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THERMODYNAMICS OF COUPLED HEAT, MASS AND MOMENTUM TRANSPORT WITH FINITE WAVE SPEED
I—BASIC IDEAS OF THEORY

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Abstract—Simultaneous mass and energy transfer in shock "second sound" wave moving with speed c_0 is investigated and relationships describing diffusive fluxes of mass $\mathbf{J}_i$ and energy $\mathbf{J}_q$ vs. concentration and enthalpy increments in wave front are found. Applying these relationships to the well known thermodynamic formula for deviation of entropy from equilibrium leads to an important relationship which defines the so-called relaxation entropy, Δs_r, as entropy deviation resulting from the presence of diffusive fluxes. A generalized expression for Δs_r including momentum transfer in incompressible fluids is also given.

It is shown that the presence of relaxation entropy in the entropy balance modifies the entropy source in the form that leads to phenomenological equations with inertial terms or, in a special case of uncoupled process, to the Cattaneo (1958) equation [1] and Maxwell equation for a visco-elastic fluid, Luikov (1966) [2]. The general theory of transformations of phenomenological equations and relaxation coefficient matrices is developed.

NOMENCLATURE

$\mathbf{C}$,	$\frac{\partial \mathbf{z}}{\partial \mathbf{u}} = [c_{ik}]$, thermostatic matrix of capacities;
C_p,	specific heat;
$\mathbf{C}^*$,	$= \frac{\partial \mathbf{z}^*}{\partial \mathbf{u}^*}$, new matrix of capacities;
c_0,	$= \sqrt{(G/\rho)}$, constant speed of second sound wave propagation;
$\mathbf{F}$, $\mathbf{F}^*$,	ordinary and new thermodynamic forces (including relaxation terms and gradients of transport potentials);
G,	modulus of shear rigidity;
h,	specific enthalpy;
Δh,	deviation of enthalpy, enthalpy increment in wave front (Fig. 2);
$\mathbf{J}_q$,	vector of density of diffusive energy flux;
$\mathbf{J}_i$,	vectors of densities of diffusive mass fluxes, $1 \leqslant i \leqslant n-1$;
$\mathbf{J}$,	col $(\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1}, \mathbf{J}_q)$, column matrix containing all independent fluxes;
$\mathbf{J}^*$,	new matrix of fluxes as a result of transformation of matrix $\mathbf{J}$;
$\mathbf{L}$, $\mathbf{L}^*$,	ordinary and transformed Onsager matrix, respectively;
$\mathbf{n}$,	unit normal vector;
$\mathbf{P}$, $\mathbf{Q}$,	matrices of transformations of fluxes and forces, respectively;
p, $\mathbf{P}'$,	pressure and pressure tensor, respectively;
s, s',	specific classical entropy and total specific entropy of disturbed region, respectively (Fig. 2);
Δs_r,	relaxation entropy of unit volume;
R,	universal gas constant;
T,	temperature;
t,	time;
$\mathbf{U}$,	unit tensor;
$\mathbf{u}$,	$= \mathrm{col}\left(\frac{\mu_n - \mu_1}{T} \ldots \frac{\mu_n - \mu_{n-1}}{T}, \frac{1}{T}\right)$, column matrix of ordinary transfer potentials;
$\mathbf{u}^*$,	transformed matrix $\mathbf{u}$;
V,	$= \rho^{-1}$, specific volume;
$\mathbf{w}$,	barycentric velocity;
$\mathbf{X}$,	$= \mathrm{col}\left(\mathrm{grad}\,\frac{\mu_n - \mu_1}{T}, \ldots, \mathrm{grad}\,\frac{\mu_n - \mu_{n-1}}{T}, \mathrm{grad}\,\frac{1}{T}\right)$, column matrix of classical thermodynamic forces;
$\mathbf{X}^*$,	transformed matrix $\mathbf{X}$;
y_i,	mass fraction of ith component;
$\mathbf{y}$,	$= \mathrm{col}\,(y_1, y_2 \ldots y_{n-1})$, column matrix of independent mass fractions;
$\mathbf{z}$,	$= \mathrm{col}\,(y_1, y_2 \ldots y_{n-1}, h)$, column matrix of thermodynamic state (for $P = \mathrm{const}$);
$\mathbf{z}^*$,	transformed matrix $\mathbf{z}$;
Δ,	deviation, increment;
σ,	entropy source;
σ_d, σ_r,	contributions to entropy source resulting from diffusion and relaxation, respectively;
η,	dynamic viscosity;
ρ,	mass density;
$\boldsymbol{\tau}$, $\boldsymbol{\tau}^*$,	original and new relaxation coefficient matrix, respectively;

π,	diffusional part of pressure tensor;
μ_i,	chemical potential of ith component.

Subscripts

0,	undisturbed state;
1,	state at wave front on disturbed medium side;
d,	diffusion of mass or energy;
h,	heat;
i,	ith component;
n,	component in normal direction;
q,	energy in coupled process;
r,	relaxation;
w,	shock wave.

Superscripts

$'$	total entropy;
T,	transpose matrix;
*,	quantities obtained as a result of transformations;
-1,	reverse matrix;
o,	deviator of tensor.

1. INTRODUCTION

THE PHYSICALLY natural demand that the partial differential equations for transport processes should secure the finite velocity of propagation of thermodynamic state perturbation has caused a certain dispraise of the well known conventional theory of energy, mass and momentum transfer based on parabolic equations. In many papers [1–15] it was emphasized that parabolic equations imply an infinite speed of propagation and, therefore, they should be replaced by adequate hyperbolic equations obtained by combining the phenomenological relationships of the non-Fourier (or more generally, non-Onsager) type and conservation equations. A considerable number of these papers dealt with uncoupled processes as, for example, pure heat conduction in solids [1–3, 5–14], isothermal mass diffusion [2, 4, 14], and momentum diffusion [2, 8, 14].

Just lately a more general theory has been developed [15] featuring coupled processes in which simultaneous mass and energy transfer takes place. In this theory, however, thermodynamic problems connected with the finite speed of propagation of disturbances were not analyzed. To this theory [15] and also to the author's earlier paper [14] the reader is referred before studying this paper.†

The relaxation terms in the non-Onsager phenomenological equations, that associate thermodynamic fluxes and forces, indeed secure the hyperbolic character of the resulting partial differential equations [15]. But at the same time a proof is required that both the phenomenological equations (with relaxation terms) and the respective wave equations are consistent with the non-equilibrium thermodynamics in the sense that they secure positiveness of the entropy source σ. The present paper will consider this problem on the example of simultaneous mass and energy transfer in n-component isobaric solutions.

