TRANSPORT PHENOMENA IN MULTIVELOCITY, MULTITEMPERATURE GAS MIXTURES

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A physical analysis is given and the mathematical properties and conditions of applicability of the equations of hydrodynamics of multitemperature and multivelocity gas mixtures are indicated /1, 2/. The momentum and energy equations are given for the whole mixture as well as the equations describing the velocity and temperature separation of the mixture components. The system of Boltzmann equations is used to obtain and study the equations of entropy balance and expressions for the entropy density, and the flow and source of entropy in a multivelocity and multitemperature mixture. It is shown that in the linear transport equations the kinetic coefficients satisfy the Onsager reciprocity relations.

The methods of determining the macroscopic equations of motion for gas mixtures from the system of Boltzmann equations are known. The first approach, based on the Chapman-Enskog method of solving Boltzmann Eqs./3/ leads to the Euler, Navier-Stokes, Barnett, etc. equations. A description of all the components of the mixture in terms of a single temperature and a single, mass-averaged velocity, presuppose that due to the mixing of the component molecules in phase space the mixture state is nearly equilibrium. The second approach given in /1/, describes situations when the mixing processes are not completed and the state of the mixture is far from equilibrium. The method leads to the equations of the hydrodynamics of a multivelocity and multitemperature mixture. Various versions of the momentum equations exist for such mixtures /4-6/.

A number of papers have appeared within the last few years dealing with the equations /1, 2/ in which a complete set of conservation laws (divergent forms) was established /7/, the equation of entropy balance was obtained and studied (for a binary mixture) /8/, additional terms were computed in the equations containing the velocity and temperature differences of the mixture components in higher powers /9/, a generalization to the case of dense gases was made /lo/ and their application to solving specific problems was given in /ll/. In spite of all this, a number of still unsolved problems remain in this area, and some of them are discussed below.

1. Hydrodynamic equations. The hydrodynamic equations for the multitemperature and multivelocity mixture /1, 2/ corresponding to the Navier-Stokes approximation in the usual mixtures, can be transformed to a form suitable for physical analysis, Thus, the zero approximation equations have the form

$$\frac{\partial}{\partial t}n_i + \nabla \cdot (n_i \mathbf{u}_i) = 0 \quad (i = 1, 2, \dots, N)$$
(1.1)

$$\rho_i \left(\frac{\partial}{\partial t} u_{i\alpha} + u_i \cdot \nabla u_{i\alpha} \right) = -\frac{\partial}{\partial r_\alpha} p_i - \sum_{j(\neq i)} F_{ij\alpha}^{(0)}$$
(1.2)

$$\frac{3}{2}n_ik\left(\frac{\partial}{\partial t}T_i + \mathbf{u}_i \cdot \nabla T_i\right) = -p_i \nabla \cdot \mathbf{u}_i - \sum_{j(\neq i)} \beta_{ij} F_{ij}^{(0)} \cdot \mathbf{u}_{ij}$$
(1.3)

$$\mathbf{F}_{ij}^{(0)} = \frac{16\rho_i \rho_j}{3 (m_i + m_j)} \, \Omega_{ij}^{(1,1)} \mathbf{u}_{ij}, \quad \mathbf{u}_{ij} = \mathbf{u}_i - \mathbf{u}_j \tag{1.4}$$

$$Q_{ij}^{(0)} = \frac{16\rho_i \rho_j k T_{ij}}{(m_i + m_j)^3} \left(\Omega_{ij}^{(1,1)} + u^2_{ij} \frac{\frac{2}{3} \Omega_{ij}^{(1,2)} - \Omega_{ij}^{(1,1)}}{v_{iT}^2 + v_{jT}^2} \right), \quad T_{ij} = T_i - T_j$$
(1.5)

$$p_{i} = n_{i}kT_{i}, \quad \beta_{ij} = \frac{v_{iT}^{2}}{v_{iT}^{2} + v_{jT}^{2}}, \quad v_{iT}^{2} = \frac{2kT_{i}}{m_{i}}$$
(1.6)

(here and henceforth the Latin indices denote the components of the mixture, and Greek indices the vector and tensor components).

