THERMODYNAMICS OF REACTING MIXTURES FOR MICROPOLAR FLUIDS

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The balance laws and linear constitutive equations of the theory of reacting mixtures for micropolar fluids are derived. Theoretical relations include the assumptions that the elements of micropolar fluids do not undergo deformations and have different temperature and concentration fields of constituents of the mixture. The theory is developed for prediction of flow, heat and mass transfer in fluid suspensions. Diffusion through the layer of fluid suspension is studied as the example.

At present the specialized theories of microcontinuum have been applied to the description of flow[1] and heat transfer[2-4] in fluid suspensions. They enable to predict the complex effect of particles of the suspension on the mentioned transfer phenomena. This effect is due to rotation and migration of particles, distribution of the local volume concentration of particles, different thermal conductivity of particles and the suspending fluid *etc*. But there have been made attempts to employ the specialized theories of microcontinuum also for prediction of mass transfer. The thermodynamics of reacting mixtures for micromorphic fluids is proposed in the article[5] on the basis of specialized thermodynamics of mixtures[6,7], which in their generality is for description of mass transfer in fluid suspensions applicable. However, the proposed theory of mixtures is for practical purposes too complicated. Here an attempt has been made to simplify the earlier proposed relations[5] and to demonstrate their application on an example.

BALANCE LAWS

In the recent study[5] is generally assumed that the inner structure of the fluid formed in the fluid suspensions by the suspended particles is deformable. But if we limit ourselves to the description of suspension with solid particles we obtain easily a considerable simplification of the balance laws given in the paper[5]. These balance laws are modified to the form considering motion of primitive particles of micromorphic fluid in such a form which is characteristic for the so-called micropolar fluids[8]. The velocity of this characteristic motion is represented by a certain translation

velocity v_k similarly as the motion of the classical fluid and by some mean relative velocity of primitive particles toward the mass centre of the volume element represented by the microrotation vector v_k. The velocity of the primitive particle v'_k whose position in the volume element is given by the vector ξ_k is thus

$$v_k^{'} = v_k - \varepsilon_{klm} v_m \xi_1 . \tag{1}$$

Analogously to representation of the velocity of motion of primitive particles it has been assumed at the derivation of balance laws in ref.[5] that the temperature Θ, in the volume element can be expressed as

$$\frac{1}{\Theta'} = \frac{1}{\Theta} + \frac{1}{\Theta^2} \vartheta_k \xi_k , \tag{2}$$

where Θ is the temperature in the mass centre of the volume element and ϑ_k represents the variation of temperature in respect to the temperature of the mass centre.

Similarly it has been assumed that the distribution of concentration $c^{\alpha'}$ and of the reduced chemical potential $\mu^{\alpha'}$ of the constituent α in the volume element can be expressed as

$$c^{\alpha'} = c^\alpha + c_k^\alpha \xi_k , \tag{3}$$

where c^α is the concentration of the constituent α in the mass centre and c_k^α is the variation of concentration in respect to the concentration in the mass centre and

$$\mu^{\alpha'} = \mu^\alpha + \mu_k^\alpha \xi_k , \tag{4}$$

where μ^α is the reduced chemical potential of the constituent in the mass centre and μ_k^α is the reduced chemical micropotential of the constituent representing the variation of the reduced chemical potential with respect to its value in the mass centre.

At the given assumption (1) concerning the motion of primitive particles of micropolar fluid, the balance equations of micropolar mixture of $N + 1$ constituents have the following form which results from the balance laws[5].
The conservation of mass gives

$$\frac{\partial \varrho}{\partial t} + (\varrho v_k)_{,k} = 0 , \tag{5}$$

where ϱ is the mass density of the mixture. An index following a comma indicates partial derivative with respect to the spatial rectangular coordinates x_k i.e. $(\varrho v_k)_{,k} \equiv \equiv \partial(\varrho v_k)/\partial x_k$. The summation convention on the repeated indices over the range 1, 2, 3 is understood.