The state of the investigated solutions will be defined by $n-1$ mass fractions y_i and the enthalpy h. In the description of the transport phenomena the densities of diffusive mass fluxes, $\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1}$, and the density of diffusive energy flux $\mathbf{J}_q$ as well as transfer potentials,

$$\frac{\mu_n-\mu_1}{T}, \quad \frac{\mu_n-\mu_2}{T}, \ldots \frac{\mu_n-\mu_{n-1}}{T}, \quad \frac{1}{T},$$

will be used. The matrix notation will be frequently exploited for which

$$\mathbf{z} = \operatorname{col}(y_1, y_2 \ldots y_{n-1}, h),$$

$$\mathbf{u} = \operatorname{col}\left(\frac{\mu_n-\mu_1}{T}, \frac{\mu_n-\mu_2}{T} \ldots \frac{\mu_n-\mu_{n-1}}{T}, \frac{1}{T}\right),$$

$$\mathbf{J} = \operatorname{col}(\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1}, \mathbf{J}_q).$$

It may seem that the non-Onsager phenomenological equations with relaxation terms [for instance the matrix equation (30) in Section 3] are incorrect because non-negativness of the classical expression for the entropy source

$$\sigma_d = \sum_{k=1}^{n} \mathbf{J}_k \cdot \operatorname{grad} \mathbf{u}_k = \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \operatorname{grad}\left(\frac{\mu_n-\mu_i}{T}\right) + \mathbf{J}_q \cdot \operatorname{grad}\left(\frac{1}{T}\right) (p = \text{const.}), \quad (1)$$

is not secured for such phenomenological equations.

However, this contradiction to a local formulation of the second law of thermodynamics is only apparent because, as is seen from what follows, equation (1) does not precisely describe the entropy source in the non-classical case where relaxation effects play a part. That is why equation (1) cannot provide a basis for the correctness of the non-Onsager equations to be verified.

In the present (two-part) work it is shown that this basis is provided by a certain generalized form of equation (1) which accounts for the presence of inertial forces associated with the time derivative of fluxes‡. Development of the method of obtaining such a basis is one of the objectives of this paper. If generalization of (1) could be found, then the phenomenological equations containing the relaxation terms would result from the condition $\sigma \geqslant 0$ as in the classical case.

Different generalizations of the entropy source have already been given in the case of heat [16] and momentum [17, 18] diffusion. These generalizations lead, among other things, to justification of the form of the Cattaneo equation [1] which describes pure heat transfer. However, these generalizations are somewhat

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† In the papers quoted the reader will also find many other valuable references concerning wave equations for transport processes.

‡ E.g. the matrix equation (26) in this paper.

formal and therefore (even in simple cases) not all of the new coefficients have been defined. Also the explanation of how the entropy source is modified when the coupled processes, such as, for instance, simultaneous mass and energy transfer, take place.

In the present work, attention is directed towards a general method of derivation of the equations which describe entropy and entropy source in the presence of relaxation effects for the processes of coupled mass and energy transfer in chemically non-reacting solutions of negligible compressibility.

This method is based on the analysis of the physical situation in the "second sound" shock wave front and on the well known classical formula for the square approximation of entropy deviation from equilibrium [19–21]. Owing to the latter fact all of the coefficients appearing in the present theory are well defined. Also presented is a certain generalization of the theory involving momentum transfer in incompressible fluids. It will be also shown (Part II) that the present theory always leads to the results which correspond to the well-known particular cases.

The classical non-equilibrium thermodynamics is based on the local equilibrium postulate [20–22]. As a consequence of this postulate, the theory (in the investigated isobaric case) makes use of the equilibrium form of the relationship which expresses the entropy s in terms of the enthalpy h and concentrations y_i. Such an approach results in a linear dependence of transport potential gradients on fluxes described by the Onsager equations.

In the present work we give up the local equilibrium postulate and assume *a priori* local non-equilibrium of continuum. The entropy of the disturbed non-equilibrium state differs at every point of the continuum from the local equilibrium entropy $s(h, y)$, with the difference $\Delta s = s' - s$ being a function of all the independent diffusive fluxes $\mathbf{J}_1, \mathbf{J}_2, \dots \mathbf{J}_{n-1}, \mathbf{J}_q$, see equation (16). This function is called the relaxation entropy because it is associated with the tendency of every element of the continuum to recover thermodynamic equilibrium during vanishing of fluxes $\mathbf{J}$ or relaxation of stresses π(max $s' = s$ for $\mathbf{J} = 0$ and $\pi = 0$). Since such a process is thermodynamically irreversible, the relaxation entropy $\Delta s = s' - s$ is a negative quantity. The present approach to a certain extent resembles that used in dynamical problems of the elasticity theory [23] where, however, the free energy potential (rather than entropy) is usually used.

The project of our analysis is as follows. In Section 2 of this paper, the coupled heat and mass transport occurring in the front of a shock wave, moving with a constant speed c_0, is investigated and the expression describing the entropy of disturbed state as a sum of classical entropy and relaxation entropy is worked out. This expression is then used (Section 3) to derive a generalized formula (26) containing an entropy source with relaxation terms. From this formula, the generalized matrix phenomenological equation of the non-Onsager type results together with the definition of the matrix of relaxation coefficients. Then in Section 4, the invariency of phenomenological equation in relation to linear transformations of thermodynamic fluxes and forces is discussed. In Section 5, a generalization of the theory, including momentum transfer in incompressible fluids (leading to the Maxwell equation for viscoelastic fluid) is given.

In Part II of this work (a separate paper), examples of linear transformations of fluxes and forces are given. This treatment is used to define new forms of the non-classical entropy source and phenomenological equations that relate new fluxes and forces. Then, on the basis of the most suitable phenomenological equations, a system of hyperbolic-type partial differential equations, describing thermal diffusion in multicomponent systems, is derived. Finally, simplifications of the theory to be applied to particular cases known from the literature are discussed.

In paper [24], the significance of relaxation entropy for formulation of the variational principles that lead to the non-Onsager phenomenological equations and conservation equations is treated.

2. THE COUPLED MASS AND ENERGY TRANSFER IN A SHOCK WAVE

Consider a non-stationary shock wave in which there is a simultaneous energy and mass transfer.

The motion of the wave is a change in position of a certain surface of discontinuity, Fig. 1. Of course, the wave velocity has nothing in common with the barycentric velocity of the medium (solid or fluid). In the frame fixed with respect to the undisturbed part of the medium the wave speed is of the same order as that of sound [7]. On the other hand, the barycentric velocity in the disturbed part is close to zero and, in media exhibiting small compressibility, may not be taken into account. In the case of an incompresssible continuum the moving wave front leaves behind a thermodynamically disturbed part of the medium which is at rest.

In the present consideration the conditions that describe the jumps of thermodynamic quantities in the wave front will be important. These conditions will be defined by analyzing an arbitrary element of the wave front and investigating the physical phenomena in the frame fixed with respect to this element (in such a frame formulation of the conditions is the easiest). The conditions, however, will be expressed in terms of the quantities which characterize the original frame (fixed in relation to the undisturbed part) in which the diffusion of mass and energy is usually described.