In the following approximation the right-hand sides of the momentum Eq.(1.2) and energy Eq.(1.3) are supplemented, respectively, by the terms (1.7) and (1.8) *Prikl.Matem.Mekhan., 50, 1, 83-90, 1986

$$-\frac{\partial}{\partial r_{\beta}} p_{i\alpha\beta} - \sum_{j(\neq i)} F_{ij\alpha}^{(1)}$$
(1.7)

$$-\nabla \cdot \mathbf{q}_{i} - p_{i\alpha\beta} \frac{\partial u_{i\alpha}}{\partial r_{\beta}} + \sum_{j(\neq i)} \beta_{ij} \mathbf{F}_{ij}^{(1)} \cdot \mathbf{u}_{ij}$$
(1.8)

$$p_{i\alpha\beta} = -2\mu_i \left(e_{i\alpha\beta} - \sum_{j(\neq i)} E_{ij} \langle u_{ij\alpha} u_{ij\beta} \rangle \right)$$
(1.9)

$$\mathbf{q}_{i} = -\lambda_{i} \left(\nabla T_{i} - \sum_{j \neq i} H_{ij} \mathbf{u}_{ij} \right)$$
(1.10)

$$\mathbf{F}_{ij}^{(1)} = \frac{64\alpha_{ij}}{15(m_i + m_j)(v_{iT}^2 + v_{jT}^2)} (\rho_j \mathbf{q}_i - \rho_i \mathbf{q}_j)$$
(1.11)

$$\langle \Gamma_{\alpha\beta} \rangle \equiv \frac{1}{2} \left(\Gamma_{\alpha\beta} + \Gamma_{\beta\alpha} \right) - \frac{1}{3} \delta_{\alpha\beta} \Gamma_{\gamma\gamma}, \quad e_{i\alpha\beta} = \left\langle \frac{\partial u_{i\alpha}}{\partial r_{\beta}} \right\rangle$$

$$E_{ij} = \frac{8n_j m_i m_j}{3kT_i} \left(\beta_{ij} \Omega_{ij}^{(1,1)} - \frac{4kT_{ij}}{(m_i + m_j) (v_{iT}^2 + v_{jT}^2)} \Omega_{ij}^{(1,2)} - \frac{3m_j}{5 (m_i + m_j)} \Omega_{ij}^{(a,s)} \right)$$

$$(1.12)$$

$$H_{ij} = \frac{32n_j m_i m_j}{15k(m_i + m_j)} \left[\frac{5}{2} \beta_{ij} \left(1 + \frac{2m_i}{m_i + m_j} \frac{T_{ij}}{T_i} \right) \Omega_{ij}^{(1,1)} - \frac{1}{\beta_{ij}} \left(\frac{m_j}{m_i + m_j} \right)^2 \left(1 + \frac{12k^4 T_{ij}^2}{m_j^2 (v_{iT}^2 + v_{jT}^2)} \right) \Omega_{ij}^{(1,2)} - \frac{2m_i m_j}{(m_i + m_j)^4} \frac{T_{ij}}{T_i} \Omega_{ij}^{(8,2)} \right]$$
(1.13)

Here F_{ij} , which is the force of interaction between the *i*-th and *j*-th component of the mixture, contains within itself the transfer of momentum between the components due to the non-coincidence of the component velocities and the thermal force caused by the partial temperature gradients. The thermal forces vanish in the Maxwellian gas, and have opposite signs for the hard and soft potentials of intermolecular interaction, which is described by the multiplier

$$\alpha_{ij} = \Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)}$$
(1.14)

in (1.11), Q_{ij} is the heat transfer between the components due to their temperature differences, $\mathbf{F}_{ij} \cdot \mathbf{u}_{ij}$ is the work done by the interaction, β_{ij} is its fraction which becomes the internal energy of the *i*-th component, $(\beta_{ij} < 1, \beta_{ij} + \beta_{ji} = 1)$, $p_{i\alpha\beta\chi} \mathbf{q}_i$ are the partial stress tensor and thermal flux, μ_i , λ_i are the viscosity and thermal conductivity of the pure gas of the *i*-th kind. A number of terms ($\sim u_i^3$, $p_{i\alpha\beta}u_{i\beta}$) are omitted from the equations by virtue of condition (1.15). Equations (1.1) - (1.13) were derived and their coefficients calculated for an arbitrary interaction potential between the molecules in the first approximation, using the Sonin polynomials. Taking into account the further terms in the expansions written in terms of the Sonin polynomials does not affect the structure and physical meaning of the terms in (1.1) - (1.3), and merely increases the accuracy of the coefficients.

