# Transformations of the equations of the first approximation of Chapman–Enskog methods and vector transport relations for mixtures of polyatomic gases[☆]

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## Abstract

Transformations of the systems of equations of the first approximation of the classical and generalized Chapman–Enskog methods are proposed for those terms of the distribution functions by means of which one can calculate the vector transport relations for mixtures of polyatomic gases, connecting the diffusion and heat fluxes and gradients of the scalar gas-dynamic variables. The solutions of the transformed systems are expressed in terms of diffusion rates and gradients of the macroparameters. The derivation and formulae for the coefficients of the Stefan–Maxwell relations and their generalizations are simplified, and rigorous results for the matrices of the transport coefficients are established. Approximate vector transport relations are given for mixtures of non-equilibrium reacting polyatomic gases.

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The kinetic theory of the transport properties of mixtures of ideal gases (which obey the Clapeyron-Mendeleyev equation of state) is most developed for the case of structureless (monatomic) particles.[1] When using the Chapman–Enskog method, the linearization of the system of Boltzmann kinetic equations with respect to the locally Maxwell distribution functions gives a system of linear non-homogeneous integral equations for the perturbations of the distribution functions $\varphi_i$, which define the form and features of the vector transport relations in the Navier-Stokes approximation. On the basis of these integral equations, the reasons for the effectiveness of their approximate solution are established using sections of series in Sonin polynomials, and the Onsager symmetry relations are proved. In the representation, called below the $d$-representation, the perturbations $\varphi_i$ are given[1] by linear functions of the temperature gradient $\nabla T$ and diffusion thermodynamic forces $\mathbf{d}_j$ ($i, j = 1, 2, \ldots, N$, where $N$ is the number of components of the mixture). For diffusion velocities $\mathbf{V}_i$ and a heat flux $\mathbf{q}$ this representation is called "fluxes in terms of thermodynamic forces".[2–4]

For gas-dynamic calculations it is more effective, however, to write $\mathbf{d}_i$ and $\mathbf{q}$ in terms of $\nabla T$ and $\mathbf{V}_j$.[2–4] The expressions for the diffusion thermodynamic forces $\mathbf{d}_i$ in terms of $\mathbf{V}_j$ and $\nabla T$ are called the Stefan–Maxwell relations. Their derivation by inverting the formulae for $\mathbf{V}_i$ in the $d$-representation leads to complex expressions for the transport coefficients, and the complexity increases as the number of terms of the expansions in Sonin polynomials taken into account increases, which is necessary in a number of cases.[2–4] A cardinal simplification of these expressions is obtained by methods based on approximate solutions of systems of equations for the perturbations $\varphi_i$ in the form of series in

polynomials: the transformation of systems of linear algebraic equations for the coefficients of the expansion in Sonin polynomials[2,3] and the use of expansion in Hermite polynomials.[4] As a result, the thermodynamic forces $\nabla T$ and $\mathbf{d}_i$ are expressed linearly in terms of the reduced heat flux and diffusion velocities. The advantages of this representation of the thermodynamic forces in terms of fluxes was shown earlier in Refs. 2–4.

Another way of modifying the classical Chapman–Enskog method is to introduce a new dependent variable $\psi_i$ instead of $\varphi_i$ using the formula

$$\varphi_i = \psi_i + \frac{m_i}{kT} \mathbf{C}_i \cdot \mathbf{V}_i$$

and to eliminate the diffusion thermodynamic forces $\mathbf{d}_i$ from the system of integral equations (here $m_i$ and $\mathbf{C}_i$ are the mass and peculiar velocity of a particle of the component $i$, and $k$ is Boltzmann's constant). The dependent variables $\psi_i$ and, consequently, $\varphi_i$ are at once expressed in terms of $\nabla T$, $\mathbf{V}_j$ (below this is called the $V$-representation for $\varphi_i$). It is shown that the solution of the systems of integral equations for the functions $\psi_i$ in the form of series in Sonin polynomials gives expressions, previously obtained in Ref. 2, for the coefficients of the vector transport relations, but a sufficiently complete analysis of these transport coefficients in an exact formulation, as is usually done when using the classical Chapman–Enskog method,[1] is not given. It is important to bear in mind that the $V$-representation for $\varphi_i$ is also used to determine the boundary jumps of the macroparameters of mixtures of slightly rarefied gases on surfaces with heterogeneous processes.[5]

In Section 1 we first give a brief description of the results of using the Chapman–Enskog method in the $d$-representation for a mixture of polyatomic gases when there are no chemical reactions and when there is only a slight deviation of the state of the mixture from a local Maxwell–Boltzmann state.[6–8] The modification proposed earlier in Ref. 5 is then extended to this case, and a more complete description of it is given; when using the systems of integral equations obtained, the properties of the transport coefficients are determined (for a mixture of monatomic gases this completes the results obtained earlier in Ref. 5). Solutions of these systems of equations in the form of series in a binary system of polynomials are then obtained, and corresponding formulae are given for the transport coefficients.

Section 2 is devoted to similar modifications of the generalized Chapman–Enskog method, intended for describing the transport properties of mixtures of reacting molecular gases when there is a considerable nonequilibrium in the internal degrees of freedom of the molecules.[9–14] Particular attention is devoted to analysing the matrices of the transport coefficients for one of the modifications. The inclusion of the inelastic collision cross-sections of the gas particles in the generalized Chapman–Enskog method has, for the moment, a mainly formal character, and hence approximate procedures (Section 3) are therefore important.

## 1. A slight departure from local equilibrium

The Chapman–Enskog method gives the correction

$$f_{i\alpha}^{(0)}(\varphi_{i\alpha}^{(I)} + \varphi_{i\alpha}^{(II)} + \varphi_{i\alpha}^{(III)})$$

to the local Maxwell–Boltzmann distribution function

$$f_{i\alpha}^{(0)} = n_i \frac{S_{i\alpha}}{Q_i} \left( \frac{m_i}{2\pi kT} \right)^{3/2} \exp(-W_i^2 - \varepsilon_{i\alpha})$$

$$Q_i = \sum_\beta S_{i\beta} \exp(-\varepsilon_{i\beta}), \quad W_i^2 = \frac{m_i}{2kT} C_i^2, \quad \varepsilon_{i\alpha} = \frac{E_{i\alpha}}{kT} \tag{1.1}$$

Here and everywhere henceforth $i = 1, 2, \ldots, N$, $\alpha = 0, 1, 2, \ldots, N^{(i)}$, where $N^{(i)}$ is the number of excited levels of the particles of component $i$, $n_i$ is the number of particles of chemical sort $i$ per unit volume, $m_i$ and $\mathbf{C}_i = \xi_i - \mathbf{v}$ is the mass and peculiar velocity of the $i$-th particle, $v$ is the mean-mass velocity of the gas mixture, $T$ is the temperature of the mixture of molecular gases, calculated[6–8] from the translational and internal energy of the particles, $E_{i\alpha}$ is the internal energy of particles of sort $i$ in the quantum energy state $\alpha$, $S_{i\alpha}$ is the statistical weight of state $i\alpha$, and $k$ is Boltzmann's constant. Chemical reactions are not considered. To simplify the notation we will omit the commas in the

sets of subscripts, so that, for example, $i\alpha \equiv i, \alpha$. In the general case the subscript $\alpha$ is a finite set of subscripts, which depend on the properties of the particles and the degree of excitation of the quantum levels (for example, $\alpha = \alpha_R \alpha_V^{(m)} \alpha_e$, where $\alpha_R$, $\alpha_V^{(m)}$ and $\alpha_e$ are the rotational, vibrational (mode $m$) and electron quantum energy levels respectively, and $m = 1, 2, \ldots, q$). For molecular low-temperature gases usually $\alpha = \alpha_R$, while for ionized inert gases $\alpha = \alpha_e$. In the case of monatomic particles, the subscript $\alpha$ will be omitted.

The zero approximation (1.1) defines the gas-dynamic variables $\{n_i(\mathbf{r}, t), v(\mathbf{r}, t), T(\mathbf{r}, t)\}$, for which the Chapman–Enskog method gives the closed system of conservation equations

$$\frac{Dn_i}{Dt} + n_i \nabla \cdot \mathbf{v} + \nabla \cdot n_i \mathbf{V}_i = 0, \quad \rho \frac{D\mathbf{v}}{Dt} + \nabla \cdot \mathbf{\Pi} = \sum_i \rho_i \mathbf{F}_i$$

$$\rho \frac{DU}{Dt} + \mathbf{\Pi} : \nabla \mathbf{v} + \nabla \cdot \mathbf{q} - \sum_i \rho_i \mathbf{V}_i \cdot \mathbf{F}_i = 0; \quad \frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \tag{1.2}$$

where $U$ is the internal energy of unit mass of the medium.

Expressions for the terms of the perturbation of the distribution function $\varphi_{i\alpha}^{(k)}$, $k =$ I, II, III, include the diad $\mathbf{C}_i \mathbf{C}_i$, the vector $\mathbf{C}_i$ and the scalar $C_i^0$ respectively. The first and third terms define the non-equilibrium contribution to the pressure tensor, in this case equal to

$$\mathbf{\Pi} = (p + \varsigma \nabla \cdot \mathbf{v})\mathbf{I} - 2\eta \mathbf{S}, \quad p = nkT$$

Here $\eta$ and $\varsigma$ are the coefficients of the shear and bulk viscosity respectively, $\mathbf{I}$ is the unit tensor and $\mathbf{S}$ is a tensor with the components

$$S_{mn} = \frac{1}{2}\left(\frac{\partial v_m}{\partial r_n} + \frac{\partial v_n}{\partial r_m}\right) - \frac{1}{3}I_{mn}\nabla \cdot \mathbf{v}; \quad m, n = 1, 2, 3$$

where $r_1$, $r_2$ and $r_3$ are the components of the radius vector.

