}. \tag{12}$$

An important fact was emphasized that equations (4), (11) and (12) are due to local non-equilibrium in the continuum and also that the assumption of a local equilibrium according to the classical irreversible thermodynamics simplifies the theory to that of Onsager's one. See also some remarks about the range of the theory at the end of this paper.

In this paper, just as in [1], non-reacting fluids and solids will be investigated under the conditions of negligible compressibility. Examples of transformations, that can be found in the classical non-equilibrium thermodynamics [5] and that will be used here, will be given for the case of a finite speed of propagation. As a result, several equivalent expressions for the non-classical entropy source and non-Onsager phenomenological equations will be obtained. Because of the variety of expressions derived, it will be possible to select the best formula for specific application which usually resolves itself into finding and solving the hyperbolic-type partial differential equations that describe the transport potential fields. Finally, simplifications of the theory that lead to the well known specific cases will be discussed. It will be shown that the present theory is consistent with the results given in literature for the familiar specific cases and it also provides a consequent generalization that ensures a uniform description of coupled processes with a finite wave speed.

‡ Some special findings (that can be derived from the present theory as special cases) were obtained earlier in the author's work [2]. These are only connected with binary systems and not supported by thermodynamic analysis.

2. TRANSFORMATIONS LEADING TO THE HEAT FLUX J_h

In the conventional theory of mass and energy transfer, it is a typical approach not to use the energy flux $\mathbf{J}_q$ and the mass fluxes $\mathbf{J}_1 \dots \mathbf{J}_{n-1}$ (in [1] all the formulae were derived for this set of fluxes), but, leaving unchanged the mass fluxes ($\mathbf{J}_i = \mathbf{J}_i^*$), to use a heat flux which is defined in [5] as:

$$\mathbf{J}_h = \mathbf{J}_q^* = \mathbf{J}_q - \sum_1^n h_i \mathbf{J}_i = \mathbf{J}_q + \sum_1^{n-1} (h_n - h_i) \mathbf{J}_i. \tag{13}$$

We will now develop in detail the theory of this transformation‡. Denoting the differences $h_n - h_i$, $\mu_n - \mu_i$ etc., respectively as $\tilde{h}_i$, $\tilde{\mu}_i$ etc. and treating $\mathbf{J}_h$ as a new flux (i.e. $\mathbf{J}_h = \mathbf{J}_q^*$), the transformation analyzed can be written as:

$$\mathbf{J}_i^* = \mathbf{J}_i, \quad i = 1, 2 \dots n-1, \tag{14}$$

$$\mathbf{J}_h = \mathbf{J}_q^* = \mathbf{J}_q + \tilde{h}_i \mathbf{J}_i. \tag{15}$$

The above equations enable one to express the transformation matrix $\mathbf{P}$, equation (6), as:

$$\mathbf{P} = \begin{bmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \hline \tilde{h}_1 & \tilde{h}_2 & \dots & 1 \end{bmatrix} \tag{16}$$

Before we proceed to describe the new matrices $\mathbf{L^*}$ and $\mathbf{C^*}$, let us consider an interesting interpretation of transformation (14) and (15) from the viewpoint of the phenomena occurring in the wave front. Multiplying equations (1) and (2) by a unit normal vector $\mathbf{n}$, we find

$$J_i = \rho_0 c_0 n_0 \Delta y_i \tag{17}$$

$$J_q = \rho_0 c_0 n_0 \Delta h \tag{18}$$

where $\Delta y_i = y_{i0} - y_{i1}$ and $\Delta h = h_0 - h_1$ represent the increments of the undisturbed concentration y_{i0} and enthalpy h_0 in relation to the disturbed concentration y_{i1} and enthalpy h_1, respectively (only the latter variables are used in the final equations for the process [1]).

Using equations (17) and (18) in (15) and employing the well known formula for the enthalpy differential at a constant pressure, we find that

$$J_h = J_q^* = \rho_0 c_0 n_0 C_p \Delta T, \tag{19}$$

which shows clearly that the isobaric flux J_h is related with a non-equilibrium temperature increment. When p is not constant, this flux is related with the enthalpy increment without a change in concentration. If we let Δh_y to represent this increment, then the anlogues of equations (17) and (18) for the new fluxes and forces will have the following form

$$J_i^* = \rho c_0 n_0 \Delta y_i, \tag{20}$$

$$J_q^* = J_h = \rho_0 c_0 n_0 \Delta h_y. \tag{21}$$

Thus, it is found that the transformation converts the primary equations (17) and (18) into similar equations that operate with the increments of certain new variables of state. The presentation of the results is

concise when the matrix notation is used. The set of equations (17) and (18) thus becomes

$$\mathbf{J} = \rho_0 c_0 \mathbf{n}_0 \Delta \mathbf{z}, \qquad (22)$$

where $\mathbf{J} = \mathrm{col}(\mathbf{J}_1, \ldots \mathbf{J}_{n-1}, \mathbf{J}_q)$ and $\mathbf{z} = \mathrm{col}(y_1 \ldots y_{n-1}, h)$. As a result of the transformation analyzed we get

$$\mathbf{J}^* = \rho_0 c_0 \mathbf{n}_0 \Delta \mathbf{z}^*, \qquad (23)$$

where $\mathbf{J}^* = \mathrm{col}(\mathbf{J}_1 \ldots \mathbf{J}_{n-1}, \mathbf{J}_h)$ and $\mathbf{z}^* = \mathrm{col}(y_1 \ldots y_{n-1}, h_y)$. Equations (22) and (23) express a certain kind of covariancy of fluxes $\mathbf{J}$ and $\mathbf{J}^*$ with the variables of state $\mathbf{z}$ and $\mathbf{z}^*$ respectively.

