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THE INERTIAL RELAXATION TERMS AND THE VARIATIONAL PRINCIPLES OF LEAST ACTION TYPE FOR NON-STATIONARY ENERGY AND MASS DIFFUSION

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Abstract — Considering several variational formulations of the classical type, the role of the entropy of diffusive fluxes of mass and energy, called relaxation entropy, is investigated. Various functionals of thermodynamic action are presented having the dimension of the product of entropy and time. Applying the Eulerian (field) representation, the stationarity conditions for the action functional are the phenomenological and conservation equations describing multicomponent non-stationary diffusion of mass and energy with finite propagation speed. Using the Lagrangian representation the least action principle for the Maxwell–Stefan equations is obtained.

NOMENCLATURE

$\mathbf{a} = (a_1, a_2, a_3)$, $\mathbf{b} = (b_1, b_2, b_3)$,	Lagrangian coordinates of components A and B, respectively;
$\mathbf{C}$,	thermostatic matrix of capacities, $[c_{ik}]$;
c_v,	specific heat at constant volume;
c_0,	constant speed of propagation of disturbances;
D, $\mathbf{D}$,	diffusivity and generalized diffusivity matrix, equation (29), respectively;
e, f,	specific internal energy and free energy, respectively;
G,	modulus of shear rigidity, ρc_0^2;
$\mathbf{H}_i$,	Biot vector connected with flux $\mathbf{J}_i$ $(i = 1, 2 \ldots n)$;
$\mathbf{H}$,	column matrix of Biot vectors, col $(\mathbf{H}_1, \mathbf{H}_2 \ldots \mathbf{H}_{n-1}, \mathbf{H}_q)$;
$\mathbf{J}_q$,	vector of density of diffusive energy flux;
$\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1}$,	vectors of densities of diffusive mass fluxes;
$\mathbf{J}$,	column matrix of all independent fluxes, col $(\mathbf{J}_1, \mathbf{J}_2 \ldots \mathbf{J}_{n-1}, \mathbf{J}_q)$;
$\mathbf{L}$,	Onsager matrix $[L_{ik}]$;
M, m,	molar mass and mass of particle, respectively;
P, p,	total and partial pressure, respectively;
R,	universal gas constant;
S,	action functional;
s, s',	specific static entropy and total entropy, respectively;
Δs_r,	relaxation entropy of unit volume;
T,	temperature;
t,	time;
$\mathbf{u}$,	column matrix of transfer potentials, col $(\mu_n - \mu_1)/T \ldots (\mu_n - \mu_{n-1})/T, 1/T)$;
V,	volume;
$\mathbf{V}$, $\mathbf{v}_A$,	barycentric velocity of solution and velocity of component A, respectively;
X,	Jacobian of transformation $\mathbf{a} \rightarrow \mathbf{x}$;
$x_{ij} = \partial x_i/\partial a_j$, $X_{ij} = \partial X/\partial x_{ij}$,	components of Jacobian matrix and Jacobian derivatives, respectively;
$\mathbf{x}$, $\mathbf{x}_A$,	radius vector and position at time t of Ath component, respectively;
$y_A, y_B \ldots y_j$,	mass fractions of components A, B and j, respectively;
$\mathbf{z}$,	column matrix of thermostatic state, col $(y_1, y_2 \ldots y_{n-1}\ e)$.

Greek symbols

∇,	nabla operator;
δ,	variational symbol;
η,	dynamic viscosity;
Λ,	Lagrangian density;
μ, μ_i,	chemical potential of the particles and of component i, respectively $(\tilde{\mu}_A = \mu_n - \mu_A)$;
ρ,	mass density;
σ, σ',	classical and non-classical entropy source, respectively;
$\boldsymbol{\tau}$, τ,	relaxation matrix and relaxation time, respectively;
Φ,	gravitational potential.

Subscripts

q,	energy in coupled process;
0,	time, $t = 0$.

Superscripts

$^{\mathrm{T}}$,	transpose matrix;
$^{-1}$,	reverse matrix;
$\square$,	specified distribution of potentials, $\mathbf{u} = \mathbf{u}^{\square}$ or specified normal component of vector $\mathbf{H}_i$ $(\mathbf{H}_i^{\square} \equiv \mathbf{H}_i \cdot \mathbf{n})$;
$\tilde{}$,	general functional (for irreversible process).

1. INTRODUCTION

When describing variationally macroscopic physical systems difficulties appear in obtaining exact functionals (that is classical Hamilton-type functionals [1, 2]. This is especially so in the case of thermodynamically irreversible, coupled, non-stationary processes, such as simultaneous heat and mass transfer.

The variational formulations allow the transfer equations to be solved by direct variational methods. Action functionals are known in: mechanics [3], field theory [4], elasticity theory [5], and nonequilibrium thermodynamics [6, 7]. However most variational principles for irreversible processes are of 'non-classical' character, i.e. are related either to the so-called "restricted variations" or to the so-called "quasi-variational" formulation; such approaches are criticized in ref. [2]. From this group the most commonly known are: Natanson's thermokinetic principle [8], Glansdorff and Prigogine's method of a local potential [7, 9], Biot's principle [10–12], Lambermont and Lebon's principle [13], various principles of thermoelasticity [14, 15], Ainola principle [16] as well as Reddy's principles [17].

When the finite propagation speed of disturbances is taken into account hyperbolic equations appear [18, 19]. In refs. [20–22] variational formulations for hyperbolic equations of transient heat conduction are given, as well their extension to other uncoupled transport processes [22]. A common feature of these works is the presence of the exponential term, $\exp(t/\tau)$, that includes the relaxation time, τ, in the functions proposed. For coupled heat and mass diffusion it has been shown [23] that an important role is played by the matrix exponential function $\exp(t\tau^{-1})$ where τ is the relaxation matrix. However, the importance of this function for the variational formulation leading to the coupled non-Fourier phenomenological equations, relating thermodynamic forces with fluxes, has not been investigated.

For the uncoupled process of pure heat conduction such a principle has been given [1], that variational treatment leading to Cattaneo's [24] equation. Therefore, in the first part of this work we formulate, in a Eulerian (field) representation, an appropriate generalization of Lebon's linear result for a more general class of coupled processes in which simultaneous heat and mass transfer occurs. This is done in Section 3. Since, however, in the Eulerian representation of motion the analogy of the continuum with a discrete system of particles is lost the Lagrangian representation of diffusion, conserving the analogy, seems to be promising. In Sections 4 and 5 it is shown that this is really so, and the classical least action principle is extended to the irreversible processes of binary isothermal diffusion. As a result of the variational approach the Maxwell–Stefan equations of diffusion are derived. This proves the effectiveness of the method in which the inertial or relaxation terms play a significant role.

