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Discrete velocity models for mixtures of noble and chemically active gases

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BASING on the ideas of our previous paper [13], we present constructions of DVM for mixtures of noble gases and of those with binary chemical reactions. The first step in our constructions is to postulate the form of the space of collisional invariants. Owing to this, we determine this space for previously existing models. We show that DVM, in their present form, cannot be applied to models of gases with chemical reactions unless the principle of detailed balance is satisfied.

Opierając się na założeniach poprzedniej pracy [13], podajemy konstrukcje modeli z dyskretnymi prędkościami dla mieszanin gazów szlachetnych i gazów z binarnymi reakcjami chemicznymi. Pierwszym krokiem proponowanych konstrukcji jest postulat dotyczący budowy przestrzeni niezmienników zderzeń. Dzięki temu wyznaczamy te przestrzenie dla modeli istniejących wcześniej. Pokazujemy, że modele z dyskretnymi prędkościami nie mogą w swej obecnej postaci być stosowane do gazów z reakcjami chemicznymi, o ile nie jest spełniona zasada szczegółowego bilansu.

Опираясь на предположениях предыдущей работы [13], приводим построение моделей с дискретными скоростями для смесей инертных газов и газов с бинарными химическими реакциями. Первым шагом предлагаемого построения является постулат, касающийся построения пространства инвариантов столкновений. Благодаря этому определяем эти пространства для моделей существующих раньше. Показываем, что модели с дискретными скоростями не могут, в своем теперешнем виде, быть применены к газам с химическими реакциями, если не удовлетворен принцип детального баланса.

1. Introduction

IN THE LAST quarter of this century the discrete voelocity models of the Boltzmann equation have acquired a firm position in the kinetic theory of gases (see [1, 2]).

The main idea of these models is that the gas particles can take only a finite number, say p, of the velocities $\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_p$, all of them are d-dimensional real vectors of $\mathbf{R}^d$. Owing to the discretization of velocities, the one-particle distribution function $f(t, \mathbf{x}, \mathbf{c})$, $(\mathbf{x} \in \mathbf{R}^d)$ is replaced by a p-dimensional vector field $N(t, \mathbf{x})$ with the components $N_m(t, \mathbf{x})$, $m = 1, 2, \ldots, p$ and a system of p semilinear partial differential equations for $N_1(t, \mathbf{x})$, $N_2(t, \mathbf{x}), \ldots, N_p(t, \mathbf{x})$ is considered instead of the integro-differential Boltzmann equation.

The admissible velocities $\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_p$ are assumed to satisfy the following relations:

$$\mathbf{c}_i + \mathbf{c}_j = \mathbf{c}_k + \mathbf{c}_l \tag{1.1}$$

and

$$(\mathbf{c}_i)^2 + (\mathbf{c}_j)^2 = (\mathbf{c}_k)^2 + (\mathbf{c}_l)^2, \tag{1.2}$$

for some nontrivial quadruplets of indices i, j, k, l $(1 \leqslant i, j, k, l \leqslant p)$. These relations are interpreted as discrete analogues of the momentum and energy conservation principles.

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CABANNES [3] was the first who posed and solved with specific examples the following problem:

given ν models with $p_\alpha (\alpha = 1, 2, \ldots, \nu)$ velocities $\mathbf{c}_1^\alpha, \mathbf{c}_2^\alpha, \ldots, \mathbf{c}_{p_\alpha}^\alpha$ and densities N_1^α, $N_2^\alpha, \ldots, N_{p_\alpha}^\alpha$. Should the case be that

$$\mathbf{c}_i^\alpha + \mathbf{c}_j^\beta = \mathbf{c}_k^\alpha + \mathbf{c}_l^\beta \tag{1.3}$$

and

$$(\mathbf{c}_i^\alpha)^2 + (\mathbf{c}_j^\beta)^2 = (\mathbf{c}_k^\alpha) + (\mathbf{c}_l^\beta)^2 \tag{1.4}$$

for some $i, j, k, l (1 \leqslant i, k \leqslant p_\alpha, 1 \leqslant j, l \leqslant p_\beta)$ not only for $\beta = \alpha$, but also for some $\beta \neq \alpha (1 \leqslant \alpha, \beta \leqslant \nu)$, then we can form a new model with

$$p = \sum_{\alpha=1}^{\nu} p_\alpha \tag{1.5}$$

velocities $(\mathbf{c}_1^1, \ldots, \mathbf{c}_{p_1}^1, \mathbf{c}_1^2, \ldots, \mathbf{c}_{p_2}^2, \ldots, \mathbf{c}_1^\nu, \ldots, \mathbf{c}_{p_\nu}^\nu)$, and p densities $(N_1^1, \ldots, N_{p_1}^1, N_1^2, \ldots, \ldots, N_{p_2}^2, \ldots, N_1^\nu, \ldots N_{p_\nu}^\nu)$.

Following this idea, new specific models were constructed by GATIGNOL [1] and, recently, by CABANNES [4].

BELLOMO and de SOCIO [5] generalized Cabannes' idea by postulating

$$m_\alpha \mathbf{c}_i^\alpha + m_\beta \mathbf{c}_j^\beta = m_\alpha \mathbf{c}_k^\alpha + m_\beta \mathbf{c}_l^\beta, \tag{1.6}$$

and

$$m_\alpha (\mathbf{c}_i^\alpha)^2 + m_\beta (\mathbf{c}_j^\beta)^2 = m_\alpha (\mathbf{c}_k^\alpha)^2 + m_\beta (\mathbf{c}_i^\beta)^2 \tag{1.7}$$

instead of Eqs. (1.3) and (1.4). Here m_α, m_β are some positive coefficients which they interpreted as molecular masses of the α and β components of the mixture.

BELLOMO and de SOCIO assumed in [5] that each separate component of the mixture is the BROADWELL gas ([6]).

Following their ideas, other models of gas mixtures were constructed, and MONACO and PŁATKOWSKI [7] organized them into a methodology of constructing discrete velocity models of gas mixtures.

Despite a very short history of discrete velocity models of gas mixtures, some interesting results relevant to the gas dynamics of mixtures were obtained. MONACO [8, 9] and PŁATKOWSKI [10] considered the problem of shock wave structure in a binary mixture of Broadwell gases, LONGO [11] and LONGO and MONACO [12] studied the steady Couette flow and the Rayleigh problem, respectively. It is important to note that they obtained analytical solutions.

This paper is a continuation of our previous paper [13]. Its aim is to show how to apply a new method proposed in [13] to the problem of construction of discrete velocity models of gas mixtures. As a result we obtain easily a very general class of models, of which the models discussed in [7] are just particular cases. Additionally, we construct such discrete velocity models that can be interpreted as those for mixtures of gases with chemical reactions.

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2. Rational construction of discrete velocity models

For future reference we outline here the theory of modelling developed in [13].

Let $p \geqslant 2$ be a given integer, and let P be the set of all unordered pairs of integers (i,j), $1 \leqslant i,j \leqslant p$. Every element of the Cartesian product $P \times P$ is called a collision; a collision formed of two pairs (i,j) and (k,l) is denoted by $(i,j;k,l)$. By definition, a symbol $\gamma(i,j;k,l)$ of the collision $(i,j;k,l)$ is a p-dimensional vector, whose m-th coordinate $\gamma_m(i,j;k,l)$ $(1 \leqslant m \leqslant p)$ is given by

$$\gamma_m(i,j;k,l) = \delta_{mk} + \delta_{ml} - \delta_{mi} - \delta_{mj}, \tag{2.1}$$

where δ_{ij} is the Kronecker's delta symbol.

We say that two or more collisions are independent if their symbols are linearly independent vectors of the Euclidean space $\mathbf{R}^p$.

The core of our construction is to choose somehow a set Q of $p-q$ independent collisions, with $1 \leqslant q \leqslant p$. This set is called the set of basic collisions.

Let Q be of the form

$$Q = \{(i_1,j_1;k_1,l_1), (i_2,j_2;k_2,l_2), \ldots, (i_{p-q},j_{p-q};k_{p-q},l_{p-q})\}, \tag{2.2}$$

and let $\gamma(i_m,j_m;k_m,l_m)$ $(m = 1,2,\ldots,p-q)$ be symbols of the collisions forming Q. The set $\bar{Q}$ of admissible collisions consists, by definition, of all collisions belonging to $P \times P$ whose symbols can be represented as linear combinations of $\gamma(i_1,j_1;k_1,l_1)$, $\gamma(i_2,j_2;k_2,l_2)$, ..., $\gamma(i_{p-q},j_{p-q};k_{p-q},l_{p-q})$.