Everywhere below we will consider only the term

$$\varphi_{i\alpha}^{(\text{II})} \equiv \varphi_{i\alpha}$$

which defines the vector transport relations.

The system of equations for $\varphi_{i\alpha}$ has the form

$$L_{i\alpha}(\varphi) = f_{i\alpha}^{(0)}\left[H_{i\alpha}\mathbf{C}_i \cdot \nabla \ln T + \frac{n}{n_i}\mathbf{C}_i \cdot \mathbf{d}_i\right]$$

$$H_{i\alpha} = W_i^2 - \frac{5}{2} + \varepsilon_{i\alpha} - \bar{\varepsilon}_i; \quad i = 1, 2, \ldots, N; \quad \alpha = 0, 1, 2, \ldots, N^{(i)} \tag{1.3}$$

The linearized collision operator is given by the expression

$$L_{i\alpha}(\varphi) = \sum_{j, \beta, \alpha', \beta'} \int f_{i\alpha}^{(0)} f_{j\beta}^{(0)} (\varphi'_{i\alpha'} + \varphi'_{j\beta'} - \varphi_{i\alpha} - \varphi_{j\beta}) d\Gamma, \quad d\Gamma = g_{ij}\sigma_X^Y d\Omega d\mathbf{C}_j$$

$$X = i\alpha j\beta, \quad Y = i\alpha' j\beta', \quad g_{ij} = |\mathbf{C}_i - \mathbf{C}_j| \tag{1.4}$$

The summation is carried out over all values of the subscripts

$$j = 1, 2, \ldots, N; \quad \beta = 0, 1, \ldots, N^{(j)}; \quad \alpha' = 0, 1, \ldots, N^{(i)}; \quad \beta' = 0, 1, \ldots, N^{(j)}$$

The prime denotes values after a collision, $\sigma$ is the differential scattering cross-section of molecules, characterizing the probability density of the transfer $(\mathbf{C}_i, \mathbf{C}_j, E_{i\alpha}, E_{j\beta}) \rightarrow (\mathbf{C}'_i, \mathbf{C}'_j, E_{i\alpha'}, E_{j\beta'})$ and $d\Omega$ is an element of the scattering solid angle, and when $j = i$ the peculiar velocity of a particle $\mathbf{C}_j$ is replaced by $\mathbf{C}_{i1}$. The diffusion thermodynamic force

of component $i$ is given by the formula

$$\mathbf{d}_i = \nabla x_i + \left(x_i - \frac{\rho_i}{\rho}\right)\nabla \ln p - \frac{\rho_i}{p}\left(\mathbf{F}_i - \sum_j \frac{\rho_j}{\rho}\mathbf{F}_j\right), \quad \sum_i \mathbf{d}_i = 0$$

$$x_i = \frac{n_i}{n}, \quad n = \sum_i n_i, \quad \rho_i = m_i n_i, \quad \rho = \sum_i \rho_i \tag{1.5}$$

$\mathbf{F}_i = \mathbf{F}_i(\mathbf{z}, t)$ is the external force, referred to $m_i$, $\mathbf{r}$ is the radius vector and $t$ is the time. The dimensionless mean internal energy of the molecules of component $i$

$$\varepsilon_i = \frac{1}{Q_i}\sum_\alpha S_{i\alpha}\varepsilon_{i\alpha}\exp(-\varepsilon_{i\alpha})$$

In the $d$-representation of the Chapman–Enskog method[6–8] the solution of system of Eqs. (1.3), (1.4) is sought in the form

$$\varphi_{i\alpha} = -\frac{1}{n}A_{i\alpha}(W^2, \varepsilon)\mathbf{C}_i \cdot \nabla \ln T - \frac{1}{n}\sum_j D_{i\alpha}^j(W^2, \varepsilon)\mathbf{C}_i \cdot \mathbf{d}_j \tag{1.6}$$

i.e. the perturbations $\varphi_i$ are expressed in terms of the thermodynamic forces $\nabla T$, $\mathbf{d}_j$.

The vectors $A_{i\alpha}\mathbf{C}_i$, $D_{i\alpha}^j\mathbf{C}_i$ satisfy systems of linear inhomogeneous integral equations $i, k = 1, 2, \ldots, N$; $\alpha = 0, 1, \ldots, N^{(i)}$

$$L_{i\alpha}(A\mathbf{C}) = -n f_{i\alpha}^{(0)} H_{i\alpha}\mathbf{C}_i \tag{1.7}$$

$$L_{i\alpha}(D^k\mathbf{C}) = -\frac{n}{x_i} f_{i\alpha}^{(0)}\left(\delta_{ik} - \frac{\rho_i}{\rho}\right)\mathbf{C}_i \tag{1.8}$$

Here $\delta_{ik}$ is the Kronecker delta.

Conditions of uniqueness of the solution of the integral equations

$$\sum_{i,\alpha} m_i \int f_{i\alpha}^{(0)}\varphi_{i\alpha}\mathbf{C}_i d\mathbf{C}_i = 0 \Rightarrow \sum_{i,\alpha} \int f_{i\alpha}^{(0)}(A_{i\alpha}; D_{i\alpha}^k)W_i^2 d\mathbf{C}_i = 0, \quad k = 1, 2, \ldots, N \tag{1.9}$$

which are a consequence of the determination of the mean-mass velocity, are imposed on the required functions.

When deriving the second term on the right-hand side of formula (1.6) and system of Eq. (1.8), the linear dependence of the vectors $\mathbf{d}_i$ is taken into account. The condition that the solution of the problem of determining the vector $D_{i\alpha}^k\mathbf{C}_i$ should be single-valued gives the equality

$$\sum_k \rho_k D_{i\alpha}^k = 0; \quad i = 1, 2, \ldots, N; \quad \alpha = 0, 1, \ldots, N^{(i)} \tag{1.10}$$

which is obtained using a well-known procedure.[1]

Using expressions (1.6)–(1.9) we obtain the following expressions for the vector transport relations ($i, j = 1, 2, \ldots, N$):the diffusion velocity of component $i$

$$\mathbf{V}_i = \frac{1}{n_i}\sum_\alpha \int f_{i\alpha}^{(0)}\varphi_{i\alpha}\mathbf{C}_i d\mathbf{C}_i = -\sum_j D_{ij}\mathbf{d}_j - D_{Ti}\nabla \ln T$$

$$(D_{ij}; D_{Ti}) = \frac{1}{3nn_i}\sum_\alpha \int f_{i\alpha}^{(0)}(D_{i\alpha}^j; A_{i\alpha})C_i^2 d\mathbf{C}_i \tag{1.11}$$

and the total heat flux

$$\mathbf{q} = \sum_{i,\alpha} \int f_{i\alpha}^{(0)} \varphi_{i\alpha} \mathbf{C}_i \left( \frac{m_i}{2} C_i^2 + E_{i\alpha} \right) d\mathbf{C}_i = \mathbf{h} + kT \sum_i \left( \frac{5}{2} + \varepsilon_i \right) n_i \mathbf{V}_i$$

$$\mathbf{h} = kT \sum_{i,\alpha} \int f_{i\alpha}^{(0)} \varphi_{i\alpha} \mathbf{C}_i H_{i\alpha} d\mathbf{C}_i = -\lambda' \nabla T - p \sum_i D_{Ti} \mathbf{d}_i$$

(1.12)

The formulae for $\mathbf{V}_i$ and $\mathbf{h}$ correspond to the "fluxes in terms of thermodynamic forces" representation.[2–4]

Here $\lambda'$ is the partial thermal conductivity, and $D_{ij}$ and $D_{Ti}$ are the diffusion and thermal diffusion coefficients of the multicomponent mixture of molecular gases.

We will now consider a modification of the Chapman–Enskog method, the purpose of which is to obtain expressions for the perturbations $\varphi_{i\alpha}$ in the *V*-representation, i.e. in the form of linear functions of the vectors $\nabla T$, $\mathbf{V}$. Extending the approach proposed earlier in Ref. 5, we will introduce the new dependent variable $\psi_{i\alpha}$ by the formula

$$\varphi_{i\alpha} = \psi_{i\alpha} + \chi_i; \quad \chi_i = \frac{m_i}{kT} \mathbf{C}_i \cdot \mathbf{V}_i$$

(1.13)

By virtue of definition (1.11), the diffusion velocity $\mathbf{V}_i$ must satisfy the requirement

$$\sum_\alpha \int f_{i\alpha}^{(0)} \psi_{i\alpha} \mathbf{C}_i d\mathbf{C}_i = 0$$

(1.14)

Multiplying Eq. (1.3) by $m_i \mathbf{C}_i$, we integrate over $\mathbf{C}_i$ and sum over $\alpha$. We have

$$\mathbf{d}_i = \mathbf{R}_i(\chi + \psi)$$

The operator $\mathbf{R}_i$ is defined by the formula

$$\mathbf{R}_i(\nu) \equiv \frac{1}{p} \sum_\alpha m_i \int \mathbf{C}_i L_{i\alpha}(\nu) d\mathbf{C}_i$$

(1.15)

Eliminating $\mathbf{d}_i$ using the expression obtained, we reduce system of Eq. (1.3) to the form

$$K_{i\alpha}(\psi) = f_{i\alpha}^{(0)} H_{i\alpha} \mathbf{C}_i \cdot \nabla \ln T - K_{i\alpha}(\chi)$$

(1.16)

The operator $K_{i\alpha}$ is given by the formula

$$K_{i\alpha}(\nu) = L_{i\alpha}(\nu) - f_{i\alpha}^{(0)} \frac{1}{x_i} \mathbf{C}_i \cdot \mathbf{R}_i(\nu); \quad \nu = \psi, \chi$$

(1.17)

taking definition (1.15) into account.