2. THE THERMODYNAMICS OF COUPLED ENERGY AND MASS TRANSFER IN THE PRESENCE OF FLUX RELAXATION

In highly non-stationary processes the local equilibrium hypothesis is not valid and the relaxation of diffusional fluxes $\mathbf{J}_i$ should be taken into account in Gibbs equation. The generalized Gibbs equation can be written as [19, 25]

$$\mathrm{d}s' = T^{-1}\,\mathrm{d}e + T^{-1}P\,\mathrm{d}\rho^{-1} + \sum_{i=1}^{n-1}[(\mu_n - \mu_i)/T]\,\mathrm{d}y_i + \mathbf{J}^{\mathrm{T}}(\mathbf{C}^{-1}/G)\,\mathrm{d}\mathbf{J} \quad (1)$$

or in the integrated form, correct for linear theory

$$s' = s + \frac{1}{2}\mathbf{J}^{\mathrm{T}}(\mathbf{C}^{-1}/G)\,\mathbf{J}. \quad (2)$$

For coupled transfer of mass and energy occurring in solutions the set of phenomenological equations relating fluxes and forces can be derived from entropy source [19, 21] via the known procedure. When equations (1) or (2) are applied instead, the classical result, the relaxation (matrix) equation, is obtained*

$$\mathbf{J} - \frac{\mathbf{L}\,\mathbf{C}^{-1}}{G}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t} = \mathbf{L}\,\mathrm{grad}\,\mathbf{u}. \quad (3)$$

De Groot's [6] notation for the vector set is used where

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

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

$$\mathbf{u} = \mathrm{col}\,[(\mu_n - \mu_1)/T, \ldots (\mu_n - \mu_{n-1})/T, 1/T]$$

$\mathrm{grad}\,\mathbf{u} = \mathrm{col}[\mathrm{grad}\,(\mu_n - \mu_1)/T \ldots, \mathrm{grad}\,(\mu_n - \mu_{n-1})/T, \mathrm{grad}\ 1/T]$ etc. The thermostatic capacity matrix appearing in equations (1)–(3) can be computed as

$$\mathbf{C} = \frac{\partial \mathbf{z}}{\partial \mathbf{u}} = \left(\frac{\partial^2 s}{\partial z_i \partial z_k}\right)^{-1}.$$

The quantity G is the modulus of shear rigidity or the product ρc_0^2 where c_0 is the propagation speed [18]. Matrix $\mathbf{L}$, equation (3), is the well-known kinetic Onsager matrix [6]. The properties of the relaxation matrix, $\tau = \mathbf{L}\,\mathbf{C}^{-1}/G$, are known [19, 23]. For the purposes of this work, it is important to assume the constancy of matrices $\mathbf{C}$ and $\mathbf{L}$ and keep in mind their symmetry. A feature characteristic of equation (3), the negligible compressibility, should also be remembered. Equation (3) remains unchanged even in a gravitational external field because in this case the generalized mass driving force $(\mu_n - \mu_k)/T + (\Phi_n - \Phi_k)/T$ is unaffected by Φ as $\Phi_i = \Phi_k$.

Transforming equation (3) into the form

$$\mathrm{grad}\,\mathbf{u} + (\mathbf{C}^{-1}/G)\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t} = \mathbf{L}^{-1}\,\mathbf{J} \quad (4)$$

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* See equations (9a) and (10) for the justification of the structure of equation (3).

and multiplying both sides of the above result the following scalar equation is obtained

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\mathbf{J}}{2G}\right)=\mathbf{J}^{\mathrm{T}}\mathbf{L}^{-1}\mathbf{J}-\mathbf{J}^{\mathrm{T}}\,\mathrm{grad}\,\mathbf{u}. \tag{5}$$

In equation (5) the term $\mathbf{J}^{\mathrm{T}}$ grad $\mathbf{u}$, represents, in matrix notation, the *classical* expression for the local entropy production

$$\begin{aligned}\sigma &= \mathbf{J}^{\mathrm{T}}\,\mathrm{grad}\,\mathbf{u}\\ &= \sum_{i=1}^{n-1}\mathbf{J}_i\cdot\mathrm{grad}\,[(\mu_n-\mu_j)/T]+\mathbf{J}_q\cdot\mathrm{grad}\frac{1}{T}.\end{aligned} \tag{6}$$

However it will be shown that this expression does not characterize the total dissipation here.

The LHS of equation (5) expresses the time-derivative of the so-called relaxation entropy of unit volume [19]

$$\Delta s_r=\mathbf{J}^{\mathrm{T}}\frac{\mathbf{C}^{-1}}{2G}\mathbf{J} \tag{7}$$

i.e. the entropy of the $\mathbf{J}_i$ fluxes. The question then arises: which term of equation (5) represents the true entropy source?

The answer can be found by considering the well-known expression for the static entropy change which has, in our notation, the following form:

$$\rho\frac{\mathrm{d}s}{\mathrm{d}t}=-\,\mathrm{div}\left[\left(\mathbf{J}_q-\sum_{1}^{n}\mu_i\mathbf{J}_i\right)\Big/T\right]+\mathbf{J}^{\mathrm{T}}\,\mathrm{grad}\,\mathbf{u}. \tag{8}$$

It is well-known [6] that equation (8) is independent of the relations between the fluxes and forces. For this reason the form of equation (8) is also conserved in the non-Fourier cases considered here. Adding equation (5) and (8) we obtain for the constant ρ a balance of the total entropy, which includes the static entropy and the entropy of diffusive fluxes

$$\begin{aligned}&\rho\frac{\mathrm{d}}{\mathrm{d}t}\left(s+\frac{1}{2G\rho}\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\mathbf{J}\right)\\ &\qquad=-\,\mathrm{div}\left[\left(\mathbf{J}_q-\sum_{1}^{n}\mu_i\mathbf{J}_i\right)\Big/T\right]+\mathbf{J}^{\mathrm{T}}\mathbf{L}^{-1}\mathbf{J}.\end{aligned} \tag{9}$$

From the above result we conclude that, for the equation (3) given, the entropy source is represented in equation (5) by the term $\mathbf{J}^{\mathrm{T}}\mathbf{L}^{-1}\mathbf{J}$ and not the expression (6).