In the wave front frame, Fig. 1, the elements of the continuum pass through the surface of discontinuity. On this surface there must be a continuous mass flux (the medium flows from side 0 to side 1), that is

$$\rho_0(\mathbf{w}_0 - \mathbf{w}_w) \cdot \mathbf{n}_0 = \rho_1(\mathbf{w}_1 - \mathbf{w}_w) \cdot \mathbf{n}_0 = \mathbf{j}_0 \cdot \mathbf{n}_0. \quad (2)$$

The symbol $\mathbf{n}_0$ denotes the unit vector of the external normal to the surface of the front, while the symbol $\mathbf{w}_w$ denotes the velocity of the wave front. The velocity $\mathbf{w}_w$ is determined along the normals $\mathbf{n}_1 = -\mathbf{n}_0$ (the

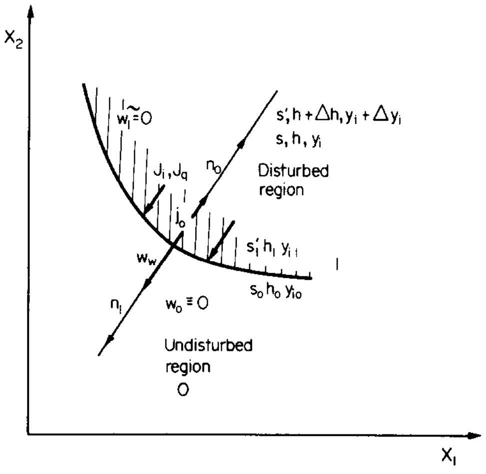

FIG. 1. Designation of basic quantities characterizing the shock wave.

direction of wave motion). Since for barycentric velocities $\mathbf{w}_0 \simeq \mathbf{w}_1 \simeq 0$, equations (2) yield

$$\mathbf{j}_0 \cdot \mathbf{n}_0 = \mathbf{j}_1 \cdot \mathbf{n}_0 = -\mathbf{j}_1 \cdot \mathbf{n}_1 = \rho_0 c_0, \tag{3}$$

where the scalar

$$c_0 = -\mathbf{w}_w \cdot \mathbf{n}_0 = \mathbf{w}_w \cdot \mathbf{n}_1 \tag{4}$$

is the propagation speed. The above definitions secure $c_0 > 0$. Also, $j = \mathbf{j}_0 \cdot \mathbf{n}_0 > 0$.

The mass balance of the component i is†

$$y_{i0} \mathbf{j}_0 \cdot \mathbf{n}_0 + (\mathbf{J}_i + y_{i1} \mathbf{j}_1) \cdot \mathbf{n}_1 = 0. \tag{5}$$

Therefore, on the basis of (3) and (5)

$$\mathbf{J}_i \cdot \mathbf{n}_1 = \rho_0 c_0 (y_{i1} - y_{i0}). \tag{6}$$

In a similar way the energy balance is obtained as

$$h_0 \mathbf{j}_0 \cdot \mathbf{n}_0 + (\mathbf{J}_q + h_1 \mathbf{j}_1) \cdot \mathbf{n}_1 = 0, \tag{7}$$

or, using (3) and (7),‡

$$\mathbf{J}_q \cdot \mathbf{n}_1 = \rho_0 c_0 (h_1 - h_0). \tag{8}$$

In the medium close to the wave front, on the undisturbed side, all the physical parameters are constant. That is why this allows the statement that the motion of the disturbed region is a motion of isoenthalpy (and at the same time of the isotherm, isobar, etc.) surrounding the disturbed region and having the same enthalpy (temperature, concentrations and other properties) such as the undisturbed region. Let this enthalpy (and concentrations) be continuous when passing the surface of the wave front. It means that an assumption is made that the continuum on the disturbed side of the wave front has two enthalpies, h_0 and h_1 (and two other sets of parameters), which describe it. Here occurs, so to say, an extension of the state $\mathbf{z}_0 = \mathrm{col}(y_{10}, y_{20} \ldots y_{n-10}, h_0)$ to the disturbed side, Fig. 2. This concept can also be applied to the interior of the disturbed part. Then, a variable extended state for an arbitrary point of the medium can be considered. Consequently, the local state of the mixture is described by the vector $\mathbf{z} = \mathrm{col}(y_1, y_2, \ldots y_{n-1}, h)$, and the extended state, by the vector $\mathbf{z} + \Delta\mathbf{z} = \mathrm{col}(y_1 + \Delta y_1, y_2 + \Delta y_2 \ldots h + \Delta h)$ (Fig. 2). In what follows, advantage will be taken of such a representation of the state of continuum. Now, let us return to investigation of the physical situation close to the wave front.

The diffusive fluxes of mass and energy are directed along the normal $\mathbf{n}$ towards the wave front, i.e. they are orthogonal to an 'equipotential' surface of the undisturbed front side. This being so,

$$\mathbf{J}_i \cdot \mathbf{n}_1 = J_i, \tag{9}$$

$$\mathbf{J}_q \cdot \mathbf{n}_1 = J_q. \tag{10}$$

Therefore, on the basis of equations (6), (8), (9) and (10)

$$\mathbf{J}_i^2 = \rho_0^2 c_0^2 (y_{i1} - y_{i0})^2, \tag{11}$$

$$\mathbf{J}_q^2 = \rho_0^2 c_0^2 (h_1 - h_0)^2. \tag{12}$$

The directions of $\mathbf{J}_i$ and $\mathbf{J}_q$ are the same [$\cos\alpha(\mathbf{J}_i, \mathbf{J}_q) = 1$] and therefore

$$\mathbf{J}_i \cdot \mathbf{J}_q = \rho_0^2 c_0^2 (y_{i1} - y_{i0})(h_1 - h_0). \tag{13}$$

Equations (11)–(13) constitute an important result—they express the state disturbance, $\Delta z_i \overset{\text{def.}}{\equiv} z_{i0} - z_{i1}$, in terms of the diffusive fluxes $\mathbf{J}_i$.

We shall now describe the deficiency of entropy close to the wave front caused by disturbances. This deficiency, that is $s_1' - s_1$, must disappear in the state (h_1, y_{i1}) and must be negative beyond this state, because the entropy of deviated state s_1' must have a maximum equal to s_1 for $h = h_1$ and $y_i = y_{i1}$. This means that the first partial derivatives of s_1' with respect to the increments $\Delta h = h - h_1$ and $\Delta y_i = y_i - y_{i1}$ must vanish for $h = h_1$ and $y_i = y_{i1}$, or that the expansion of s_1' about s_1 must begin with square terms (should the linear terms appear in this expansion, the first derivatives would be different from zero and the local equilibrium entropy would not be maximum).