In view of the linearity we have

$$\psi_{i\alpha} = \psi_{i\alpha}^T + \psi_{i\alpha}^V$$

(1.18)

where $\psi_{i\alpha}^T$ and $\psi_{i\alpha}^V$ satisfy the following systems of equations respectively

$$K_{i\alpha}(\psi^T) = f_{i\alpha}^{(0)} H_{i\alpha} \mathbf{C}_i \cdot \nabla \ln T$$

(1.19)

$$K_{i\alpha}(\psi^V) = -K_{i\alpha}(\chi)$$

(1.20)

The mathematical properties of systems of Eqs. (1.19) and (1.20) are analogous to the properties of the simpler systems for the case of a mixture of monatomic gases.[5] We will supplement the earlier comment in Ref. 5 on the solvability of these systems by the following. In the classical Chapman–Enskog method[1] the integral operators of the systems of equations for the perturbations $\varphi_i$ are self-adjoint, and the additional requirements imposed on the solution make it unique. The left-hand side of Eq. (1.16) becomes self-adjoint when condition (1.14) is satisfied. In fact, suppose

$\tilde{\psi}_{i\alpha}$ is a certain function from the class of functions defined by this condition. Multiplying the operator $K_{i\alpha}(\psi)$ by $\tilde{\psi}_{i\alpha}$, integrating over $\mathbf{C}_i$ and summing over $\alpha$, we obtain

$$\sum_\alpha \int \tilde{\psi}_{i\alpha} K_{i\alpha}(\psi) d\mathbf{C}_i \;=\; \sum_\alpha \int \tilde{\psi}_{i\alpha} L_{i\alpha}(\psi) d\mathbf{C}_i$$

since the contribution of the second term on the right-hand side of formula (1.17) for $K_{i\alpha}(\psi)$ in this expression is equal to zero in view of condition (1.14). As is well known, the operator $L_{i\alpha}(\psi)$ is self-adjoint, with an eigenfunction of this class $\psi_{i\alpha}^C = \tau(\mathbf{r}, t) \cdot \mathbf{M}_i \mathbf{C}_i$ (the right-hand sides of Eqs. (1.19) and (1.20) are orthogonal to it). Consequently, the same will apply to the operator $K_{i\alpha}(\psi)$. We will impose condition (1.14) separately on the particular solutions. We will assume the arbitrary function $\tau$ to be zero. We will write the solution of the system of Eq. (1.19) in the form

$$\psi_{i\alpha}^T \;=\; -\frac{1}{n}\mathcal{A}_{i\alpha}(W^2, \varepsilon)\mathbf{C}_i \cdot \nabla \ln T \tag{1.21}$$

The functions $\mathcal{A}_{i\alpha}$ satisfy the system of equations obtained from system (1.7) when we make the replacement $A_{i\alpha} \Rightarrow \mathcal{A}_{i\alpha}$, $L_{i\alpha} \Rightarrow K_{i\alpha}$, but instead of the first condition of (1.9) we now require that

$$\sum_\alpha \int f_{i\alpha}^{(0)} \mathcal{A}_{i\alpha} W_i^2 d\mathbf{C}_i \;=\; 0 \tag{1.22}$$

This leads to a considerable simplification of the solution in the form of an expansion in polynomials.[5]

In the same way as before,[1,5] it can be shown, taking the linear dependence of the vectors $\rho_i \mathbf{V}_i$ into account, that

$$\psi_{i\alpha}^V \;=\; -\frac{1}{n}\sum_j \mathcal{D}_{i\alpha}^j(W^2, \varepsilon)\mathbf{C}_i \cdot \mathbf{V}_j \tag{1.23}$$

The functions $\mathcal{D}_{i\alpha}^j$ satisfy the following system of equations

$$K_{i\alpha}(\mathcal{D}^h \mathbf{C}) \;=\; nK_{i\alpha}\left\{ \frac{m_i}{kT}(\mathbf{C}_i' - \mathbf{C}_i)(\delta_{jh} - \delta_{ih}) \right\}; \quad i, h \;=\; 1, 2, \ldots, N \tag{1.24}$$

The form of the right-hand side of Eq. (1.24) denotes that the difference $\chi_i' + \chi_j' - \chi_i - \chi_j$ occurring in the integrand of the operator $K_{i\alpha}(\chi)$ is replaced by the expression in braces. The law of conservation of momentum of colliding molecules

$$m_j(\mathbf{C}_j' - \mathbf{C}_j) \;=\; -m_i(\mathbf{C}_i' - \mathbf{C}_i) \tag{1.25}$$

is used.

The condition for the solution to be unique is analogous to condition (1.22) (with $\mathcal{A}_{i\alpha}$ replaced by $\mathcal{D}_{i\alpha}^j$). Instead of (1.10) the uniqueness condition here has the form[5]

$$\sum_h \mathcal{D}_{i\alpha}^h \;=\; 0 \tag{1.26}$$

Using the results obtained, we have for the reduced heat flux (see formula (1.12))

$$\mathbf{h} \;=\; kT\sum_{i,\alpha} \int f_{i\alpha}^{(0)} \psi_{i\alpha} \mathbf{C}_i H_{i\alpha} d\mathbf{C}_i \;=\; -\lambda \nabla T + p\sum_i k_{Ti}\mathbf{V}_i \tag{1.27}$$

Here the thermal conductivity is

$$\lambda \;=\; \frac{k}{3n}\sum_{i,\alpha} \int f_{i\alpha}^{(0)} \mathcal{A}_{i\alpha} H_{i\alpha} C_i^2 d\mathbf{C}_i \;=\; \frac{k}{3}[\mathcal{A}\mathbf{C}, \mathcal{A}\mathbf{C}] > 0 \tag{1.28}$$

while the thermal-diffusion ratio has the form

$$k_{Tj} = -\frac{1}{3n^2}\sum_{i,\alpha}\int f_{i\alpha}^{(0)}\mathcal{D}_{i\alpha}^{j}H_{i\alpha}C_i^2 d\mathbf{C}_i = -\frac{1}{3n}[\mathcal{D}^j\mathbf{C}, \mathcal{A}\mathbf{C}], \quad \sum_j k_{Tj} = 0 \tag{1.29}$$

When deriving formulae (1.28) and (1.29) we used Eqs. (1.19) and (1.20), definitions (1.16) and (1.17), condition (1.14), the self-adjointness of the operator $L_{i\alpha}$, and also a generalization of the well-known[1] definition of a complete integral bracket

$$[\mathbf{M}, \mathbf{J}] = \sum_{i,j}\frac{n_i n_j}{n^2}([\mathbf{M}, \mathbf{J}]_{ij}' + [\mathbf{M}, \mathbf{J}]_{ij}'') = -\frac{1}{n^2}\sum_{i,\alpha}\int \mathbf{J}_{i\alpha}\cdot L_{i\alpha}(\mathbf{M})d\mathbf{C}_i$$

where

$$[\mathbf{M}, \mathbf{M}] > 0$$

$$[\mathbf{M}, \mathbf{J}]_{ij}' = \sum_{\alpha,\beta,\alpha',\beta'}\int f_{i\alpha}^{(0)}f_{j\beta}^{(0)}\mathbf{J}_{i\alpha}\cdot(\mathbf{M}_{i\alpha} - \mathbf{M}_{i\alpha'}')d\Gamma d\mathbf{C}_i$$

$$[\mathbf{M}, \mathbf{J}]_{ij}'' = \sum_{\alpha,\beta,\alpha',\beta'}\int f_{i\alpha}^{(0)}f_{j\beta}^{(0)}\mathbf{J}_{i\alpha}\cdot(\mathbf{M}_{j\beta} - \mathbf{M}_{j\beta'}')d\Gamma d\mathbf{C}_i$$

The primes on the square brackets indicate partial integral brackets,[1] and the quantity $d\Gamma$ is defined by the second formula of (1.4). The functions $\mathbf{M}_{i\alpha}$ and $\mathbf{J}_{i\alpha}$ are proportional to the vector $\mathbf{C}_i$, and the coefficients of proportionality depend on $W_i^2$ and $\varepsilon_{i\alpha}$. The well-known property $L_{i\alpha}(\mathbf{M}) \sim \mathbf{C}_i$ is taken into account as above. The dots denote scalar products of these functions.

Taking the formulae obtained and expression (1.15) into account, we obtain the Stefan–Maxwell relations

$$\mathbf{d}_i = \mathbf{R}_i(\chi + \psi^V) + \mathbf{R}_i(\psi^T) = \sum_j \alpha_{ij}(\mathbf{V}_j - \mathbf{V}_i) - k_{Ti}\nabla\ln T \tag{1.30}$$

Equalities (1.25) and (1.26) respectively are used to calculate $\mathbf{R}_i(\chi)$ and $\mathbf{R}_i(\psi^V)$; as a result, the first term on the right-hand side of formula (1.30) is written in terms of $\mathbf{V}_j - \mathbf{V}_i$. The expression $\mathbf{R}_i(\psi^T) = -k_{Ti}\nabla\ln T$ follows, for example, from the chain of equalities

$$\sum_i k_{Ti}\mathbf{V}_i \cdot \nabla\ln T = \{f^{(0)}\psi^V \mathbf{C}H\}\cdot\nabla\ln T = \{\psi^V K(\psi^T)\} = \{\psi^V L(\psi^T)\} =$$

$$= \{\psi^T L(\psi^V)\} = \{\psi^T K(\psi^V)\} = -\{\psi^T K(\chi)\} = -\{\psi^T L(\chi)\} = \tag{1.31}$$

$$= -\{\chi L(\psi^T)\} = -\frac{1}{p}\sum_{i,\alpha}m_i\int\mathbf{C}_i\cdot\mathbf{V}_i L_{i\alpha}(\psi^T)d\mathbf{C}_i = -\sum_i \mathbf{R}_i(\psi^T)\cdot\mathbf{V}_i$$

The expressions in braces denote, for example,

$$\{f^{(0)}\psi^V \mathbf{C}H\} = \frac{kT}{p}\sum_{i,\alpha}\int f_{i\alpha}^{(0)}\psi_{i\alpha}^V \mathbf{C}_i H_{i\alpha}d\mathbf{C}_i$$

The self-adjointness of the operator $L_{i\alpha}$ is used when determining the transport relations (including in the chain of equalities (1.31)).