The next question is: what is the form of the entropy source when the equation (3) is not given? The answer is found remembering that the Second Law of Thermodynamics should use the total entropy s', not the static entropy s. Substituting the entropy s from equation (2) into equation (8) we get

$$\begin{aligned}\rho\frac{\mathrm{d}s'}{\mathrm{d}t}&=-\,\mathrm{div}\left[\left(\mathbf{J}_q-\sum_{i=1}^{n}\mu_i\mathbf{J}_i\right)\Big/T\right]\\ &\qquad+\mathbf{J}^{\mathrm{T}}\left(\mathrm{grad}\,\mathbf{u}+(\mathbf{C}^{-1}/G)\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t}\right)\end{aligned} \tag{9a}$$

which indicates that the total entropy s' corresponds to the entropy source

$$\sigma'=\mathbf{J}^{\mathrm{T}}\left(\mathrm{grad}\,\mathbf{u}+(\mathbf{C}^{-1}/G)\frac{\mathrm{d}J}{\mathrm{d}t}\right). \tag{10}$$

It is easy to see that the condition of non-negativeness of the entropy source (10) postulates equation (3). Equation (10) will be used in Section 5 to obtain the so-called kinetic energy of diffusion which is important in several variational formulations.

The irreversibility of the relaxation is seen in the case when the gradients of transport potentials are negligible and the fluxes $\mathbf{J}_i$ are significant. Then there appear inertial forces opposing the decrease of fluxes. Although gradients are not present the fluxes are still observed, decreasing in time to zero. Making the assumption that the state (e, y_i) does not change significantly from equation (9) we get

$$\begin{aligned}&-\iiint(1/2G)\,\mathbf{J}_0^{\mathrm{T}}\mathbf{C}^{-1}\mathbf{J}_0\,\mathrm{d}V\\ &\qquad\cong\iiint\int_{t_1=0}^{t_2\to\infty}\mathbf{J}^{\mathrm{T}}\mathbf{L}^{-1}\mathbf{J}\,\mathrm{d}V\,\mathrm{d}t\geqslant 0\end{aligned} \tag{11}$$

for the fluxes disappearing on the system boundaries. This inequality characterizes the irreversibility of the relaxation.

In the case of mechanical effects, related to a certain generalized form of equation (10) [19], the irreversibility of relaxation means the progressive decrease of stress for a constant strain, i.e. for a vanishing shear rate grad $\mathbf{V}$ [18, 19]. This is related with the transfer of the elastic strain energy of solid or liquid into heat.* In the same way the quenching of mass and heat fluxes is accompanied by heat production. Equation (11) expresses the entropy produced in the system related to this heat.

The state function property of the relaxation entropy, explained below, indicates the special form in which this quantity might be effective in the variational formulation of Section 3. The extended space of states $(\mathbf{J}, \mathbf{z})$ and the cyclic process at $\mathbf{z}$ = constant are now considered. From equation (7), the change in Δs_r has a reversible character, i.e. in the closed cycle of states beginning and ending at the same state $\mathbf{J}_0$ integral

$$\begin{aligned}\oint\mathrm{d}\Delta s_r&=(1/G)\oint\mathbf{J}^{\mathrm{T}}\mathbf{C}^{-1}\,\mathrm{d}\mathbf{J}\\ &=\mathbf{J}^{\mathrm{T}}(\mathbf{C}^{-1}/2G)\mathbf{J}\Big|_{\mathbf{J}_0}^{\mathbf{J}_0}=0.\end{aligned} \tag{12}$$

This result suggests that the different extended space of states, $(\mathbf{H}, \mathbf{z})$, or $(\mathbf{H}, \mathbf{u})$, without $\mathbf{J}_i$, should be appropriate to construct an action functional based on Δs_r. The simplest new state coordinates, $\mathbf{H}_i$, will be those which provide the linear variations between $\mathbf{J}_i$ and the derivatives of $\mathbf{H}_i$. The quadratic functional is then

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*When dissipation of the deformation work is dependent on velocity we talk about viscosity, when not, about friction (consider for instance the plastic resistance during flow [26]). When elastic strain energy is dissipated, it is as a result of the relaxation.

related to Δs_r. This is then recognized as Biot's description [11, 12] restricted to the time derivatives. This idea is exploited below.

3. THE VARIATIONAL PRINCIPLE FOR COUPLED HEAT AND MASS TRANSFER IN THE EULERIAN REPRESENTATION

As we are interested in a coupled process we must take into consideration n Biot vectors, that satisfy the following conditions:

$$\dot{\mathbf{H}}_1 = \mathbf{J}_1 ; \dot{\mathbf{H}}_2 = \mathbf{J}_2 \ldots \dot{\mathbf{H}}_{n-1} = \mathbf{J}_{n-1} ; \dot{\mathbf{H}}_q = \mathbf{J}_q . \tag{13}$$

We will now again employ the matrix notation, where

$$\mathbf{H} = \mathrm{col}\,(\mathbf{H}_1, \mathbf{H}_2 \ldots \mathbf{H}_{n-1}, \mathbf{H}_n = \mathbf{H}_q). \tag{14}$$

The process is now considered in the extended space of the dependent variables **H** and **u**. The relaxation entropy, equation (7), expressed by the **H** vector is

$$\Delta s_r = \frac{1}{2} \dot{\mathbf{H}}^{\mathrm{T}} (\mathbf{C}^{-1}/G) \dot{\mathbf{H}}. \tag{15}$$

We shall first discuss a simple but far less important application, the case of a thermodynamically reversible process ($\mathbf{L}^{-1} = 0$), assuming that the field, $\mathbf{E} = -\mathrm{grad}\,\mathbf{u}$ and vectors, $\mathbf{H}_i$, on the system boundaries are given. The following functional is considered:

$$S = \iint_V \iint_{t_1}^{t_2} \left[\frac{1}{2} \dot{\mathbf{H}}^{\mathrm{T}} (\mathbf{C}^{-1}/G) \dot{\mathbf{H}} + \mathbf{u}^{\mathrm{T}} \mathrm{div}\,\mathbf{H} \right] \mathrm{d}V \,\mathrm{d}t \tag{16}$$

where the relaxation entropy appears explicitly. This is an entropy functional having the dimension of the product of entropy and time. The dots pertain, in general, to substantial derivatives. We restrict ourselves to media under mechanical equilibrium (constant velocity V).