Since the vectors $\gamma(i_m,j_m;k_m,l_m)$ $(m = 1,2,\ldots,p-q)$ are linearly independent, they span a $(p-q)$-dimensional linear subspace $\mathbf{F}^{\perp} \subset \mathbf{R}^p$. An orthogonal (in the sense of $\mathbf{R}^p$) complement $\mathbf{F}$ of $\mathbf{F}^{\perp}$ to $\mathbf{R}^p$ is called the space of collisional invariants and every vector $\varphi \in \mathbf{F}$ is called a collisional invariant.

We have, of course, $\dim \mathbf{F} = q$.

It can be shown (c.f. [13]) that $\varphi = (\varphi_1, \varphi_2, \ldots, \varphi_p)$ is a collisional invariant if and only if for every $(i,j;k,l) \in \bar{Q}$

$$\varphi_i + \varphi_j = \varphi_k + \varphi_l. \tag{2.3}$$

Thus, starting from a set of $p-q$ independent collisions, we have constructed the set $\bar{Q}$ of admissible collisions and the space of collisional invariants.

Let us notice, that in some cases an inverse procedure can be useful namely we choose a system of q linearly independent vectors forming $\mathbf{F}$ and determine all nontrivial quadruplets of indices, for which relations of the type (2.3) hold. As a result we obtain the set $\bar{Q}$ of admissible collisions and, substracting from it a system of $p-q$ independent collisions, we find the set Q of basic collisions.

In our construction we did not make any use of the molecular velocities. Therefore, from the purely mathematical point of view, they can be completely arbitrary but, due to physical reasons, it is very desirable to have the usual conservation laws satisfied, i.e. relations of the type (1.1) and (1.2) should hold for every collision $(i,j;k,l) \in \bar{Q}$.

It is very easy to choose the molecular velocities in such a way that the momentum conservation principle (1, 2) is fulfilled. Indeed, let the vectors $\varphi_i (i = 1,2,\ldots,q)$ with

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the components φ_{ij} ($j = 1, 2, \ldots, p$) form a basis in $\mathbf{F}$. The molecular velocities $\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_p$ satisfy the momentum conservation principle (1.1) if and only if there exist vectors $\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_q \in \mathbf{R}^d$ such that

$$\mathbf{c}_j = \sum_{j=1}^{q} \varphi_{ij}\mathbf{v}_i, \quad i = 1, 2, \ldots, p. \tag{2.4}$$

To have the energy conservation principle satisfied, it is sufficient to demand the velocities to satisfy Eq. (1.2) for these collisions which form the set Q.

Substituting Eq. (2.4) into Eq. (1.2), we obtain a system of $p-q$ quadratic equations

$$\Big(\sum_{m=1}^{q} \varphi_{mi_s}\mathbf{v}_m\Big)^2 + \Big(\sum_{m=1}^{q} \varphi_{mj_s}\mathbf{v}_m\Big)^2 = \Big(\sum_{m=1}^{q} \varphi_{mk_s}\mathbf{v}_m\Big)^2 + \Big(\sum_{m=1}^{q} \varphi_{ml_s}\mathbf{v}_m\Big)^2, \tag{2.5}$$

for every $(i_s, j_s; k_s, l_s) \in Q$, $s = 1, 2, \ldots, p-q$.

Starting from some most basic principles we derived in [13], the following form of the collisional operator is obtained:

$$\mathscr{F}(U, V) = \frac{1}{2} \sum_{(i,j;k,l)\in\bar{Q}} A(i, j; k, l)\gamma(i, j; k, l)\,(U_l V_j + U_j V_i - U_k V_l - U_l V_k), \tag{2.6}$$

where $U = (U_1, U_2, \ldots, U_p)$, $V = (V_1, V_2, \ldots, V_p)$ are arbitrary vectors of $\mathbf{R}^p$ and $A(i, j; k, l)$ are non-negative coefficients called transition rates.

Here we devote more time to the question of determination of the transition rates because this problem was not discussed in our previous paper [13].

On the Cartesian product $P \times P$, we introduce the following equivalence relation (see also [1]):

$$(i, j) \equiv (k, l) \Leftrightarrow \varphi_i + \varphi_j = \varphi_k + \varphi_l \quad \text{for every} \quad \varphi \in \mathbf{F}. \tag{2.7}$$

This relation splits P into a certain number of equivalence classes, say $P_1, P_2, \ldots, P_{p'}$; the class of (i, j) is also denoted as $\overline{(i, j)}$.

This partition of P determines a partition of $\bar{Q}$. We have (cf. [13])

$$\bar{Q} = \bigcup_{i=1}^{p'} \bar{Q}_i, \quad \bar{Q}_i \cap \bar{Q}_j = \emptyset, \quad i \neq j,$$

where

$$\bar{Q}_i = P_i \times P_i, \quad i = 1, 2, \ldots, p'.$$

Let (i, j) P; we denote by $a(i, j; k, l)$ the probability that $(i, j; k, l) \in \bar{Q}$.

We set (cf. [1])

$$a(i, j; k, l) = 0,$$

if (i, j), (k, l) belong to two different classes, and

$$\sum_{(k,l)\in\overline{(i,j)}} a(i, j; k, l) = 1. \tag{2.8}$$

Usually it is assumed that all collisions which belong to the same class $\bar{Q}_i$ are equally probable, therefore one takes

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$$a(i,j;k,l) = \frac{1}{\text{number of elements of } \overline{(i,j)}} \tag{2.9}$$

for every $(k,l) \in \overline{(i,j)}$.

Let the molecular velocities $\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_p$ satisfy the momentum and energy conservation principles. Then

$$|\mathbf{c}_k - \mathbf{c}_l| = |\mathbf{c}_i - \mathbf{c}_j| \quad \text{for every} \quad (k,l) \in \overline{(i,j)}. \tag{2.10}$$

Under the assumption that all molecules are the same, we obtain

$$A(i,j;k,l) = S|\mathbf{c}_i - \mathbf{c}_j| a(i,j;k,l), \tag{2.11}$$

where S is proportional to the collisional cross section. If, however, the gas consists of molecules of various types, say α and β, we can replace S in Eq. (2.11) by $S_{\alpha\beta}$.

EXAMPLE 1. We take $p = 2r$, where r is an arbitrary but fixed integer, $(r = 2,3, \ldots)$.

As the set of basic collisions we take

$$Q = \bigcup_{i=1}^{r-1} \{i, i+r; i+1, i+r+1)\}. \tag{2.12}$$

The set $\overline{Q}$ of admissible collisions is

$$\overline{Q} = \bigcup_{1 \leqslant i < j \leqslant r} \{(i, i+r; j, j+r)\}. \tag{2.13}$$

We have

$$\gamma(i, i+r; j, j+r) = \sum_{k=i}^{j} \gamma(k, k+r; k+1, k+r+1) \quad (1 \leqslant i < j \leqslant r). \tag{2.14}$$

As the basis $\varphi_0, \varphi_1, \ldots, \varphi_r$ of the space $\mathbf{F}$ of collisional invariants we take

$$\begin{cases} \varphi_{0m} = 1, \\ \varphi_{im} = \delta_{im} - \delta_{i+r,m}, \\ m = 1, 2, \ldots, 2r, \quad i = 1, 2, \ldots, r. \end{cases} \tag{2.15}$$

As it follows from Eqs. (1.1) and (1.2) and the above, the momentum and energy conservation laws are satisfied if and only if

$$\begin{cases} \mathbf{c}_i = \mathbf{v}_0 + \mathbf{v}_i, \\ \mathbf{c}_{i+r} = \mathbf{v}_0 - \mathbf{v}_i, \\ i = 1, 2, \ldots, r, \end{cases} \tag{2.16}$$

where $\mathbf{v}_0, \mathbf{v}_1, \ldots, \mathbf{v}_r$ are arbitrary vectors of $\mathbf{R}^d$ such that

$$\overline{v}_i^2 = v = \text{const}, \quad i = 1, 2, \ldots, r. \tag{2.17}$$

In the case under consideration the equivalence relation defined by the relation (2.7) splits the set P of all pairs (i,j) $(1 \leqslant i,j \leqslant 2r)$ into the following equivalence classes:

one class, say P_1, consisting of r pairs of the form $(i, i+r)$, $(i = 1, 2, \ldots, r)$;

many one-element classes.