Let us now discuss the transformation of matrices $\mathbf{L}$ and $\mathbf{C}$. In the case of equations (14) and (15) the Onsager kinetic matrix $\mathbf{L}$ transforms into a certain matrix $\mathbf{L}^*$ the form of which is obtained using the $\mathbf{P}$ matrix, equation (16), in the general equation (8). The explicit form of the new matrix $\mathbf{L}^*$ will not be given here, because it is the same as that in the classical Onsager non-equilibrium thermodynamics [5]. Rather we shall discuss the capacity matrices $\mathbf{C}$ and $\mathbf{C}^*$, the specific form of which has an effect on the relaxation entropy and its contribution to the entropy source, equations (11) and (12). But since the reciprocals of $\mathbf{C}$ and $\mathbf{C}^*$ appear in these equations, in what follows we shall use the $\mathbf{C}^{-1}$ and $\mathbf{C}^{*-1}$ matrices.

Equation (9) yields

$$\mathbf{C}^{*-1} = \mathbf{P}^{-1\mathrm{T}} \mathbf{C}^{-1} \mathbf{P}^{-1}. \qquad (24)$$

For the $\mathbf{P}$ matrix, equation (16), we have

$$\mathbf{P}^{-1} = \begin{bmatrix} 1 & 0 & \ldots & 0 \\ 0 & 1 & \ldots & 0 \\ -\tilde{h}_1 & -\tilde{h}_2 & & 1 \end{bmatrix} \qquad (25)$$

$$\mathbf{P}^{-1\mathrm{T}} = \mathbf{Q} = \begin{bmatrix} 1 & 0 & \ldots & -\tilde{h}_1 \\ 0 & 1 & \ldots & -\tilde{h}_2 \\ 0 & 0 & & 1 \end{bmatrix} \qquad (26)$$

and the matrix $\mathbf{C}^{-1}$ has the following form {compare with equation (17) in [1]}:

$$\mathbf{C}^{-1} = \qquad (27)$$

$$\begin{bmatrix} \left(\dfrac{\partial \dfrac{\tilde{\mu}_1}{T}}{\partial y_1}\right)_{y_2 y_3 \ldots h} & \left(\dfrac{\partial \dfrac{\tilde{\mu}_1}{T}}{\partial y_2}\right)_{y_1 y_3 \ldots h} & \left(\dfrac{\partial \dfrac{\tilde{\mu}_1}{T}}{\partial h}\right)_{y_1 \ldots y_{n-1}} \\ \left(\dfrac{\partial \dfrac{\tilde{\mu}_2}{T}}{\partial y_1}\right)_{y_2 y_3 \ldots h} & \left(\dfrac{\partial \dfrac{\tilde{\mu}_2}{T}}{\partial y_2}\right)_{y_1 y_3 \ldots h} & \left(\dfrac{\partial \dfrac{\tilde{\mu}_2}{T}}{\partial h}\right)_{y_1 \ldots y_{n-1}} \\ \left(\dfrac{\partial T^{-1}}{\partial y_1}\right)_{y_2 y_3 \ldots h} & \left(\dfrac{\partial T^{-1}}{\partial y_2}\right)_{y_1 y_3 \ldots h} & \left(\dfrac{\partial T^{-1}}{\partial h}\right)_{y_1 \ldots y_{n-1}} \end{bmatrix}$$

The differential $(\partial T^{-1}/\partial h)_{y_1 \ldots y_{n-1}}$ in equation (27) is equal to $-1/C_p T^2$.

Using equations (24–27), we get a symmetrical matrix (28).

$$\mathbf{C}^{*-1} = \mathbf{P}^{-1\mathrm{T}} \mathbf{C}^{-1} \mathbf{P}^{-1} = \qquad (28)$$

Accounting for the differential relationship

$$\left(\frac{\partial V}{\partial a}\right)_b = \left(\frac{\partial V}{\partial a}\right)_c + \left(\frac{\partial V}{\partial c}\right)_a\left(\frac{\partial c}{\partial a}\right)_b, \qquad (29)$$

and

$$\tilde{h}_1 = -\left(\frac{\partial h}{\partial y_1}\right)_T, \quad \tilde{h}_2 = -\left(\frac{\partial h}{\partial y_2}\right)_T, \text{ etc.,}$$

the matrix (28) can be simplified to the form

$$\mathbf{C}^{*-1} = \qquad (30)$$

$$\begin{bmatrix} \left(\dfrac{\partial \dfrac{\tilde{\mu}_1}{T}}{\partial y_1}\right)_{T,y_2\ldots y_{n-1}} & \left(\dfrac{\partial \dfrac{\tilde{\mu}_1}{T}}{y_2}\right)_{T,y_1\ldots y_{n-1}} & \bigg| & 0 \\ \left(\dfrac{\partial \dfrac{\mu_2}{T}}{\partial y_1}\right)_{T,y_2\ldots y_{n-1}} & \left(\dfrac{\partial \dfrac{\mu_2}{T}}{\partial y_2}\right)_{T,y_1\ldots y_{n-1}} & \bigg| & 0 \\ \hline 0 & 0 & \bigg| & -1/(C_p T^2) \end{bmatrix}$$

The advantage of using the heat flux $\mathbf{J}_q^* = \mathbf{J}_h$ is clearly visible here. A characteristic feature of the matrices $\mathbf{C}^*$ and $\mathbf{C}^{*-1}$ is the disappearance of terms that express the thermostatic coupling. It is known from the classical thermodynamics that this property is a physical result of the statistical independence of fluctuations of certain state variables [3]. In our case this concerns the y_i and h variables. The $\mathbf{C}^{*-1}$ matrix is especially simple in the case of a binary system because it is a diagonal matrix, see also [2].