It may be verified that for inertial frames ($\mathbf{V}$ = constant) the general functional

$$\tilde{S} = \iiiint \Lambda (\dot{\mathbf{u}}, \partial \mathbf{u}/\partial \mathbf{x}, \mathbf{u}, \mathbf{x}, t) \,\mathrm{d}V \,\mathrm{d}t \tag{17}$$

has Euler's equation based on substantial derivative in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \Lambda}{\partial \dot{\mathbf{u}}}\right) + \mathrm{div}\left(\frac{\partial \Lambda}{\partial\, \mathrm{grad}\,\mathbf{u}}\right) = \frac{\partial \Lambda}{\partial \mathbf{u}}. \tag{18}$$

Thus Euler's equation for the action (16) in the case when $\mathbf{u} = f(\mathbf{x}, t)$ is

$$\mathrm{grad}\,\mathbf{u} + \mathbf{C}^{-1} \ddot{\mathbf{H}}/G = 0. \tag{19}$$

As $\dot{\mathbf{H}} = \mathbf{J}$ it agrees, for a reversible process ($\mathbf{L}^{-1} \to 0$), with equation (4).

Functional (16) is still not the desired result for a general irreversible process ($\mathbf{L}^{-1} \neq 0$), but its form gives a valuable clue for consideration. In the general variational formulation discussed below, all the so far neglected effects are taken into account. Hence, the field, $\mathbf{E} = -\mathrm{grad}\,\mathbf{u}$, is no longer a given function $f(\mathbf{x}, t)$ but an undefined function that must be found from an additional term in the action functional. Therefore a generalized functional must also be varied with respect to the **u** vector. Also definite changes of **H** and/or **u** on the boundary should be taken into account. Finally, the structure of the generalized functional must include the energy dissipation ($\mathbf{L}^{-1} \neq 0$).

When dissipation occurs, then, as shown in equation (23), the role of the matrix exponential function

$$\mathbf{M} = \exp\,(t\,\tau^{-1}) = \exp\,(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t) \tag{20}$$

should be taken into account in the basic expressions leading to partial differential equations of the hyperbolic type. As such equations are directly related to equation (3), equation (20) is helpful when formulating the general action for equations (3) or (4). However the presence of the exponential term [equation (20)] means that instead of matrix $\mathbf{C}^{-1}$ the matrix $\mathbf{C}^{-1}$ exp $(t\,\tau^{-1})$ must be used. The general action functional is

$$\begin{aligned}
\tilde{S} = \iiint\int_{t_1}^{t_2} & [(1/2G)\dot{\mathbf{H}}^{\mathrm{T}} \mathbf{C}^{-1} \exp(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)\dot{\mathbf{H}} \\
& + \mathbf{u}^{\mathrm{T}} \exp(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)\,\mathrm{div}\,\mathbf{H} + (\rho/G)\,\mathbf{u}^{\mathrm{T}} \\
& \exp\,(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)\mathbf{L}\,\dot{\mathbf{u}}]\,\mathrm{d}V \mathrm{d}t \\
& - \int_{\partial V_u} \iint_{t_1}^{t_2} [(\mathbf{H}\,\mathbf{n})^{\mathrm{T}} \\
& \exp\,(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)\,\mathbf{u}^{\square}]\,\mathrm{d}A \mathrm{d}t \\
& - \int_{\partial V_H} \iint_{t_1}^{t_2} (\mathbf{H}\,\mathbf{n} - \mathbf{H}^{\square})^{\mathrm{T}} \\
& \exp\,(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)\,\mathbf{u}\,\mathrm{d}A \mathrm{d}t
\end{aligned} \tag{21}$$

with $\mathbf{H}\,\mathbf{n} = \mathrm{col}\,(\mathbf{H}_1 \cdot \mathbf{n}, \mathbf{H}_2 \cdot \mathbf{n} \ldots \mathbf{H}_n \cdot \mathbf{n})$. Observe that the surface terms of equation (21) are related with specified functions describing the vectors **u** and **H** on the system boundaries.*

We shall prove that the function (21) leads to the set of the phenomenological and conservation equations. For this purpose it should be remembered that the matrices

$$\mathbf{A} = \mathbf{C}^{-1} \exp\,(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)$$

and

$$\mathbf{B} = \exp\,(-\mathbf{C}\,\mathbf{L}^{-1}\,G\,t)\,\mathbf{L} \tag{22}$$

are symmetrical, i.e. $\mathbf{A} = \mathbf{A}^{\mathrm{T}}$ and $\mathbf{B} = \mathbf{B}^{\mathrm{T}}$. The matrices **C** and **L** are also symmetrical. The proof is given in ref. [19] for the matrix **B**. The same method is valid for the matrix **A**.

Using the general Euler equation (18) we have found the stationarity condition of functional (21) with respect to **H** as

$$\mathrm{grad}\,\mathbf{u} = \mathbf{L}^{-1} \dot{\mathbf{H}} - (\mathbf{C}^{-1}/G)\,\ddot{\mathbf{H}}. \tag{23}$$

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* See equations (26) and (27).

Since $\dot{\mathbf{H}} = \mathbf{J}$ equation (4) represents the stationarity condition of function (21) for the $\mathbf{H}$ vector.

Whereas the Euler equation (18) for functional (21) for the vector $\mathbf{u}$ is

$$\operatorname{div}\mathbf{H} = \rho\mathbf{C}\,\mathbf{u} = -\rho\mathbf{z}. \tag{24}$$

The above relationship describes the conservation of mass and energy in Biot's formalism. Indeed, differentiating both sides of equation (24) with respect to time gives the usual matrix form of the conservation laws

$$\operatorname{div}\mathbf{J} = -\rho\mathbf{C}\dot{\mathbf{u}} = -\rho\dot{\mathbf{z}}. \tag{25}$$

It should also be noted that taking account of the surface terms of the action functional gives the following boundary conditions:

$$\mathbf{u}(\mathbf{x}, t) = \mathbf{u}^{\square}(\mathbf{x}, t), \qquad \mathbf{x} \in \partial V_u, \forall\, t, \tag{26}$$

$$\mathbf{H}(\mathbf{x}, t)\mathbf{n} = \mathbf{H}^{\square}(\mathbf{x}, t), \ \mathbf{x} \in \partial V_H, \forall\, t, \tag{27}$$

where

$$\mathbf{H}^{\square} = \operatorname{col}(\mathbf{H}_1^{\square}, \mathbf{H}_2^{\square} \ldots \mathbf{H}_q^{\square});$$

$$\mathbf{u}^{\square} = \operatorname{col}[(\mu_n^{\square} - \mu_1^{\square})/T^{\square}, \ldots 1/T^{\square}];$$

$$\mathbf{H}\,\mathbf{n} = \operatorname{col}(\mathbf{H}_1 \cdot n \ldots \mathbf{H}_q \cdot n)$$

and

$$\delta\mathbf{H} = \delta\mathbf{u} = 0 \quad \text{for } t = t_1 \text{ and } t = t_2, \forall\,\mathbf{x}.$$

We neglect here the scalar counterparts of the above relations.