This expansion (for $p = \text{const.}$) can be written in one of the alternative forms known from the classical thermodynamics [19–21]:

$$\begin{aligned} s_1' &= s_1 + \frac{1}{2}\left[\Delta h \Delta T^{-1} + \sum_{k=1}^{n-1} \Delta y_k \Delta\left(\frac{\mu_n - \mu_k}{T}\right)\right] \\ &= \frac{1}{2}\sum_i^n \sum_k^n c_{ik}\, \Delta u_i \Delta u_k \\ &= \frac{1}{2}\left[\sum_{i=1}^{n-1} \sum_{k=1}^{n-1} \frac{\partial(\mu_n - \mu_i)\, T^{-1}}{\partial y_k} \Delta y_k\, \Delta y_i \right. \\ &\quad \left. + 2\frac{\partial(\mu_n - \mu_i)\, T^{-1}}{\partial h} \Delta y_i\, \Delta h + \frac{\partial T^{-1}}{\partial h} \Delta h^2\right], \end{aligned} \tag{14}$$

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† It should be kept in mind that $\mathbf{J}_q$ and $\mathbf{J}_i$ are 'diffusive' fluxes. These are expressed in equations (5) and (7) or (6) and (8) in terms of concentration and enthalpy jumps.

‡ Note that the presence of c_0 in equations (6) and (8) does not imply that $\mathbf{J}_q$ and $\mathbf{J}_i$ are convective quantities. In fact, these are diffusive fluxes that are 'only expressed' in terms of the convective flux $\rho_0 c_0$ of equation (3).

where

$$\mathbf{u} = \mathrm{col}\,(u_1, u_2 \ldots u_{n-1}, u_n)$$

$$\overset{\text{def.}}{=} \mathrm{col}\left(\frac{\mu_n-\mu_1}{T} \ldots \frac{\mu_n-\mu_{n-1}}{T}, \frac{1}{T}\right).$$

The derivative $[\partial(\mu_n-\mu_1)T^{-1}/\partial h]_{y_{i1}}$ can be replaced in equation (14) by the derivative $(\partial T^{-1}/\partial y_i)_{h_1}$ based on the Maxwell relation. These derivatives pertain to the state T_1, p_0 and y_{i1}.

Application of equations (11–13) to express the increments $\Delta y_i = u_{i0} - y_{i1}$ and $\Delta h = h_0 - h_1$ in terms of the diffusive fluxes yields an important expression which describes the total† entropy s_1' of the disturbed side of wave front as

$$\begin{aligned} s_1' = s_1 + \frac{1}{2\rho_1^2 c_0^2} & \left\{ \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} \left[\frac{\partial(\mu_n-\mu_i)T^{-1}}{\partial y_k} \right]_{p_0 h_1} \right. \\ & \times \mathbf{J}_k \cdot \mathbf{J}_i + 2 \sum_{i=1}^{n-1} \left[\frac{\partial(\mu_n-\mu_i)\,T^{-1}}{\partial h} \right]_{p_0 y_1} \\ & \left. \times \mathbf{J}_i \cdot \mathbf{J}_q + \left(\frac{\partial T^{-1}}{\partial h} \right)_{p_0 y_1} \cdot \mathbf{J}_q^2 \right\}. \end{aligned} \tag{15}$$

Here s_1 is the function of h_1 and of all y_{i1}, known from the classical thermodynamics, and the term containing fluxes is the entropy of relaxation.

It is well known that the requirement for positiveness of the entropy source, obtained for the classical quantity s_1, leads to phenomenological relations of Onsager's type. It will be shown that a similar demand for the source of the total entropy s_1' leads to the Cattaneo–Vernotte type of generalized phenomenological equations suggested by the present author in [15] for the coupled processes without a thermodynamic justification.

Since equation (15) is derived for the wave front, we can be sure that the phenomenological equations obtained on its basis (see below) will be exact near the disturbed side of wave front. The corresponding equations for the interior of disturbed region could be, at least in principle, more general as these are associated with a less particular physical situation. At present, however, it will be arbitrarily assumed that equation (15) will hold also for each point of the disturbed region interior. The non-Onsager phenomenological equations obtained in this way will have the same form both for the disturbed side of wave front and any point of the interior of disturbed region, which physically seems to be be rather natural. (This is, in fact, a standpoint based on what has been published up till now on pure heat conduction.)

The acceptance of the standpoint that equation (15) can be applied also to the interior of disturbed region results in a fundamental relationship for the total entropy s' of an arbitrary element of the medium:

$$\begin{aligned} s'(y_1, y_2 \ldots h, \mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_q) = {} & s(y_1, y_2 \ldots h) \\ & + \frac{1}{2\rho^2 c_0^2} \left\{ \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} \left[\frac{\partial(\mu_n-\mu_i)\,T^{-1}}{\partial y_k} \right]_{p_0 h} \right. \\ & \times \mathbf{J}_k \cdot \mathbf{J}_i + 2 \sum_{i=1}^{n-1} \left[\frac{\partial(\mu_n-\mu_i)\,T^{-1}}{\partial h} \right]_{p_0 y} \\ & \left. \times \mathbf{J}_i \cdot \mathbf{J}_q + \left(\frac{\partial T^{-1}}{\partial h} \right)_{p_0 y} \mathbf{J}_q^2 \right\}. \end{aligned} \tag{16}$$

This lays emphasis on the fact that the appearance of diffusive fluxes is inseparably connected with the inherent thermodynamic non-equilibrium which causes relaxation of fluxes (see Fig. 2 for interpretation of the local values $\mathbf{z} = (h, y_j)$ and their increments $\Delta\mathbf{z}$).

It is convenient to use equation (16) in an alternative matrix form using the so-called capacities $c_{ik} = \partial z_i/\partial u_k$ [15], i.e. elements of the following matrix:

$$\mathbf{C} = \left[\begin{array}{cccc} \dfrac{\partial y_1}{\partial\left(\dfrac{\mu_n-\mu_1}{T}x\right)} & \dfrac{\partial y_1}{\partial\left(\dfrac{\mu_n-\mu_2}{T}\right)} & \dfrac{\partial y_1}{\partial\left(\dfrac{\mu_n-\mu_{n-1}}{T}\right)} & \dfrac{\partial y_1}{\partial\left(\dfrac{1}{T}\right)} \\ \dfrac{\partial y_2}{\partial\left(\dfrac{\mu_n-\mu_1}{T}\right)} & \dfrac{\partial y_2}{\partial\left(\dfrac{\mu_n-\mu_2}{T}\right)} & \dfrac{\partial y_2}{\partial\left(\dfrac{\mu_n-\mu_{n-1}}{T}\right)} & \dfrac{\partial y_2}{\partial\left(\dfrac{1}{T}\right)} \\ \hdashline \dfrac{\partial h}{\partial\left(\dfrac{\mu_n-\mu_1}{T}\right)} & \dfrac{\partial h}{\partial\left(\dfrac{\mu_n-\mu_2}{T}\right)} & \dfrac{\partial h}{\partial\left(\dfrac{\mu_n-\mu_{n-1}}{T}\right)} & \dfrac{\partial h}{\partial\left(\dfrac{1}{T}\right)} \end{array} \right] \tag{17}$$

It is important that the matrix $\mathbf{C}$ is negatively defined and symmetric [15, 19, 20] which is a consequence of the second law of thermodynamics and Maxwell relations.