Below we formulate some of the properties of the hydrodynamic equations obtained.

The equations are invariant under Galilean transformations, rotations and reflections with respect to the origin of coordinates.

The system of zero approximation equations is hyperbolic (the characteristic equation has ten different roots); therefore the associated Cauchy problem is correct.

The system of zero approximation equations has 14 linearly independent divergent forms /7/.

The zero approximation equations are irreversible (unlike the equations of the Chapman-

Enskog method) because of the relaxation terms $\mathbf{F}_{ij}^{(0)}$, $Q_{ij}^{(0)}$ in the momentum and energy equations. The equations describe flows with arbitrary ratios of the mixture component temperatures, and with relative velocities

$$u_{ij} \ll \max\left(\sqrt{2kT_i/m_i}, \sqrt{2kT_j/m_j}\right) \tag{1.15}$$

However, here the order of magnitude of the velocities u_{ij} can be equal to that of the component velocities u_i, u_j and to the smaller of the thermal velocities.

Restriction (1.15) on the quantity u_{ij} is needed in computing the moments of the collision integrals I_{ij} $(j \neq i)$

$$\int \Psi(\mathbf{v}_i) I_{ij}(f_i^{(0)}, f_j^{(n)}) d\mathbf{v}_i, \quad \Psi(\mathbf{v}_i) = \left\{ m_i \mathbf{v}_i, \quad \frac{m_i}{2} (\mathbf{v}_i - \mathbf{u}_i)^2, \\ \langle (\mathbf{v}_i - \mathbf{u}_i)_\alpha (\mathbf{v}_i - \mathbf{u}_i)_\beta \rangle, \quad (\mathbf{v}_i - \mathbf{u}_i) (\mathbf{v}_i - \mathbf{u}_i)^2 \right\}$$

$$(1.16)$$

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occurring in the hydrodynamic equations and the distribution function $f_i^{(n)} = f_i^{(0)} \Phi_i^{(n)}$. Using the symmetry properties of the collision integrals, we can write (1.16) in the form

$$\int f_i^{(0)} f_j^{(0)} \Phi_j^{(n)} \left[\Psi(\mathbf{v}_i) - \Psi(\mathbf{v}_i) \right] g_{ij} b \, db \, de \, d\mathbf{v}_j \, d\mathbf{v}_i$$

Here the velocities v_i , v_j are first expressed in terms of the velocities of the centre of mass $G_{ij} = (m_i v_i + m_j v_j) (m_i + m_j)^{-1}$ and the relative velocity $g_{ij} = v_i - v_j$, and the integration is carried out over ε and b. Further, the sum of the exponent indices in $f_i^{(0)} f_j^{(0)}$ is transformed to the form in which the dependence on u_{ij} is separated out (see e.g. /9/)

$$\begin{split} \frac{(\mathbf{v}_i - \mathbf{u}_i)^2}{v_{iT}^2} + \frac{(\mathbf{v}_j - \mathbf{u}_j)^2}{v_{jT}^3} &= \overline{G}_{ij}^2 \left(\frac{1}{v_{iT}^2} + \frac{1}{v_{jT}^2}\right) + \frac{(\mathbf{g}_{ij} - \mathbf{u}_{ij})}{v_{iT}^2 + v_{jT}^2}\\ \overline{G}_{ij} &= \mathbf{G}_{ij} - \mathbf{g}_{ij} \frac{2k\left(T_i - T_j\right)}{\left(m_i + m_j\right)\left(v_{iT}^2 + v_{jT}^2\right)} - \left(\beta_{ji}\mathbf{u}_i + \beta_{ij}\mathbf{u}_j\right) \end{split}$$

Then, using condition (1.15) we expand $\exp\left[-(g_{ij}-u_{ij})^2(v_{iT}^3+v_{jT}^2)^{-1}\right]$ in a series in u_{ij} , pass in the integrand from the variables G_{ij} , g_{ij} to \overline{G}_{ij} , g_{ij} , and integrate with respect to the latter.