Acting on both sides of equation (23) with a divergence operator and making use of equation (24), gives the following wave equation:

$$\dot{\mathbf{z}} = \mathbf{D}[\nabla^2\mathbf{z} - (\ddot{\mathbf{z}}/c_0^2)] \tag{28}$$

where

$$\mathbf{D} = -\mathbf{L}\,\mathbf{C}^{-1}/\rho \tag{29}$$

is the diffusivity matrix. The consistency of equation (29) with the classical definition of $\mathbf{D}$ is shown in ref. [19]. An alternative, equivalent, form of equation (28) which employs the transport potentials is

$$\rho\mathbf{C}\,\dot{\mathbf{u}} = -\mathbf{L}[\nabla^2\mathbf{u} - (\ddot{\mathbf{u}}/c_0^2)]. \tag{30}$$

Thus it was shown that the functional (21) leads to the basic equations of coupled energy and mass transfer. In applications, depending on convenience, various of the above discussed forms of process equations, equations (3), (25), (28) or (30), are used.

In the next part of this paper we deal with the variational principles which do not use the relaxation entropy, but rather the related quantity, the kinetic energy of diffusion.

4. THE LAGRANGIAN COORDINATES AND LEAST ACTION PRINCIPLE FOR PARTICLE DIFFUSION

Equation (10) has an interesting counterpart in the diffusion theory of some distinguished particles of a definite kind, e.g. Brownian (sol) particles. The latter process is well-understood [6] and it can be used for an additional interpretation of the kinetic terms. This interpretation is now used for the variational description of the isothermal molecular diffusion in a rigorous Hamilton (least action) form. Therefore we will briefly consider below the role of the kinetic terms in particle diffusion, showing their usefulness and appropriateness for the variational approach. Next, in Section 5, we consider molecular diffusion treated in the same (least action) style.

Consider the isothermal transport of particles of density ρ by laminar Brownian diffusion occurring in a quiescent fluid ($\mathbf{V} = 0$). The counterpart of equation (10) in this case is [6]

$$\begin{aligned}\sigma' &= \mathbf{J} \cdot \left\{\operatorname{grad}[-(\mu + \Phi)/T] - T^{-1}\frac{\mathrm{d}(\mathbf{J}/\rho)}{\mathrm{d}t}\right\} \\ &= \mathbf{J} \cdot \operatorname{grad}[-(\mu + \Phi)/T] - \rho T^{-1}\frac{\mathrm{d}v^2/2}{\mathrm{d}t}.\end{aligned} \tag{31}$$

Here $\mathbf{J} = \rho\mathbf{v}$ is the particle diffusion flux. The term with $\mathrm{d}(\mathbf{J}/\rho)$ depends on the particle acceleration, i.e. it is precisely the inertial term. From ref. [6], equation (31) is consistent with the diffusion equation*

$$\rho\left(\frac{\partial^2 x_i}{\partial t^2}\right)_{\mathbf{a}} + RTM^{-1}\frac{\partial\rho}{\partial x_i} + \rho\frac{\partial\Phi}{\partial x_i} + \rho\tau^{-1}\left(\frac{\partial x_i}{\partial t}\right)_{\mathbf{a}} = 0 \tag{32}$$

(the quantities $\mathbf{x}$, ρ, M and Φ pertain to the particles). Note the continuum-type description.

The last term on the LHS of equation (32) is the viscous term containing the relaxation time τ which is found from the Stokes law as $(3\pi\eta d)^{-1}m$. The time derivatives of equation (32) were taken at constant Lagrangian coordinates, $\mathbf{a} = (a_1, a_2, a_3)$. This means that the similarity with a system of discrete particles is preserved. In the Lagrangian representation, the equation of reversible motion ($\eta = 0$) can be derived from a variational principle fully analogous to the Hamilton least action principle. Since however the entropy (not energy) action has so far been effectively used we will postulate and prove that, in the absence of external fields, the time integral taken over the difference between the potential entropy and the kinetic entropy is stationary. As previously, in the irreversible case ($\eta \neq 0$), the term $\exp(t\tau^{-1})$ will appear as the multiplicative factor of the reversible Lagrangian.

Comparing equations (10) and (31) we note that the role of the time derivative of the volumetric relaxation entropy, is played in equation (31) by the term $-\frac{1}{2}T^{-1}\rho(\mathrm{d}v^2/\mathrm{d}t)$.† Hence the counterpart of the relaxation entropy itself (per unit mass) should be equal

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* Note the explicit presence of the gravitational potential Φ due to the change to a diffusion driving force in comparison with equation (3).

† This conclusion is also confirmed by equation (45).

to $-\frac{1}{2}T^{-1}\mathbf{v}^2$. Whereas the entropy Lagrangian must contain the Legendre transform of the quantity $s - \frac{1}{2}T^{-1}\mathbf{v}^2$ with respect to $\mathbf{v}$, i.e. it must operate with the sum $s + \frac{1}{2}T^{-1}\mathbf{v}^2$. Therefore, after introducing the term $\exp(t\tau^{-1})$, we will consider the following:

$$\tilde{S} = \iiiint \exp(t/\tau)\,\rho_0(\mathbf{a})\left[\frac{1}{2}T^{-1}\left(\frac{\partial \mathbf{x}}{\partial t}\right)_{\mathbf{a}}^2 + s(\rho, T) - T^{-1}\Phi(\mathbf{x})\right]\mathrm{d}a_1\,\mathrm{d}a_2\,\mathrm{d}a_3\,\mathrm{d}t \quad (33)$$

for variations of δx_i which vanish on the system boundary.

The Lagrangian coordinates $\mathbf{a} = (a_1, a_2, a_3)$ are used in equation (32) for the position at time $t = 0$ and $\mathbf{x} = \mathbf{x}(\mathbf{a}, t)$ is the position at time t. In this description the current density of particles, ρ, is related to their initial density, $\rho_0(\mathbf{a})$, by the Lagrangian form of continuity equation

$$\rho^{-1}(\mathbf{a}, t) = \rho_0^{-1}(\mathbf{a}, 0)X, \qquad X = \partial(x_1, x_2, x_3)/\partial(a_1, a_2, a_3). \quad (34)$$

Here X is the Jacobian of the coordinate transformation ($\mathbf{a} \to \mathbf{x}$). Using X all components of equation (32) can be written in terms of the $\mathbf{a}$ and $\mathbf{t}$ derivatives of the dependent variables $\mathbf{x}$ and ρ

$$\rho_0\left(\frac{\partial^2 x_i}{\partial t^2}\right)_{\mathbf{a}} + RTM^{-1}X_{ij}\frac{\partial \rho}{\partial a_j} + \rho_0\frac{\partial \phi}{\partial x_i} + \rho_0\tau\left(\frac{\partial x_i}{\partial t}\right)_{\mathbf{a}} = 0 \quad (35)$$

where

$$X_{ij} = \frac{\partial X}{\partial x_{ij}}, \quad x_{ij} = \frac{\partial x_i}{\partial a_j}, \quad \frac{\partial a_j}{\partial x_i} = \frac{X_{ij}}{X}. \quad (36)$$

(The double suffix summation convention is used.)