It can be shown that the partial derivatives in equation (16) are coefficients of matrix $\mathbf{C}^{-1}$. Therefore, equation (16) can be written in a concise matrix form

$$s'(\mathbf{z}, \mathbf{J}) = s(\mathbf{z}) + \frac{1}{2\rho G} \mathbf{J}^{\mathrm{T}} \mathbf{C}^{-1} \mathbf{J}. \tag{18}$$

In equation (18) the dependence [2] of modulus of shear rigidity G on the propagation velocity:

$$G = \rho c_0^2, \tag{19}$$

was exploited.‡ The significance of expression (18) lies in the fact that it allows construction of a new formal structure of the irreversible thermodynamics based on the concept of local non-equilibrium in a continuum. This means the renunciation of the fundamental

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† By the total entropy, the sum of the classical entropy and entropy of diffusional fluxes is meant.

‡ Equation (19) can alternatively be treated as a definitive equation for G in terms of c_0.

assumption of local equilibrium accepted in the classical non-equilibrium thermodynamics [20–22].

The consequences of such an approach are discussed in the next Section.

3. THE NON-CLASSICAL ENTROPY SOURCE AND NON-ONSAGER PHENOMENOLOGICAL EQUATIONS

With the help of the conventional approach of non-equilibrium thermodynamics we will find the entropy source by making use of mass and energy conservation equations in the expression for time derivative of the total entropy s'.

The conservation equations are†:

$$\rho \frac{\mathrm{d}y_i}{\mathrm{d}t} = -\operatorname{div} \mathbf{J}_i, \quad i = 1, 2 \ldots n-1, \tag{20}$$

$$\rho \frac{\mathrm{d}h}{\mathrm{d}t} = -\operatorname{div} \mathbf{J}_q, \tag{21}$$

and can be written in the following matrix form

$$\rho \frac{\mathrm{d}\mathbf{z}}{\mathrm{d}t} = -\operatorname{div} \mathbf{J}. \tag{22}$$

On the other hand, on the basis of equation (18) the expression describing time derivative of the total entropy s' is (for p = const.)

$$\frac{\mathrm{d}s'}{\mathrm{d}t} = T^{-1}\frac{\mathrm{d}h}{\mathrm{d}t} + \sum_{k=1}^{n-1}\left(\frac{\mu_n - \mu_k}{T}\right)\frac{\mathrm{d}y_k}{\mathrm{d}t} + \frac{1}{\rho G}\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}. \tag{23}$$

Making use of (20) and (21) in (23) gives

$$\rho\frac{\mathrm{d}s'}{\mathrm{d}t} = \frac{-\operatorname{div}\mathbf{J}_q}{T} - \sum_{k=1}^{n-1}\left(\frac{\mu_n - \mu_k}{T}\right) \times \operatorname{div}\mathbf{J}_k + \frac{1}{G}\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}, \tag{24}$$

that is

$$\rho\frac{\mathrm{d}s'}{\mathrm{d}t} = -\operatorname{div}\frac{\mathbf{J}_q - \sum_{k=1}^{n}\mu_k\mathbf{J}_k}{T} + \mathbf{J}_q\cdot\operatorname{grad}T^{-1} + \sum_{k=1}^{n-1}\mathbf{J}_k\cdot\operatorname{grad}\left(\frac{\mu_n - \mu_{n-1}}{T}\right) + \frac{1}{G}\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}, \tag{25}$$

(the complicated structure of the scalar in the last component of this equation should be kept in mind).

Equation (25) shows that besides the classical expression for the entropy source there is an additional term connected with relaxation. Taking into consideration that the column matrix $\mathbf{J}$ is composed of $\mathbf{J}_k$ and $\mathbf{J}_q$, the non-classical entropy source resulting from equation (25) can be written in a compact matrix form

$$\sigma = \mathbf{J}^{\mathrm{T}}\mathbf{F} = \mathbf{J}^{\mathrm{T}}\left(\operatorname{grad}\mathbf{u} + \frac{\mathbf{C}^{-1}}{G}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}\right), \tag{26}$$

where

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

Note the appearance of additional inertial forces in the generalized thermodynamic forces $\mathbf{F}_i$ of equation (26). In [24] the role of the reversible and dissipative forces in equation (26) is shown.

Let us notice also that equation (26) can be written in the form:

$$\sigma = \sigma_r + \sigma_d,$$

where

$$\sigma_d = \mathbf{J}^{\mathrm{T}}\operatorname{grad}\mathbf{u} \tag{27}$$

and‡

$$\sigma_r = \mathbf{J}^{\mathrm{T}}\frac{\mathbf{C}^{-1}}{G}\mathbf{J} \tag{28}$$

describe the classical and non-classical component of entropy source, respectively. Although such a separation is formal, sometimes it facilitates the use of equation (26) (see Section 4).

The condition of non-negativeness of entropy source (26) leads to a phenomenological matrix equation

$$\mathbf{J} = \mathbf{L}\left(\operatorname{grad}\mathbf{u} + \frac{\mathbf{C}^{-1}}{G}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}\right), \tag{29}$$

in which $\mathbf{L}$ is the Onsager matrix defined positively. Note that in the case of pure heat diffusion $c_h = -C_pT^2$, $L_h = \rho C_p a T^2 = \lambda T^2$ and equation (29) is reduced to the Cattaneo equation

$$\mathbf{J}_h + \frac{a}{c_0^2}\dot{\mathbf{J}}_h = -\lambda\operatorname{grad}T. \tag{29a}$$

Equation (29) can be replaced by a system of two equations

$$\mathbf{J} + \tau\dot{\mathbf{J}} = \mathbf{L}\operatorname{grad}\mathbf{u}, \tag{30}$$

$$\tau = -\frac{\mathbf{L}\mathbf{C}^{-1}}{G}. \tag{31}$$

For equation (29) [or (30) and (31)] the entropy source (26) takes a bilinear form:

$$\sigma = \mathbf{J}^{\mathrm{T}}\mathbf{L}^{-1}\mathbf{J} \geqslant 0 \quad (\mathbf{L} \geqslant \mathbf{O}). \tag{32}$$

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† Note that this 'general' form of conservation laws cannot be affected by the presence of relaxation or other terms. On the other hand, a purely thermodynamic relationship [see equation (23)] must undergo a change due to an additional (non-equilibrium) term which describes relaxation.

‡ Somewhat surprisingly, the static matrix $\mathbf{C}$ appears in the kinetic equation (28). This is, of course, a consequence of our expression for Δs, equation (14). In Section 7 of Part II it will be, therefore, shown that the general theory based on equation (26) simplifies to the 'special' cases known earlier from the kinetic theory.

