

Generalized Stefan-Maxwell Diffusion Equations for Multicomponent Mixtures of Polyatomic Gases

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Abstract. The generalization of Grad's moment method for the multicomponent mixture of the polyatomic gases is developed to the case when a large number of polynomials and the moments corresponding to them are taken into account in the expansion of the distribution function. The mass transport equations in the form of the Stefan-Maxwell equations and the heat flux of mixture with "true" thermal conductivity are obtained. The approximation which gives the first non-zero values of the thermal diffusion and thermal conductivity coefficients are discussed in detail. The expressions for these coefficients are distinguished by the simpler form of the corresponding results of the conventional Chapman - Enskog method.

INTRODUCTION

The formal kinetic theory of the monatomic and polyatomic gas mixtures is based on the use of a system of the kinetic equations with collision integrals in the Boltzmann or Wang Chang-Uhlenbeck forms [1,2]. In the case of low Knudsen numbers these equations are solved using the traditional Chapman-Enskog method (CEM) [1-3] or Grad's moment method (GMM) [4-6] which enable one to obtain both equations for the conservation (balance) of mass, momentum and energy for the gas mixture as well as the transport relations for the diffusion fluxes of the components of the mixture, the heat flux and viscous stress tensor for a mixture which close the conservation equations.

In the standard CEM scheme [1-3] the linear transport relations are written in a form which is solved for the diffusion fluxes and the heat flux in terms of the gradients of the molar fractions (concentration) of the components, the pressure and temperatures gradients. Using the terminology of non-equilibrium thermodynamics we shall denote this way of writing the transport equations by the term "fluxes in terms of forces".

The alternative form of the transport equations for the multicomponent gas mixture in the "forces in terms of fluxes" representation can be obtained by a certain modification of CEM scheme [7] or by direct using of GMM scheme [5,6]. It had already been shown [8] that the use of this method in the case of a multicomponent gas mixture of monatomic molecules makes it possible, in well-known approximation of 13N moments, to obtain the mass transport equations in the form of the Stefan-Maxwell equations. In this case the "thermodynamics force of diffusion" which includes the concentration and pressure gradients is expressed in terms of a linear combination of the diffusion fluxes and a thermal diffusion term which is proportional to the temperature gradient. This approach was later generalized to the case of the polyatomic gaseous mixture [9]

RESULTS OF THE CHAPMAN-ENSKOG METHOD

The conventional expressions for the mass diffusion fluxes of the components \mathbf{J}_i and the reduced heat flux of the mixture \mathbf{J}_q which are obtained by CEM can be written in the form [2]

$$\mathbf{J}_i = \rho_i \mathbf{V}_i = -\rho_i \left(\sum_{k=1}^N D_{ik} \mathbf{d}_k + D_{Ti} \nabla \ln T \right), \quad (1)$$

$$\mathbf{J}_q = -\lambda' \nabla T - \sum_{k=1}^N D_{Tk} p \mathbf{d}_k \quad (2)$$

Here n_i , $\rho_i = m_i n_i$ and $\mathbf{V}_i = \mathbf{u}_i - \mathbf{u}$ are the number density, mass density and the diffusion velocity of species i , D_{ik} and D_{Tk} are the multicomponent coefficients of diffusion and thermal diffusion of gas mixture, λ' is the "instantaneous" thermal conductivity, T is the temperature, m_i is the mass of a particle of species i , k_B is the Boltzmann constant. The thermodynamic diffusion force in the absence of external forces defined as

$$\mathbf{d}_i = \nabla \frac{n_i}{n} + \left(\frac{n_i}{n} - \frac{\rho_i}{\rho} \right) \nabla \ln p. \quad (3)$$

The expression for \mathbf{J}_i may be rewritten as

$$\mathbf{J}_i = -\rho_i \sum_{k=1}^N D_{ik} (\mathbf{d}_k + k_{Tk} \nabla \ln T), \quad (4)$$

where the thermal diffusion ratios k_{Tk} are introduced as the solutions of the linear algebraic system of the equations of N -th order

$$\sum_{k=1}^N D_{ik} k_{Tk} = D_{Ti}, \quad i, k = 1, \dots, N \quad (5)$$

Note that the coefficient λ' in Eq. (2) is the thermal conductivity of the mixture in the case that all diffusion forces vanish. It is not the customary, steady state thermal conductivity. To obtain the "true" thermal conductivity λ it is necessary to solve Eqs. (1) for the diffusion forces in terms of the mass flux vectors and the temperature gradients, substitute the result into the relation (2) and take the coefficient of the temperature gradient. The alternative expression for \mathbf{J}_q takes the form