The relaxation entropy transforms, with the form of equation (11) being preserved, see [1]. Therefore, on using equation (30), we get

$$\Delta s_r = \frac{\mathbf{J}^T\mathbf{C}^{-1}\mathbf{J}}{2G} = \frac{\mathbf{J}^{*T}\mathbf{C}^{*-1}\mathbf{J}^*}{2G}$$

$$= \frac{1}{2G}\left[\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\left(\frac{\partial \frac{\tilde{\mu}_i}{T}}{\partial y_j}\right)_{T,y} J_j J_i - \frac{1}{C_p T^2} J_h^2\right]. \quad (31)$$

In addition, for the shock-wave front we have

$$\Delta s_r = \frac{\rho}{2}\Delta\mathbf{z}^T\mathbf{C}^{-1}\Delta\mathbf{z} = \frac{\rho}{2}\Delta\mathbf{z}^{*T}\mathbf{C}^{*-1}\Delta\mathbf{z}^*$$

$$= \frac{\rho}{2}\left[\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\left(\frac{\partial \frac{\tilde{\mu}_i}{T}}{\partial y_j}\right)_{T,y} \Delta y_j \Delta y_i - \frac{1}{C_p T^2}\Delta h_y^2\right]$$

$$= \frac{\rho}{2}\left[\sum_{i=1}^{n-1}\Delta\frac{\tilde{\mu}_{Ti}}{T}\Delta y_i + \Delta T^{-1}\Delta h_y\right], \quad (32)$$

(because $\Delta h_y = C_p\Delta T$ for const. p). The last expression indicates that $\mathbf{z}^* = \text{col}(y_1 y_2 \ldots y_{n-1}, h_y)$ is the new vector of state. The new transport potential vector has the following form:

$$\mathbf{u}^* = \text{col}\left(\frac{\tilde{\mu}_{T1}}{T}, \frac{\tilde{\mu}_{T2}}{T} \frac{\tilde{\mu}_{Tn-1}}{T}, \frac{1}{T}\right),$$

where the subscript T indicates that the potentials $\tilde{\mu}_{Ti}$ are taken at a constant temperature. The new expression for Δs_r can be easily obtained directly from the original expression after a simple change of variables (i.e. even without resorting to the $\mathbf{C}$ and $\mathbf{C}^*$ matrices). Indeed, writing the former expression for Δs_r [1] as

$$\Delta s_r = \frac{\rho}{2}\left\{\sum_{i=1}^{n-1}\Delta\frac{\tilde{\mu}_i}{T}\Delta y_i + \Delta\frac{1}{T}\Delta h\right\} \quad (33)$$

and making use of the thermodynamic relation

$$\left(\frac{\partial \frac{\tilde{\mu}_i}{T}}{\partial T^{-1}}\right)_{y_1\ldots y_{n-1}} = \tilde{h}_i \quad (34)$$

and also expressing the increment Δh in equation (33) by the increments ΔT and Δy_i, we get

$$\Delta s_r = \frac{\rho}{2}\left[\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\left(\frac{\partial \frac{\tilde{\mu}_i}{T}}{\partial y_j}\right)_T \Delta y_j\Delta y_i \right.$$

$$+ \sum_{i=1}^{n-1}\left(\frac{\partial \frac{\tilde{\mu}_i}{T}}{\partial T^{-1}}\right)_y \Delta T^{-1}\Delta y_i$$

$$\left. - \sum_{i=1}^{n-1} h_i\Delta T^{-1}\Delta y_i + C_p\Delta T\Delta T^{-1}\right]$$

$$= \frac{\rho}{2}\left[\sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\left(\frac{\partial \frac{\tilde{\mu}_i}{T}}{\partial y_i}\right)_T \Delta y_j\Delta y_i - \frac{C_p(\Delta T)^2}{T^2}\right], (35)$$

which is equivalent to (32). The conclusion which can be drawn from the above is that the entropy of new diffusive fluxes, equation (31), can be obtained in a less formal way by making an adequate transformation of the state variables in the classical thermostatic expressions known from the fluctuation theory, equation (32), and making use of the analogy between the expressions of the (31)- and (32)-type (the transformation matrix of the z_i variables is also the $\mathbf{P}$ matrix, see [1]).

This approach has the advantage that usually it is quite easy to find the increments of new potentials u_i^*. In our case,

$$\mathbf{u}^* = \text{col}\left(\frac{\tilde{\mu}_{T1}}{T}, \ldots \frac{\tilde{\mu}_{Tn-1}}{T}, \frac{1}{T}\right),$$

which is in agreement with the following relationship resulting from the definition of capacities

$$\Delta\mathbf{u}^* = \mathbf{C}^{*-1}\Delta\mathbf{z} \quad (36)$$

for the matrix (30). The same result is also obtained from the general equation which expresses the transformation of the increment of transport potentials [1]:

$$\Delta\mathbf{u}^* = \mathbf{Q}\Delta\mathbf{u} = \mathbf{P}^{-1T}\Delta\mathbf{u}. \quad (37)$$

Indeed, since

$$\Delta \mathbf{u} = \mathrm{col}\left(\Delta \frac{\tilde{\mu}_1}{T} \ldots \Delta T^{-1}\right),$$

then on the basis of relations (26) and (37)

$$\Delta \mathbf{u}^* = \begin{bmatrix} \Delta \dfrac{\tilde{\mu}_1}{T} - \tilde{h}_1 \Delta T^{-1} \\ \Delta \dfrac{\tilde{\mu}_2}{T} - \tilde{h}_2 \Delta T^{-1} \\ \hline \Delta T^{-1} \end{bmatrix} = \begin{bmatrix} \Delta \dfrac{\tilde{\mu}_{T1}}{T} \\ \Delta \dfrac{\tilde{\mu}_{T2}}{T} \\ \hline \Delta T^{-1} \end{bmatrix} \quad (38)$$

according to the well known thermodynamic relation

$$\Delta \frac{\mu_i}{T} = \Delta \frac{\mu_{Ti}}{T} - h_i \frac{\Delta T}{T^2},$$

see e.g. [5]. Knowing the new transport potentials, i.e. the components of the $\mathbf{u}^*$ vector, it is easy to write an adequate equation expressing the non-classical entropy source in terms of new fluxes and forces

$$\sigma^* = \mathbf{J}^{*\mathrm{T}}\left(\mathrm{grad}\,\mathbf{u}^* + \frac{\mathbf{C}^{*-1}}{G} \frac{d\mathbf{J}^*}{dt}\right)$$

$$= \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \mathrm{grad} \frac{\tilde{\mu}_{Ti}}{T} + \mathbf{J}_h \cdot \mathrm{grad}\, T^{-1}$$

$$+ \frac{\mathbf{J}^{*\mathrm{T}} \mathbf{C}^{*-1} d\mathbf{J}^*}{G\, dt}. \quad (39)$$

The phenomenological matrix equation resulting from the non-negativeness condition of σ^* is§

$$\mathbf{J}^* = \mathbf{L}^* \,\mathrm{grad}\,\mathbf{u}^* + \frac{\mathbf{L}^* \mathbf{C}^{*-1}}{G} \frac{d\mathbf{J}^*}{dt}. \quad (40)$$

The forms of equations (39) and (40) are often too general to be applied in practice. Sometimes it is more convenient to use alternative equations, (49)–(51), described in Section 3, where the specific properties of the transformed capacity matrix are taken advantage of.