Similar equations were obtained earlier in /12/ for a plasma. However, the use in their derivation of a number of assumptions specific for a plasma (quasineutrality, large differences in the masses and temperatures of the electrons and ions, the Landau collision integral, etc.) make it impossible to use the equations for mixtures of neutral gases.

In some cases it may be better to describe the mixture in terms of the velocity common to the whole mixture and temperature, given by the relations

$$\rho \mathbf{u} = \sum_{i} \rho_{i} \mathbf{u}_{i}, \quad \frac{3}{2} nkT = \frac{3}{2} \sum_{i} n_{i} kT_{i} + \frac{1}{2} \sum_{i} \rho_{i} V_{i}^{2}$$
(1.17)

where $\mathbf{V}_i = \mathbf{u}_i - \mathbf{u} = \rho^{-1} \sum_j \rho_j \mathbf{u}_{ij}$ is the diffusion velocity of the *i*-th component, and in terms of

the component velocity and temperature differences

$$u_{ij} = u_i - u_j, \ T_{ij} = T_i - T_j$$
 (1.18)

The partial velocities and temperatures are expressed in terms of these quantities as follows:

$$\mathbf{u}_{i} = \mathbf{u} + \mathbf{V}_{i}, \quad T_{i} = T + \frac{1}{n} \sum_{j} n_{j} T_{ij} - \frac{1}{3kn} \sum_{j} \rho_{j} V_{j}^{3}$$
 (1.19)

Addition and pairwise subtraction of Eqs.(1.2) yields, respectively, the momentum equation for the whole mixture and equations for the velocity differences in the mixture components. Using (1.17) - (1.19) we can write them as follows:

$$\rho\left(\frac{\partial}{\partial t}u_{\alpha}+\mathbf{u}\cdot\nabla u_{\alpha}\right)=-\frac{\partial}{\partial r_{\alpha}}p-\frac{\partial}{\partial r_{\beta}}p_{\alpha\beta}$$
(1.20)

$$\frac{\partial}{\partial t} u_{ij\alpha} + \mathbf{u} \cdot \nabla u_{ij\alpha} = -\mathbf{u}_{ij} \cdot \nabla u_{\alpha} - (\mathbf{V}_i \cdot \nabla V_{i\alpha} - \mathbf{V}_j \cdot \nabla V_{j\alpha}) -$$
(1.21)

$$\left(\frac{1}{\rho_{i}} \frac{\partial}{\partial r_{\beta}} p_{i\alpha\beta} - \frac{1}{\rho_{j}} \frac{\partial}{\partial r_{\beta}} p_{j\alpha\beta}\right) - \left(\frac{1}{\rho_{i}} \frac{\partial}{\partial r_{\alpha}} p_{i} - \frac{1}{\rho_{j}} \frac{\partial}{\partial r_{\alpha}} p_{j}\right) - \sum_{k} \left(\frac{1}{\rho_{i}} F_{ik\alpha} - \frac{1}{\rho_{j}} F_{jk\alpha}\right) \quad p = nkT$$

$$p_{\alpha\beta} = \sum_{k} p_{i\alpha\beta} + \sum_{k} \rho_{i} \langle V_{i\alpha} V_{i\beta} \rangle$$

The stress tensor components $p_{\alpha\beta}$ of the mixture contain, in addition to the Navier-Stokes stresses, the Karman stresses and a series of Barnett terms /13/.

Similarly we obtain, for Eqs.(1.3), the energy equation for the mixture and for the component temperature differences

$$\frac{3}{2} kn \left(\frac{\partial}{\partial t} T + \mathbf{u} \cdot \nabla T \right) = -p \nabla \cdot \mathbf{u} - \nabla \cdot \mathbf{q} - p_{\alpha\beta} \frac{\partial u_{\alpha}}{\partial r_{\beta}} +$$

$$\frac{3}{2} kT \nabla \cdot \left(\sum_{i} n_{i} \mathbf{V}_{i} \right) - \frac{5}{2} k \sum_{i} \sum_{j} \nabla \cdot \left(\frac{n_{i} n_{j}}{n} T_{ij} \mathbf{V}_{i} \right) + \dots$$

$$\mathbf{q} = \sum_{i} \mathbf{q}_{i} + \frac{5}{2} kT \sum_{i} n_{i} \mathbf{V}_{i}$$