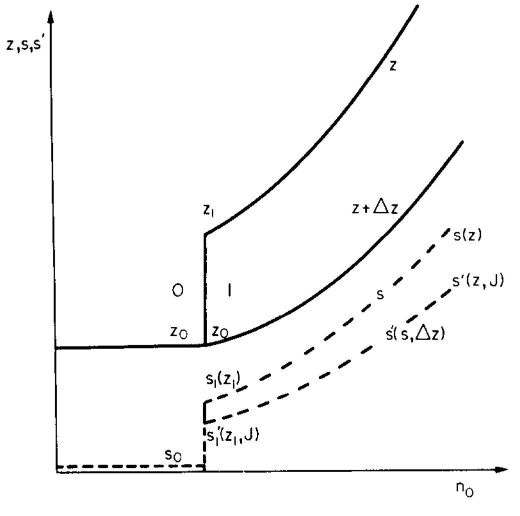

FIG. 2. Interpretation of disturbed and extended states.

Equation (30) constitutes a generalization of the Cataneo equation (29a) for coupled processes, while equation (31) defines the matrix of relaxation coefficients by two basic matrices: the kinetic (Onsager) matrix **L** and the thermostatic capacity matrix **C**. Equations (30) and (31) have been predicted rather than proved by the author in the earlier work [15] but their thermodynamic origin has not been then discovered as yet.

The present theory shows that these result from renunciation of the postulate of local equilibrium which is one of the basic postulates in the classical irreversible thermodynamics. Consequently, the relaxation terms appear as a result of application of a more proper expression for entropy, equation (16). Thus, no essentially new technique is required to obtain the Cattaneo-type non-Onsager equations or related wave equations.

It is important that here all of the new parameters and functions (describing relaxation effects) are determined quantitatively and that they are expressed in terms of the known and measurable physical quantities. Note that in the limiting case $c_0 \to \infty$ the classical description based on the local equilibrium is recovered.

4. THE GENERALIZED THEORY OF TRANSFORMATION OF FLUXES AND FORCES AND THE INVARIANCY OF THE PHENOMENOLOGICAL EQUATION (29)

The bracketed expression in equation (26) is a matrix thermodynamic force of simultaneous energy and mass transport with relaxation. In what follows this force will be denoted by $\mathbf{F} = \mathrm{col}\,(\mathbf{F}_1, \mathbf{F}_2 \ldots \mathbf{F}_{n-1}, \mathbf{F}_q = \mathbf{F}_n)$, while the component $\mathbf{F}_k$ is†

$$\mathbf{F}_k = \mathrm{grad}\, u_k + \sum_{i=1}^{n} \frac{C_{ki}^{-1}}{G} \frac{\mathrm{d}\mathbf{J}_i}{\mathrm{d}t}. \tag{33}$$

One can see that each of the generalized forces $\mathbf{F}_k$ includes inertial components which depend on all the fluxes. Equation (29) expressed in terms of the matrix **F** has a simple form

$$\mathbf{J} = \mathbf{L}\mathbf{F}. \tag{34}$$

Suppose it is required to describe the process with the aid of new fluxes $\mathbf{J}_i^*$ and new forces $\mathbf{F}^*$ which are linear functions of the former fluxes $\mathbf{J}_i$ and forces $\mathbf{F}_i$, respectively, that is

$$\mathbf{J}^* = \mathbf{P}\mathbf{J}, \tag{35}$$

$$\mathbf{F}^* = \mathbf{Q}\mathbf{F} \tag{36}$$

where **P** and **Q** are the matrices of the transformation. As is shown below, only one of these can be freely chosen [see equation (40)].

The physical objectiveness of the entropy source (26) and relaxation entropy $s' - s$, equation (18), demands that each of these quantities be transformed invariantly with respect to transformations (35) and (36). That means that

$$\mathbf{J}^{\mathrm{T}}\,\mathbf{F} = \mathbf{J}^{*\mathrm{T}}\,\mathbf{F}^* \tag{37}$$

and

$$\frac{1}{2\rho\, G} \mathbf{J}^{\mathrm{T}}\,\mathbf{C}^{-1}\,\mathbf{J} = \frac{1}{2\rho\, G} \mathbf{J}^{*\mathrm{T}}\,\mathbf{C}^{*-1}\,\mathbf{J}^*. \tag{38}$$

We will prove that the conditions (37) and (38) lead to the transformation rules of the basic quantities describing the process, i.e. for $\mathbf{L}\tau\mathbf{C}$, σ_r, σ_d, **u**, **z** and grad **u**, and imply the invariancy of the form of phenomenological equation (29) with respect to (35) and (36).

Substituting the RHS of equations (35) and (36) into a new entropy source, $\mathbf{J}^{*\mathrm{T}}\,\mathbf{F}^*$, and using equation (37), we get

$$\sigma = \mathbf{J}^{*\mathrm{T}}\,\mathbf{F}^* = \mathbf{J}^{\mathrm{T}}\,\mathbf{P}^{\mathrm{T}}\,\mathbf{Q}\mathbf{F} = \mathbf{J}^{\mathrm{T}}\,\mathbf{F}. \tag{39}$$

Therefore, $\mathbf{P}^{\mathrm{T}}\mathbf{Q}$ is the unit matrix **E**‡. Hence

$$\mathbf{Q} = (\mathbf{P}^{\mathrm{T}})^{-1}, \tag{40}$$

which gives a rule for computing the matrix **Q** if the matrix **P** is given (or the reverse).

As the new entropy source is $\mathbf{J}^{*\mathrm{T}}\,\mathbf{F}^*$, then the new phenomenological equation should have the form:

$$\mathbf{J}^* = \mathbf{L}^*\,\mathbf{F}^*. \tag{41}$$

Equations (34), (35), (36) and (41) yield

$$\mathbf{L}^* = \mathbf{P}\mathbf{L}\mathbf{Q}^{-1} \tag{42}$$

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† An equation of this type is given in [20]. It takes into account the kinetic energy of diffusion only and not the available energy of local non-equilibrium state, as equation (33) does. Note, therefore, the agreement of equation (33) with the results obtained from the kinetic theory, see Section 7 of Part II.

‡ In the absence of external magnetic field.

and equations (40) and (42) yield

$$\mathbf{L}^* = \mathbf{P}\mathbf{L}\mathbf{P}^{\mathrm{T}}. \tag{43}$$

This expression describes the new Onsager matrix. On the basis of the symmetry of **L** with account for (43), we obtain

$$\mathbf{L}^* = \mathbf{P}\mathbf{L}\mathbf{P}^{\mathrm{T}} = \mathbf{P}\mathbf{L}^{\mathrm{T}}\mathbf{P}^{\mathrm{T}} = (\mathbf{P}\mathbf{L}\mathbf{P}^{\mathrm{T}})^{\mathrm{T}} = \mathbf{L}^{*\mathrm{T}}, \tag{44}$$

i.e. the new matrix $\mathbf{L}^*$ is also symmetric.