Using formulae (1.27) and (1.30) and taking the last equality of (1.29) into account, we obtain the following expressions in a representation previously called "thermodynamic forces in terms of flows" (Refs. 2–4)

$$\nabla T = -\frac{1}{\lambda}\mathbf{h} + \frac{p}{\lambda}\sum_i k_{Ti}\mathbf{V}_i, \quad \mathbf{d}_i = \frac{1}{T\lambda}k_{Ti}\mathbf{h} + \sum_j\left(\alpha_{ij} - \frac{p}{T\lambda}k_{Ti}k_{Tj}\right)(\mathbf{V}_j - \mathbf{V}_i)$$

As is usually done,[6–8,15] we will seek the functions $\psi_{i\alpha}^T$ and $\psi_{i\alpha}^V$ in the form of expansions in systems of polynomials

$$(\mathcal{A}_{i\alpha}; \mathcal{D}_{i\alpha}^j) = \frac{m_i}{2kT}\sum_{r,q}(-a_{i,rq}; d_{i,rq}^j)S_{3/2}^{(r)}(W_i^2)P^{(q)}(\varepsilon_{i\alpha}), \quad r+q \geq 1$$

$$r = 0, 1, 2, ..., R; \quad q = 0, 1, 2, ..., Q; \quad i, j = 1, 2, ..., N; \quad \alpha = 0, 1, 2, ..., N^{(i)}$$

(1.32)

Unlike the $d$-representation in expansions (1.32) there are no terms with $(r, q) = 0$, proportional to the factors $a_{i,00}$ and $d_{i,00}^j$, which simplifies the systems of equations for the coefficients of these expansions.

Relations for determining the Sonin polynomials $S_{3/2}^{(r)}$ are well known.[1] The orthogonality relations for the Waldman-Trubenbacher polynomials have the form: the quantity $\langle P^{(m)}P^{(n)}\rangle$ is equal to zero and $\langle P^{(m)^2}\rangle$ when $m \neq n$ and $m = n$ respectively, and $P^{(0)} = 1$, $P^{(1)} = \langle \varepsilon_{i\alpha}\rangle - \varepsilon_{i\alpha}$, etc. The following notation is used

$$\langle Z_{i\alpha}\rangle = \left(\sum_\alpha S_{i\alpha}\exp(-\varepsilon_{i\alpha})\right)^{-1}\sum_\alpha Z_{i\alpha}S_{i\alpha}\exp(-\varepsilon_{i\alpha}); \quad \langle \varepsilon_{i\alpha}\rangle = \varepsilon_i, \quad \langle P^{(1)^2}\rangle = \frac{c_{vi}}{k}$$

The heat capacity at constant volume of the component $i$, due to internal degrees of freedom of the molecules, is given by the expressions

$$c_{vi} = \frac{\partial}{\partial T}(\langle \varepsilon_{i\alpha}\rangle kT) = k(\langle \varepsilon_{i\alpha}^2\rangle - \varepsilon_i^2)$$

The following formulae are obtained for the transport coefficients (1.28) and (1.29)

$$\lambda = \frac{1}{2}\sum_i x_i\left(\frac{5}{2}ka_{i,10} + c_{vi}a_{i,01}\right), \quad k_{Ti} = \frac{1}{2n}\sum_j x_j\left(\frac{5}{2}d_{j,10}^i + \frac{c_{vi}}{k}d_{j,01}^i\right)$$

(1.33)

We substitute the expansions in polynomials into the integral equations for the required functions (1.32), we multiply them scalarly by the product

$$\mathbf{Q}_{i\alpha}^{rq} = \mathbf{W}_iS_{3/2}^{(r)}(W_i^2)P^{(q)}(\varepsilon_{i\alpha}), \quad r+q \geq 1$$

we integrate over $\mathbf{C}_i$ and sum over $\alpha$. We find, respectively,

$$\sum_{j}\sum_{r_1,q_1}\Lambda_{rr_1qq_1}^{ij}a_{j,r_1q_1} = \frac{3}{2}kTx_i\left(5\delta_{r1}\delta_{q0} + 2\frac{c_{vi}}{k}\delta_{r0}\delta_{q1}\right)$$

(1.34)

$$\sum_{j}\sum_{r_1,q_1}\Lambda_{rr_1qq_1}^{ij}d_{j,r_1q_1}^h = 2n\Lambda_{r0q0}^{ih}$$

$$i, h = 1, 2, ..., N; \quad r, r_1 = 0, 1, 2, ..., R; \quad q, q_1 = 0, 1, 2, ..., Q; \quad r+q \geq 1; \quad r_1+q_1 \geq 1$$

(1.35)

where $R$ and $Q$ are the maximum indices of the polynomials considered.

It is important to emphasise that, when solving the problem in the form of series in polynomials, in the initial systems of Eqs. (1.19) and (1.20) we can immediately replace the operators $K_{i\alpha}$ by the operators $L_{i\alpha}$ (Ref. 5) and obtain systems of equations with known properties.[6] This is based on the fact that the expression obtained by multiplying the second term on the right-hand side of formula (1.17) scalarly by $\mathbf{Q}_{i\alpha}^{rq}$, integrating over $\mathbf{C}_i$ and summing over $\alpha$, is equal to zero.

The coefficients in Eqs. (1.34) and (1.35) are given by the expression

$$\Lambda_{rr_1qq_1}^{ij} = \sqrt{m_im_j}\left(\delta_{ij}\sum_k x_ix_k[\mathbf{Q}^{r_1q_1}, \mathbf{Q}^{rq}]_{ik}' + x_ix_j[\mathbf{Q}^{r_1q_1}, \mathbf{Q}^{rq}]_{ij}''\right), \quad i, j, k = 1, 2, ..., N$$

The approximate expressions for these coefficients, which are necessary in order to calculate the transport coefficients in the lowest approximation in polynomials, were derived previously in Refs. 7,8,15. When deriving the expression

for the right-hand side of Eq. (1.35) we used the equality

$$[\mathbf{Q}^{00}, \mathbf{Q}^{rq}]'_{ih} = -\sqrt{m_h/m_i}[\mathbf{Q}^{00}, \mathbf{Q}^{rq}]''_{ih}$$

obtained taking the conservation law (1.25) into account. By virtue of this law, we also have

$$\sum_h \Lambda^{ih}_{r0q0} = 0 \Rightarrow \sum_h d^h_{j, r_1 q_1} = 0$$

The last equality, which is obtained by summing Eq. (1.35) over $h$, shows that condition (1.26) is satisfied for system (1.35).

Unlike the analogous systems of equations of the $d$-representations,[6–8] systems of Eqs. (1.34) and (1.35) are linearly independent, since they do not contain equations corresponding to values of the indices $r$ and $q$ equal to zero.

Taking the above relations into account, we obtain the following equation for the factor $\alpha_{ij}$ in the Stefan–Maxwell relation (1.30)

$$\alpha_{ij} = \frac{x_i x_j}{\mathscr{D}_{ij}} + \frac{1}{3kT} \sum_{h=1}^{N} \sum_{r, q} \Lambda^{ih}_{r0q0} d^j_{h, rq}, \quad r + q \geq 1 \tag{1.36}$$

where

$$\mathscr{D}_{ij} = 3kT(2nm_i[\mathbf{W}, \mathbf{W}]'_{ij})^{-1} \tag{1.37}$$

In formula (1.36) the coefficients $d^j_{h, rq}$ are the solution of the system of linear algebraic Eq. (1.35). The coefficient of binary diffusion of molecular gases $\mathscr{D}_{ij}$ in the lowest approximation in polynomials, like the remaining transport coefficients, depends on the elastic and inelastic collision cross-sections. In the case of a mixture of monatomic gases, formula (1.37) defines the binary diffusion coefficient in a first approximation in Sonin polynomials.

The solutions of systems of linear algebraic Eqs. (1.34) and (1.35) and then formulae for the transport coefficients $\lambda$, $k_{Ti}$ and $\alpha_{ij}$ can be written in terms of determinants. For a mixture of monatomic gases, the relations obtained are identical with the well-known relations,[2–4] apart from the notation. In books on the kinetic theory of transport phenomena in polyatomic gases,[7,8,15,16] no expressions are given for the transport coefficients in terms of determinants. This is due not only to their complexity and the availability of computer mathematics. Effective algorithms for calculating these systems, based, in particular, on the iteration method,[7,8] are used instead of Cramer's rule.

A formula for $\alpha_{ij}$ was obtained earlier in Refs. 7,8 in the lowest approximation in polynomials.

## 2. An arbitrary departure from local equilibrium with respect to internal degrees of freedom of molecules

In flows of high-temperature polyatomic reacting gases there are, generally speaking, regions with different levels of excitation of the internal degrees of freedom of the molecules. To describe these regions, the appropriate gas-dynamic models hold, and a continuous calculation of the whole field of flow can be carried out using the system of general equations of physico-chemical gas dynamics – equations with level kinetics over all the quantum levels of the molecules. It includes the system of equations for the populations

$$\frac{Dn_{i\alpha}}{Dt} + n_{i\alpha}\nabla \cdot \mathbf{v} + \nabla \cdot n_{i\alpha}\mathbf{V}_{i\alpha} = \dot{N}_{i\alpha}$$

and the equations of momentum and energy, i.e. the second and third equations of (1.2), where now

$$\mathbf{\Pi} = p\mathbf{I} - 2\eta\mathbf{S}, \quad p = nkT_t$$

The vector transport relations and the quantity $U$ are given by more complex expressions.