Therefore,

$$\overline{Q} = P_1 \times P_1.$$

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Assuming all collisions of $\bar{Q}$ to be equally probable, we obtain on the basis of Eq. (2.11)

$$A(i, i+r; j, j+r) = \frac{2vS}{r} \quad (1 \leqslant i < j \leqslant r), \tag{2.18}$$

$$A(i, j; k, l) = 0 \quad \text{in other cases.} \tag{2.19}$$

Owing to Eqs. (2.6), (2.13) and Eqs. (2.18), (2.19), the collisional operator $\mathscr{F}$ is of the form

$$\mathscr{F}(N, N) = \frac{2vS}{r} \sum_{1 \leqslant i < j \leqslant r} \gamma(i, i+r; j, j+r)\,(N_i N_{i+r} - N_j N_{j+r}). \tag{2.20}$$

Usually the following convention is introduced: for every quantity, say W, depending on the indices $i_1, i_2, \ldots, i_s$, we set

$$W(i_1, i_2, \ldots, i_s) = W(j_1, j_2, \ldots, j_s) \quad \text{if} \quad i_k = j_k (\mathrm{mod}\, 2r), \quad k = 1, 2, \ldots, s. \tag{2.21}$$

Using this convention, we can represent the collisional operator $\mathscr{F}$ (N, N) in the well-known form ([1], [2])

$$\mathscr{F}_i(N, N) = \frac{2vS}{r} \sum_{j=1}^{r} (N_{i+j} N_{i+j+r} - N_i N_{i+r}), \tag{2.22}$$

where $\mathscr{F}_i (i = 1, 2, \ldots, 2r)$ is the i-th component of $\mathscr{F}$. Particular cases:

i) We put $d = 2$, and

$$\mathbf{v}_i = v\left(\cos\frac{(i-1)\pi}{r}, \sin\frac{(i-1)\pi}{r}\right), \quad i = 1, 2, \ldots, r. \tag{2.23}$$

The resulting model is the so-called plane $2r$ velocity model introduced by GATIGNOL [1],

ii) We put $d = 3$, $r = 3$, and

$$\mathbf{v}_1 = v\begin{pmatrix}1\\0\\0\end{pmatrix}, \quad \mathbf{v}_2 = v\begin{pmatrix}0\\1\\0\end{pmatrix}, \quad \mathbf{v}_3 = v\begin{pmatrix}0\\0\\1\end{pmatrix}. \tag{2.24}$$

This is the celebrated space BROADWELL model [6].

iii) if we set $d = 3$, $r = 6$, and take

$$\begin{aligned} \mathbf{v}_i &= v\left(\cos\alpha, \sin\alpha\cos\frac{2i\pi}{3}, \sin\alpha\sin\frac{2i\pi}{3}\right), \quad i = 1, 2, 3, \\ \mathbf{v}_i &= v\left(\cos\beta, \sin\beta\cos\frac{(2i+1)\pi}{3}, \sin\beta\sin\frac{(2i+1)\pi}{3}\right), \quad i = 4, 5, 6, \end{aligned} \tag{2.25}$$

where

$$\tan\alpha = 3 - \sqrt{5}, \quad \alpha = 37^{\circ}.377,$$

$$\tan\beta = 3 + \sqrt{5}, \quad \beta = 79^{\circ}.187,$$

we obtain the so-called regular space model with 12 velocities. This model was introduced by CABANNES [14].

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3. General construction of DVM for gas mixtures

Let us assume that we have a certain number, say ν, of discrete velocity models of the Boltzmann equation.

Let the α-th model be represented with a p_α-dimensional density vector

$$N^\alpha = (N_1^\alpha, N_2^\alpha, \ldots, N_{p_\alpha}^\alpha) \in \mathbf{R}^{p_\alpha} \tag{3.1}$$

and with p_α velocities

$$\mathbf{c}_1^\alpha, \mathbf{c}_2^\alpha, \ldots, \mathbf{c}_{p_\alpha}^\alpha \in \mathbf{R}^d. \tag{3.2}$$

We will represent also the mixture with a p_0-dimensional density vector N

$$N = (N_1^1, \ldots, N_{p_1}^1, N_1^2, \ldots, N_{p_2}^2, \ldots, N_1^\nu, \ldots, N_{p_\nu}^\nu) \in \mathbf{R}^{p_0} \tag{3.3}$$

where

$$p_0 = \sum_{\alpha=1}^{\nu} p_\alpha, \tag{3.4}$$

and with the mixture the set of admissible velocities

$$V = \{\mathbf{c}_1^1, \ldots, \mathbf{c}_{p_1}^1, \mathbf{c}_1^2, \ldots, \mathbf{c}_{p_2}^2, \ldots, \mathbf{c}_1^\nu, \ldots, \mathbf{c}_{p_\nu}^\nu\}. \tag{3.5}$$

Inversely, let a p_0-dimensional vector N

$$N = (N_1, N_2, \ldots, N_{p_0})$$

be given. With it we can form a p_α-dimensional vector by projecting $\mathbf{R}^{p_0}$ on the p_α-dimensional subspace $\mathbf{R}_\alpha = \mathbf{R}^{p_\alpha}$ with the aid of a projection operator P_α defined by

$$P_\alpha N = N^\alpha = (N_{r_\alpha+1}, N_{r_\alpha+2}, \ldots, N_{r_{\alpha+1}}), \tag{3.6}$$

where

$$\begin{aligned} r_1 &= 0, \\ r_\alpha &= \sum_{\beta=1}^{\alpha-1} p_\beta, \qquad \alpha = 2, 3, \ldots, \nu. \end{aligned} \tag{3.7}$$

Similarly, if a set of p_0 velocity vectors $\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_{p_0}$ is given, then the subset $\mathbf{c}_{r_\alpha+1}$, $\mathbf{c}_{r_\alpha+2}, \ldots, \mathbf{c}_{r_{\alpha+1}}$ can be treated as the set of velocities of the α-th model. According to the philosophy of [13], it is sufficient to form a set of (mixture) basic collisions in order to obtain the desired model.

We assume that all collisions which take place for the α-th model when isolated take place also when in the mixture. Accordingly, let Q_α be the set of basic collisions of the α-th model, i.e.

$$\begin{aligned} Q_\alpha = \{&(i_1, j_1; k_1, l_1), \ldots, (i_{p_\alpha - q_\alpha}, j_{p_\alpha - q_\alpha}; k_{p_\alpha - q_\alpha}, l_{p_\alpha - q_\alpha})\}, \\ &1 \leqslant i_s, j_s, k_s, l_s \leqslant p_\alpha, \qquad s = 1, 2, \ldots, p_\alpha - q_\alpha, \end{aligned}$$

where q_α is the dimension of the space of collisional invariants of the α-th model. Since in the joint p-dimensional representation of the mixture the places from $r_\alpha+1$ to $r_{\alpha+1}$ are reserved for the α-th model, we rewrite Q_α as

$$\begin{aligned} Q_\alpha = Q_{\alpha\alpha} = \{&(r_\alpha+i_1, r_\alpha+j_1; r_\alpha+k_1, r_\alpha+l_1) \ldots \\ &(r_\alpha+i_{p_\alpha-q_\alpha}, r_\alpha+j_{p_\alpha-q_\alpha}; r_\alpha+k_{p_\alpha-q_\alpha}, r_\alpha+1_{p_\alpha-q_\alpha})\}. \end{aligned}$$

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The set

$$Q_s = \bigcup_{\alpha=1}^{\nu} Q_{\alpha\alpha}$$

is called the set of basic self-collisions.

To the set of basic self-collisions we have to add a set of basic cross-collisions, i.e. collisions between particles of different types. Let them be

$$Q_{\alpha\beta} = \{(i_1, j_1; k_1, l_1), \ldots, (i_{c_{\alpha\beta}}, j_{c_{\alpha\beta}}; k_{c_{\alpha\beta}}, l_{c_{\alpha\beta}})\} = Q_{\beta\alpha},$$

where $c_{\alpha\beta}$ is the number of collisions of the type $\alpha, \beta \leftrightarrow \alpha, \beta$, and

$$r_\alpha < i_s, k_s \leqslant r_{\alpha+1}$$
$$r_\beta < j_s, l_s \leqslant r_{\beta+1},$$
$$s = 1, 2, \ldots, c_{\alpha\beta}, \quad 1 \leqslant \alpha < \beta \leqslant \nu.$$

These sets of collisions can be chosen in a principally arbitrary way; the unique constraint s that the total number of mixture basic collisions

$$c = \sum_{1 \leqslant \alpha \leqslant \beta \leqslant \nu} c_{\alpha\beta},$$

where $c_{\alpha\alpha} = p_\alpha - q_\alpha$, does not exceed p_0.

The difference $q_0 = p_0 - c$ is equal to the dimension of the mixture space of collisional invariants.