Substituting **J** from (35) into the relation

$$\Delta s_r = \mathbf{J}^{\mathrm{T}} \frac{\mathbf{C}^{-1}}{2G} \mathbf{J}, \tag{45}$$

which describes the relaxation entropy of a unit volume, we get

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

$$= \mathbf{J}^{*\mathrm{T}} (\mathbf{P}^{\mathrm{T}})^{-1} \frac{\mathbf{C}^{-1}}{2G} \mathbf{P}^{-1}\mathbf{J}^*. \tag{46}$$

We may see that the invariancy of Δs_r will be assured [meaning that equality (38) will be true] if we use a new capacity matrix defined as

$$\mathbf{C}^* = \mathbf{P}\mathbf{C}\mathbf{P}^{\mathrm{T}}. \tag{47}$$

In the same fashion as for the matrix $\mathbf{L}^*$ one can prove that the new capacity matrix $\mathbf{C}^*$ is symmetric and that it results from the symmetry of the former matrix **C**.

Actually, on the basis of equation (47) and for $\mathbf{C} = \mathbf{C}^{\mathrm{T}}$:

$$\mathbf{C}^* = \mathbf{P}\mathbf{C}^{\mathrm{T}}\mathbf{P}^{\mathrm{T}} = (\mathbf{P}\mathbf{C}\mathbf{P}^{\mathrm{T}})^{\mathrm{T}} = \mathbf{C}^{*\mathrm{T}}. \tag{48}$$

Application of (47) and (35) to (28) gives

$$\sigma_r = \mathbf{J}^{\mathrm{T}} \frac{\mathbf{C}^{-1}}{G} \mathbf{J} = \mathbf{J}^{*\mathrm{T}} \frac{\mathbf{C}^{*1}}{G} \mathbf{J}^* \tag{49}$$

which means that contribution of relaxation to the entropy source is also an invariant of the transformation (35).

Due to invariancy of the total entropy source and the relation $\sigma = \sigma_d + \sigma_r$, the quantity σ_d, equations (1) and (27), should be also invariant. This means that

$$\mathbf{J}^{\mathrm{T}} \operatorname{grad} \mathbf{u} = \mathbf{J}^{*\mathrm{T}} \operatorname{grad} \mathbf{u}^*, \tag{50}$$

just as in the classical process without relaxation. From equations (35), (40) and (50) we get a *transformation rule for the gradients of transfer potentials*

$$\operatorname{grad} \mathbf{u}^* = \mathbf{P}^{-1\mathrm{T}} \operatorname{grad} \mathbf{u} = \mathbf{Q} \operatorname{grad} \mathbf{u}, \tag{51}$$

which is similar as to the total forces $\mathbf{F}_i$, equation (36). Equation (51) also implies that

$$\Delta\mathbf{u}^* = \mathbf{Q}\Delta\mathbf{u}. \tag{52}$$

Finally, after considering the capacity definition and equations (40), (47) and (52) we get

$$\Delta\mathbf{z}^* = \mathbf{P}\Delta\mathbf{z}, \tag{53}$$

i.e. the state variables, z_i, are transformed in the same way as the fluxes $\mathbf{J}_i$.

One can presume that the phenomenological equation (29) has a form invariant with respect to the investigated transformations. Let us check this. For the factor before the derivative $\mathrm{d}\mathbf{J}/\mathrm{d}t$, equation (29), on having used (43) and (47), we have

$$-\tau = \frac{\mathbf{L}\mathbf{C}^{-1}}{G} = \frac{\mathbf{P}^{-1}\mathbf{L}^*\mathbf{P}^{-1\mathrm{T}}(\mathbf{P}^{-1}\mathbf{C}^*\mathbf{P}^{-1\mathrm{T}})^{-1}}{G}$$

$$= \frac{\mathbf{P}^{-1}\mathbf{L}^*\mathbf{P}^{-1\mathrm{T}}\mathbf{P}^{\mathrm{T}}\mathbf{C}^{*-1}\mathbf{P}}{G} = \frac{\mathbf{P}^{-1}\mathbf{L}^*\mathbf{C}^{*-1}\mathbf{P}}{G}. \tag{54}$$

Applying equation (54) to (29) and using relations (35), (43) and (51), we get

$$\mathbf{P}^{-1}\mathbf{J}^* = G^{-1}\mathbf{P}^{-1}\mathbf{L}^*\mathbf{C}^{*-1}\mathbf{P}\,\mathbf{P}^{-1}\dot{\mathbf{J}}^*$$

$$+\mathbf{P}^{-1}\mathbf{L}^*\mathbf{P}^{-1\mathrm{T}}\mathbf{P}^{\mathrm{T}} \operatorname{grad} \mathbf{u}^*, \tag{55}$$

or (after multiplication of the both sides by **P** and simplifications)

$$\mathbf{J}^* = \mathbf{L}^* \left(\operatorname{grad} \mathbf{u}^* + \frac{\mathbf{C}^{*-1}}{G} \frac{\mathrm{d}\mathbf{J}^*}{\mathrm{d}t} \right). \tag{56}$$

It is therefore proved that for the linear transformations (35), (36) and (40), the form of the phenomenological equation will not alter [compare equations (29) and (56)]. This fact means that the structure of (56) is admissible in view of the transformations investigated.

Equation (56) yields a new relaxation matrix

$$\tau^* = \frac{-\mathbf{L}^*\mathbf{C}^{*-1}}{G}, \tag{57}$$

that is, the definition of τ^* does not change [compare equations (31) and (57)]. This does not mean, however, that $\tau = \tau^*$. The use of (57) *in the last component of* (54) gives an important relation

$$\tau^* = \mathbf{P}\tau\mathbf{P}^{-1}, \tag{58}$$

which defines the transformation rule for the relaxation matrix. On the basis of equation (56) it is also easy to prove that the new forces F_i can be represented by an expression obtained from (33) by adding stars to the symbols.

Examples of definite transformations taken from the classical theory of mass and energy transfer need rather a long discussion and, therefore, are considered in a separate paper (Part II). Now we shall pass to a certain generalization of the theory.

5. AN APPROXIMATE DESCRIPTION INCLUDING MOMENTUM TRANSFER

We have generalized our analysis to construct an expression for the relaxation entropy in an incompressible fluid with a certain velocity field **w**:

$$\Delta s_r = \frac{1}{2G} \mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\mathbf{J} - \frac{1}{4GT} \mathring{\pi}:\mathring{\pi}, \tag{59}$$

where $\mathring{\pi}$ is a deviator of the viscous part of pressure tensor. Then, substituting a more exact energy equation, c.f. [26],

$$\rho\frac{\mathrm{d}h}{\mathrm{d}t} = -\operatorname{div}\mathbf{J}_q + \frac{\mathrm{d}p}{\mathrm{d}t} - \mathring{\boldsymbol{\pi}}:\mathrm{gr\mathring{a}d}\,\mathbf{w}, \tag{60}$$

and equation (20) into the thermodynamic formula for $\mathrm{d}s'/\mathrm{d}t$ we find:

$$\begin{aligned}\rho\frac{\mathrm{d}s'}{\mathrm{d}t} = &-T\operatorname{div}\mathbf{J}_q - T^{-1}\mathring{\pi}:\mathrm{gr\mathring{a}d}\,\mathbf{w}\\ &-\sum_{i=1}^{n-1}\frac{\mu_n-\mu_i}{T}\operatorname{div}\mathbf{J}_i\\ &+\frac{1}{G}\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t} - \frac{1}{2GT}\mathring{\pi}:\frac{\mathrm{d}\mathring{\pi}}{\mathrm{d}t}\end{aligned} \tag{61}$$

from which the entropy source is obtained† in matrix notation as

$$\begin{aligned}\sigma = \mathbf{J}\left(\operatorname{grad}\mathbf{u} + \frac{\mathbf{C}^{-1}}{G}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}\right) - \mathring{\boldsymbol{\pi}}:&\\ \times\left(T^{-1}\,\mathrm{gr\mathring{a}d}\,\mathbf{w} + \frac{T^{-1}}{2G}\frac{\mathrm{d}\mathring{\pi}}{\mathrm{d}t}\right)&,\end{aligned} \tag{62}$$