3. RELAXATION MATRIX, GENERALIZED DIFFUSIVITY MATRIX AND DESCRIPTION OF STATIONARY THERMAL DIFFUSION

We will now investigate at length the relaxation coefficient matrix τ^*, which corresponds to the transformed fluxes $\mathbf{J}^*$. The matrix τ^* depends on two, already discussed, matrices $\mathbf{L}^*$ and $\mathbf{C}^*$. Because of the characteristic form of the transformed capacity matrix ($C_{iq}^* = C_{qi}^* = 0$ for $i = 1, 2, 3 \ldots n-1$) and for the sake of a better elucidation of the role of mass fluxes $\mathbf{J}_i$ in relation to the heat flux $\mathbf{J}_h$, we shall separate in the $\mathbf{C}^{*-1}$ matrix, equation (30), a sub-matrix

$$\mathbf{C}_m^{-1} = \left(\hat{c}\,\frac{\tilde{\mu}}{Ti}/\partial y_j\right)_T,$$

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§ In the same way, the phenomenological equations (49) and (50), given later, result from the alternative form of σ^*, equation (51).

which is related to the isothermal transport of mass. Furthermore, in the $\mathbf{C}^{*-1}$ matrix, we shall take into account the null sub-matrices (column and row) that describe the lack of thermostatic couplings. As a result, we shall write the $\mathbf{C}^{*-1}$ matrix in the following form

$$\mathbf{C}^{*-1} = \begin{bmatrix} \mathbf{C}_m^{-1} & \vdots & \mathbf{O} \\ \hline \mathbf{O} & \vdots & \begin{array}{c} 1 \\ \overline{C_p T^2} \end{array} \end{bmatrix}. \quad (41)$$

In the same way we shall formulate the Onsager symmetrical matrix $\mathbf{L}^*$ separating in it the sub-matrices $\mathbf{L}_m$, $\mathbf{L}_T$ and the one-element sub-matrix $L_{qq} = \lambda T^2$. These are related to diffusion, thermal diffusion and thermal conductivity, respectively. We shall get

$$\mathbf{L}^* = \begin{bmatrix} \mathbf{L}_m & \vdots & \mathbf{L}_T \\ \hline \mathbf{L}_T^\mathrm{T} & \vdots & \lambda T^2 \end{bmatrix} \quad (42)$$

Because of this, the relaxation coefficient matrix has the following structure

$$\tau^* = -\frac{\mathbf{L}^* \mathbf{C}^{*-1}}{\rho c_0^2} = \frac{1}{c_0^2}\begin{bmatrix} \dfrac{-\mathbf{L}_m \mathbf{C}_m^{-1}}{\rho} & \vdots & \dfrac{\mathbf{L}_T}{\rho C_p T^2} \\ \hline \dfrac{-\mathbf{L}_T^\mathrm{T} \mathbf{C}_m^{-1}}{\rho} & \vdots & \dfrac{\lambda}{\rho C_p} \end{bmatrix} \quad (43)$$

But the sub-matrix $-\mathbf{L}_m \mathbf{C}_m^{-1}/\rho$ is a mass diffusivity matrix $\mathbf{D}_m$, according to the well known definition, see e.g. [5]. Also $\lambda/\rho C_p$ is the thermal diffusivity, a. That is why the expression (43) defines a certain generalized diffusivity matrix $\mathbf{D}^*$ such that

$$\mathbf{L}^* = \frac{\mathbf{D}^*}{c_0^2} \quad (44)$$

and

$$\mathbf{D}^* = \begin{bmatrix} \mathbf{D}_m & \vdots & \dfrac{\mathbf{L}_T}{\rho T^2 C_p} \\ \hline \dfrac{-\mathbf{L}_T^\mathrm{T} \mathbf{C}_m^{-1}}{\rho} & \vdots & a \end{bmatrix} \quad (45)$$

(the matrix $\mathbf{D}^*$ is usually non-symmetric).

Equation (44) constitutes a simple and important matrix generalization of expression $\tau_h = a/c_0^2$, which is well known in the theory of pure heat conduction. On the other hand, equation (45) expresses the general diffusivity matrix including effects of isothermal mass diffusion, thermal mass diffusion as well as diffusion of heat. It is possible in this equation to define the column matrix $\mathbf{L}_T/\rho C_p T^2$ as a matrix which characterizes the thermal diffusion quantitatively. However, the elements of this matrix would be given in $\mathrm{kg}\,\mathrm{m}^2\,\mathrm{s}^{-1}\,\mathrm{J}^{-1}$ and such a definition would be less suitable for practical applications. That is why, we shall define the thermal diffusion matrix in another way, i.e. as

$$\mathbf{D}_T = \frac{\mathbf{L}_T}{\rho T}. \quad (46)$$

Because of this, every element of this matrix will

have a typical dimension of $m^2 s^{-1}$. This definition is sometimes used also in the classical non-equilibrium thermodynamics [6]. After making use of (46) in equations (44) and (45), we get

$$\mathbf{D^*} = \tau^* c_0^2 = \left[\begin{array}{c|c} \mathbf{D}_m & \dfrac{\tilde{\mathbf{D}}_T}{C_p T} \\ \hline -T\tilde{\mathbf{D}}_T^T \mathbf{C}_m^{-1} & a \end{array} \right]. \quad (47)$$

Equation (47) is applied to the general phenomenological equation (40), which with the use of (36) is transformed to

$$\mathbf{J^*} = -\rho \mathbf{D^*} \, \text{grad} \, z^* - \frac{\mathbf{D^*}}{c_0^2} \frac{d\mathbf{J^*}}{dt}. \quad (48)$$