$$\frac{\partial}{\partial t} T_{ij} + \mathbf{u} \cdot \nabla T_{ij} = -\frac{2}{3} T_{ij} \nabla \cdot \mathbf{u} - \frac{2}{3} T \nabla \cdot \mathbf{u}_{ij} - \mathbf{u}_{ij} \cdot \nabla T -$$
(1.23)

$$k \sum_{k} \left[\mathbf{V}_{i} \cdot \nabla \left(\frac{n_{k}}{n} T_{ik} \right) - \mathbf{V}_{j} \cdot \nabla \left(\frac{n_{k}}{n} T_{jk} \right) + \frac{2}{3} \frac{n_{k}}{n} \left(T_{ik} \nabla \cdot \mathbf{V}_{i} - T_{jk} \nabla \cdot \mathbf{V}_{j} \right) \right] - \left(\frac{1}{n_{i}} \nabla \cdot \mathbf{q}_{i} - \frac{1}{n_{j}} \nabla \cdot \mathbf{q}_{j} \right) - \left(\frac{1}{n_{i}} p_{i\alpha\beta} - \frac{1}{n_{j}} p_{j\alpha\beta} \right) \frac{\partial u_{\alpha}}{\partial r_{\beta}} - \sum_{k} \left(\frac{Q_{ik}}{n_{i}} - \frac{Q_{jk}}{n_{j}} \right) + \sum_{k} \left(\frac{\beta_{ik}}{n_{i}} \mathbf{F}_{ik} \cdot \mathbf{u}_{ik} - \frac{\beta_{jk}}{n_{j}} \mathbf{F}_{jk} \cdot \mathbf{u}_{jk} \right) + \dots$$

Here the terms $\sim u_{ij}^{s}$, $p_{i\alpha\beta}u_{ij\beta}$ are denoted by repeated dots. They are not written out, since terms of this order were already neglected when deriving Eqs.(1.1)-(1.13). In the case of a binary mixture of Maxwellian molecules (1.21), (1.23) are identical with the analogous equations of /5/, provided that the terms $\sim u_{ij}^{s}$, $p_{i\alpha\beta}u_{ij\beta}$ are neglected in the latter. Assuming that the relaxation times u_{ij} and T_{ij} are small compared with the characteristic

Assuming that the relaxation times u_{ij} and T_{ij} are small compared with the characteristic hydrodynamic time we can show, following /5/, that to a first approximation (1.21) yields the relation

$$-\frac{1}{\rho_i} \nabla (n_i kT) + \frac{1}{\rho_j} \nabla (n_j kT) = \sum_k \left(\frac{1}{\rho_i} \mathbf{F}_{ik} - \frac{1}{\rho_j} \mathbf{F}_{jk} \right)$$

for determining \mathbf{u}_{ij} , and T_{ij} are second-order quantities with respect to the gradients of the macroscopic quantities. Solving these relations for \mathbf{u}_{ij} we can obtain expressions for the diffusion velocities. The termodiffusive term in the diffusion velocity is determined by the thermal forces in \mathbf{F}_{ij} and the thermodiffusive effect in the heat flux by the terms $\sim \mathbf{u}_{ij}$ and \mathbf{q}_i . After this Eqs.(1.20) become the Navier-Stokes equations and (1.22) transforms into the energy equation of a normal mixture. However, the viscosity and thermal conductivity in them are sums of the viscosity and thermal conductivity of the mixture components.

2. Equations of entropy balance. Introducing the definition of specific entropy

$$\rho s = \sum_{i} \rho_{i} s_{i} = -k \sum_{i} \int f_{i} \left(\ln f_{i} - 1 \right) d\mathbf{v}_{i}$$

$$(2.1)$$

we can use standard methods /14/ to obtain the entropy balance equation of the form $(J_s$ is the entropy flux and σ denotes the entropy source)

$$\frac{\partial}{\partial t} \rho s = -\nabla \cdot \left(\sum_{i} \rho_{i} s_{i} \mathbf{u}_{i} + \mathbf{J}_{s} \right) + \sigma$$

$$\mathbf{J}_{s} = -k \sum_{i} \int \left(\mathbf{v}_{i} - \mathbf{u}_{i} \right) f_{i} \left(\ln f_{i} - 1 \right) d\mathbf{v}_{i}$$

$$\sigma = -k \sum_{i} \sum_{i} \int I_{ij} \left(f_{i}, f_{j} \right) \ln f_{i} d\mathbf{v}_{i} \ge 0$$
(2.2)