The static entropy of particles is related to the variables ρ and T by

$$\mathrm{d}s = c_v T^{-1}\,\mathrm{d}T - \left(\frac{\partial p}{\partial T}\right)_\rho \frac{\mathrm{d}\rho}{\rho^2}. \quad (37)$$

For the ideal "dilute solution of the particles" their pressure $p = \rho RTM^{-1}$ and hence

$$\mathrm{d}s = c_v T^{-1}\,\mathrm{d}T - RM^{-1}\rho^{-1}\,\mathrm{d}\rho. \quad (38)$$

Using the above equation a variation δx_i in equation (33) is now considered. It should be noted that due to the continuity equation (34), the entropy $s(\rho, T)$ depends on the derivatives $x_{ij} = \partial x_i/\partial a_j$. Hence, for the constant T, Euler equation of the function (33) is

$$\rho_0(\mathbf{a})T^{-1}\left(\frac{\partial^2 x_i}{\partial t^2}\right)_{\mathbf{a}} + \rho_0(\mathbf{a})T^{-1}\tau^{-1}\left(\frac{\partial x_i}{\partial t}\right)_{\mathbf{a}} + \frac{\partial}{\partial a_j}\left[\rho_0(\mathbf{a})\left(\frac{\partial s}{\partial \rho}\right)_T \frac{\partial \rho}{\partial x_{ij}}\right] + \rho_0(\mathbf{a})T^{-1}\frac{\partial \Phi}{\partial x_i} = 0. \quad (39)$$

But from equations (34) and (36)

$$\frac{\partial \rho}{\partial x_{ij}} = -\frac{\rho^2}{\rho_0}X_{ij}. \quad (40)$$

Therefore, using equations (38) and (40)

$$\frac{\partial}{\partial a_j}\left[\rho_0(\mathbf{a})\left(\frac{\partial s}{\partial \rho}\right)_T \frac{\partial \rho}{\partial x_{ij}}\right] = RM^{-1}\frac{\partial}{\partial a_j}(\rho X_{ij}) = RM^{-1}X_{ij}\frac{\partial \rho}{\partial a_j}. \quad (41)$$

(In the above transformation the identity $\sum_j \frac{\partial X_{ij}}{\partial a_j} = 0$ has been used.)

From equations (41) and (39) we find that equation (39) transforms into equation (35) which is equivalent to equation (32). Thus the exact 'least action' functional, equation (33), leading to equation (32) is established.

It should be recognized that the stationarity of the entropy action (33) was derived for an ideal solution where the Clapeyron law holds. By the analogous reasoning it can be shown that the action functional containing the free energy of particles $f(\rho, T) = e(\rho, T) - Ts(\rho, T)$ can be used alternatively having the form

$$\tilde{S}_F = \int_{t_1}^{t_2}(E_k - E_p - F)\exp(t/\tau)\,\mathrm{d}t = \iiiint \exp(t/\tau)\,\rho_0(f)\left[\tfrac{1}{2}(\partial \mathbf{x}/\partial t)^2 - \mathbf{a}(\rho, T) - \phi(\mathbf{x})\right] \times \mathrm{d}a_1\,\mathrm{d}a_2\,\mathrm{d}a_3\,\mathrm{d}t \quad (42)$$

which is also unknown in the literature. For vanishing viscosity ($\eta \to 0$, $\tau \to \infty$) equation (42) represents exactly the Hamilton principle of an isothermal process. Because $(\partial f/\partial \rho)_T = p/\rho^2 \cong RT/M\rho$ the equation (32) is again obtained. When Clapeyron's law does not apply the term $\partial p/\partial x_i$ will appear in equation (32) instead of $RTM^{-1}\,\partial \rho/\partial x_i$. Since, however, we are not sure that the pressure gradient is a correct force, in a rigorous sense, for the non-ideal case (the gradient of pressure activity might be considered as a more proper force) it cannot be stated which action, equation (33) or (42), should be preferred in the non-ideal case.* We can only be sure that, in the ideal case, both actions, (33) or (42), are equivalent.

5. HAMILTON'S (LEAST ACTION) PRINCIPLE FOR THE MAXWELL–STEFAN EQUATIONS OF DIFFUSION

Let us now look for the molecular counterpart of equation (31). Comparing equation (31) with equation (10) taken at the constant ρ we expect that the non-classical term of equation (10) is related to the kinetic energy of diffusion. To show this we consider the binary† molecular diffusion in an ideal isothermal

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* However the free energy function could be more proper from the viewpoint of classical thermodynamic ideas.

† The generalization of the theory for the multicomponent case is direct only if a single relaxation time and diffusivity are assumed.

solution composed of the two species A and B under the approximation $M_A \cong M_B \cong M$. In this case one has

$$C^{-1} = \frac{\partial(\tilde{\mu} T^{-1})_T}{\partial y_A} \cong -RM^{-1}(y_A^{-1} + y_B^{-1}), \quad (43)$$

$$G = P \cong \rho RTM^{-1} \quad (44)$$

and the total entropy

$$s' = s + (C^{-1}/2G\rho)\mathbf{J}_A^2 \cong s - (1/2\rho^2 T)(y_A^{-1} + y_B^{-1})\mathbf{J}_A^2 = s - \frac{1}{2T}\left[y_A\left(\frac{\partial x_A}{\partial t}\right)_a^2 + y_B\left(\frac{\partial x_B}{\partial t}\right)_b^2\right] \quad (45)$$

$(\mathbf{J}_A = -\mathbf{J}_B = \mathbf{J})$.

Hence the entropy source σ' can be approximated by the equation

$$\sigma' = \mathbf{J}_A \cdot \text{grad}\,[-(\mu_A + \phi_A)/T] - \rho T^{-1}\frac{d}{dt} \times \left(\frac{v_A^2}{2}y_A + \frac{v_B^2}{2}y_B\right) + \mathbf{J}_B \cdot \text{grad}\,[-(\mu_B + \phi_B)/T] \quad (46)$$

which is very similar to equation (31). The velocities $v_A = (\partial x_A/\partial t)$ and $v_B = (\partial x_B/\partial t)$ in equation (45) and (46) are taken in the reference frame in which the fluid rests. Thus the middle term of the RHS of equation (46) is related to the kinetic energy of diffusion [6]. Since equation (31) and (46) are similar we can expect that, as previously, the kinetic energy of diffusion will play an important role in the variational formulation sought for the *molecular* diffusion. However, due to the only approximate equivalency of equations (10) and (46) it cannot be claimed that the approaches in Sections 3 and 5, differing substantially in the process description, are equivalent for the binary case with constant T. The approach of Section 3 is more related to phenomenological nonequilibrium thermodynamics whereas that of Section 5 is more related to the kinetic theory.