It is taken into account that $\mathbf{J^*} = \text{col}(\mathbf{J}_m, \mathbf{J}_h)$, where $\mathbf{J}_m = \text{col}(\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1})$ and that grad $z^* = \text{col}(\text{grad } y, C_p \text{ grad } T)$, where $y = \text{col}(y_1, y_2 \ldots, y_{n-1})$. As a result, we get the basic set of phenomenological equations in the form, which is most suitable for direct applications:|

$$\mathbf{J}_m = -\rho \mathbf{D}_m \, \text{grad} \, y - \frac{\rho \tilde{\mathbf{D}}_T}{T} \, \text{grad} \, T$$

$$- \frac{\mathbf{D}_m}{c_0^2} \frac{d\mathbf{J}_m}{dt} - \frac{\tilde{\mathbf{D}}_T}{c_0^2 C_p T} \frac{d\mathbf{J}_h}{dt}, \quad (49)$$

$$\mathbf{J}_h = \rho T \tilde{\mathbf{D}}_T^T \mathbf{C}_m^{-1} \, \text{grad} \, y - \lambda \, \text{grad} \, T$$

$$+ \frac{T\tilde{\mathbf{D}}_T^T \mathbf{C}_m^{-1}}{c_0^2} \frac{d\mathbf{J}_m}{dt} - \frac{\lambda}{\rho C_p c_0^2} \frac{d\mathbf{J}_h}{dt}. \quad (50)$$

Note, that this set can also be derived from the entropy source (39) expressed as

$$\sigma^* = \mathbf{J}_m^T \left(\text{grad} \, \frac{\tilde{\mu}}{T} + \frac{C_m^{-1}}{G} \frac{d\mathbf{J}_m}{dt} \right)$$

$$+ \mathbf{J}_h \left(\text{grad} \, T^{-1} - \frac{1}{GC_p T^2} \frac{d\mathbf{J}_h}{dt} \right) \geq 0, \quad (51)$$

which clearly shows the role of inertial forces. The importance of equations such as (49), (50) and (51) lies in the fact that they operate exclusively with the commonly known quantities ($c_0^2 = G/\rho$).

The first of the two equations (49) and (50) give a matrix presentation of the diffusion of $n-1$ components, the second expresses the diffusion of heat. These equations describe a coupled transport of mass and heat, with a finite wave speed. When $c_0 \to \infty$ they

turn into the well known equations of the classical theory of multi-component thermal diffusion.

For the special case of a two-component system and with the use of a different thermal diffusion coefficient D_T, such that $\tilde{D}_T = D_T y_1 y_2 T$, equations (49) and (50) simplify into equations (86) and (87), which were given in our earlier work [2].

4. HYPERBOLIC EQUATIONS OF MULTI-COMPONENT THERMAL DIFFUSION

Acting on the both sides of equations (49) and (50) with the divergence operator, assuming that the coefficients in these equations are constant and making use of the equations of the conservation of mass and sensible heat, we get the following set of hyperbolic equations:

$$\rho \frac{dy}{dt} = \rho \mathbf{D}_m \left(\nabla^2 y - \frac{d^2 y}{c_0^2 \, dt^2} \right)$$

$$+ \frac{\rho \tilde{\mathbf{D}}_T}{T} \left(\nabla^2 T - \frac{d^2 T}{c_0^2 \, dt^2} \right), \quad (52)$$

$$\rho C_p \frac{dT}{dt} = -\rho T \tilde{\mathbf{D}}_T^T \mathbf{C}_m^{-1} \left(\nabla^2 y - \frac{d^2 y}{c_0^2 \, dt^2} \right)$$

$$+ \lambda \left(\nabla^2 T - \frac{d^2 T}{c_0^2 \, dt^2} \right). \quad (53)$$

Equations (52) and (53) express the Galilean representation of simultaneous heat and mass transfer with finite wave speed.

For a stationary medium, these equations include the d'Alembert operators and not (as it is in the classical equations) the Laplace operators. The presence of the former in the partial differential equations of change is a rule if the relaxation effects are to be accounted for.

It is expected that equations (52) and (53) will describe the mass and heat transport better than the classical ones, especially in the case of strong non-stationarities, e.g. during travel of sound waves through the fluid when the thermal diffusion is being intensified. The relaxation terms should also be important in the application of these equations to dispersed media and non-Newtonian fluids that are described by the Maxwell fluid model.

5. TRANSFORMATIONS LEADING TO ENTROPY STREAMS

We will give here an outline of the formalism using other fluxes and forces. Leaving the definitions of mass fluxes unchanged, we shall be using here the entropy flux $\mathbf{J}_s$ instead of the original energy flux $\mathbf{J}_q$. It is generally known that

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| Using the Gibbs–Duhem equation, it is possible to bring the first (classical) term of the RHS of equation (50) to the form commonly used in literature:

$$-\rho T \tilde{\mathbf{D}}_T^T \mathbf{A} \left(\frac{\partial \dfrac{\mu}{T}}{\partial y} \right) \text{grad } y,$$

where the matrix

$$\mathbf{A} = [A_{ik}] \equiv \left(\delta_{ik} + \frac{y_k}{y_n} \right) \text{for } i, k = 1, 2 \ldots n-1,$$

see e.g. [6].

$$\mathbf{J}_s = T^{-1} \left(\mathbf{J}_q - \sum_{k=1}^{n} \mu_k \mathbf{J}_k \right) = T^{-1} \left(\sum_{k=1}^{n-1} \tilde{\mu}_k \mathbf{J}_k + \mathbf{J}_q \right).$$

$$(54)$$

On the ground of equations (17), (18) and (54), the new flux $\mathbf{J}_n^* = \mathbf{J}_s$ satisfies the equation:

$$\mathbf{J}_s = \rho_0 c_0 \mathbf{n}_0 \, \Delta s, \qquad (55)$$

i.e. it is directly related to the entropy increment in the shock wave front.