To derive this system of general equations of physico-chemical gas dynamics, a generalized Chapman–Enskog method has been developed.[9–13]

Instead of system (1.3) for the perturbations $\varphi_{i\alpha}^{(II)} \equiv \varphi_{i\alpha}$, in the generalized Chapman–Enskog method there is a system of integral linear inhomogeneous equations

$$L_{i\alpha}^{S}(\varphi) = f_{i\alpha}^{(0)} \left[ H_i \mathbf{C}_i \cdot \nabla \ln T_t + \frac{n}{n_{i\alpha}} \mathbf{C}_i \cdot \mathbf{d}_{i\alpha} \right], \quad H_i = W_{ti}^2 - \frac{5}{2} \tag{2.1}$$

where

$$f_{i\alpha}^{(0)} = y_{i\alpha} f_i^{(0)}, \quad y_{i\alpha} = \frac{n_{i\alpha}}{n_i}, \quad \sum_{\alpha} y_{i\alpha} = 1, \quad n_i = \sum_{\alpha} n_{i\alpha}$$

$$f_i^{(0)} = n_i \left( \frac{m_i}{2\pi k T_t} \right)^{3/2} \exp(-W_{ti}^2), \quad W_{ti}^2 = \frac{m_i}{2kT_t} C_i^2 \tag{2.2}$$

In the above expressions $f_i^{(0)}$ is the locally Maxwell distribution function for the component $i$, $L_{i\alpha}^{S}(\varphi)$ is the linearized symmetrized collision operator, $n_{i\alpha}$ is the number of particles of sort $i$ in the quantum state $\alpha$ per unit volume (the population of the quantum state $\alpha$ of particles of sort $i$), $\mathbf{V}_{i\alpha}$ is the diffusion velocity of the component $i\alpha$, $\dot{N}_{i\alpha}$ is the production of particles of sort $i$ in quantum state $\alpha$ as a result of transitions between energy levels and as a result of chemical reactions, $T_t$ is the translational temperature of the reacting mixture of ideal gases, the quantities $n_i$ and $\mathbf{C}_i$ are defined in Section 1, $y_{i\alpha}$ is the relative population, and

$$\mathbf{d}_{i\alpha} = \nabla \frac{n_{i\alpha}}{n} + \left( \frac{n_{i\alpha}}{n} - \frac{m_i n_{i\alpha}}{\rho} \right) \nabla \ln p - \frac{m_i n_{i\alpha}}{p} \left( \mathbf{F}_i - \sum_j \frac{\rho_j}{\rho} \mathbf{F}_j \right) \equiv y_{i\alpha} \mathbf{d}_i + x_i \nabla y_{i\alpha} \tag{2.3}$$

$$\mathbf{d}_i = \sum_{\alpha} \mathbf{d}_{i\alpha}, \quad p = nkT_t$$

The quantity $\mathbf{d}_i$ is defined by formula (1.5) with the replacement $T \Rightarrow T_t$. The vectors $\nabla y_{i\alpha}$ are linearly dependent

$$\sum_{\alpha} \nabla y_{i\alpha} = 0 \tag{2.4}$$

In the approximation of this method employed, the distribution function is

$$f_{i\alpha} = f_{i\alpha}^{(0)}(1 + \varphi_{i\alpha})$$

By definition, it is the mathematical expectation of the number of particles of chemical sort $i$, which possess internal energy $E_{i\alpha}$, in an element of phase space $d\Sigma_i$. This number of particles is

$$dn_{i\alpha} = f_{i\alpha} d\Sigma_i, \quad f_{i\alpha} = f(\mathbf{C}_i, E_{i\alpha}, \mathbf{r}, t), \quad d\Sigma_i = d\mathbf{r} d\mathbf{C}_i$$

In Section 1 we use the same definition, but the relative population $y_{i\alpha}$ there is the Boltzmann distribution. The collision operator $L_{i\alpha}^{S}$ is self-adjoint, and, taking into account bimolecular chemical reactions ($2 \rightleftarrows 2$), it is given by the expression[9]

$$L_{i\alpha}^{S}(\varphi) = \sum_{j, \beta, k, \gamma, l, \delta} \int \frac{1}{2} \{\Phi\}(\varphi_{k\gamma}' + \varphi_{l\delta}' - \varphi_{i\alpha} - \varphi_{j\beta}) g_{ij} \sigma_{i\alpha j\beta}^{k\gamma l\delta} d\Omega d\mathbf{C}_j$$

$$\Phi = \frac{S_{i\alpha} S_{j\beta}}{S_{k\gamma} S_{l\delta}} \left( \frac{m_i m_j}{m_k m_l} \right)^3 f_{k\gamma}^{(0)'} f_{l\delta}^{(0)'} + f_{i\alpha}^{(0)} f_{j\beta}^{(0)} \tag{2.5}$$

$$k \equiv k', \quad \gamma \equiv \gamma', \quad l \equiv l', \quad \delta \equiv \delta'; \quad i, j, k', l' = 1, 2, ..., N; \quad \gamma' = 0, 1, ..., N^{(k)}; \quad \delta' = 0, 1, ..., N^{(l)}$$

As above, the primes denote quantities after a collision, and the quantum states are denoted by Greek subscripts. If a particle of sort $i$ does not react, the subscripts $k'$ and $l'$ are replaced by $i$ and $j$, and the summation is carried out over $j$, $\beta$, $\gamma'$ and $\delta'$. If they react, the same replacement is made in the terms of the operator (2.5), describing the collisions of particles of sort $i$ with non-reacting particles. Collision operators for more complex chemical reactions are also given in Refs 7,8,16,17. Linearization and symmetrization of these operators was also carried out previously in Ref. 14.

In this paper we will not consider the version of the method in which the non-self-conjugate integral operator $L_{i\alpha}$ is used.[17] The difference between the versions of the generalized Chapman–Enskog method[9–13] is characterised by the procedure for calculating the perturbations $\varphi_{i\alpha}^{(III)}$, which depend on the modulus of the vector of the peculiar velocity of a particle $\mathbf{C}_i$. When determining the transport relations in the asymptotically principal approximation with respect to small Knudsen numbers, this difference disappears, and we can require all the gas-dynamic variables to be given by the zero approximation

$$n_{i\alpha} = \int f_{i\alpha}^{(0)} d\mathbf{C}_i, \quad T_t = \frac{1}{3nk}\sum_{i,\alpha}\int f_{i\alpha}^{(0)} m_i C_i^2 d\mathbf{C}_i = \frac{p}{nk}, \quad \mathbf{v} = \frac{1}{\rho}\sum_{i,\alpha}\int f_{i\alpha}^{(0)} m_i \xi_i d\mathbf{C}_i$$

As a result of solving system of equations (2.1) we find that the perturbation $\varphi_{i\alpha}$ and, consequently, the diffusion velocities $\mathbf{V}_{i\alpha}$ and the heat flux $\mathbf{q}$ are linear functions of the vectors $\nabla T_t$, $d_{j\beta}$ (or $\nabla T_t$, $\mathbf{d}_j$, $\nabla y_{j\beta}$):

$$\mathbf{V}_{i\alpha} = \frac{1}{n_{i\alpha}}\int f_{i\alpha}^{(0)} \varphi_{i\alpha} \mathbf{C}_i d\mathbf{C}_i, \quad \mathbf{V}_i = \sum_{\alpha} y_{i\alpha} \mathbf{V}_{i\alpha}$$

$$\mathbf{q} = \sum_{i,\alpha}\int f_{i\alpha}^{(0)} \varphi_{i\alpha}\left(\frac{m_i}{2}C_i^2 + E_{i\alpha} + E_i^{\text{ch}}\right)\mathbf{C}_i d\mathbf{C}_i \qquad (2.6)$$

Here $E_i^{\text{ch}}$ is the energy of the formation of a chemical element of sort $i$. In the modification of the method proposed earlier in Ref. 14, instead of $\varphi_{i\alpha}$ a new dependent variable $\vartheta_{i\alpha}$ was introduced, as given by the formula

$$\varphi_{i\alpha} = \vartheta_{i\alpha} + \frac{m_i}{kT_t}\mathbf{V}_{i\alpha}\cdot\mathbf{C}_i$$

and the quantities $\mathbf{d}_{i\alpha}$ were eliminated from Eq. (2.1) and an expansion in Sonin polynomials was used. The complete theory is constructed in the same way as was done in Section 1. The vectors $\mathbf{d}_{i\alpha}$ and $\mathbf{q}$ are given by linear combinations of the vector $\nabla T_t$, $\mathbf{V}_{j\beta}$.

We will consider another modification, which is more convenient for converting the general equations of physico-chemical gas dynamics on changing to special cases.[18] We introduce a new dependent variable $\psi_{i\alpha}$, analogous to relations (1.13)

$$\varphi_{i\alpha} = \psi_{i\alpha} + \chi_i, \quad \chi_i = \frac{m_i}{kT_t}\mathbf{V}_i\cdot\mathbf{C}_i \qquad (2.7)$$

retaining the notation. We substitute the right-hand side of formula (2.3) into Eq. (2.1) instead of $\mathbf{d}_{i\alpha}$, then we use the replacement (2.7), multiply by $m_i\mathbf{C}_i$, integrate over $\mathbf{C}_i$ and sum over $\alpha$.