In the following analysis we will assume that the diffusion is accompanied by macroscopic motion having the velocity $\mathbf{V}$. The state variables for components A and B are the spatial coordinates x_{Ai} and x_{Bi}. As the concentrations we will use the mass densities ρ_A and ρ_B; of course $\rho_A + \rho_B = \rho$. The continuity equations for species A and B written in the Lagrangian forms are

$$\begin{aligned} \rho_A^{-1}(\mathbf{a}, t) &= \rho_{A0}^{-1}(a, 0)\,X_A, \\ \rho_B^{-1}(a_1 t) &= \rho_{B0}^{-1}(\mathbf{a}, 0)\,X_B, \end{aligned} \quad (47)$$

$$X_A = \frac{\partial(x_{A1}, x_{A2}, x_{A3})}{\partial(a_1, a_2, a_3)}, \quad X_B = \frac{\partial(x_{B1}, x_{B2}, x_{B3})}{\partial(b_1, b_2, b_3)} \quad (48)$$

where $\mathbf{a} = (a_1, a_2, a_3)$ and $\mathbf{b} = (b_1, b_2, b_3)$ are the Lagrangian coordinates of A and B respectively. The reason for our earlier assumption that a macroscopic motion $\mathbf{V}$ occurs is that, in the present case, we cannot consider the fluid as a quiescent medium because the various velocities of A and B will generally result in a non-vanishing barycentric velocity $\mathbf{V}$. Since

$$(\rho_A + \rho_B)\mathbf{V} = \rho_A \mathbf{v}_A + \rho_B \mathbf{v}_B \quad (49)$$

$\mathbf{V}$ obeys the integral condition

$$\iiiint [\rho_A(\mathbf{v}_A - \mathbf{V}) + \rho_B(\mathbf{v}_B - \mathbf{V})] \exp(t/\tau) \times \delta\mathbf{V}\,dx\,dy\,dz\,dt = 0 \quad (\delta\mathbf{V} \neq 0) \quad (50)$$

for the arbitrary volume and time interval. It results from equations (47) and (48) that in Lagrangian coordinates equation (50) becomes

$$\iiiint \rho_{A0}\left(\frac{\partial \mathbf{x}_A}{\partial t} - \mathbf{V}\right)\delta\mathbf{V} \exp(t/\tau)\,da_1\,da_2\,da_3\,dt + \iiiint \rho_{B0}\left(\frac{\partial \mathbf{x}_B}{\partial t} - \mathbf{V}\right)\delta\mathbf{V} \exp(t/\tau)\,db_1 db_2 db_3 dt. \quad (51)$$

The above relationship should be an additional result obtained from the variational principle together with equations of motion for species A and B. It means that the action function sought must contain $\mathbf{V}$ as an additional state variable. Remembering the role of the kinetic energy of diffusion we take the action functional in the form

$$\begin{aligned} \tilde{S} = {} & \iiiint \exp(t/\tau)\,\rho_{A0}\left[\frac{1}{2}T^{-1}\left(\frac{\partial \mathbf{x}_A}{\partial t} - \mathbf{V}\right)^2 + s_A(\rho_A, T) - T^{-1}\Phi_A(\mathbf{x}_A)\right] da_1 da_2 da_3 dt \\ & + \iiiint \exp(t/\tau)\,\rho_{B0}\left[\frac{1}{2}T^{-1}\left(\frac{\partial \mathbf{x}_B}{\partial t} - \mathbf{V}\right)^2 + s_B(\rho_B, T) - T^{-1}\Phi_B(\mathbf{x}_B)\right] \\ & \times db_1 db_2 db_3 dt. \end{aligned} \quad (52)$$

Here $s_A(\rho_A, T)$ and $s_B(\rho_B, T)$ are the partial specific entropies of A and B.* As is known from statistical mechanics [27], for the partial entropies s_A and s_B in an ideal solution

$$ds_N = c_{vN} T^{-1} dT - RM_N^{-1}\rho_N^{-1} d\rho_N \quad (N = A, B). \quad (53)$$

When the above result is used together with equations (40) and (41) taken for the components A and B, and the variation of the functional $\tilde{S}$ [equation (52)] is performed with respect to x_{Ai} and x_{Bi} the following equations of motion are obtained:

$$\rho_{A0}\frac{\partial^2 x_{Ai}}{\partial t^2} + \rho_{A0}\tau^{-1}\left(\frac{\partial x_{Ai}}{\partial t} - V_i\right) + X_{Aij}\frac{\partial p_A}{\partial a_j} + \rho_{A0}\frac{\partial \Phi_A}{\partial x_{Ai}} - \rho_{A0}w_i = 0 \quad (54)$$

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* The specific entropy of the fluid $s = y_A s_A + y_B s_B$ is not explicity present in the action functional.

$$\rho_{\mathrm{B0}}\frac{\partial^2 x_{\mathrm{B}i}}{\partial t^2} + \rho_{\mathrm{B0}}\tau^{-1}\left(\frac{\partial x_{\mathrm{B}i}}{\partial t} - V_i\right) + X_{\mathrm{B}ij}\frac{\partial p_{\mathrm{B}}}{\partial b_j} + \rho_{\mathrm{B0}}\frac{\partial \Phi_{\mathrm{B}}}{\partial x_{\mathrm{B}i}} - \rho_{\mathrm{B0}}w_i = 0 \quad (55)$$

where w_i is the acceleration related to V_i. In addition the vanishing variation of $\tilde{S}$ versus V_i defines the velocity $\mathbf{V}$ as the barycentric velocity obeying equation (51) or (49). Using the continuity relations, equations (36), (47) and (48) we find

$$X_{\mathrm{A}ij}\frac{\partial p_{\mathrm{A}}}{\partial a_j} = \frac{\rho_{\mathrm{A0}}}{\rho_{\mathrm{A}}}\frac{\partial p_{\mathrm{A}}}{\partial x_i}, \qquad X_{\mathrm{B}ij}\frac{\partial p_{\mathrm{B}}}{\partial b_j} = \frac{\rho_{\mathrm{B0}}}{\rho_{\mathrm{B}}}\frac{\partial p_{\mathrm{B}}}{\partial x_i}. \quad (56)$$

Equations (54), (55) and (56) are the Maxwell–Stefan equations in the Lagrangian representation.