The flux $\mathbf{J}_s$ takes an account of the entropy transfer by diffusion of mass and heat [5]. There is also a possibility of using the second entropy flux $\mathbf{J}_{sh}$, which is related exclusively to the diffusion of heat [5]. The flux $\mathbf{J}_{sh}$ satisfies the equation

$$\mathbf{J}_{sh} = \mathbf{J}_s - \sum_{k=1}^{n} s_k \mathbf{J}_k = \mathbf{J}_s + \sum_{k=1}^{n-1} \tilde{s}_k \mathbf{J}_k. \qquad (56)$$

If the situation in the shock wave front is described, then the stream $\mathbf{J}_{sh}$ satisfies also the second equation

$$\mathbf{J}_s = \rho_0 c_0 \mathbf{n}_0 \left(\Delta s - \sum_{1}^{n} s_k \, \Delta y_k \right) = \rho_0 c_0 \mathbf{n}_0 C_p \frac{\Delta T}{T}. \qquad (57)$$

Comparison of equations (19) and (57) shows that

$\mathbf{J}_{sh} = T^{-1} \mathbf{J}_h$. The same conclusions can be drawn from equations (54), (56) and (13). It means that it would suffice to substitute $\mathbf{J}_h = T \mathbf{J}_{sh}$ into all the previous equations involving $\mathbf{J}_h$¶ to obtain the suitable equations involving $\mathbf{J}_{sh}$. This applies especially to expressions (31) and (32) for the relaxation entropy which, after introducing $\mathbf{J}_{sh}$ and using the mass capacity matrix

$$\mathbf{C}_m = \left[\left(\frac{\partial \mu_i}{T} \Big/ \partial y_j \right)_T \right],$$

can be written as

$$\Delta s_r = \frac{1}{2G} \left[\mathbf{J}_m^T C_m^{-1} \mathbf{J}_m - \frac{\mathbf{J}_{sh}^2}{C_p} \right]$$

$$= \frac{\rho}{2T} \left[\sum_{i=1}^{n-1} \Delta \tilde{\mu}_{Ti} \, \Delta y_i - \frac{\Delta s_v^2}{C_p} \right]. \qquad (58)$$

¶ Note that the condition of linearity of transformation makes it necessary to assume T constant in $T \mathbf{J}_{sh}$.

To this expression there corresponds the following form of the total entropy source

$$\sigma_{sh} = \mathbf{J}_m^T \left(\text{grad} \, \frac{\tilde{\mu}_T}{T} + \frac{C_m^{-1}}{G} \frac{d\mathbf{J}_m}{dt} \right) -$$

$$\mathbf{J}_{sh} \times \left(\text{grad} \ln T + \frac{1}{GC_p} \frac{d\mathbf{J}_{sh}}{dt} \right) \qquad (59)$$

as well as certain phenomenological equations obtained for the generalized forces appearing in brackets in equation (59). They can be brought to equations (49) and (50) if it is taken into account that $\mathbf{J}_{sh} = T^{-1} \mathbf{J}_h$ and that the already discussed definition of $\mathbf{D}_T$ is kept.

The transformation of the $\mathbf{J}_q$ flux into $\mathbf{J}_s$ [equation (54)] corresponds to the following transformation matrix:

$$\mathbf{P} = \begin{bmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \frac{\tilde{\mu}_1}{T} & \frac{\tilde{\mu}_2}{T} & \dots & \frac{1}{T} \end{bmatrix} \qquad (60)$$

The knowledge of $\mathbf{P}$ enables one to find the reciprocal of the new capacity matrix $\mathbf{C}_s$ related with the fluxes $\mathbf{J}_1, \mathbf{J}_2 \dots \mathbf{J}_{n-1}, \mathbf{J}_s$. We get

$$\mathbf{C}_s^{-1} = \mathbf{P}^{-1T} \mathbf{C}^{-1} \mathbf{P}^{-1} = \begin{bmatrix} \frac{1}{T}\left(\frac{\partial \tilde{\mu}_1}{\partial y_1}\right)_{s,y_2} & \frac{1}{T}\left(\frac{\partial \tilde{\mu}_1}{\partial y_2}\right)_{s,y_1} \cdots & \frac{1}{T}\left(\frac{\partial \tilde{\mu}_1}{\partial s}\right)_{y,y} \\ \frac{1}{T}\left(\frac{\partial \tilde{\mu}_2}{\partial y_1}\right)_{s,y_2} & \frac{1}{T}\left(\frac{\partial \tilde{\mu}_2}{\partial y_2}\right)_{s,y_2} & \frac{1}{T}\left(\frac{\partial \tilde{\mu}_2}{\partial s}\right)_{y,y} \\ \cdots & \cdots & \cdots \\ -\frac{1}{T}\left(\frac{\partial T}{\partial y_1}\right)_{s,y_2} & -\frac{1}{T}\left(\frac{\partial T}{\partial y_2}\right)_{s,y_1} & -C_p^{-1} \end{bmatrix} \qquad (61)$$

where

$$-\left(\frac{\partial T}{\partial y_i}\right)_{sy_j} = \left(\frac{\partial \tilde{\mu}_i}{\partial s}\right)_{y_1 y_2}$$

is Maxwell's relation. This yields the following expressions for the relaxation entropy†† and entropy source:

$$\Delta s_r = \frac{1}{2G} \left[\sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \frac{1}{T} \left(\frac{\partial \tilde{\mu}_i}{\partial y_j} \right)_{s,y} \right.$$

$$\times \mathbf{J}_j \mathbf{J}_i - \frac{2}{T} \sum_{i=1}^{n-1} \left(\frac{\partial T}{\partial y_i} \right)_{s,y} \mathbf{J}_i \mathbf{J}_s - \frac{\mathbf{J}_s^2}{C_p} \Bigg]. \qquad (62)$$

†† Equation (62) can also express the value

$$\Delta s_r = -\frac{\Delta h_r}{T} = \frac{\rho}{2T} \left(\sum_{i}^{n-1} \Delta \tilde{\mu}_i \, \Delta y_i - \Delta T \Delta s \right)$$

as the function of $\mathbf{J}_i$ and $\mathbf{J}_s$, on using equations (17) and (55).

$$\sigma_s = \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \left[T^{-1} \operatorname{grad} \tilde{\mu}_i - \frac{T^{-1}}{G} \right.$$

$$\sum_{j=1}^{n-1} \left(\frac{\partial \tilde{\mu}_i}{\partial y_j} \right) \frac{d\mathbf{J}_j}{dt} - \frac{T^{-1}}{G} \left(\frac{\partial T}{\partial y_i} \right) \frac{d\mathbf{J}_s}{dt} \right]$$

$$- \mathbf{J}_s \cdot \left[\operatorname{grad} \ln T + \frac{T^{-1}}{G} \right.$$

$$\sum_{i=1}^{n-1} \left(\frac{\partial T}{\partial y_i} \right) \frac{d\mathbf{J}}{dt} + \frac{1}{GC_p} \frac{d\mathbf{J}_s}{dt} \right] \tag{63}$$

in which the generalized thermodynamic forces (terms in brackets) contain inertial forces. If $G \to \infty$, we get the classical formula for σ_s.