We obtain for the vector $\mathbf{d}_i$

$$\mathbf{d}_i = \mathbf{R}_i^S(\chi + \psi) \equiv \frac{1}{p}\sum_{\alpha} m_i \int \mathbf{C}_i L_{i\alpha}^S(\chi + \psi) d\mathbf{C}_i \qquad (2.8)$$

Eliminating $\mathbf{d}_i$ using this formula, we reduce Eq. (2.1) to the form

$$K_{i\alpha}^S(\psi) = f_{i\alpha}^{(0)}[H_i\mathbf{C}_i\cdot\nabla\ln T_t + \mathbf{C}_i\cdot\nabla\ln y_{i\alpha}] - K_{i\alpha}^S(\chi) \qquad (2.9)$$

The operator $K_{i\alpha}^S$ is given by expression (1.17) with $L_{i\alpha}$ and $\mathbf{R}_i$ replaced by $L_{i\alpha}^S$, $\mathbf{R}_i^S$. The quantity $H_i$ is defined by the second relation of (2.1).

As in Section 1, we will assume the existence of a solution of the problem in the class of functions defined by requirement (1.14). The analysis of system of Eq. (2.9) is similar to the analysis of system (1.16), taking into account the linear dependence of the groups of vectors $\nabla y_{i\alpha}$ and $\rho_i\mathbf{V}_i$. The solution will be sought in the form

$$\psi_{i\alpha} = \psi_{i\alpha}^T + \psi_{i\alpha}^Y + \psi_{i\alpha}^V, \quad \sum_{\alpha}\int f_{i\alpha}^{(0)}(\psi_{i\alpha}^T; \psi_{i\alpha}^Y; \psi_{i\alpha}^V)\mathbf{C}_i d\mathbf{C}_i = 0 \qquad (2.10)$$

The second equation of (2.10) is a consequence of requirement (1.14). The functions $\psi_{i\alpha}^T, \psi_{i\alpha}^Y, \psi_{i\alpha}^V$ satisfy the following systems of equations

$$K_{i\alpha}^S(\psi^T) = f_{i\alpha}^{(0)} H_i \mathbf{C}_i \cdot \nabla \ln T_t, \quad K_{i\alpha}^S(\psi^Y) = f_{i\alpha}^{(0)} \mathbf{C}_i \cdot \nabla \ln y_{i\alpha}, \quad K_{i\alpha}^S(\psi^V) = -K_{i\alpha}^S(\chi) \tag{2.11}$$

and are represented by the following expressions

$$\psi_{i\alpha}^T = -\frac{1}{n}\tilde{A}_{i\alpha}\mathbf{C}_i \cdot \nabla \ln T_t, \quad \psi_{i\alpha}^Y = -\frac{1}{n}\sum_{h,\sigma} G_{i\alpha}^{h\sigma}\mathbf{C}_i \cdot \nabla y_{h\sigma}, \quad \psi_{i\alpha}^V = -\frac{1}{n}\sum_h \tilde{D}_{i\alpha}^h \mathbf{C}_i \cdot \mathbf{V}_h \tag{2.12}$$

$$i = 1, 2, ..., N; \quad h = 1, 2, ..., N; \quad \sigma = 0, 1, ..., N^{(h)}$$

The required functions $\tilde{A}_{i\alpha}, G_{i\alpha}^{h\sigma}, \tilde{D}_{i\alpha}^h$ satisfy the following systems of inhomogeneous linear integral equations

$$K_{i\alpha}^S(\tilde{A}\mathbf{C}) = -n f_{i\alpha}^{(0)} H_i \mathbf{C}_i, \quad K_{i\alpha}^S(G^{h\sigma}\mathbf{C}) = -\frac{n}{y_{i\alpha}} f_{i\alpha}^{(0)}(\delta_{ih}\delta_{\alpha\sigma} - \delta_{ih}y_{h\alpha})\mathbf{C}_i$$

$$K_{i\alpha}^S(\tilde{D}^h \mathbf{C}) = n K_{i\alpha}^S \left\{ \frac{1}{kT_t}[m_k \mathbf{C}_k' \Delta_{kh} + m_l \mathbf{C}_l' \Delta_{lh} - m_j \mathbf{C}_j \Delta_{jh}] \right\} \tag{2.13}$$

where

$$\Delta_{nh} = \delta_{nh} - \delta_{ih}; \quad n = k, l, j; \quad k \equiv k'; \quad l \equiv l'$$

When $k = i$, $l = j$ and $T_t = T$ we obtain the right-hand side of Eq. (1.24). The right-hand side of the last equation of (2.13) is written for the case (2.5).

The solution of the problem for $\psi_{i\alpha}^Y$ is constructed in the same way as indicated in Ref. 1. We will put $\mathbf{b}_{i\alpha} = \nabla y_{i\alpha}$. Taking equality (2.4) into account, we introduce the following system of linearly independent vectors $\mathbf{b}_{i\alpha}^*$ by the formula

$$\mathbf{b}_{i\alpha} = \mathbf{b}_{i\alpha}^* - y_{i\alpha}\sum_\beta \mathbf{b}_{i\beta}^*$$

We will represent the function $\psi_{i\alpha}^Y$ by the sum $-n^{-1}\sum_{h,\sigma} G_{i\alpha}^{h\sigma}\mathbf{C}_i \cdot \mathbf{b}_{h\sigma}^*$. Substituting it into the second equation of (2.11), we find the second equation of (2.13). When it is multiplied by $y_{h\sigma}$ and summed over $h$ and $\sigma$ the right-hand side of this equation vanishes. Without loss of generality we will assume

$$\sum_{h,\sigma} y_{h\sigma} G_{i\alpha}^{h\sigma} = 0 \tag{2.14}$$

which enables us, in the sum for $\psi_{i\alpha}^Y$, to replace the vector $\mathbf{b}_{i\alpha}^*$ by the vector $\mathbf{b}_{i\alpha}$. Finally we obtain the required solution in the form of the second formula of (2.12).

Similarly, we will write the solution for $\psi_{i\alpha}^V$ in the form of a sum over the system of linearly independent vectors $\mathbf{B}_h$

$$\psi_{i\alpha}^V = -\frac{1}{n}\sum_h H_{i\alpha}^h \mathbf{C}_i \cdot \mathbf{B}_h, \quad \rho_i \mathbf{V}_i = \sum_h \left(\delta_{ih} - \frac{\rho_i}{\rho}\right)\mathbf{B}_h, \quad \mathbf{V}_j - \mathbf{V}_i = \sum_h \frac{1}{\rho_h}(\delta_{jh} - \delta_{ih})\mathbf{B}_h \tag{2.15}$$

Using the last two equalities, the law of conservation of momentum of the colliding particles and definition (2.7), we convert the difference

$$\chi_k' + \chi_l' - \chi_i - \chi_j = \sum_h \rho_h^{-1}\mathbf{B}_h \cdot \left\{ \frac{1}{kT_t}[m_k \mathbf{C}_k' \Delta_{kh} + m_l \mathbf{C}_l' \Delta_{lh} - m_j \mathbf{C}_j \Delta_{jh}] \right\}$$

which occurs in the integrands of the right-hand side of the third equation of (2.11).

Substituting this expression and the first expression of (2.15) into the third equation of (2.11) and putting $D_{i\alpha}^h = \rho_h H_{i\alpha}^h$, we obtain the third equation of (2.13). On summing over $h$, its right-hand side vanishes, and hence, similar to

relations (1.26) and (2.14), we assume

$$\sum_h \tilde{D}_{i\alpha}^h = 0 \tag{2.16}$$

which enables us to replace $\mathbf{B}_h$ by $\rho_h \mathbf{V}_h$ in the first formula of (2.15) and to obtain an expression for $\psi_{i\alpha}^V$ according to the second equality of (2.12).

Using definitions (2.6), (2.7) and (2.10), we obtain for the vector transport relations

$$\mathbf{q} = \tilde{\mathbf{h}} + \sum_i \left( \frac{5}{2} k T_t + E_i + E_i^{\mathrm{ch}} \right) n_i \mathbf{V}_i + \sum_{i,\,\alpha} n_{i\alpha} E_{i\alpha} (\mathbf{V}_{i\alpha} - \mathbf{V}_i), \quad E_i = \sum_\alpha y_{i\alpha} E_{i\alpha}$$

$$\tilde{\mathbf{h}} = k T_t \sum_{i,\,\alpha} \int f_{i\alpha}^{(0)} \psi_{i\alpha} H_i \mathbf{C}_i d\mathbf{C}_i, \quad \mathbf{V}_{i\alpha} - \mathbf{V}_i = \frac{1}{n_{i\alpha}} \int f_{i\alpha}^{(0)} \psi_{i\alpha} \mathbf{C}_i d\mathbf{C}_i \tag{2.17}$$

$$\mathbf{d}_i \equiv \mathbf{R}_i^S (\psi + \chi) = \frac{1}{p} \sum_\alpha m_i \int \mathbf{C}_i L_{i\alpha}^S (\psi^T + \psi^Y + \psi^V + \chi) d\mathbf{C}_i$$

The last relations are given in a form which demonstrates crossover effects

$$\tilde{\mathbf{h}} = -\lambda^T \nabla T_t - \sum_{i,\,\alpha} p_i k_{i\alpha}^Y \nabla y_{i\alpha} + p \sum_i k_{Ti}^V \mathbf{V}_i, \quad p_i = n_i k T_t$$

$$\mathbf{V}_{i\alpha} - \mathbf{V}_i = -k_{i\alpha}^Y \nabla \ln T_t - \sum_{j,\,\beta} D_{i\alpha,\,j\beta}^Y \nabla y_{j\beta} - \sum_j D_{i\alpha,\,j}^V \mathbf{V}_j \tag{2.18}$$

$$\mathbf{d}_i \equiv \mathbf{R}_i^S (\psi + \chi) = -k_{Ti}^V \nabla \ln T_t + \sum_{j,\,\beta} \frac{n_j}{n} D_{j\beta,\,i}^V \nabla y_{j\beta} + \sum_j \tilde{\alpha}_{ij} (\mathbf{V}_j - \mathbf{V}_i)$$