As the mixture set of basic collisions we take

$$Q_M = \bigcup_{1 \leqslant \alpha \leqslant \beta \leqslant \nu} Q_{\alpha\beta}.$$

Having constructed it we can proceed exactly in the way described in Sect. 2 and obtain the desired discrete velocity model of the mixture.

We consider in more detail a special, but in our opinion the most interesting case. Namely, let us assume that each of the models we use to form a mixture has the same set of basic collisions. More precisely, we assume that

$$p_1 = p_2 = \ldots = p_\nu = p$$

and

$$Q_1 = Q_2 = \ldots = Q_\nu = Q.$$

Let $\mathbf{F}$ be the common, for every model, space of collisional invariants, and let $\varphi_0, \varphi_1, \ldots, \varphi_{q-1}$ with $\varphi_0 = (1, 1, \ldots, 1)$, be its basis.

As the mixture space of collisional invariants we take a linear $(q+\nu-1)$-dimensional subspace $\mathbf{F}_M$ of $\mathbf{R}^{p\nu}$ spanned by the vectors

$$\Phi_1 = (\varphi_0, 0, \ldots, 0),$$
$$\Phi_1 = (0, \varphi_0, \ldots, 0),$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\Phi_\nu = (0, 0, \ldots, \varphi_0),$$
$$\Phi_{\nu+1} = (\varphi_1, \varphi_1, \ldots, \varphi_1),$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\Phi_{q+\nu-1} = (\varphi_{q-1}, \varphi_{q-1}, \ldots, \varphi_{q-1}),$$

where 0 stands for the p-dimensional null vector.

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Let $\bar{Q}$ be common for all models, when separate set of admissible collisions. As it follows from the set (3.8), the following types of collisions are possible:

$$(i,j;k,l)\in\bar{Q}\Rightarrow(r_\alpha+i,r_\beta+j;r_\alpha+k,r_\beta+l)\in\bar{Q}_M,$$
$$(r_\alpha+i,r_\beta+j;r_\beta+k,r_\alpha+l)\in\bar{Q}_M,$$
$$(r_\beta+i,r_\alpha+j;r_\alpha+k,r_\beta+l)\in\bar{Q}_M,$$
$$(r_\beta+i,r_\alpha+j;r_\beta+k,r_\alpha+l)\in\bar{Q}_M$$
$$(1\leqslant\alpha\leqslant\beta\leqslant\nu),$$

where $\bar{Q}_M$ is the set of the mixture admissible collisions, and

$$r_\alpha=p(\alpha-1),\qquad\alpha=1,2,\ldots,\nu.$$

Moreover, we have collisions of the type

$$(r_\alpha+i,r_\beta+j;r_\alpha+j,r_\beta+i)\in\bar{Q}_M$$

for every $1\leqslant i<j\leqslant p$ and $1\leqslant\alpha<\beta\leqslant\nu$.

Therefore the set $\bar{Q}_M$ of mixture admissible collisions is of the form

$$\bar{Q}_M=\bigcup_{1\leqslant\alpha\leqslant\beta\leqslant\nu}\ \bigcup_{(i,j;k,l)\in\bar{Q}}\{(r_\alpha+i,r_\beta+j;r_\alpha+k,r_\beta+l),$$
$$(r_\alpha+i,r_\beta+j;r_\beta+k,r_\alpha+l),(r_\beta+i,r_\alpha+j;r_\alpha+k,r_\beta+l),(r_\beta+i,r_\alpha+j;$$
$$r_\beta+k,r_\alpha+l)\}\cup\bigcup_{1\leqslant\alpha\leqslant\beta\leqslant\nu}\ \bigcup_{1\leqslant i<j\leqslant p}\{(r_\alpha+i,r_\beta+j;r_\alpha+j,r_\beta+i)\}.\tag{3.9}$$

We have to indicate a set of mixture basic collisions.

Let us notice first that this set consists of $\nu p-(q+\nu-1)=\nu(p-1)-(q-1)$ collisions.

We have $\nu(p-q)$ independent self-collisions.

$$Q_M^{(s)}=\bigcup_{\alpha=1}^{\nu}\{(r_\alpha+i_1,r_\alpha+j_1;r_\alpha+k_1,r_\alpha+l_1),$$
$$\ldots,(r_\alpha+j_{p-q},r_\alpha+j_{p-q};r_\alpha+k_{p-q},r_\alpha+l_{p-q})\},\tag{3.10}$$

where $(i_s,j_s;k_s,l_s)$, $(s=1,2,\ldots,p-q)$ are the basic collisions of Q. As the lacking $\nu(p-1)-(q-1)-\nu(p-q)=(\nu-1)(q-1)$ independent collisions, we may take the following set of cross-collisions:

$$Q_M^{(c)}=\bigcup_{\alpha=1}^{\nu-1}\bigcup_{i=1}^{q-1}\{(r_\alpha+i,r_{\alpha+1}+i+1;r_\alpha+i+1,r_{\alpha+1}+1)\},\tag{3.11}$$

provided that $q>1$.

Hence the set

$$Q_M=Q_M^{(c)}\cup Q_M^{(s)}\tag{3.12}$$

is a set of basic collisions for the mixture under consideration.

Owing to Eq. (3.9) and the general theory of collisional operators given in [13], the mixture collisional operator is of the form

$$\mathscr{F}(N,N)=\sum_{1\leqslant\alpha\leqslant\beta\leqslant\nu}\ \sum_{(i,j;k,l)\in\bar{Q}}[A_{\alpha\beta}^{\alpha\beta}(i,j;k,l)\gamma_{\alpha\beta}^{\alpha\beta}(i,j;k,l)(N_{r_\alpha+i}N_{r_\beta+j}-N_{r_\alpha+k}N_{r_\beta+l})\tag{3.13}$$

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(3.13) [cont.)

$$+A^{\alpha\beta}_{\beta\alpha}(i,j;k,l)\gamma^{\alpha\beta}_{\beta\alpha}(i,j;k,l)\,(N_{r_\alpha+1}N_{r_\beta+j}-N_{r_\alpha+l}N_{r_\beta+k})$$
$$+A^{\beta\alpha}_{\alpha\beta}(i,j;k,l)\gamma^{\beta\alpha}_{\alpha\beta}(i,j;k,l)\,(N_{r_\alpha+j}N_{r_\beta+i}-N_{r_\alpha+k}N_{r_\beta+l})$$
$$+A^{\beta\alpha}_{\beta\alpha}(i,j;k,l)\gamma^{\beta\alpha}_{\beta\alpha}(i,j;k,l)\,(N_{r_\alpha+j}N_{r_\beta+i}-N_{r_\alpha+l}N_{r_\beta+k})]$$
$$+\sum_{1\leqslant\alpha\leqslant\beta\leqslant\nu}\ \sum_{1\leqslant i<j\leqslant p}A^{\alpha\beta}_{\alpha\beta}(i,j;j,i)\gamma^{\alpha\beta}_{\alpha\beta}(i,j;j,i)\,(N_{r_\alpha+i}N_{r_\beta+j}-N_{r_\alpha+j}N_{r_\beta+i}),$$

where

$$A^{\alpha\beta}_{\gamma\delta}(i,j;k,l)=A(r_\alpha+i,r_\beta+j;r_\gamma+k,r_\delta+l), \tag{3.14}$$

$$\gamma^{\alpha\beta}_{\gamma\delta}(i,j;k,l)=\gamma(r_\alpha+i,r_\beta+j;r_\gamma+k,r_\delta+l)\in\mathbf{R}^{\nu p}. \tag{3.15}$$