$$\mathbf{J}_q = -\lambda \nabla T + p \sum_{k=1}^N k_{Tk} \mathbf{V}_k, \quad (6)$$

where

$$\lambda = \lambda' - \frac{p}{T} \sum_{k=1}^N k_{Tk} D_{Tk}. \quad (7)$$

For the monatomic gas mixture all the coefficients in these relations, that is, multicomponent coefficients of diffusion and thermal diffusion and thermal conductivity, are described in the form of the ratios of determinants of order $N\xi+1$ to determinants of order $N\xi$ which are obtained as the result of solving a truncated infinite system of the algebraic equations using Kramer's rules. Here, N is the number of components in the mixture and ξ is the order of the approximations (the number of terms which are retained in finding the transport coefficients in the form of series in orthogonal Sonine polynomials in the Chapman-Cowling method). We note that, according to existing terminology [2], retention of the first non-zero coefficients in the expansion for the transport coefficients - this is the first approximation ($\xi = 1$) in the case of diffusion coefficients and the second approximation ($\xi = 2$) in the case of thermal conductivity and thermal diffusion.

In the solutions obtained the elements of the determinants are expressed in terms of so-called “integral brackets” of Sonine polynomials of different orders which, in their turn, are represented in the form of linear combinations of Ω -integrals which are function of the temperature and also depend on the parameters of the interaction potentials between particles. In the case of the binary gas mixture, for example, binary coefficients of diffusion in the first approximation is defined by the expression [1]

$$[D_{ik}]_1 = \frac{3k_B T}{16n\mu_{ik}\Omega_{ik}^{(1,1)}(T)} \quad (8)$$

where μ_{ik} is the reduced mass of the particles of species i and k . It is known that the thermal diffusion is more sensitive to the exact nature of the collision process. For the binary gas mixture the thermal-diffusion factor k_T is linear in the quantity $(6C_{ik}^* - 5)$, where

$$C_{ik}^* = \Omega_{ik}^{(1,2)} / 3\Omega_{ik}^{(1,1)} \quad (9)$$

For the hard elastic sphere collision model, $C_{ik}^* = 1$ and for “maxwellian” molecules, $C_{ik}^* = 0$.

The usual procedure of CEM gives the needlessly cumbersome expressions for the “instantaneous” thermal conductivity and thermal diffusion coefficients. We also have the very complex form of the expression for the “true” thermal conductivity (8). The expressions for the second approximation to these coefficients are proportional to the ratio of two determinations, one of order $2N+1$, the other of order $2N$ [3]. Some modification of the calculating procedure which makes possible to obtain the more simple expressions in the least approximation has been proposed in [10, 2]

The additional terms and the new polynomials arise in the expansion of the distribution function in the case of the polyatomic gas mixture. These terms are related to consideration of the internal energy of the molecules. The linear relations for \mathbf{J}_i and \mathbf{J}_q has the form identical with those of the monatomic gas mixture. Taking into account in the expansion of the distribution function only one polynomial by Wang Chang – Uhlenbeck we obtain that multicomponent thermal diffusion and thermal conductivity coefficients are described in the form of the ratios of determinants of order $N(\zeta+1)+1$ to determinants of order $N(\zeta+1)$. The elements of the determinants in this case are expressed in terms of the integral brackets not only of the Sonine polynomials but of a new polynomial as well. The generalized Ω -integrals are also introduced which include the summation with respect to the internal states of the colliding molecules.

The disadvantage and the complexity of the CEM procedure are also retained in this case. The usual approximation which gives the first non-zero values of the thermal diffusion and thermal conductivity leads to the coefficients which are described in the form of the ratios of determinants of order $3N+1$ to determinants of order $3N$. The derivation of the Stefan-Maxwell equations for the polyatomic gas mixture using CEM procedure has been carried on in the work [11]. Some modification of the calculating scheme makes possible to obtain the thermal diffusion factor which in the least approximation has been expressed in terms of the ratios of determinants of orders $2N+1$ and N .