In the method of solving the Boltzmann equations given in /1/, it was assumed that the cross collision integrals

$$I_{ij}(f_i, f_j) \sim K I_{ii}(f_i, f_i)$$
 (2.3)

and the distribution functions were written in the form of series in terms of the Knudsen number K

$$f_{i}(t, \mathbf{r}, \mathbf{v}_{i}) = f_{i}^{(0)} \left(1 + \sum_{n=1}^{\infty} K^{n} \Phi_{i}^{(n)}\right)$$

$$f_{i}^{(0)} = n_{i} \left(\frac{m_{i}}{2\pi kT_{i}}\right)^{1/2} \exp\left[-\frac{m_{i} (\mathbf{v}_{i} - \mathbf{u}_{i})^{2}}{2kT_{i}}\right]$$
(2.4)

Using (2.3), (2.4) we can also write the quantities ρ_s, J_s, σ in the form of series in K whose first two terms are:

$$\rho s^{(0)} = -k \sum_{i} \int f_{i}^{(0)} (\ln f_{i}^{(0)} - 1) d\mathbf{v}_{i} = k \sum_{i} \left[\frac{3}{2} n_{i} - n_{i} \ln \left(\frac{n_{i}}{e} \left(\frac{m_{i}}{2\pi k T_{i}} \right)^{s/s} \right) \right]$$

$$\rho s^{(1)} = -k \sum_{i} \int f_{i}^{(0)} \Phi_{i}^{(1)} \ln f_{i}^{(0)} d\mathbf{v}_{i} = 0$$

$$\mathbf{J}_{s}^{(0)} = -k \sum_{i} \int (\mathbf{v}_{i} - \mathbf{u}_{i}) f_{i}^{(0)} (\ln f_{i}^{(0)} - 1) d\mathbf{v}_{i} = 0$$
(2.5)

$$\begin{aligned} \mathbf{J}_{s}^{(1)} &= -k \sum_{i} \int (\mathbf{v}_{i} - \mathbf{u}_{i}) f_{i}^{(0)} \Phi_{i}^{(1)} \ln f_{i}^{(0)} d\mathbf{v}_{i} = \sum_{i} \frac{q_{i}^{(1)}}{T_{i}} \\ \sigma^{(0)} &= -k \sum_{i \neq j} \int I_{ij} (f_{i}^{(0)}, f_{j}^{(0)}) \ln f_{i}^{(0)} d\mathbf{v}_{i} \neq 0 \\ \sigma^{(1)} &= -k \sum_{i} \int \Phi_{i}^{(1)} [I_{ii} (f_{i}^{(1)}, f_{i}^{(0)}) + I_{ii} (f_{i}^{(0)}, f_{i}^{(1)})] d\mathbf{v}_{i} - \\ k \sum_{i \neq j} \int \{\Phi_{j}^{(1)} I_{ij} (f_{i}^{(0)}, f_{j}^{(0)}) + [I_{ij} (f_{i}^{(0)}, f_{j}^{(1)}) + I_{ij} (f_{i}^{(1)}, f_{j}^{(0)})] \ln f_{i}^{(0)} \} d\mathbf{v}_{i} \end{aligned}$$

In deriving the second and fourth relation in (2.5) we have used the conditions of uniqueness on $f_i^{(1)}$ and the definition of thermal fluxes /1/.

To a first approximation in K, the entropy density is represented, by virtue of definition (2.1), as the sum of partial entropies which are functions of the local T_i and n_i such as they would be if every component were in a state of equilibrium with specific temperature T_i . The entropy flux is determined by the partial heat fluxes. We note that, unlike in the usual mixtures, the entropy source in the zero approximation is different from zero by virtue of the velocity and temperature relaxation processes of the mixture components. This indicates the irreversibility of the hydrodynamic equations in the zero approximation.