The expressions for the coefficients in formulae (2.18) have the form

$$\lambda^T = k \sum_{i,\,\alpha} \langle \tilde{A}_{i\alpha} H_i \rangle = \frac{k}{3} [\tilde{A} \mathbf{C}, \tilde{A} \mathbf{C}] > 0$$

$$k_{i\alpha}^Y = \frac{1}{n_i} \sum_{j,\,\beta} \langle G_{j\beta}^{i\alpha} H_j \rangle = \frac{1}{n_{i\alpha}} \langle \tilde{A}_{i\alpha} \rangle = \frac{1}{3n_i} [G^{i\alpha} \mathbf{C}, \tilde{A} \mathbf{C}]$$

$$k_{Ti}^V = -\frac{1}{n} \sum_{j,\,\beta} \langle \tilde{D}_{j\beta}^i H_j \rangle = \frac{1}{p} \sum_\alpha \int m_i \mathbf{C}_i \cdot L_{i\alpha}^S (\tilde{A} \mathbf{C}) d\mathbf{C}_i = -\frac{1}{3n} [\tilde{D}^i \mathbf{C}, \tilde{A} \mathbf{C}] \tag{2.19}$$

$$D_{i\alpha,\,j\beta}^Y = \frac{1}{n_{i\alpha}} \langle G_{i\alpha}^{j\beta} \rangle = \frac{1}{3n_i} [G^{i\alpha} \mathbf{C}, G^{j\beta} \mathbf{C}], \quad D_{i\alpha,\,i\alpha}^Y > 0$$

$$D_{i\alpha,\,j}^V = \frac{1}{n_{i\alpha}} \langle \tilde{D}_{i\alpha}^j \rangle = \frac{1}{3n_i} [G^{i\alpha} \mathbf{C}, \tilde{D}^j \mathbf{C}]$$

We have introduced the notation

$$\langle X_{i\alpha} Y_i \rangle = \frac{1}{3n} \int f_{i\alpha}^{(0)} X_{i\alpha} Y_i C_i^2 d\mathbf{C}_i, \quad [\mathbf{F}, \mathbf{J}]^S = -\frac{1}{n^2} \sum_{i,\,\alpha} \int \mathbf{J}_{i\alpha} \cdot L_{i\alpha}^S (\mathbf{M}) d\mathbf{C}_i$$

The total integral bracket $[\ldots]^S$ is defined in the same way as in Section 1.

The procedures for obtaining the relations derived above are similar to the derivation of formulae (1.28) and (1.29). We used the last expressions of (2.7), (2.10) and (2.11), formulae (2.12) and the first two equations of (2.13). The self-adjointness of the operator $L_{i\alpha}^S$ was taken into account. The specific form of the operator $L_{i\alpha}^S(\chi)$ was not used, so that the results (2.18) and (2.9) are general.

For example, we will express the quantity $\mathbf{R}_i^S(\psi^Y)$ in terms of the coefficients $D_{h\sigma,i}^V$. By definition

$$\mathbf{R}_i^S(\psi^Y) = \frac{1}{p}\sum_\alpha \int m_i \mathbf{C}_i L_{i\alpha}^S(\psi^Y) d\mathbf{C}_i = \sum_{h,\sigma} \Gamma_i^{h\sigma} \nabla y_{h\sigma}$$

$$\Gamma_i^{h\sigma} \equiv -\frac{m_i}{3pn}\sum_\alpha \int \mathbf{C}_i \cdot L_{i\alpha}^S(G^{h\sigma}\mathbf{C})d\mathbf{C}_i$$

(2.20)

We will put

$$\{\Omega\} \equiv -\frac{1}{n^2}\sum_{i,\alpha}\int \Omega d\mathbf{C}_i, \quad \mathbf{G}_{i\alpha}^{h\sigma} \equiv G_{i\alpha}^{h\sigma}\mathbf{C}_i, \quad \tilde{\mathbf{D}}_{i\alpha}^j \equiv \tilde{D}_{i\alpha}^j\mathbf{C}_i$$

and we will consider the expression $\Delta \equiv \{\chi_i L_{i\alpha}^S(\mathbf{G}^{h\sigma})\}$, which can be written in the form

$$\Delta = \sum_i \Gamma_i^{h\sigma}\mathbf{V}_i$$

(2.21)

The quantity $\Gamma_i^{h\sigma}$ is defined by the last formula of (2.20). On the other hand, in the same way as for (1.31) we obtain the chain of equalities

$$\Delta = \{\mathbf{G}_{i\alpha}^{h\sigma}L_{i\alpha}^S(\chi)\} = \{\mathbf{G}_{i\alpha}^{h\sigma}K_{i\alpha}^S(\chi)\} = -\{\mathbf{G}_{i\alpha}^{h\sigma}K_{i\alpha}^S(\psi^V)\} =$$

$$= \frac{1}{n}\left\{\mathbf{G}_{i\alpha}^{h\sigma}K_{i\alpha}^S\left(\sum_j \tilde{\mathbf{D}}^j \cdot \mathbf{V}_j\right)\right\} = \frac{1}{3n}\sum_j \mathbf{V}_j\{\mathbf{G}_{i\alpha}^{h\sigma} \cdot L_{i\alpha}^S(\tilde{\mathbf{D}}^j)\} =$$

$$= \frac{1}{3n}\sum_j \mathbf{V}_j\{\tilde{\mathbf{D}}_{i\alpha}^j \cdot L_{i\alpha}^S(\mathbf{G}^{h\sigma})\} = \frac{1}{3n}\sum_j \mathbf{V}_j\{\tilde{\mathbf{D}}_{i\alpha}^j \cdot K_{i\alpha}^S(\mathbf{G}^{h\sigma})\} =$$

$$= \frac{1}{3n}\sum_j \mathbf{V}_j\left\{-\tilde{\mathbf{D}}_{i\alpha}^j \cdot f_{i\alpha}^{(0)}\frac{n}{y_{i\alpha}}\delta_{ih}(\delta_{\alpha\sigma}-y_{h\alpha})\mathbf{C}_i\right\} = \sum_j \mathbf{V}_j\frac{n_h}{n}D_{h\sigma,j}^V$$

Comparing the results obtained with definitions (2.20) and (2.21), we find

$$\sum_i \Gamma_i^{h\sigma}\mathbf{V}_i = \sum_j \mathbf{V}_j\frac{n_h}{n}D_{h\sigma,j}^V \Rightarrow \mathbf{R}_i^S(\psi^Y) = \sum_{h,\sigma}\frac{n_h}{n}D_{h\sigma,i}^V\nabla y_{h\sigma}$$

The last equality was used to derive the third formula of (2.18).

Hence, we have obtained relations (2.18) and (2.19) between the coefficients of the expressions for the vector transport relations. We can use an expansion of the solution in series in polynomials, but the results obtained in this way will have a formal form, since the cross sections of the physico-chemical processes are insufficiently well known, whereas the purpose of this section is to provide rigorous results. In practice, approximate procedures are employed, the results of which are considered in the next section.

We will change to a special case in formulae (2.18) and (2.19) by replacing the relative populations $y_{i\alpha}$ by their asymptotically principal expressions[19] (for small Knudsen numbers). For example, in the case considered in Section 1, in the first formula of (2.17) the difference $\mathbf{V}_{i\alpha} - \mathbf{V}_i$ is eliminated, and then, in the expressions for $\mathbf{q}$ and $\mathbf{d}_i$, the variable $y_{i\alpha}$ is replaced by the Boltzmann function, which occurs in formula (1.1), and the translational temperature $T_t$ is replaced by the temperature $T$.

## 3. Approximate relations

In the procedure proposed earlier in Ref. 9, the internal degrees of freedom of the particles are split into two groups, so that the subscript $\alpha = \alpha_1\alpha_2 \equiv \alpha_1, \alpha_2$. On the left-hand side of Eq. (2.1) the linearized collision operators for the $\alpha_2$-processes are assumed to be small; these, and also the collision operators which determine the chemical reactions, are neglected. It is assumed that the energy of the particles and the collision cross-sections for the $\alpha_1$-processes are independent of the $\alpha_2$-states of the particles, i.e. this energy is equal to $E_{i\alpha_1}$, while for the cross sections and total internal energy of the particle the following equalities respectively hold

$$\sigma_A^B = \sigma_X^\Delta, \quad E_{i\alpha} = E_{i\alpha_1} + E_{i\alpha_2}$$
$$A = i\alpha_1\alpha_2 j\beta_1\beta_2, \quad B = i\gamma_1'\alpha_2 j\delta_1'\beta_2, \quad X = i\alpha_1 j\beta_1, \quad \Delta = i\gamma_1' j\delta_1'$$

(3.1)

In practice, one also usually neglects the collision operators for the $\alpha_1$-processes. In this case $\alpha \equiv \alpha_2$, and only the elastic-collision operators are taken into account. This leads to the non-equilibrium (generalized) Hirschfelder-Eucken approximation,[9,19] when the effect of the internal degrees of freedom of the particles on the transport relations is only taken into account in terms of the diffusion of their internal energy. The structure of the expression for the pressure tensor is not changed. The shear viscosity coefficients $\eta$, the reduced heat flux $\tilde{\mathbf{h}}$ (see (2.17)) and the vector $\mathbf{d}_i$ (the Stefan–Maxwell relation) are given by the corresponding expressions for an *N*-component mixture of monatomic gases.[1] The following formula holds

$$\mathbf{V}_{i\alpha} - \mathbf{V}_i = -\left(\sum_j \frac{x_j}{\mathscr{D}_{ij}}\right)^{-1} \nabla \ln y_{i\alpha}, \quad x_j = \frac{n_j}{n}$$

where $\mathscr{D}_{ij} \equiv [\mathscr{D}_{ij}]_\mathrm{I}$ is the binary diffusion coefficient of monatomic gases in a first approximation in Sonin polynomials[1] (the second approximation was also analysed earlier in Ref. 19). Data, characterizing the accuracy of the Eucken correction to the thermal conductivity are given for a number of single-component polyatomic gases, for example, in Ref. 20.