With account for the Curie symmetry principle [20], equation (62) leads to the phenomenological equation (29) already discussed above for the coupled mass and energy diffusion, as well as to the equation

$$\mathring{\pi} = -T^{-1}L_\pi\left(\mathrm{gr\mathring{a}d}\,\mathbf{w} + \frac{1}{2G}\frac{\mathrm{d}\mathring{\pi}}{\mathrm{d}t}\right), \tag{63}$$

which describes momentum diffusion. For $G \to \infty$ this equation must become the Newton equation. Therefore the Onsager coefficient $L_\pi = 2\eta T$, in agreement with [20]. As a result, we come to the Maxwell equation for a viscoelastic fluid

$$\mathring{\boldsymbol{\pi}} = -2\eta\,\mathrm{gr\mathring{a}d}\,\mathbf{w} - \frac{\eta}{G}\frac{\mathrm{d}\mathring{\pi}}{\mathrm{d}t}. \tag{64}$$

Thus, we have obtained the consistent thermodynamic theory that leads to both the phenomenological Cattaneo equation (for pure heat diffusion) and Maxwell equation (for momentum diffusion). This theory justifies these equations from the point of view of the second law of thermodynamics and extends the first of them to the case of coupled transfer processes. It is also important that the theory allows a quantitative evaluation of the role of heat and mass relaxation effects in non-Newtonian fluids described by the Maxwell body model.

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† The classical expression for the entropy flux has been assumed, which can turn out to be an approximation, see e.g. [18].

THERMODYNAMIQUE DES TRANSPORTS COUPLES DE CHALEUR, DE MASSE ET DE QUANTITE DE MOUVEMENT AVEC UNE VITESSE FINIE D'ONDE: I—IDEES THEORIQUES FONDAMENTALES

Résumé—On considère les transferts simultanés de masse et d'énergie dans une onde de choc "second son", se déplaçant à la vitesse C_0 et on trouve des relations décrivant les flux de diffusion de masse J_i et d'énergie J_q en fonction des sauts de concentration et d'enthalpie dans l'onde. En appliquant ces relations aux formules classiques de la thermodynamique pour la variation d'entropie à partir de l'équilibre, on est conduit à une relation importante qui défini l'entropie de relaxation ΔS_r comme l'écart d'entropie résultant de la présence des flux de diffusion. Une expression générale de ΔS_r est donnée qui inclut le transfert de quantité de mouvement pour les fluides incompressibles.

On montre que la présence de l'entropie de relaxation dans le bilan d'entropie modifie la source d'entropie d'une façon qui conduit à des équations phénoménologiques avec des termes d'inertie ou, dans un cas spécial de processus sans couplage, à l'équation de Cattaneo [1] et à l'équation de Maxwell pour un fluide viscoélastique [2]. On développe la théorie générale des transformations des équations phénoménologiques et des matrices de coefficients de relaxation.

THERMODYNAMIK DES GEKOPPELTEN WÄRME-, STOFF- UND IMPULSTRANSPORTS MIT ENDLICHER WELLENGESCHWINDIGKEIT

Zusammenfassung—Es wird der gleichzeitige Stoff- und Energietransport in Stoßwellen zweiter Art, die sich mit der Geschwindigkeit c_0 bewegen, untersucht. Die ermittelten Beziehungen beschreiben die Diffusionsströme von Masse J_i und Energie J_q in Abhängigkeit von Konzentrations- und Enthalpieanstieg in der Wellenfront. Die Anwendung dieser Beziehungen auf die bekannte thermodynamische Gleichung für die Abweichung der Entropie vom Gleichgewichtszustand führt auf eine wichtige Beziehung, die die sogenannte Relaxations entropie $\Delta\ s_r$ als Entropieabweichung definiert, die sich aufgrund der auftretenden Diffusionsströme ergibt. Ein allgemeiner Ausdruck für $\Delta\ s_r$, der den Impulstransport in inkompressiblen Strömungen enthält, wird ebenfalls angegeben. Weiter wird gezeigt, daß das Auftreten der Relaxationsentropie in der Entropiebilanz die Entropiequelle in der Weise verändert, daß sich phänomenologische Gleichungen mit Trägheitsgliedern oder in einem speziellen Fall bei nichtgekoppeltem Prozeß die Cattaneo-Gleichung [1] und die Maxwell-Gleichung für ein viscoelastisches Fluid [2] ergeben. Es wird die allgemeine Theorie der Transformation von phänomenologischen Gleichungen und Relaxationskoeffizienten Matrizen entwickelt.

ТЕРМОДИНАМИКА ВЗАИМОСВЯЗАННЫХ ПРОЦЕССОВ ПЕРЕНОСА ТЕПЛА, МАССЫ И ИМПУЛЬСА С КОНЕЧНОЙ СКОРОСТЬЮ РАСПРОСТРАНЕНИЯ ВОЛНЫ.

I — ОСНОВНЫЕ ПОЛОЖЕНИЯ ТЕОРИИ

Аннотация — Исследуется одновременный перенос массы и энергии в ударной «второй звуковой» волне, движущейся со скоростью c_0, и получены выражения, описывающие диффузионные потоки массы J_i и энергии J_q в зависимости от роста концентрации и энтальпии во фронте волны. Подстановка этих соотношений в известную термодинамическую формулу, описывающую отклонение энтропии от равновесного состояния, приводит к важному соотношению, с помощью которого можно определить так называемую энтропию релаксации ΔS_r как отклонение энтропии под действием диффузионных потоков. Приведено обобщенное выражение для ΔS_r, учитывающее перенос импульса в несжимаемых жидкостях.

Показано, что наличие энтропии релаксации в энтропийном балансе позволяет выразить источник энтропии в виде, удобном для вывода феноменологических уравнений, содержащих инерционные слагаемые, или в отдельном несопряженном случае — уравнения Каттанео [1] и уравнения Максвелла для вязкоупругой жидкости [2]. Разработана общая теория преобразования феноменологических уравнений и матриц коэффициентов релаксации.