Using the integral equations for $\Phi_i^{(1)}$ and definitions of the quantities $Q_{ij}, \mathbf{F}_{ij}, \mathbf{q}_i$ and

 $p_{i\alpha\beta}$ /l/, we can write the expression for the entropy source in the form of the sum of products of fluxes and thermodynamic forces associated with them, as is the practice in the thermodynamics of irreversible processes

$$\sigma^{(0)} + \sigma^{(1)} = \sum_{i < j} \sum_{q_{ij}} Q_{ij} \left(\frac{1}{T_j} - \frac{1}{T_i} \right) + \sum_{i < j} \sum_{q_{ij}} F_{ij} \cdot \left(\frac{\beta_{ij}}{T_i} + \frac{\beta_{ji}}{T_j} \right) \mathbf{u}_{ij} + \sum_{i} \mathbf{q}_i \cdot \nabla \frac{1}{T_i} - \sum_{i} p_{i\alpha\beta} \frac{\mathbf{v}_{i\alpha\beta}}{T_i}$$
(2.6)

Here Q_{ij} , \mathbf{F}_{ij} , \mathbf{q}_i , $p_{i\alpha\beta}$ denote the fluxes and $(T_j^{-1} - T_i^{-1})$, $(T_i^{-1}\beta_{ij} + T_j^{-1}\beta_{ji}) \mathbf{u}_{ij}$, ∇T_i^{-1} , $-T_i^{-1}e_{i\alpha\beta}$ are the conjugate thermodynamic forces.

The linear laws connecting the fluxes with the forces can be derived from (1.4), (1.5), (1.9) - (1.13) under the condition that $|T_i - T_j| \ll (T_i + T_j)$ (the smallness of the remaining forces has already been assumed in deriving the hydrodynamic equations). They have the form

$$Q_{ij} = L_{Q_{ij}Q_{ij}} \left(\frac{1}{T_j} - \frac{1}{T_i}\right), \quad \mathbf{F}_{ij} = L_{F_{ij}F_{ij}} \frac{1}{T} \mathbf{u}_{ij} + \sum_{\substack{k(\neq i, j) \\ k \neq i, j}} \left(L_{F_{ij}F_{ik}} \frac{1}{T} \mathbf{u}_{ik} + L_{F_{ij}F_{kj}} \frac{1}{T} \mathbf{u}_{kj}\right) + L_{F_{ij}q_i} \nabla \frac{1}{T_i} + L_{F_{ij}q_j} \nabla \frac{1}{T_j}$$

$$\mathbf{q}_i = L_{q_iq_i} \nabla \frac{1}{T_i} + \sum_{j(\neq i)} L_{q_iF_{ij}} \frac{1}{T} \mathbf{u}_{ij}, \quad p_{i\alpha\beta} = -L_{p_ip_i} \frac{1}{T} e_{i\alpha\beta}$$
(2.7)

When the velocity and temperature differences in the components of the mixture are small, doubts may arise concerning the validity of the multivelocity and multitemperature description of the mixture. However, in the Chapman-Enskog method leading to a one-velocity and one-temperature description u_{ij} is the rate of diffusion, $\sim Kc_0 (c_0)$ is the speed of sound in the mixture) and the temperature difference $\sim u_{ij}^2 \sim K^2 c_0^3$ (see (1.19)). Therefore we have assumed above that $\max(v_{iT}, v_{jT}) \gg |u_{ij}| \gg Kc_0$ and $(T_i + T_j) \gg |T_i - T_j| \gg K^2 (T_i + T_j)$.

When the transport phenomena have a vector character (interaction between the components and thermal conductivity), we have crossover effects and the corresponding coefficients satisfy the Onsager-Casimir reciprocity relations

$$L_{F_{ij}q_{i}} = -L_{q_{i}F_{ij}} = 32 \frac{m_{i}m_{j}\rho_{j}T\lambda_{i}\alpha_{ij}}{(m_{i}+m_{j})^{3}}, \quad L_{F_{ij}q_{j}} = -L_{q_{j}F_{ij}}$$
(2.8)