The assumption of linear relations between the fluxes and generalized forces ensures the non-negativeness of σ_s and leads to phenomenological equations

$$\mathbf{J}_i = \sum_{k=1}^{n-1} L_{ik} \left[T^{-1} \operatorname{grad} \tilde{\mu}_k + \frac{T^{-1}}{G} \right.$$

$$\times \sum_{j=1}^{n-1} \frac{\partial \tilde{\mu}_k}{\partial y_j} \frac{d\mathbf{J}_j}{dt} - \frac{T^{-1}}{G} \frac{\partial T}{\partial y_k} \frac{\partial \mathbf{J}_s}{dt} \right]$$

$$- L_{is} \left[\operatorname{grad} \ln T + \frac{T^{-1}}{G} \right.$$

$$\times \sum_{j=1}^{n-1} \frac{\partial T}{\partial y_j} \frac{d\mathbf{J}_j}{dt} + \frac{1}{GC_p} \frac{d\mathbf{J}_s}{dt} \right] \tag{64}$$

$$\mathbf{J}_s = \sum_{i=1}^{n-1} L_{is} \left[T^{-1} \operatorname{grad} \tilde{\mu}_i + \frac{T^{-1}}{G} \right.$$

$$\times \sum_{j=1}^{n-1} \frac{\partial \tilde{\mu}_i}{\partial y_j} \frac{d\mathbf{J}_j}{dt} - \frac{T^{-1}}{G} \frac{\partial T}{\partial y_i} \frac{d\mathbf{J}_s}{dt} \right]$$

$$- L_{ss} \left[\operatorname{grad} \ln T + \frac{T^{-1}}{G} \right.$$

$$\times \sum_{j=1}^{n-1} \frac{\partial T}{\partial y_j} \frac{d\mathbf{J}_j}{dt} + \frac{1}{GC_p} \frac{d\mathbf{J}_s}{dt} \right] \tag{65}$$

having again well-defined inertial terms. Here, we make use of the Onsager coefficients and not the coefficients of diffusion. It is expected that the phenomenological equations (64) and (65) will be employed in the description of highly non-stationary thermoelectric phenomena (the classical counterparts of these equations [5] should essentially deal with stationary phenomena).

6. ADDITIONAL REMARKS

Before concluding the discussion of various forms of phenomenological equations of coupled heat and mass transfer, it is worthwhile to mention, see [1], that if the momentum diffusion is accounted, for, then, under the assumption of small compressibility, the expression for the relaxation entropy can be generalized into

$$\Delta s_r = \frac{1}{2G} \mathbf{J}^T \mathbf{C}^{-1} \mathbf{J} - \frac{1}{4GT} \overset{\circ}{\pi} : \overset{\circ}{\pi} \tag{66}$$

($\overset{\circ}{\pi}$ is the deviatoric part of the pressure tensor). It was shown in [1] that if the second term of equation (66) is accounted for, then we get an additional phenomenological equation in which we recognize the Maxwell equation for a visco-elastic fluid, with the relaxation time $\tau_\pi = \eta/G$.

Under the assumption mentioned, the flux transformations and related phenomenological equations are little dependent on changes in the pressure tensor. However, in the case of a compressible fluid, especially if any chemical reactions take place, the effects of the second viscosity might be important and the form of phenomenological equations may become more complicated. Some conclusions on this subject were presented in [7]. It can hardly be said that this problem is solved, since the analysis presented in [7] was too formal, some new coefficients obtained were physically undefined and only non-reacting fluids were accounted for. That is why the thermodynamics of transport phenomena with the finite wave speed, as applied to compressible fluid in the presence of chemical reactions, should be the subject of further works.

7. SIMPLIFICATIONS OF THE THEORY FOR THE FAMILIAR SPECIAL CASES

Already Natanson [8] expressed the opinion, that all the relaxation times for the transport of momentum, heat and mass must be interrelated, saying that "this is an important, yet still an unknown law". In the present theory the relations between the relaxation coefficients come as a consequence of the unity of transport phenomena in the second sound wave, in which the propagation of momentum, heat and mass with the same speed c_0 takes place.

Maxwell's equation of a visco-elastic fluid, with the relaxation time $\tau_\pi = \eta/G$, is one of the specific relations, known earlier, to which the present theory is simplified. Let us discuss other cases. The literature data deal mainly with the perfect gas.

For isothermal binary diffusion the present theory gives $\tau_d = \rho D/G$. Hence, for the perfect gas $\tau_d = \rho D/P$—the result already known to Natanson [8]. Naturally, for pure heat conduction, we get the well known formula $\tau_h = a/c_0^2$.