Usually we are interested in the projection

$$\mathscr{F}^\alpha(N,N)=P_\alpha\mathscr{F}(N,N)$$

of the collisional operator on $\mathbf{R}_\alpha(\alpha=1,2,\ldots,\nu)$. From Eq. (3.13) we obtain

$$\mathscr{F}^\alpha(N,N)=\sum_{(i,j;k,l)\in\bar{Q}}A^{\alpha\alpha}_{\alpha\alpha}(i,j;k,l)\gamma(i,j;k,l)\,(N^\alpha_iN^\alpha_j-N^\alpha_kN^\alpha_l) \tag{3.16}$$
$$+\sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{\nu}\Big\{\sum_{(i,j;k,l)\in\bar{Q}}[A^{\alpha\beta}_{\alpha\beta}(i,j;k,l)\gamma(i,k)\,(N^\alpha_iN^\beta_j-N^\alpha_kN^\beta_l)$$
$$+A^{\alpha\beta}_{\beta\alpha}(i,j;k,l)\gamma(i,l)\,(N^\alpha_iN^\beta_j-N^\alpha_lN^\beta_k)+A^{\beta\alpha}_{\alpha\beta}(i,j;k,l)\gamma(j,k)\,(N^\alpha_jN^\beta_i-N^\alpha_kN^\beta_l)$$
$$+A^{\beta\alpha}_{\beta\alpha}(i,j;k,l)\gamma(j,l)\,(N^\alpha_jN^\beta_i-N^\alpha_lN^\beta_k)]+\sum_{1\leqslant i<j\leqslant p}A^{\alpha\beta}_{\alpha\beta}(i,j;j,i)\gamma(i,j)\,(N^\alpha_iN^\beta_j-N^\alpha_jN^\beta_i),$$

where $\gamma(i,j;k,l)\in\mathbf{R}^p$ is the symbol of the collision $(i,j;k,l)\in\bar{Q}$, and $\gamma(i,j)$ is a p-dimensional vector whose m-th component is defined by

$$\gamma_m(i,j)=\delta_{mj}-\delta_{mi},\qquad m=1,2,\ldots,p. \tag{3.17}$$

When deriving Eq. (3.16), we made use of the following equalities:

$$P_\alpha\gamma^{\alpha\alpha}_{\alpha\alpha}(i,j;k,l)=\gamma(i,j;k,l),$$
$$P_\alpha\gamma^{\alpha\beta}_{\alpha\beta}(i,j;k,l)=\gamma(i,k),\qquad\beta\neq\alpha,$$

which result from the definition of the symbol (2.1) and that of the projector (3.6).

Let

$$\varphi_j=(\varphi_{j1},\varphi_{j2},\ldots,\varphi_{jp}),\qquad j=1,2,\ldots,q-1$$

be the basis in $\mathbf{F}$. The mixture momentum vector

$$(m_1\mathbf{c}^1_1,\ldots,m_1\mathbf{c}^1_p,m_2\mathbf{c}^2_1,\ldots,m_2\mathbf{c}^2_p,\ldots,m_\nu\mathbf{c}^\nu_1,\ldots,m_\nu\mathbf{c}^\nu_p) \tag{3.18}$$

is an element of $\mathbf{F}_M$ if and only if

$$\mathbf{c}^\alpha_i=\mathbf{v}^\alpha_0+\mu_\alpha\sum_{j=1}^{q-1}\mathbf{v}_j\varphi_{ji},\qquad i=1,2,\ldots,p,\qquad\alpha=1,2,\ldots,\nu, \tag{3.19}$$

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where $\mathbf{v}_0^\alpha$ and $\mathbf{v}_j$ are arbitrary vectors of $\mathbf{R}^d$, and

$$\mu_\alpha = \frac{m_1}{m_\alpha}, \quad \alpha = 1, 2, \ldots, \nu. \tag{3.20}$$

The mixture energy vector

$$\left(m_1(\mathbf{c}_1^1)^2, \ldots, m_1(\mathbf{c}_p^1)^2, m_2(\mathbf{c}_1^2)^2, \ldots, m_2(\mathbf{c}_p^2), \ldots, m_\nu(\mathbf{c}_1^\nu)^2, \ldots, m_\nu(\mathbf{c}_p^\nu)^2\right) \tag{3.21}$$

is a collisional invariant if and only if it is orthogonal to the symbols of any collision of Q_M.

According to Eqs. (3.10), (3.11) and (3.22), we obtain after some manipulations

$$\left(\sum_{m=1}^{q-1} \mathbf{v}_m \varphi_{mi}\right)^2 + \left(\sum_{m=1}^{q-1} \mathbf{v}_m \varphi_{mj}\right)^2 = \left(\sum_{m=1}^{q-1} \mathbf{v}_m \varphi_{mk}\right)^2 + \left(\sum_{m=1}^{q-1} \mathbf{v}_m \varphi_{ml}\right)^2 \tag{3.22}$$

for every $(i, j; k, l) \in Q$, and

$$\left[v_0^\alpha - v_0^{\alpha+1} - (\mu_{\alpha+1} - \mu_\alpha) \sum_{m=1}^{q-1} \mathbf{v}_m \frac{\varphi_{mi} + \varphi_{m,i+1}}{2}\right] \sum_{m=1}^{q-1} v_m(\varphi_{mi} - \varphi_{m,i+1}) = 0, \tag{3.23}$$

$$\alpha = 1, 2, \ldots, \nu-1, \quad i = 1, 2, \ldots, q-1.$$

A model is said to be regular if

$$\left(\sum_{m=1}^{q-1} \mathbf{v}_m \varphi_{mi}\right)^2 = v^2, \quad i = 1, 2, \ldots, p. \tag{3.24}$$

For regular models the relations (3.22) are satisfied identically, and Eq. (3.23) reduces to

$$(\mathbf{v}_0^\alpha - \mathbf{v}_0^{\alpha+1}) \cdot \sum_{m=1}^{q-1} \mathbf{v}_m(\varphi_{mi} - \varphi_{m,i+1}) = 0. \tag{3.25}$$

Assuming that $q > d$ and that the vectors

$$\sum_{m=1}^{q-1} \mathbf{v}_m(\varphi_{mi} - \varphi_{m,i+1}), \quad i = 1, 2, \ldots, d \tag{3.26}$$

are linearly independent, we obtain from Eq. (3.25)

$$\mathbf{v}_0^\alpha = \mathbf{v}_0, \quad \alpha = 1, 2, \ldots, \nu. \tag{3.27}$$

Bearing in mind the Gallilean transformation, we can set $\mathbf{v}_0 = 0$ without losing generality. Hence we obtained for regular models

$$\mathbf{c}_i^\alpha = \mu_\alpha \sum_{m=1}^{q-1} \mathbf{v}_m \varphi_{mi}, \quad i = 1, 2, \ldots, p. \tag{3.28}$$

EXAMPLE 2. We consider a mixture of ν gases each of them modelled as in Example 1 of Sect. 2.

Since these models are regular, the molecular velocities are

$$\begin{aligned} \mathbf{c}_i^\alpha &= \mu_\alpha \mathbf{v}_i, \quad i = 1, 2, \ldots, r, \\ \mathbf{c}_{i+r}^\alpha &= -\mu_\alpha \mathbf{v}_i, \end{aligned} \tag{3.29}$$

where $\mathbf{v}_i \in \mathbf{R}^d$ $(i = 1, 2, \ldots, r)$ and have the same modulus.

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Now, we proceed to determine the nontrivial classes of equivalence into which the relation (2.7) splits the set P of all (unordered) pairs (i,j) $(1 \leqslant i,j \leqslant p)$.

Using the definition (2.7) of the equivalence relation as well as the relations (2.16) and (3.8), we obtain

i) ν classes of the form

$$\bigcup_{i=1} \{(2r(\alpha-1)+i,\ 2r(\alpha-1)+i+r)\}, \qquad \alpha = 1, 2, \ldots, \nu.$$

Each class contains r pairs, therefore due to Eq. (2.9).

$$a^{\alpha\alpha}_{\alpha\alpha}(i, i+r; j, j+r) = \frac{1}{r}, \qquad \alpha = 1, 2, \ldots, \nu, \qquad 1 \leqslant i < j \leqslant r.$$

The relative velocities are

$$|\mathbf{c}^{\alpha}_{i} - \mathbf{c}^{\alpha}_{i+r}| = |\mathbf{c}^{\alpha}_{j} - \mathbf{c}^{\alpha}_{j+r}| = 2\mu_{\alpha} v, \qquad \alpha = 1, 2, \ldots, \nu, \qquad 1 \leqslant i < j \leqslant r.$$

The collisions which can be formed of pairs of the same class can be physically interpreted as head-on collisions between particles of the same gas with subsequent scattering into $2r$ directions.