(since the force ∇T_i^{-1} is an even function and $T^{-1}u_{ij}$ is an odd function of the molecular velocities). Unlike the binary mixtures /8/, in multicomponent mixtures the force \mathbf{F}_{ij} depends not only on \mathbf{u}_{ij} , but also on \mathbf{u}_{ik} and \mathbf{u}_{jk} ($k \neq i, j$), which are conjugated with \mathbf{F}_{ik} and \mathbf{F}_{jk} . The corresponding coefficients are connected by the Onsager reciprocity relations

$$L_{F_{ij}F_{ik}} = L_{F_{ik}F_{ij}} = -\left(\frac{32}{15}\right)^2 \frac{m_i^{\mathfrak{a}}m_j m_k \rho_j \rho_k \lambda_i \alpha_{ij} \alpha_{ik}}{k^{\mathfrak{a}} (m_i + m_j)^{\mathfrak{a}} (m_i + m_k)^{\mathfrak{a}}}$$

$$L_{F_{ij}F_{kj}} = L_{F_{kj}F_{ij}}$$
(2.9)

where $L_{F_{ij}q_i}, L_{F_{ij}F_{kj}}$ are obtained from $L_{F_{ij}q_i}, L_{F_{ij}F_{ik}}$ by mutual interchange of the indices *i*, *j*. The remaining coefficients of (2.7) are determined by the relations

$$L_{Q_{ij}Q_{ij}} = \frac{16\rho_i \rho_j kT^{a}}{(m_i + m_j)^{a}} \Omega_{ij}^{(1,1)}, \quad L_{F_{ij}F_{ij}} = L_{F_{ij}F_{ij}}^{(0)} + L_{F_{ij}F_{ij}}^{(1)} = \frac{16\rho_i \rho_j T}{3(m_i + m_j)} \Omega_{ij}^{(1,1)} - \left(\frac{32}{15}\right)^{a} \frac{m_i^{a}m_j^{a}(\rho_j^{a}\lambda_i + \rho_i^{a}\lambda_j)\alpha_{ij}}{k^{a}(m_i + m_j)^{a}}$$

$$L_{q_iq_i} = \lambda_i T^{a}, \quad L_{p_ip_i} = 2\mu_i T$$
(2.10)

In order for the entropy source to be always positive, the matrix of the kinetic coefficients $L_{nm}(n, m = Q_{ij}, F_{ij}, q_i, p_i)$ must satisfy certain conditions /14/

$$L_{nn} \ge 0, \left\| \begin{array}{cc} L_{F_{ij}F_{ij}} & L_{F_{ij}q_i} \\ L_{q_iF_{ij}} & L_{q_iq_i} \end{array} \right\| = L_{q_iq_i} L_{F_{ij}F_{ij}}^{(0)} \left(1 - \frac{L_{F_{ij}F_{ij}}^{(1)}}{L_{F_{ij}F_{ij}}^{(0)}} \right) + L_{q_iF_{ij}}^{a} \ge 0$$

$$(2.11)$$

The non-negativity of $L_{F_{ij}F_{ij}}$ follows from the inequality

$$\frac{L_{F_{ij}F_{ij}}^{(0)}}{L_{F_{ij}F_{ij}}^{(0)}} = 2 \left(\frac{\alpha_{ij}}{\Omega_{ij}^{(1,1)}}\right)^2 \left[\frac{n_j \Omega_{ij}^{(1,1)}}{n_i \Omega_i^{(3,2)}} \left(\frac{m_i}{m_i + m_j}\right)^3 + \frac{n_j \Omega_{ij}^{(1,1)}}{n_j \Omega_j^{(2,3)}} \left(\frac{m_j}{m_i + m_j}\right)^3\right] < 1$$
(2.12)

which holds by virtue of the condition $n_i\Omega_{ij} \ll n_i\Omega_i$ (a corollary of the initial assumption (2.3)) and of the condition $\alpha_{ij}(\Omega_{ij}^{(1,1)})^{-1} < 1$. The non-negativity of the remaining components L_{nn} clearly follows from (2.10). When inequality (2.11) holds, the second condition of (2.11) also holds.

The mutuality relations (2.8), (2.9) and the inequalities (2.11) are established using the transport coefficients calculated in the first-order approximation in terms of the Sonin polynomials. However, it can be shown that they also remain valid for the exact expressions for the transport coefficients.

Expression (2.6) for the entropy source was derived under the same assumptions as the hydrodynamic equations, i.e. for arbitrary temperature differences of the mixture components and under the constraint (1.15) imposed on u_{ij} . The Onsager reciprocity relations, however, hold only when the differences in the temperature and velocity components are small. Thus in order for the laws of thermodynamics of irreversible processes to hold in the system in question, the local equilibrium must extend outside each component.

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