Lebon [7] made use of Enskog's iteration method [9, 10], commonly used in the kinetic theory of gases, for obtaining expressions for entropy and entropy flux with the accuracy to the 2nd-order terms. Considering the transport of heat and momentum in the case of a one-component monatomic perfect gas, this author concluded that the 2nd-order correction for the entropy density is a sum of the term containing the square of the heat flux $\mathbf{J}_h^2$ and the square of the deviatoric part of the momentum flux $\overset{\circ}{\pi} : \overset{\circ}{\pi}$, with the coefficients of proportionality equal, respectively, to

$$\alpha' = \frac{-\rho}{5TP^2} \tag{67}$$

$$\gamma' = -\frac{1}{4PT} \cdot \tag{68}$$

We will show that the present theory, equation (66), simplifies to relations (67) and (68). In the special case analyzed $J = J_h$, $G = P$ and $C_p = 5/2\,RM^{-1}$, where R is gas constant. Thus, the coefficients at the squares of the fluxes, resulting from equation (66), are

$$\frac{C^{-1}}{2G} = -\frac{1}{2C_p T^2 P} = -\frac{M}{5RT^2 P} = -\frac{\rho}{5TP^2} = \alpha' \tag{69}$$

and

$$-\frac{1}{4GT} = -\frac{1}{4PT} = \gamma' \tag{70}$$

in complete agreement with [7]. The thermal relaxation time can be derived from the general equation (5) as

$$\tau_h = -\frac{L_h C_h^{-1}}{G} = \frac{\lambda}{C_p P}. \tag{71}$$

But for the monatomic gas

$$\lambda = \frac{5}{2}\eta C_r = \frac{3}{2}\eta C_p. \tag{72}$$

That is why, on the grounds of (71) and (72)

$$\tau_h = \frac{3}{2}\frac{\eta}{P}, \tag{73}$$

which agrees with [8, 11] and [12].

As can be seen, the theory presented resolves itself into the special cases known from literature. At the same time it gives many new results for non-ideal multi-component media in which there are coupled transport phenomena. This fact confirms the concept adopted here, that the basis quantities characterizing the relaxation effects, can, in principle, be defined on the ground of thermodynamics alone [see equation (33) which expresses the square approximation of the deviation of entropy from equilibrium] as well as confirms equations (14–16) of Part I describing the entropy of relaxation.

The effectiveness of thermodynamic approaches exploiting entropy deficiency function, equation (33), has been lately confirmed also in other applications, for instance, in research on thermodynamic stability [4] and qualitative analysis of the properties of flow process trajectories [16] as well as in some optimization problems [17]. Regardless of the generality of the results reached here and the definitiveness of all the new coefficients and functions characterizing relaxation effects, it is necessary to bear in mind that the accuracy of an approximation, such as in equation (33), can prove unsatisfactory in the case of large disturbances Δy_i and Δh. Also the static character of

the C matrix in equations (11) and (12) can prove to be an approximation, like the one in the theory of electromagnetic infinite lines, where in the case of a small energy dissipation the proportionality of inductance to the reciprocal of capacitance is accepted [18–20] (it is a result of the fact that the electromagnetic field carries along the same amount of magnetic and electric energy). As a result, in the most complicated cases it might prove to be necessary to use a matrix, which differs from C and which does not have a thermostatic character.‡‡

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‡‡ For barycentric velocity $v \neq$ const., some controversies regarding the so-called principle of material frame-indifference may arise, see for instance [7, 15]. But the opinions on this subject are still not clear [15] whereas we are interested mainly in the case when $v =$ const.

THERMODYNAMIQUE DES TRANSPORTS COUPLES DE CHALEUR, DE MASSE ET DE
QUANTITE DE MOUVEMENT AVEC UNE VITESSE FINIE D'ONDE: II—EXEMPLES DE
TRANSFORMATIONS DE FLUX ET DE FORCES

Résumé—En utilisant la théorie développée dans la partie I de ce travail [1], les transformations linéaires des flux et des forces thermodynamiques sont exploitées pour les transferts couplés de masse et d'énergie avec une vitesse finie C_0 de propagation. Les cas considérés englobent les transformations bien connues de la thermodynamique classique des phénomènes irréversibles. On obtient des équations phénoménologiques différentes de celles d'Onsager et un système d'équations hyperboliques (52) et (53) qui décrivent la diffusion thermique de plusieurs composants. On montre la généralité d'une approche thermodynamique basée sur l'entropie de relaxation et on discute des simplifications de la théorie pour des cas spéciaux connus.

THERMODYNAMIK DES GEKOPPELTEN WÄRME-, STOFF- UND IMPULSTRANSPORTS
MIT ENDLICHER WELLENGESCHWINDIGKEIT
II—BEISPIELE FÜR TRANSFORMATIONEN VON STROMDICHTEN
UND KRÄFTEN

Zusammenfassung—Unter Verwendung der in Teil I dieser Arbeit [1] entwickelten Theorie werden lineare Transformationen von thermodynamischen Stromdichten und Kräften umfassend für den gekoppelten Massen- und Energietransport mit endlicher Ausbreitungsgeschwindigkeit c_0 untersucht. Die betrachteten Fälle enthalten Transformationen, welche in der klassischen irreversiblen Thermodynamik gut bekannt sind. Verschiedene phänomenologische nicht-Onsager-Gleichungen und ein Standardsatz hyperbolischer Gleichungen, Gleichung (52) und (53), welche die Mehrkomponenten-Thermodiffusion beschreiben, werden erhalten. Es wird die Allgemeingültigkeit eines thermodynamischen Ansatzes, welcher auf einer sogenannten Relaxationsentropie beruht, gezeigt und Vereinfachungen der Theorie für bekannte Spezialfälle erörtert.

ТЕРМОДИНАМИКА ВЗАИМОСВЯЗАННЫХ ПРОЦЕССОВ ПЕРЕНОСА ТЕПЛА,
МАССЫ И ИМПУЛЬСА С КОНЕЧНОЙ СКОРОСТЬЮ РАСПРОСТРАНЕНИЯ ВОЛНЫ.
II — ПРИМЕРЫ ПРЕОБРАЗОВАНИЯ ПОТОКОВ И СИЛ

Аннотация — С помощью разработанной в части I настоящей работы [1] теории подробно исследуются линейные преобразования термодинамических потоков и сил для взаимосвязанных процессов переноса массы и энергии, протекающих с конечной скоростью c_0. Рассматриваются преобразования, хорошо известные из классической термодинамики необратимых процессов. Получены различные неонзагеровские феноменологические уравнения и основная система гиперболических уравнений, (52), (53), описывающие многокомпонентную диффузию тепла. Показана общность термодинамического подхода, основанного на так называемой энтропии релаксации, и обсуждаются упрощения теории на известные частные случаи.