The transition rates are

$$A^{\alpha\alpha}_{\alpha\alpha}(i, i+r; j, j+r) = \frac{2v\mu_{\alpha}}{r} S_{\alpha\alpha}, \qquad \alpha = 1, 2, \ldots, \nu, \qquad 1 \leqslant i < j \leqslant r, \tag{3.30}$$

where $S_{\alpha\alpha}$ s the collisional cross-section for self-collisions.

ii) $\frac{\nu}{2}(\nu-1)$ classes of the following form:

$$\bigcup_{i=1}^{r} \{(2r(\alpha-1)+i,\ 2r(\beta-1)+i+r),\ (2r(\alpha-1)+i+r,\ 2r(\beta-1)+i)\},$$

$$1 \leqslant \alpha < \beta < \nu.$$

Each class contains $2r$ pairs, therefore the transition probabilities are

$$a^{\alpha\beta}_{\alpha\beta}(i, i+r; j, j+r) = a^{\alpha\beta}_{\beta\alpha}(i, i+r; j, j+r) = a^{\beta\alpha}_{\alpha\beta}(i, i+r; j, j+r)$$

$$= a^{\beta\alpha}_{\beta\alpha}(i, i+r; j, j+1) = \frac{1}{2r},$$

$$1 \leqslant \alpha < \beta \leqslant \nu, \qquad 1 \leqslant i \leqslant j \leqslant r.$$

The relative velocities are

$$|\mathbf{c}^{\alpha}_{i} - \mathbf{c}^{\beta}_{i+r}| = |\mathbf{c}^{\alpha}_{j} - \mathbf{c}^{\beta}_{j+r}| = v(\mu_{\alpha} + \mu_{\beta}), \qquad 1 \leqslant \alpha < \beta \leqslant \nu, \qquad 1 \leqslant i \leqslant j \leqslant r.$$

Hence the transition rates become

$$A^{\alpha\beta}_{\alpha\beta}(i, i+r; j, j+r) = A^{\alpha\beta}_{\beta\alpha}(i, i+r; j, j+r)$$

$$= A^{\beta\alpha}_{\alpha\beta}(i, i+r; j, j+r) = A^{\beta\alpha}_{\beta\alpha}(i, i+r; j, j+r) = \frac{v}{2r} S_{\alpha\beta}(\mu_{\alpha} + \mu_{\beta}), \tag{3.31}$$

where $S_{\alpha\beta}$ is the collisional cross-section for cross collisions.

Physically, the collisions that may be formed of the elements of the same class represent collisions between particles of different components with subsequent scattering into $2r$ equally probable directions.

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iii) $rv(r-1)\,(v-1)$ classes consisting of just two pairs

$$\{(2r(\alpha-1)+i,\ 2r(\beta-1)+j),\ (2r(\alpha-1)+j,\ 2r(\beta-1)+i)\},$$
$$1 \leqslant \alpha < \beta \leqslant v, \quad 1 \leqslant i < j \leqslant 2r, \quad j \neq i+r.$$

The transition probabilities are, consequently,

$$a^{\alpha\beta}_{\beta\alpha}(i,j;j,i) = a^{\beta\alpha}_{\alpha\beta}(i,j;j,i) = \frac{1}{2},$$

and the relative velocities are given by

$$|\mathbf{c}^{\alpha}_{i} - \mathbf{c}^{\beta}_{j}| = |\mathbf{c}^{\alpha}_{j} - \mathbf{c}^{\beta}_{i}| = v\sqrt{\mu_\alpha^2 + \mu_\beta^2 - 2\mu_\alpha\mu_\beta\cos\psi_{ij}},$$

where ψ_{ij} is the angle between $\mathbf{v}_i$ and $\mathbf{v}_j$.

Taking now

$$\frac{1}{r}S_{\alpha\beta}$$

as the collisional cross-section, we obtain

$$A^{\alpha\beta}_{\beta\alpha}(i,j;k,l) = \frac{v}{2r}S_{\alpha\beta}\sqrt{\mu_\alpha^2 + \mu_\beta^2 - 2\mu_\alpha\mu_\beta\cos\psi_{ij}}, \tag{3.32}$$
$$1 \leqslant \alpha < \beta \leqslant v, \quad 1 \leqslant i < j \leqslant 2r, \quad j \neq i+r.$$

iv) Numerous one-element classes. They are of no significance because by using just one pair it is impossible to build a non-trivial collision.

Now, using Eqs. (2.14) and (3.30)–(3.32) as well as the convention (2.21), we obtain from Eq. (3.16) the collisional operator of the model under consideration.

The corresponding model equations are (cf. [7])

$$\left(\frac{\partial}{\partial t} + \mu_\alpha \mathbf{c}_m \nabla_x\right) N^{\alpha}_{m} = \frac{v}{2r}\sum_{\beta=1}^{v} S_{\alpha\beta}(\mu_\alpha + \mu_\beta)\sum_{j=1}^{2r}[N^{\alpha}_{m+j}N^{\beta}_{m+j+r} - N^{\alpha}_{m}N^{\beta}_{m+r}] \tag{3.33}$$
$$+ \frac{v}{2r}\sum_{\beta=1}^{v} S_{\alpha\beta}\sum_{j=1}^{2r}\sqrt{\mu_\alpha^2 + \mu_\beta^2 - 2\mu_\alpha\mu_\beta\cos\psi_{m,\,m+j}}\ (N^{\alpha}_{m+j}N^{\beta}_{m} - N^{\alpha}_{m}N^{\beta}_{m+j}),$$

where

$$\mathbf{c}_m = \mathbf{v}_m,$$
$$\mathbf{c}_{m+r} = -\mathbf{v}_m, \quad m = 1, 2, \ldots, r.$$

4. Construction of DVM for mixtures of reactive gases

In order to illustrate better our ideas of modelling, we present here a construction of such discrete velocity models which can be interpreted as those for mixtures with chemical reactions.

Our modelling is based on the theory of real gases which is given in [15] and [16] (see also, for example [17, 18, 19] or other textbooks).

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In the theory of real gases each molecule is identified by both its chemical type and by its internal quantum state. In this paper, for the sake of simplicity, we take into account changes in chemical character and ignore those in internal quantum state.

We assume that we know from chemistry this assortment of molecules B_α ($\alpha = 1, 2, \ldots, \nu$) which can be present in the gas mixture.

Let the molecule B_α consist of atoms $A^{(\lambda)}(\lambda = 1, 2, \ldots, \varkappa)$. The atomic composition of a molecule is represented in the form of a chemical formula ([15])

$$B_\alpha = A^{(1)}_{K_{1\alpha}} A^{(2)}_{K_{2\alpha}} \ldots A^{(\varkappa)}_{K_{\varkappa\alpha}}, \tag{4.1}$$

where $K_{\beta\alpha}(\beta = 1, 2, \ldots, \varkappa, \alpha = 1, 2, \ldots, \nu)$ is the number of atoms of the β type in the molecule B_α. These numbers are assumed to be known from chemistry. We consider only binary reactions, i.e. such reactions when, as a result of a collision of two molecules of any sort, we obtain again two molecules but in general of different types. Hence we admit binary inelastic collisions of the type

$$B_\alpha + B_\beta \leftrightarrow B_\gamma + B_\delta. \tag{4.2}$$

We assume again that we know from chemistry the set of all types of reactions which can occur in the mixture.

We use the shorthand

$$(\alpha, \beta \leftrightarrow \gamma, \delta)$$

to denote a reaction of the type (4.2). Let $\mathscr{R}$ be the set of all types of reactions which occur in the mixture.

In this Chapter we follow the general lines of the previous Chapter, i.e. we consider ν models, each of them having the same number of velocities p and the same set of basic collisions Q.

We start from constructing the mixture space $\mathbf{F}_M \subset \mathbf{R}^{\nu p}$ of collisional invariants.

First, the total number of molecules is conserved because the outcome of a collision of two molecules are again two particles.

Consequently, the vector

$$\Phi_0 = (\varphi_0, \varphi_0, \ldots, \varphi_0) \in \mathbf{R}^{\nu p}, \tag{4.3}$$

where, as previously, $\varphi_0 = (1, 1, \ldots, 1) \in \mathbf{R}^p$ is a collisional invariant.

The next conservation law expresses the conservation of the number of atoms in molecules before and after a collision. This can be expressed as

$$K_{\lambda\alpha} + K_{\lambda\beta} = K_{\lambda\gamma} + K_{\lambda\delta}, \quad \lambda = 1, 2, \ldots, \varkappa, \quad (\alpha, \beta \to \gamma, \delta) \in \mathscr{R}. \tag{4.4}$$

Hence the following vectors

$$\begin{aligned} \Phi_1 &= (K_{11}\varphi_0, K_{12}\varphi_0, \ldots, K_{1\nu}\varphi_0) \in \mathbf{R}^{\nu p}, \\ \Phi_2 &= (K_{21}\varphi_0, K_{22}\varphi_0, \ldots, K_{2\nu}\varphi_0) \in \mathbf{R}^{\nu p}, \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \Phi_\varkappa &= (K_{\varkappa 1}\varphi_0, K_{\varkappa 2}\varphi_0, \ldots, K_{\varkappa\nu}\varphi_0) \in \mathbf{R}^{\nu p} \end{aligned} \tag{4.5}$$

should be numbered among the space of collisional invariants.