The conservation of microinertia gives

$$\dot{j}_{kl} + (\varepsilon_{krs}j_{rl} + \varepsilon_{lrs}j_{rk}) \, v_s = 0 \, . \tag{6}$$

In Eq. (6) denotes j_{kl} the tensor of microinertia and ε_{klm} the Levi–Civita symbol. The superposed dot denotes the material derivative

$$\dot{j}_{kl} \equiv \frac{\partial j_{kl}}{\partial t} + j_{kl,m}v_m \, .$$

The conservation of mass of constituent α gives

$$h^\alpha_{k,k} - \varrho \dot{c}^\alpha = m^\alpha \, , \quad (\alpha = 1, ..., N) \, , \tag{7}$$

where h^α_k denotes the relative mass flux of the constituent α defined as $h^\alpha_k = \varrho^\alpha$. $. \, (v^\alpha_k - v_k)$ where ϱ^α is the density and v^α_k the velocity of constituent α (no sum on α is assumed, see Eq. (11)). The mass supply m^α to constituent α is due to chemical reactions. The concentration c^α of the constituent α is defined as $c^\alpha \equiv \varrho^\alpha/\varrho$.
The conservation of mass moment of constituent α gives

$$h^\alpha_{kl,k} + h^\alpha_l - \bar{h}^\alpha_l - \varrho j_{lk}\dot{c}^\alpha_k = m^\alpha_l \, , \quad (\alpha = 1, ..., N) \, . \tag{8}$$

In Eq. (8) is h^α_{kl} the relative mass flux moment of constituent α, $\bar{h}^\alpha_k$ the mean relative mass flux of constituent α and m^α_k is the mass supply moment to constituent α. Balance of momentum gives

$$t_{kl,k} + \varrho(f_l - \dot{v}_l) = 0 \, , \tag{9}$$

where t_{kl} represents the stress tensor and f_l the body force density. The balance of the first-order moment of momentum gives

$$m_{kr,k} + \varepsilon_{rkl}t_{kl} + \varrho l_r - \varrho(\dot{\overline{j_{rl}v_l}}) = 0 \, , \tag{10}$$

where m_{kl} is the couple stress tensor and l_k the body couple vector. Conservation of energy

$$-\varrho\dot{\varepsilon} + t_{kl}(v_{l,k} - \varepsilon_{klr}v_r) + m_{kl}v_{l,k} + q_{k,k} + (\mu^\alpha h^\alpha_k)_{,k} + \varrho r = 0 \, . \tag{11}$$

In Eq. (11) denotes ε the internal energy, q_k the heat flux and r the heat source. The reduced chemical potential μ^α of constituent α is defined[5] as $\mu^\alpha \equiv \partial\psi/\partial c^\alpha$, where ψ is the free energy. The reduced chemical micropotential μ^α_k of constituent α is defined[5] as $\mu^\alpha_k \equiv (\partial\psi/\partial c^\alpha_l) j_{kl}$.

We employ the summation convention from 1 to N over repeated Greek index α. Validity of the summation convention over the greek index α is assumed also in the next part of this study. Balance of the first-order moment of energy gives

$$-\varrho\dot{\varepsilon}_n + \varrho\varepsilon_1\varepsilon_{r1n}v_r + 2\varepsilon_{rn1}m_{kr}(v_{1,k} - \varepsilon_{k1r}v_r) + q_{kn,k} +$$

$$+ q_n - \bar{q}_n + \left(\frac{\Theta}{|\vartheta_n|^2}\vartheta_n\mu_n^\alpha h_{kn}^\alpha\right)_{,k} + \mu^\alpha h_n^\alpha - \mu^\alpha \bar{h}_n^\alpha + \varrho r_n = 0\,, \qquad (12)$$

where ε_k is the moment of energy, q_{k1} the moment of heat flux, $\bar{q}_k$ the mean heat flux and v_k the moment of heat source.

The entropy inequality holds

$$\varrho\dot{\eta} - \varrho(\Theta^{-1}r + \Theta^{-2}\vartheta_k r_k) - (\Theta^{-1}q_k + \Theta^{-2}\vartheta_1 q_{k1})_{,k} \geqq 0\,, \qquad (13)$$

where η denotes entropy.