LINEARIZED MOMENT METHOD FOR THE MULTICOMPONENT GAS MIXTURE OF THE POLYATOMIC MOLECULES

The non-equilibrium state of a multicomponent gas mixture of polyatomic molecules is described by the distribution function of particles of species i in an α -th quantum state which we will seek in the form

$$f_{i\alpha} = f_{i\alpha}^{(0)} (1 + \phi_{\alpha i}) , \quad f_{i\alpha}^{(0)} = n_i \left(\frac{\beta_i}{\pi} \right)^{3/2} Q_i^{-1} \exp(-\beta_i c_i^2 - \varepsilon_{i\alpha}) , \quad (10)$$

where $f_{i\alpha}^{(0)}$ is the local Maxwell-Boltzmann distribution, $\phi_{i\alpha}$ is a small correction ($|\phi_{i\alpha}| \ll 1$), $\beta_i = m_i / 2k_B T$, $\mathbf{c}_i = \mathbf{v}_i - \mathbf{u}$. The values $\varepsilon_{i\alpha}$ and Q_i are defined as

$$\varepsilon_{i\alpha} = E_{i\alpha}/k_B T \quad , \quad Q_i = \sum_{\alpha} \exp(-\varepsilon_{i\alpha}) \quad (11)$$

Here $E_{i\alpha}$ is the internal energy of the particles of species i in an α -th quantum state.

The system of the linearized kinetic equations, which the correction $\phi_{i\alpha}$ satisfies, is written as

$$\left[\frac{d\phi_{i\alpha}}{dt} + (\mathbf{c}_i \cdot \nabla) \phi_{i\alpha} + \frac{n}{n_i} (\mathbf{c}_i \cdot \mathbf{d}_i) + \left(\beta_i c_i^2 - \frac{5}{2} + \varepsilon_{i\alpha} - \langle \varepsilon_i \rangle \right) (\mathbf{c}_i \cdot \nabla) \ln T \right] = \sum_k L_{ik}^{\alpha} (\phi_{i\alpha} + \phi_{k\beta}) , \quad (12)$$

where Wang Chang – Uhlenbeck linearized collision operator defined, for any function of the dynamical variables for a binary collision between species i and k , by the equation

$$L_{ik}^{\alpha} (Y) = \sum_{\beta\gamma\delta} \int \int f_{k\beta}^{(0)} (Y' - Y) g \sigma_{\alpha\beta}^{\gamma\delta} (g, \chi, \varphi) \sin \chi d\chi d\varphi d\mathbf{c}_k \quad (13)$$

Here, the primes indicate values after the binary collision, $\sigma_{\alpha\beta}^{\gamma\delta}$ is the inelastic differential scattering cross section for the process $\alpha, \beta \rightarrow \gamma, \delta$, g is the initial relative velocity of particles of species i and k , χ is the scattering angle and φ is the polar angle.

On the left-hand side of Eqs. (12) we omitted the terms which include the scalar and tensorial function of \mathbf{c}_i , corresponding to taking into account the shear and volume viscosities.

The expansion of the correction $\phi_{i\alpha}$ in the general moment method can be represented in the form

$$\phi_{i\alpha} = \sum_{mnq} \mathbf{a}_i^{mnq} \mathbf{P}_i^{mn}(\mathbf{W}_i) R_i^{(q)}(\varepsilon_{i\alpha}) \quad (14)$$

Here $\mathbf{P}_i^{mn}(\mathbf{W}_i)$ are the irreducible tensorial polynomials where $\mathbf{W}_i = \beta_i^{1/2} \mathbf{c}_i$ is the dimensionless velocity of particles of species i . Within the multiplier these polynomials are the irreducible tensorial Hermite polynomials [4]. The $R_i^{(q)}$ are the polynomials of Wang Chang- Uhlenbeck of the dimensionless internal energy of molecule of species i in the state α . For the vector values ($m=1$) the polynomials $\mathbf{P}_i^{1n}(\mathbf{W}_i)$ can be written as

$$\mathbf{P}_i^{1n}(\mathbf{W}_i) = \gamma_n S_{3/2}^n(W^2) \mathbf{W} \quad (15)$$

where $S_{3/2}^n(W^2)$ are the Sonine polynomials, γ_{1n} is the normalization factor. The first several polynomials \mathbf{P} and R are as follow

$$\mathbf{P}^{00}=1, \quad \mathbf{P}_i^{10}=(2)^{1/2} \mathbf{W}, \quad \mathbf{P}_i^{11}=\left(\frac{4}{5}\right)^{1/2} \left(W^2 - \frac{5}{2}\right) \mathbf{W}, \quad R_{i\alpha}^{(0)}=1, \quad R_{i\alpha}^{(1)}=\varepsilon_{i\alpha} - \langle \varepsilon_i \rangle \quad (16)$$

Because of the orthogonality of the polynomials the expansion coefficients are expressed in terms of the moments of the distribution function. The first several vector coefficients are related to the diffusion velocity \mathbf{V}_i and the reduced heat fluxes of species i \mathbf{J}_{qi}^{tr} and \mathbf{J}_{qi}^{int} which correspond to the translational and internal degrees of freedom of the particles

$$a_i^{000}=0, \quad \mathbf{a}_i^{100}=(2)^{1/2} \beta_i^{1/2} \mathbf{V}_i, \quad \mathbf{a}_i^{110}=\left(\frac{4}{5}\right)^{1/2} \beta_i^{1/2} \frac{\mathbf{J}_{qi}^{tr}}{p_i}, \quad \mathbf{a}_i^{101}=(2)^{1/2} \beta_i^{1/2} \frac{\mathbf{J}_{qi}^{int}}{n_i c_i^{int} T} \quad (17)$$