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Under the additional assumption which follows from physico-chemical reasons and claims that the component atoms $A^{(1)}, A^{(2)}, \ldots, A^{(\varkappa)}$ are included in the assortment of the molecules B_α, i.e. assuming that there is at least one β $(\varkappa+1 \leqslant \beta \leqslant \nu)$ such that

$$\sum_{\alpha=1}^{\varkappa} K_{\alpha\beta} \neq 1, \tag{4.6}$$

it can be proved (cf. [15]) that the vectors $\Phi_0, \Phi_1, \ldots, \Phi_\varkappa$ are linearly independent.

Finally, we assume that the other quantities represented now by the vectors $\varphi_1, \varphi_2, \ldots, \varphi_{q-1}$ are conserved during each collision, be it elastic or inelastic.

Hence the vectors

$$\begin{aligned} \Phi_{\varkappa+1} &= (\varphi_1, \varphi_1, \ldots, \varphi_1) \in \mathbf{R}^{\nu p}, \\ \Phi_{\varkappa+2} &= (\varphi_2, \varphi_2, \ldots, \varphi_2) \in \mathbf{R}^{\nu p}, \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \Phi_{q+\varkappa-1} &= (\varphi_{q-1}, \varphi_{q-1}, \ldots, \varphi_{q-1}) \in \mathbf{R}^{\nu p}, \end{aligned} \tag{4.7}$$

are elements of $\mathbf{F}_M$.

Under the assumption (4.6) the vectors $\Phi_0, \Phi_1, \ldots, \Phi_{q+\varkappa-1}$ are linearly independent, and we take them as the basis of the mixture space of collisional invariants.

Evidently

$$\dim \mathbf{F}_M = q+\varkappa.$$

Applying the general method of construction of the discrete velocity models presented in Sect. 2, we can determine the set of admissible collisions $\bar{Q}_M$. By direct inspection of the basis (4.3), (4.5) and (4.7) of $\mathbf{F}_M$, we obtain

$$\begin{aligned} \bar{Q}_M = \bigcup_{(\alpha,\beta<\!\!-\!\!>\gamma,\delta)\in\mathscr{R}} \Big[\bigcup_{(i,j;k,l)\in\bar{Q}} \{(r_\alpha+i, r_\beta+j; r_\gamma+k, r_\delta+1)\} \\ \cup \bigcup_{1\leqslant i<j\leqslant p} \{(r_\alpha+i, r_\beta+j; r_\delta+j, r_\delta+i)\}, \end{aligned} \tag{4.8}$$

where

$$r_\alpha = (\alpha-1)p.$$

Using that in Eq. (2.6), we obtain the joint mixture collisional operator as a mapping from $\mathbf{R}^{\nu p} \times \mathbf{R}^{\nu p}$ into $\mathbf{R}^{\nu p}$. However, one is usually interested in a partial collisional operator, i.e. in a collisional operator describing changes of the densities N_α due to all types of collisions the α molecules can experience.

It is convenient to split the set $\mathscr{R}$ of all types of collisions (reactions) into two subsets:

i) the subsets $\mathscr{R}_e$ of elastic collisions, i.e. such collisions which preserve the identities of two colliding partners

$$\mathscr{R}_e = \bigcup_{1\leqslant\alpha\leqslant\beta\leqslant\nu} \{(\alpha, \beta \leftrightarrow \beta, \alpha)\};$$

ii) the subset $\mathscr{R}_{\text{in}}$ of inelastic collisions, i.e. such reactions between a pair of molecules that result in the emergence of two chemically different molecules.

We distinguish two types of inelastic collisions:

$$\mathscr{R}^{(1)}_{\text{in},\alpha} = \bigcup_{\substack{\beta,\delta=1 \\ \beta\neq\alpha \text{ or } \delta\neq\alpha}}^{\nu} \{(\alpha, \alpha \leftrightarrow \beta, \delta)\}$$

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and

$$\mathscr{R}^{(2)}_{\mathrm{in},\alpha} = \bigcup_{\substack{\beta,\delta,\varepsilon=1 \\ \beta\neq\alpha,\delta\neq\alpha,\varepsilon\neq\alpha \\ \delta\neq\beta \text{ or } \varepsilon\neq\beta}}^{\nu} \{(\alpha,\beta\leftrightarrow\delta,\varepsilon)\}.$$

Of course

$$\mathscr{R}_{\mathrm{in}} = \bigcup_{\alpha=1}^{\nu} \mathscr{R}^{(1)}_{\mathrm{in},\alpha} \cup \bigcup_{\alpha=1}^{\nu} \mathscr{R}^{(2)}_{\mathrm{in},\alpha},$$

$$\mathscr{R}_e \cup \mathscr{R}_{\mathrm{in}} = \mathscr{R}.$$

Accordingly, we split the collisional operators into two parts: one part responsible for the elastic collisions, $\mathscr{F}_{e,\alpha}$, and the second part describing the inelastic collisions, $\mathscr{F}_{\mathrm{in},\alpha}$ i.e. we write

$$\mathscr{F}_\alpha(N,N) = \mathscr{F}_{e,\alpha}(N,N) + \mathscr{F}_{\mathrm{in},\alpha}(N,N). \tag{4.9}$$

The elastic part $\mathscr{F}_{e,\alpha}$ is given by the form of the operator (3.13), whereas the inelastic part $\mathscr{F}_{\mathrm{in},\alpha}(N,N)$ is of the form

$$\begin{aligned}
\mathscr{F}_{\mathrm{in},\alpha} = \sum_{(\alpha,\alpha<->\beta,\delta)\in\mathscr{R}^{(1)}_{\mathrm{in},\alpha}} \Big\{ \sum_{(i,j;k,l)\in\bar{Q}} & [A^{\alpha\alpha}_{\beta\delta}(i,j;k,l)g(i,j)(N^\beta_k N^\delta_l - N^\alpha_i N^\alpha_j) \\
& + A^{\alpha\alpha}_{\delta\beta}(i,j;k,l)g(i,j)(N^\beta_l N^\delta_k - N^\alpha_i N^\alpha_j) + A^{\beta\delta}_{\alpha\alpha}(i,j;k,l)g(k,l)(N^\beta_i N^\delta_j - N^\alpha_k - N^\alpha_l) \\
& + A^{\delta\beta}_{\alpha\alpha}(i,j;k,l)g(k,l)(N^\beta_j N^\delta_i - N^\alpha_k N^\alpha_l) + \sum_{1\leqslant i<j\leqslant p} [A^{\alpha\alpha}_{\beta\delta}(i,j;i,j)g(i,j)(N^\beta_i N^\delta_j - N^\alpha_i N^\alpha_j) \\
& + [A^{\alpha\alpha}_{\delta\beta}(i,j;i,j)g(i,j)(N^\beta_j N^\delta_i - N^\alpha_i N^\alpha_j)]\Big\} + \sum_{(\alpha,\beta<->\delta,\varepsilon)\in\mathscr{R}^{(2)}_{\mathrm{in},\alpha}} \Big\{ \sum_{(i,j;k,l)\in\bar{Q}} \\
& + [A^{\alpha\beta}_{\delta\varepsilon}(i,j;k,l)h(i)(N^\delta_k N^\varepsilon_l - N^\alpha_i N^\beta_j) + A^{\alpha\beta}_{\varepsilon\delta}(i,j;k,l)h(i)(N^\delta_l N^\varepsilon_k - N^\alpha_i N^\beta_j) \\
& + A^{\beta\alpha}_{\delta\varepsilon}(i,j;k,l)h(j)(N^\delta_k N^\varepsilon_l - N^\alpha_j N^\beta_i) + A^{\beta\alpha}_{\varepsilon\delta}(i,j;k,l)h(j)(N^\delta_l N^\varepsilon_k - N^\alpha_j N^\beta_i) \\
& + A^{\delta\varepsilon}_{\alpha\beta}(i,j;k,l)h(k)(N^\delta_i N^\varepsilon_j - N^\alpha_k N^\beta_l) + A^{\varepsilon\delta}_{\alpha\beta}(i,j;k,l)h(k)(N^\delta_j N^\varepsilon_i - N^\alpha_k N^\beta_l) \\
& + A^{\delta\varepsilon}_{\beta\alpha}(i,j;k,l)h(l)(N^\delta_i N^\varepsilon_j - N^\alpha_l N^\beta_k) + A^{\varepsilon\alpha}_{\beta\alpha}(i,j;k,l)h(l)(N^\delta_j N^\varepsilon_i - N^\alpha_l N^\beta_k) \\
& + \sum_{1\leqslant i<j\leqslant p} [A^{\alpha\beta}_{\varepsilon\delta}(i,j;i,j)h(i)(N^\delta_i N^\varepsilon_j - N^\alpha_i N^\beta_j) + A^{\alpha\beta}_{\varepsilon\delta}(i,j;i,j)h(i)(N^\delta_j N^\varepsilon_i - N^\alpha_i N^\beta_j) \\
& + A^{\beta\alpha}_{\varepsilon\delta}(i,j;i,j)h(j)(N^\delta_i N^\varepsilon_j - N^\alpha_j N^\beta_i) + A^{\beta\alpha}_{\delta\varepsilon}(i,j;i,j,j)h(j)(N^\delta_j N^\varepsilon_i - N^\alpha_j N^\beta_i)\Big\}.
\end{aligned} \tag{4.10}$$