The balance laws (7), (8), (11) and (12) are postulated for constituents $\alpha = 1, \ldots, N$. But these laws are satisfied also for the constituent $N + 1$ if we define

$$c^{N+1} = 1 - \sum_{\alpha=1}^{N} c^\alpha\,, \quad \delta^{N+1} = -\sum_{\alpha=1}^{N}\delta^\alpha\,, \qquad (14)$$

where the symbol δ is succeedingly equal to $\delta = (c_k, h_k, \bar{h}_k, h_{k1}, m, m_k)$, and if we define

$$\mu^\alpha = \mu^{\alpha*} - \mu^{N+1*}\,, \quad \mu_k^\alpha = \mu_k^{\alpha*} - \mu_k^{N+1*}\,, \qquad (15)$$

where $\mu^{\alpha*}$ is the chemical potential of constituent α and $\mu_k^{\alpha*}$ the chemical micropotential of constituent α. From relation (15) results that μ^{N+1} and μ_k^{N+1} are identically equal to zero.

CONSTITUTIVE EQUATIONS

We shall define the micropolar fluid mixture by the constitutive equations

$$\mathscr{L} = \tilde{\mathscr{L}}(\mathscr{S})\,. \qquad (16)$$

In relation (16) $\mathscr{L}$ represents the set of dependent constitutive variables

$$\mathscr{L} = \{t_{k1}, m_{k1}, q_k, q_{k1}, \bar{q}_k, \varepsilon, \varepsilon_k, \eta, h_k^\alpha, h_{k1}^\alpha, \bar{h}_k^\alpha, m^\alpha, m_k^\alpha\} \qquad (17)$$

and $\mathscr{S}$ the set of independent constitutive variables

$$\mathscr{S} = \{d_{k1}, c_{k1}, a_{k1m}, \Theta, \Theta_{,k}, \vartheta_k, \vartheta_{k,1}, c, c_{,k}, c_k, c_{k,1}, \varrho^{-1}, j_{k1}\}\,, \qquad (18)$$

where

$$d_{kl} = \tfrac{1}{2}(v_{k,l} + v_{l,k}), \quad c_{kl} = \tfrac{1}{2}(v_{l,k} - v_{k,l}) - \varepsilon_{klr}v_r, \quad a_{klm} = -\varepsilon_{klr}v_{r,m},$$

and where

$$c = (c^1, ..., c^N), \quad c_{,k} = (c_{,k}^1, ..., c_{,k}^N),$$

$$c_k = (c_k^1, ..., c_k^N), \quad c_{k,l} = (c_{k,l}^1, ..., c_{k,l}^N).$$

Symbol $\hat{\mathscr{L}}$ denotes the response function.

We shall formulate the constitutive equations (*16*) by use of the constitutive theory[9,10] in the form given in ref.[11]. If we limit ourselves finally to the linear form of the constitutive equations, we obtain

$$t_{kl} = (-\pi + \lambda_v v_{r,r} + \lambda_1 \vartheta_{r,r} + \lambda_2 c_{r,r}) \delta_{kl} + \mu_v(v_{k,l} + v_{l,k}) +$$
$$+ \kappa_v(v_{l,k} - \varepsilon_{rkl}v_r) + \mu_1 \vartheta_{k,l} + \mu_2 \vartheta_{l,k} + \mu_3 c_{k,l} + \mu_4 c_{l,k}, \qquad (19)$$

where π is the thermodynamic pressure defined by $\pi \equiv -(\partial\psi/\partial\varrho^{-1})$,

$$m_{kl} = \alpha_v v_{r,r}\delta_{kl} + \beta_v v_{k,l} + \gamma_v v_{l,k} + \varepsilon_{klm}(\alpha\Theta_{,m} + \alpha_0\vartheta_m + \beta c_{,m} + \beta_0 c_m), \quad (20)$$

$$h_k^{\alpha} = \chi_1\Theta_{,k} + \chi_2\vartheta_k + \chi_3 c_{,k} + \chi_4 c_k + \varepsilon_0\varepsilon_{klm}v_{l,m}, \qquad (21)$$

$$\bar{h}_k^{\alpha} = (\chi_1 - \varphi_1)\Theta_{,k} + (\chi_2 - \varphi_2)\vartheta_k + (\chi_3 - \varphi_3)c_{,k} +$$
$$+ (\chi_4 - \varphi_4)c_k + (\varepsilon_0 - \tau_0)\varepsilon_{klm}v_{l,m}, \qquad (22)$$