When the gradients of partial pressures p_{A} and p_{B} are accepted as the driving forces even in the non-ideal case, equations (54), (55) and (56) can alternatively be obtained from the action functional based on the partial free energies

$$\tilde{S}_F = \iiiint \exp(t/\tau)\rho_{\mathrm{A0}}\left[\frac{1}{2}\left(\frac{\partial \mathbf{x}_{\mathrm{A}}}{\partial t} - \mathbf{V}\right)^2 - f_{\mathrm{A}}(\rho_{\mathrm{A}}, T) - \Phi_{\mathrm{A}}(\mathbf{x}_{\mathrm{A}})\right]\mathrm{d}a_1\mathrm{d}a_2\mathrm{d}a_3\mathrm{d}t + \iiiint \exp(t/\tau)\rho_{\mathrm{B0}}\left[\frac{1}{2}\left(\frac{\partial \mathbf{x}_{\mathrm{B}}}{\partial t} - \mathbf{V}\right)^2 - f_{\mathrm{B}}(\rho_{\mathrm{B}}, T) - \Phi_{\mathrm{B}}(\mathbf{x}_{\mathrm{B}})\right]\mathrm{d}b_1\mathrm{d}b_2\mathrm{d}b_3\mathrm{d}t. \quad (57)$$

Using equations (54)–(56) and passing to the Eulerian representation, the usual form of Maxwell–Stefan equations is obtained

$$\rho_{\mathrm{A}}\left[\frac{\partial \mathbf{v}_{\mathrm{A}}}{\partial t} + (\mathbf{v}_{\mathrm{A}}\nabla)\mathbf{v}_{\mathrm{A}}\right] - \rho_{\mathrm{A}}w + \nabla p_{\mathrm{A}} + \rho_{\mathrm{A}}\nabla\Phi_{\mathrm{A}} + \frac{\rho_{\mathrm{A}}\rho_{\mathrm{B}}}{\rho\tau}(\mathbf{v}_{\mathrm{A}} - \mathbf{v}_{\mathrm{B}}) = 0, \quad (58)$$

$$\rho_{\mathrm{B}}\left[\frac{\partial \mathbf{v}_{\mathrm{B}}}{\partial t} + (\mathbf{v}_{\mathrm{B}}\nabla)\mathbf{v}_{\mathrm{B}}\right] - \rho_{\mathrm{B}}w + \nabla p_{\mathrm{B}} + \rho_{\mathrm{B}}\nabla\Phi_{\mathrm{B}} + \frac{\rho_{\mathrm{A}}\rho_{\mathrm{B}}}{\rho\tau}(\mathbf{v}_{\mathrm{B}} - \mathbf{v}_{\mathrm{A}}) = 0. \quad (59)$$

When

$$\tau = \rho D P^{-1} = DM(RT)^{-1} \quad (60)$$

is applied to equations (58) and (59) and under assumption of equimolar diffusion, these equations lead to Fick's law assuming that the external and inertial forces are neglected. On the other hand when the inertial terms are conserved, equations (58) and (59) give the more proper description leading (under suitable assumptions, less restrictive than those of Fick) to the hyperbolic equations of change containing the quantity $c_0 = (p\rho^{-1})^{1/2} = (RTM^{-1})^{1/2}$ as the propagation speed. The details are described elsewhere [28].

The extension of the theory, equation (52) and (57), and equations (58) and (59) for the non-isothermal case should be the subject of further study.

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LES TERMES D'INERTIE/RELAXATION ET LES PRINCIPES VARIATIONNELS DU TYPE DE MOINDRE ACTION POUR LA DIFFUSION INSTATIONNAIRE DE MASSE ET D'ENERGIE

Résumé—Considérant plusieurs formulations variationnelles de type classique, le rôle de l'entropie des flux diffusifs de masse et d'énergie, appelée entropie de relaxation, est étudié. Plusieurs fonctionnelles d'action thermodynamique sont présentées qui ont la dimension du produit de l'entropie par un temps. Appliquant la représentation eulerienne, les conditions stationnaires pour la fonctionnelle d'action sont les équations phénoménologiques et de conservation qui décrivent la diffusion de chaleur et de masse avec une vitesse finite de propagation. On obtient le principe de moindre action pour les équations de Maxwell–Stefan, à partir de la représentation lagrangienne.

DIE TRÄGHEITS-/RELAXATIONS-GLIEDER UND DIE VARIATIONSPRINZIPIEN DER KLEINSTEN WIRKUNG FÜR DIE NICHTSTATIONÄRE ENERGIE- UND MASSENDIFFUSION

Zussammenfassung—Betrachtet werden einige Variationsgleichungen des klassischen Typs, wobei die Rolle der Entropie der Diffusionsströme von Masse und Energie, genannt Relaxationsentropie, untersucht wird. Zahlreiche thermodyamische Funktionale mit der Dimension eines Produkts aus Entropie und Zeit werden angegeben. Bei Anwendung der Eulerischen Feld-Darstellung sind die Stationaritätsbedingungen für das Wirkungsfunktional die phänomologischen und Bilanzgleichungen, die die instationäre Vielkomponentendiffusion von Masse und Energie mit endlicher Ausbreitungsgeschwindigkeit beschreiben. Bei Anwendung der Lagrange-Darstellung wird das Prinzip der kleinsten Wirkung für die Stefan-Maxwell-Gleichungen erhalten.

ИНЕРЦИОННЫЕ (РЕЛАКСАЦИОННЫЕ) ВКЛАДЫ И ВАРИАЦИОННЫЕ ПРИНЦИПЫ ТИПА НАИМЕНЬШЕГО ДЕЙСТВИЯ ДЛЯ НЕСТАЦИОНАРНОЙ ДИФФУЗИИ ЭНЕРГИИ И МАССЫ

Аннотация—С учетом нескольких вариационных формулировок классического вида исследована роль энтропии диффузионных потоков массы и энергии, называемой релаксационной энтропией. Приведены различные функционалы термодинамического действия, размерность которых равна произведению размерностей энтропии и времени. С помощью эйлеровского (полевого) описания условия стационарности для функционала действия представляются в виде феноменологических уравнений и уравнений сохранения, описывающих многокомпонентную нестационарную диффузию массы и энергии с конечной скоростью распространения. На основе представления Лагранжа сформулирован принцип наименьшего действия для уравнений Максвелла-Стефана.