$$\alpha = 1,2,\ldots,\nu,$$

where the symbols $A^{\alpha\beta}_{\delta\varepsilon}(i,j;k,l)$ are defined by Eq. (3.14), and $g(i,j)$ and $h(i)$ are p-dimensional vectors whose components $g_m(i,j)$ and $h_m(i)$ are given by

$$\begin{aligned}
g_m(i,j) &= \delta_{im} + \delta_{jm}, \qquad m = 1,2,\ldots,p, \\
h_m(i) &= \delta_{im}, \qquad m = 1,2,\ldots,p,
\end{aligned}$$

respectively.

Physical collisional invariants

Now, we proceed to the determination of the molecular velocities $\mathbf{c}^\alpha_i$, $i = 1,2,\ldots,p$, $\alpha = 1,2,\ldots,\nu$.

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First, because the momentum is conserved in any type of collision, the pv-dimensional vectors of the mixture momentum (3.18) must be elements of $\mathbf{F}_M$. This results in

$$\mathbf{c}_i^\alpha = \mu_\alpha(\mathbf{A}^\alpha + \mathbf{B}_i), \tag{4.11}$$

where

$$\mathbf{A}^\alpha = \sum_{j=1}^{\varkappa} K_{j\alpha}\mathbf{a}_j, \quad \alpha = 1, 2, \ldots, \nu,$$

$$\mathbf{B}_i = \sum_{j=1}^{q_0-1} \varphi_{ji}\mathbf{b}_j, \quad i = 1, 2, \ldots, p. \tag{4.12}$$

Here $\mathbf{a}_1, \ldots, \mathbf{a}_\varkappa, \mathbf{b}_1, \ldots, \mathbf{b}_{q-1}$ are arbitrary vectors from $\mathbf{R}^d$, $\mu_\alpha = m_1/m_\alpha$, and φ_{ji}, $i = 1, 2, \ldots, p$ are components of $\varphi_j \in \mathbf{R}^p$, $(j = 1, 2, \ldots, q-1)$.

The inelastic collisions do not preserve the translational energy but they preserve the sum of the translational and internal energies. Therefore the following vector

$$\left(\frac{1}{2}m, (\mathbf{c}_1^1)^2 + E_1, \ldots, \frac{1}{2}m_1(\mathbf{c}_p^1)^2 + E_1, \ldots, \frac{1}{2}m_\nu(\mathbf{c}_1^\nu)^2 + E_\nu, \ldots, \frac{1}{2}m_\nu(\mathbf{c}_\nu^\nu) + E_\nu\right), \tag{4.13}$$

where E_α is the internal energy of the molecule B_α, is a collisional invariant instead of the vector (3.21).

Thus we get the following relations:

$$\frac{1}{2}m_\alpha\mu_\alpha^2(A^\alpha + B_i)^2 + \frac{1}{2}m_\beta\mu_\beta^2(A^\beta + B_j)^2 + E_\alpha + E_\beta = \frac{1}{2}m_\delta\mu_\delta^2(A^\delta + B_j)^2 + \frac{1}{2}m_\varepsilon\mu_\varepsilon^2(A^\varepsilon + B_l)^2 + E_\delta + E_\varepsilon \tag{4.14}$$

for every $(\alpha, \beta \leftrightarrow \delta, \varepsilon) \in \mathscr{R}$ and $(i, j; k, l) \in \bar{Q}$.

Of these relations merely $\nu p - \dim \mathbf{F}_M = \nu p - q - \varkappa$ is independent.

It is convenient to treat the internal energies $E_1, E_2, \ldots, E_\nu$ as unknown. As a result, we get more unknowns (their total number is equal to $d(\varkappa+q) \neq 1+\nu$), what can be helpful in constructing "physically interesting models". For instance, assuming

$$A^\alpha = 0, \quad \alpha = 1, \ldots, \nu, \quad B_i^2 = B^2, \quad i = 1, 2, \ldots, p$$

we get from (4.14)

$$E_\alpha + E_\beta - E_\delta - E_\varepsilon = \frac{1}{2}(m_\delta\mu_\delta^2 + m_\varepsilon\mu_\varepsilon^2 - m_\alpha\mu_\alpha^2 - m_\beta\mu_\beta^2)B^2. \tag{4.15}$$

The difference of internal energies does not vanish due to the difference of masses of the colliding and emerging molecules.

The polyatomic molecules cannot be treated as spherically symmetric and, therefore, (in the case of $d = 3$) we have an additional collisional invariant which is the angular momentum ([19])

$$m_\alpha \mathbf{x} \wedge \mathbf{c}_i^\alpha + \mathbf{I}_\alpha, \quad \alpha = 1, 2, \ldots, \nu, \quad i = 1, 2, \ldots, p, \tag{4.16}$$

where for any two three-dimensional vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{a} \wedge \mathbf{b}$ stands for their vectorial product. In relations (4.16) $\mathbf{x}$ denotes the position of the center of colliding molecule and $\mathbf{I}_\alpha$ is the mean angular momentum of the α molecules.

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Usually, the distance between the centers of the colliding molecules is neglected owing to its shortness. This means that, as a matter of fact, the molecular mean angular momentum $\mathbf{I}_\alpha$ is conserved. Since $\mathbf{I}_\alpha$ does not depend on the molecular velocities $\mathbf{c}_i^\alpha$, then the angular momentum is a collisional invariant if and only if

$$\mathbf{I}_\alpha = \sum_{\alpha=1}^{\varkappa} K_{\beta\alpha} \vec{\mathscr{I}}_\beta, \qquad \alpha = 1, 2, \ldots, \varkappa,$$

where $\vec{\mathscr{I}}_\beta \in \mathbf{R}^3$ are arbitrary vectors ($\beta = 1, 2, \ldots, \varkappa$).

Maxwellian

A Maxwellian is, by definition (cf. [1, 13]), a νp-dimensional vector with positive components whose logarithm is a collisional invariant.

In the case under consideration, we obtain from this definition and from the vectors (4.3), (4.5) and (4.7)

$$N_i^\alpha = A \exp\Big[\sum_{\lambda=1}^{\varkappa} K_{\lambda\alpha}\mu_\lambda + \sum_{j=1}^{q_0-1} \varphi_{ji} C_j\Big], \qquad i = 1, 2, \ldots, p, \qquad \alpha = 1, 2, \ldots, \nu, \tag{4.17}$$

where $A, \mu_1, \ldots, \mu_\varkappa, C_1, \ldots, C_{q-1}$ are arbitrary constants.

The quantities

$$\sum_{\lambda=1}^{\varkappa} K_{\lambda\alpha}\mu_\lambda, \qquad \alpha = 1, 2, \ldots, \nu$$

can be interpreted as chemical potentials.

In the full theory (see [15]), in the case of isotropic mixtures in equilibrium, the Maxwellian $f_\alpha(\xi)$ is of the form

$$f_\alpha(\xi) = A \exp\left[\sum_{\lambda=1}^{\varkappa} K_{\lambda\alpha}\mu_\lambda - \frac{\frac{1}{2} m_\alpha \xi^2 + E_\alpha}{kT}\right], \tag{4.18}$$

where ξ is the molecular velocity, T is the temperature, and k is the Boltzmann constant provided that the so-called principle of detailed balance is satisfied.

If, however, the principle of the detailed balance is not satisfied, a distribution different from Eq. (4.18) takes place in the state of equilibrium ([20]).

Hence the principle of detailed balance is, in a sense, equivalent to establishing a Maxwellian as an equilibrium distribution ([15]).

Since for the proposed DVM the Maxwellian is a unique equilibrium distribution, these models can be applied to such mixtures for which the principle of detailed balance holds. Should we like to have other distributions in the state of equilibrium, we ought to construct a new theory of discrete velocity models. Hence the DVM in their present form cannot be applied to models of these gas mixtures for which the principle of detailed balance is ont satisfied.

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