$$h_{kl}^{\alpha} = -(\delta_1 v_{r,r} + \delta_2 \vartheta_{r,r} + \delta_3 c_{r,r})\delta_{kl} - \delta_v(v_{k,l} + v_{l,k}) -$$
$$- \delta_0(v_{l,k} - \varepsilon_{rkl}v_r) - \delta_4\vartheta_{k,l} - \delta_5\vartheta_{l,k} - \delta_6 c_{k,l} - \delta_7 c_{l,k}, \qquad (23)$$

$$q_k = \kappa\Theta_{,k} + \omega\vartheta_k + \kappa_1 c_{,k} + \omega_1 c_k + \beta\varepsilon_{klm}v_{l,m}, \qquad (24)$$

$$\bar{q}_k = (\kappa - \kappa_0)\Theta_{,k} + (\omega - \omega_0)\vartheta_k + (\kappa_1 - \kappa_2)c_{,k} +$$
$$+ (\omega_1 - \omega_2)c_k + (\beta - \xi)\varepsilon_{klm}v_{l,m}, \qquad (25)$$

$$q_{kl} = -(\sigma_1 v_{r,r} + \sigma_2 \vartheta_{r,r} + \sigma_3 c_{r,r})\delta_{kl} - \sigma_v(v_{k,l} + v_{l,k}) -$$
$$- \sigma_0(v_{l,k} - \varepsilon_{rkl}v_r) - \sigma_4\vartheta_{k,l} - \sigma_5\vartheta_{l,k} - \sigma_6 c_{k,l} - \sigma_7 c_{l,k}, \qquad (26)$$

$$m^{\alpha} = \alpha_1 + \alpha_2 c, \qquad (27)$$

$$m_k^a = \beta_1 \Theta_{,k} + \beta_2 \vartheta_k + \beta_3 c_{,k} + \beta_4 c_k + \beta_5 \varepsilon_{klm} v_{l,m} , \qquad (28)$$

$$\varepsilon = \psi - \Theta^{-1} \vartheta_k \varepsilon_k + \Theta \eta , \quad \varepsilon_k = \Theta \frac{\partial \psi}{\partial \delta_k} , \qquad (29)$$

$$\eta = - \frac{\partial \psi}{\partial \Theta} - \frac{1}{\Theta} \vartheta_k \frac{\partial \psi}{\partial \vartheta_k} , \qquad (30)$$

where

$$\psi = \hat{\psi}(\Theta, \vartheta_k, c, c_k, \varrho^{-1}, j_{kl})$$

may be expressed

$$\psi = \gamma_0 + \gamma_1 \frac{1}{\varrho} + \gamma_2 \Theta + \gamma_3 \Theta^2 + \gamma_4 c + \gamma_5 c^2 + \gamma_6 \vartheta_k \vartheta_k + \gamma_7 c_k c_k . \qquad (31)$$

In the constitutive equations $\lambda_v, \lambda_1, \lambda_2$ *etc.* represent the material coefficients, which are in general functions of Θ, c, ϱ^{-1} and of invariants of the tensor of micro-inertia j_{kl}. With respect to the used notation, the coefficients of $c, c_{,k}, c_k$ and $c_{k,l}$ represent N coefficients e.g. $\lambda_2 = (\lambda_{21}, \lambda_{22}, ..., \lambda_{2N})$. The values of material moduli are further restricted by the entropy inequality *(13)*.

The constitutive equations *(19)*−*(31)* connect the effects of kinematic, thermo-dynamic and concentration quantities and of their gradients on the flux of mo-mentum, mass *(21)* (generalized Fick law for diffusion), heat *(24)* (generalized Fourier law) and on the flux of their mean quantities and moments.

By substituting the constitutive equations *(19)*−*(31)* into the balance laws *(5)*−*(12)* the field equations are obtained. If the values f_k, l_k, r and r_k are given, the field equa-tions constitute the complete set of partial differential equations for the determina-tion of fields $\varrho, j_{kl}, v_k, v_k, \Theta, \vartheta_k, c$ and c_k. The solution of the set for the appropriate initial and boundary conditions is the result of the application of the proposed theory to the description of transport phenomena in fluid suspensions. In the next section of this study the theory is applied to the solution of the problem of gas diffusion in the stationary layer of fluid suspension.