Here

$$\mathbf{J}_{qi}^{tr} = \mathbf{q}_i^{tr} - \frac{5}{2} p_i \mathbf{V}_i, \quad \mathbf{J}_{qi}^{int} = \mathbf{q}_i^{int} - \langle \varepsilon_i \rangle p_i \mathbf{V}_i \quad (18)$$

where \mathbf{q}_i^{tr} and \mathbf{q}_i^{int} are the corresponding total heat fluxes of species i .

The set of the equations for the coefficients \mathbf{a}_i^{lnq} is obtained after multiplying the linearized kinetic equation (12) by the values $f_i^{(0)} \mathbf{P}_i^{1n}(\mathbf{W}_i) R_i^{(q)}(\varepsilon_{i\alpha})$, integrating over velocities and summation over all the internal states. The closed system of the moment equations for any n is obtained in this report.

We shall consider the approximation to the distribution function when the polynomials (6) together with the coefficients (17) should be only conserved in the expansion (14). This approximation gives the first non-zero values of the thermal diffusion and thermal conductivity coefficients. The associated system of equations for $\mathbf{J}_i = \rho_i \mathbf{V}_i$, \mathbf{J}_{qi}^{tr} and \mathbf{J}_{qi}^{int} in this approximation becomes

$$\frac{d\mathbf{J}_i}{dt} + p\mathbf{d}_i = \mathbf{R}_i^{100}, \quad \frac{d\mathbf{J}_{qi}^{tr}}{dt} + \frac{5}{2} \frac{k_B}{m_i} p_i \nabla T = \mathbf{R}_i^{110}, \quad \frac{d\mathbf{J}_{qi}^{int}}{dt} + \frac{c_i^{int}}{m_i} p_i \nabla T = \mathbf{R}_i^{101} \quad (19)$$

The values \mathbf{R}_i^{1nq} are the moments with respect to the collision integrals of the kinetic equation. After the using of the expansion (14) these values are expressed in terms of a linear set of the coefficients (17).

GENERALIZED STEFAN-MAXWELL DIFFUSION EQUATIONS AND HEAT FLUX

The analysis shows that the order of coefficients at the moments on the right-hand side of the Eqs. (19) is mainly determined by the values of τ_{ik}^{-1} or $(c_i^{tr}/k_B)\tau_{ik}$ where τ_{ik} is the characteristic time between collisions for i and k molecules. For the slow changing states of a gas we have the condition $\tau_{ik} \ll \tau_L$ where τ_L is the characteristic time of change of gas macroscopic parameters. These considerations allow us to neglect the time derivatives of the values \mathbf{J}_i , \mathbf{J}_{qi}^{tr} and \mathbf{J}_{qi}^{int} on the left-hand sides of the Eqs. (19). The resulting system of linear algebraic equations of the diffusion velocities and reduced heat fluxes of species is as follow

$$\sum_{k \neq i} \frac{n_i n_k k_B T}{n [D_{ik}]_1} (\mathbf{V}_i - \mathbf{V}_k) = -p\mathbf{d}_i - \sum_{k \neq i} \frac{m_k}{m_i + m_k} \frac{n_i n_k k_B T}{n [D_{ik}]_1} \left(\frac{6}{5} C_{ik}^* - 1 \right) \left(\frac{\mathbf{J}_{qi}^{tr}}{p_i} - \frac{m_i}{m_k} \frac{\mathbf{J}_{qk}^{tr}}{p_k} \right) - \sum_{k \neq i} \frac{n_i n_k k_B T}{n [D_{ik}]_1} \left(E_{ik}^* \frac{\mathbf{J}_{qi}^{int}}{n_i c_i^{int} T} - E_{ki}^* \frac{\mathbf{J}_{qk}^{int}}{n_k c_k^{int} T} \right), \quad (20)$$

$$-p_i \nabla \ln T - \sum_{k \neq i} \frac{m_k}{m_i + m_k} \frac{n_i n_k k_B T}{n [D_{ik}]_1} \left(\frac{6}{5} C_{ik}^* - 1 \right) (\mathbf{V}_i - \mathbf{V}_k) = \frac{p^2}{T} \left(\sum_k \Lambda_{ik} \frac{\mathbf{J}_k^{tr}}{p_k} + \sum_k \frac{k_B}{c_k^{int}} \Lambda'_{ik} \frac{\mathbf{J}_{qk}^{int}}{p_k} \right) \quad (21)$$