We will now take into account the collision operators for the $\alpha_1$-processes. In the generalized Chapman–Enskog method the situations are considered, generally speaking, when the distribution function of the molecules over the energy $E_{i\alpha_1}$ differs considerably from the locally equilibrium distribution. We will make an additional assumption regarding the closeness of this function to the Boltzmann function, which holds, for example, for an important class of flows,[15,16] when the rotational levels relate to the $\alpha_1$-levels, and the vibrational and electronic levels relate to the $\alpha_2$-levels. The distribution function of the zero approximation is given by the expression

$$f_{i\alpha}^{(0)} = n_{i\alpha_2} \frac{S_{i\alpha_1}}{Q_i^1} \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp(-W_i^2 - \varepsilon_{i\alpha_1})$$

$$n_{i\alpha_2} = \sum_{\alpha_1} n_{i\alpha}, \quad W_i^2 = \frac{m_i}{2kT} C_i^2, \quad \varepsilon_{i\alpha_1} = \frac{E_{i\alpha_1}}{kT}$$

(3.2)

Here and below $\alpha \equiv \alpha_1\alpha_2$, $n_{i\alpha_2}$ is the population of the vibrational and electronic levels of the particles of sort *i*, and *T* is the temperature, determined taking into account the translational energy of the particles and their internal energy $E_{i\alpha_1}$. In the zero approximation (3.2), the gas-dynamic variables are $n_{i\alpha_2}$, $\mathbf{v}$, $T$, which satisfy the momentum and energy equations and also the system of equations

$$\frac{Dn_{i\alpha_2}}{Dt} + n_{i\alpha_2}\nabla \cdot \mathbf{v} + \nabla \cdot n_{i\alpha_2}\mathbf{V}_{i\alpha_2} = \dot{N}_{i\alpha_2}; \quad n_{i\alpha_2}\mathbf{V}_{i\alpha_2} = \sum_{\alpha_1} n_{i\alpha}\mathbf{V}_{i\alpha}$$

(3.3)

obtained by summing the overall system of equations of the populations $n_{i\alpha}$ over $\alpha_1$.

Following the procedure proposed earlier in Ref. 9, it can be shown that the perturbation of the distribution function $\varphi_{i\alpha}^{(II)} \equiv \varphi_{i\alpha}$, which determines the vector transport relations, is given by the following formula in the case considered

$$\varphi_{i\alpha} = \varphi_{i\alpha_1} - Q_{i\alpha_1} \mathbf{C}_i \cdot \nabla \ln y_{i\alpha_2}; \quad y_{i\alpha_2} = \frac{n_{i\alpha_2}}{n_i}, \quad \sum_{\alpha_2} y_{i\alpha_2} = 1 \tag{3.4}$$

Expressions for the function $\varphi_{i\alpha_1}$ follow from relations (1.6)–(1.8) and from relations (1.13) and (1.21)–(1.24) by replacing the subscript $\alpha$ by $\alpha_1$ in the $d$-representation and $V$-representation respectively. The effect of the $i\alpha_2$-levels is characterized by the term with the factor $Q$. These factors satisfy the following system of equations

$$\sum_{j, \beta_1, \gamma_1, \delta_1} \int f_{i\alpha_1}^{(0)} f_{j\beta_1}^{(0)} (Q_{i\gamma_1}' \mathbf{C}_i' - Q_{i\alpha_1} \mathbf{C}_i) g_{ij} \sigma_X^\Delta d\Omega d\mathbf{C}_j = -f_{i\alpha_1}^{(0)} \mathbf{C}_i$$

$$Q_{i\gamma_1}' = Q(W_i'^2, \varepsilon_{i\gamma_1}'), \quad Q_{i\alpha_1} = Q(W_i^2, \varepsilon_{i\alpha_1}), \quad \gamma_1 \equiv \gamma_1', \quad \delta_1 \equiv \delta_1' \tag{3.5}$$

Here we have used the notation (3.1) for $X$ and $\Delta$.

The solution of system (3.5) is sought in the form of a series in the binary system of polynomials (1.32). Confining ourselves to one term of the expansion, we obtain

$$Q_{i\alpha_1} \approx q_{i,00} = \frac{m_i}{kT} \left( \sum_j \frac{x_j}{\mathscr{D}_{ij}} \right)^{-1}, \quad x_j = \frac{n_j}{n} \tag{3.6}$$

where $\mathscr{D}_{ij}$ is the binary diffusion coefficient of polyatomic gases, which is given by formula (1.37) with the replacement $\alpha \Rightarrow \alpha_1$ and depends on the elastic collision cross-sections and the cross-sections of the $i\alpha_1$-processes.

By virtue of solution (3.4), using the equality

$$\sum_{\alpha_2} \nabla y_{i\alpha_2} = 0$$

we obtain the following results. The vectors $\mathbf{V}_i$ and $\mathbf{d}_i$ are given by formulae (1.11) and (1.13). We will write the total heat flux vector in the form $\mathbf{q} = \mathbf{q}_1 + \mathbf{q}_2$. The term $\mathbf{q}_1$ is calculated from formulae (1.12) or (1.27) (in the corresponding expressions in Section 1 for the transport coefficients, the subscript $\alpha$ is replaced by $\alpha_1$). The effect of $i\alpha_2$-processes is taken into account via the diffusion velocity $\mathbf{V}_{i\alpha_2}$ (the definition is given by the second equality of (3.3)) and the term of the heat flux $\mathbf{q}_2$

$$\mathbf{q}_2 = \sum_i (E_i^{(2)} + E_i^{\mathrm{ch}}) n_i \mathbf{V}_i + \sum_{i, \alpha_2} n_{i\alpha_2} E_{i\alpha_2} (\mathbf{V}_{i\alpha_2} - \mathbf{V}_i) =$$

$$= \sum_i (\varepsilon_i^{(2)} + \varepsilon_i^{\mathrm{ch}}) p_i \mathbf{V}_i - \sum_i \frac{p_i}{m_i} q_{i,00} \nabla E_i^{(2)} \tag{3.7}$$

$$\mathbf{V}_{i\alpha_2} - \mathbf{V}_i = -\frac{kT}{m_i} q_{i,00} \nabla \ln y_{i\alpha_2}, \quad E_i^{(2)} = \sum_{\alpha_2} y_{i\alpha_2} E_{i\alpha_2} \tag{3.8}$$

The quantity $q_{i,00}$ is defined by relation (3.6). The corresponding expressions for the non-equilibrium Hirshfelder-Eucken approximation follow from expressions (3.4), (3.5), etc., if we omit the subscripts $\alpha_1$, $\beta_1$, etc. and put $\alpha \equiv \alpha_2$.

Eq. (3.3), together with the momentum and energy equations, describe, in particular, flows with vibrational-chemical relaxation, when the rotational levels belong to the quantum levels $\alpha_1$, and the vibrational levels belong to the quantum levels $\alpha_2$ (the electron levels are frozen). Using the procedure described, expressions for the vector transport properties are determined assuming that the rotational energy and the collision cross-sections of the molecules are independent of the vibrational levels. These expressions in the $d$-representation were obtained previously using the modified Chapman–Enskog method without these assumptions.[15] In this method it is assumed that the operators describing the excitation of the vibrational and chemical processes are asymptotically small together with the Knudsen number by comparison with the operators for the $i\alpha_1$-processes.

In the procedure based on the generalized Chapman–Enskog method, it is assumed that the effect of these operators on the transport coefficients being investigated is small from the practical point of view, and they are neglected. Consequently, the results of this section for the transport properties (and, in general, the results of the generalized Chapman–Enskog method for such flows[21–24]) hold not only for the relaxation case, but also for states close to quasi-stationary.

Suppose, for example, in the zero approximation (3.2), the relative population of the vibrational levels $y_{i\alpha_2}$ is a Boltzmann function of the vibrational temperature $T_{vi}$. Then, from system (3.3) we obtain a simpler system of equations for the temperatures $T_{vi}$, and in expressions (3.7) and (3.8) the quantity $y_{i\alpha_2}$ is replaced by this function of $T_{vi}$, so that instead of $\nabla y_{i\alpha_2}$ we will have the gradients $\nabla T_{vi}$.

In conclusion we emphasize that the generalized Chapman–Enskog method (Sections 2 and 3) hold for weak translational non-equilibrium, when the state of the gas medium is close to locally Maxwellian. However, the non-equilibrium of the internal degrees of freedom of the particles may be considerable. The mathematical theory of the corresponding dynamic equations are at the stage of development. In Section 2 we indicated possible modifications of the generalized Chapman–Enskog method, and the procedure employed was illustrated using one of these, when the perturbation of the distribution function is expressed linearly in terms of the diffusion velocities of the chemical components $\mathbf{V}_i$ and the temperature and relative-population gradients. This representation is convenient to use in the problem of the Knudsen layer on surfaces with heterogeneous processes[25] (for example, in evaporation-condensation[26]). The properties of the transport-coefficient matrix have been proved, and a relation has been established between the crossover effects. For applications it is important to develop simplified models of the transport relations. In Section 3 we gave examples of the use of an algorithm for the approximate solution of the integral equations of the generalized Chapman–Enskog method.

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