DIFFUSION THROUGH THE LAYER OF FLUID SUSPENSION

From the point of view of theory of mixture for micropolar fluids the gas forms with the fluid suspension a two constituent mixture of gas and fluid. The effect of suspended solid particles on motion, heat transfer and diffusion is in the proposed theory impli-citely included. For simplicity let us assume that the fluid suspension is trapped between two flat infinite parallel membranes a distance $2L$ apart. The diffusion flux is caused by different concentration on the surface of the fluid layer. The fluid

is stationary with uniform temperature. The constituents of the mixture do not react chemically.

Let us introduce the rectangular Cartesian coordinate system with the x-axis coincident with the center line and the y-axis normal to y. The balance laws $(5)-(12)$ provide for the case under consideration the following system of equations

$$\frac{dh_y}{dy} = 0, \quad \frac{dh_{yy}}{dy} + h_y - \bar{h}_y = 0, \tag{32}$$

where for simplicity the penetrating constituent is not specially denoted. The constitutive equations have the form

$$h_y = \chi_3 \frac{dc}{dy} + \chi_4 c_y, \tag{33}$$

$$\bar{h}_y = (\chi_3 - \varphi_3)\frac{dc}{dy} + (\chi_4 - \varphi_4) c_y, \tag{34}$$

$$h_{yy} = -\delta \frac{dc_y}{dy}, \tag{35}$$

where c and c_y denote the concentration and the change of concentration of gas and $\delta = \delta_3 + \delta_6 + \delta_7$.

Assuming constant constitutive coefficients it is possible for the boundary conditions

$$y = L: \quad c = c_1, \quad c_y = k\frac{dc}{dy},$$

$$y = -L: \quad c = c_2, \quad c_y = k\frac{dc}{dy}, \tag{36}$$

where k is the parameter dependent on the volume concentration of particles, to obtain easily the solution of system (32) in the closed form. The solutions *i.e.* the functional dependences of the concentration c and variation of concentration c_y of gas on the position and properties of the mixture represented by the constitutive coefficients are given and discussed in ref.[12].

From the physical point of view the variation of concentration c_y to the component of "local" concentration gradient represents the change of the gas concentration due to the suspended particles in small volume of the fluid suspension with the mean concentration c. In the limiting case at zero volume concentration of suspended

particles the value of the concentration variation c_y is equal to the negative value of the concentration gradient[12].

For evaluation of the fields c and c_y the values of the constitutive coefficients χ_3, χ_4, φ_3, φ_4 and δ are needed. These constitutive coefficients are in ref.[12] expressed as functions of the volume concentration of particles and of diffusion coefficients of fluid and particles *i.e.* as the functions of "primitive" properties of the mixture.

From the comparison of the classical solution of the diffusion through the layer[13] and the solution obtained here results: The classical solution of distribution of the gas concentration is independent of the properties of the fluid suspension. Here the solution depends on properties of fluid suspension. It demonstrates how different diffusion coefficients of the suspending fluid and suspended particles can affect the distribution of concentration c and variation of concentration c_y. This effect is due to different distribution of particles at the surface of the layer and in the layer. It is necessary to mention that the effect is not significant and the difference between the classical distribution of concentration c and the here obtained distribution is about 2% at maximum.

The above result does not justify the use of the relatively complicated theory for description of diffusion in fluid suspensions. Nevertheless, by use of the specialized theory of microcontinuum proposed in[4] it is possible to obtain information on distribution of the volume concentration of particles in flowing fluid suspension. When fluid suspension undergoes steady flow between the membranes a particle-depleted layer occurs at the wall[4]. Then the local values of coefficients in the balance equations $(33)-(35)$ can be easily determined. It means that by use of the theory proposed here, it is possible to evaluate the change in the value of the diffusion flux which is due to the redistribution of particles at flowing suspensions. This change reaches the order of magnitude of tens of %.

The most important reason which justifies the use of the proposed theory of mixtures for micropolar fluids is the fact resulting from the constitutive Eqs $(21)-(23)$ *i.e.* that it is possible to evaluate the effect of moving particles on diffusion through the layer. This effect is — as the experimental results reveal — substantial and increases the diffusion flux several times. The classical theory cannot deal with this problem in another way than through experimental determination of mean diffusion coefficients for flowing fluid suspensions[14].

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