$$-p_i \frac{c_i^{int}}{k_B} \nabla \ln T - \sum_{k \neq i} \frac{n_i n_k k_B T}{n [D_{ik}]_1} E_{ik}^* (\mathbf{V}_i - \mathbf{V}_k) = \frac{p^2}{T} \left(\sum_k G_{ik} \frac{\mathbf{J}_k^{tr}}{p_k} + \sum_k \frac{k_B}{c_k^{int}} G'_{ik} \frac{\mathbf{J}_{qk}^{int}}{p_k} \right) \quad (22)$$

Resolving Eqs. (21) and (22) with respect to \mathbf{J}_{qi}^{tr} and \mathbf{J}_{qi}^{int} and substituting the expressions obtained into (20) we are led to the diffusion equations in a form of the generalized Stefan-Maxwell equations

$$\sum_{k \neq i} \frac{n_i n_k}{n^2 [D_{ik}]_1} (1 - \Delta_{ik}^{(2)}) (\mathbf{V}_i - \mathbf{V}_k) = -\mathbf{d}_i - k_{Ti} \nabla \ln T \quad (23)$$

The coefficient of binary diffusion $[D_{ik}]_1$ is defined by Eq. (9), $\Delta_{ik}^{(2)}$ is the correction of the higher approximation to the coefficient of binary diffusion. The thermal diffusion ratios k_{Ti} identical to the coefficients as occur in the equation for \mathbf{J}_i (5). At the same time the expressions obtained by moment method are more simple and are described in the form of the ratios of determinants of order $2N+1$ to determinants of order $2N$ in place of ratios of determinants of order $3N+1$ and $3N$ as it is in the conventional CEM procedure. The expression for k_{Ti} has a form

$$k_{Ti} = \sum_{k \neq i}^N \frac{n_i n_k}{k_B n^2 [D_{ik}]_1} \left[\mu_{ik} \left(\frac{6}{5} C_{ik}^* - 1 \right) \left(\frac{\lambda_k^{tr}}{m_k n_k} - \frac{\lambda_i^{tr}}{m_i n_i} \right) + \left(E_{ki}^* \frac{k_B}{c_k^{int}} \frac{\lambda_k^{int}}{m_k n_k} - E_{ik}^* \frac{k_B}{c_i^{int}} \frac{\lambda_i^{int}}{m_i n_i} \right) \right] \quad (24)$$

Here λ_i^{tr} and λ_i^{int} are the partial thermal conductivities corresponding to the transport of the translational and internal energies of the particles of species i . The expressions for these parameters are described in the form of the ratios of determinants of order $2N+1$ and $2N$ and given in [9].

An important consideration following from the expression (24) is that the thermal diffusion ratios along with the usual term proportional to the factor $(6/5)C_{ik}^* - 1$ as in the case of a mixture of monatomic molecules includes the terms proportional to E_{ki}^* and E_{ik}^* essentially related to the inelastic interaction of molecules. For the most mixtures of the polyatomic gases the calculations of the thermal diffusion coefficients based on the theory of the monatomic gases give, as a rule, fairly satisfactory results. However, for the mixtures with the close masses of the molecules (A-CO₂, D₂-HT, ³He-HD etc) the contribution of the inelastic terms may become quite significant.

Resolving Eqs. (21) and (22) with respect to \mathbf{J}_{qi}^{tr} and \mathbf{J}_{qi}^{int} and using the definitions (18) we can also obtain the expression for the total heat flux of mixture $\mathbf{q} = \sum_i (\mathbf{q}_i^{tr} + \mathbf{q}_i^{int})$ which is written at once with the true thermal conductivity λ . This expression acquires the form

$$\mathbf{q} = -\lambda \nabla T + \sum_{k=1}^N \left(\frac{5}{2} + \langle \varepsilon_k \rangle \right) p_k \mathbf{V}_k + p \sum_{k=1}^N k_{TK} \mathbf{V}_k \quad (25)$$

where

$$\lambda = \sum_{k=1}^N (\lambda_k^{tr} + \lambda_k^{int})$$

The thermal conductivity coefficient and thermal diffusion ratios correspond to the results of the full second approximation of the CEM. They are distinguished by the simpler form of the corresponding quantities of the usual CEM procedure where these coefficients are expressed in terms of the ratio of determinants of order $3N+1$ to determinants of order $3N$ while the expressions obtained above include the ratios of $(2N+1)$ -th and $2N$ -th order determinants.

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