5 Entropy, Quasiequilibrium, and Projectors Field

Projection operators P_y contribute both to the invariance equation (3.2), and to the film extension of the dynamics (4.5). Limiting results, exact solutions, etc. only weakly depend on the particular choice of projectors, or do not depend on it at all. However, validity of approximations obtained on each iteration step towards the limit strongly depends on the choice of the projector. Moreover, if we want each approximate solution to be consistent with such physically crucial conditions as the second law of thermodynamics (the entropy of the isolated systems increases), then the choice of the projector becomes practically unique.

In this chapter we consider the main ingredients for constructing the projector, based on the two additional structures:

(a) The moment parameterization,
(b) The entropy and the entropic scalar product.

5.1 Moment Parameterization

Same as in the previous chapters, let a regular map (projection) is defined, $\Pi : U \to W$. We consider only maps $F : W \to U$ which satisfy $\Pi \circ F = 1$. We seek slow invariant manifolds among such maps. (A remark is in order here: sometimes one has to consider F which are defined not on the whole W but only on some subset of it.) In this case, the unique projector consistent with the given structure is the superposition of the differentials (the chain rule):

$$P_y = (D_y F)_y \circ (D_x \Pi)_{F(y)} \ . \tag{5.1}$$

In the language of differential equations (5.1) has the following significance: First, equation (3.1) is projected,

$$\frac{\mathrm{d}y}{\mathrm{d}t} = (D_x \Pi)_{F(y)} J(F(y)) \ . \tag{5.2}$$

Second, the latter equation is lifted back to U with the help of F and its differential,

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$$\begin{aligned} & x(t) = F(y(t)) \; ; \\ & \left.\frac{\mathrm{d}x}{\mathrm{d}t}\right|_{x=F(y)} = (D_y F)_y \left(\frac{\mathrm{d}y}{\mathrm{d}t}\right) = (D_y F)_y ((D_x \Pi)_{F(y)} J(F(y))) = P_y J(F(y)) \; . \end{aligned} \tag{5.3}$$

The most standard example of the construction just described is as follows: x is the distribution density, $y = \Pi(x)$ is the set of selected moments of this density, $F : y \to x$ is a "closure assumption", a distribution density parameterized by the values of the moments y. Another standard example is relevant to problems of chemical kinetics: x is a detailed description of the reacting mixture (including all intermediates and radicals), y are concentrations of stable reactants and products of the reaction.

The moment parameterization and moment projectors (5.1) are often encountered in applications. However, they have certain shortcomings. In particular, it is by far not always the case that the moment projection *transforms a dissipative system into another dissipative system*. Of course, for invariant $F(y)$ *any* projector transforms the dissipative system into a dissipative system. However, for various approximations to invariant manifolds (closure assumptions) this is not readilyso[1]. The property of projectors to *preserve the type of the dynamics* will be imposed below as one of the requirements.

5.2 Entropy and Quasiequilibrium

The dissipation properties of the system (3.1) are described by specifying the *entropy* S, the distinguished *Lyapunov function* which monotonically increases along solutions of equation (3.1). In a certain sense, this Lyapunov function is more fundamental than the system (3.1) itself. That is, usually, the entropy is known much better than the right hand side of equation (3.1). For example, in chemical kinetics, the entropy is obtained from the *equilibrium* data. The same holds for other Lyapunov functions, which are defined by the entropy and by a specification of the reaction conditions (the free energy, $U - TS$, for the isothermal isochoric processes, the free enthalpy, $U - TH$, for the isothermal isobaric processes etc.). On physical grounds, all these entropic Lyapunov functions are proportional (up to additive constants) to the entropy of the minimal isolated system which includes the system under study [115]. In general, with some abuse of language, we term the Lyapunov functional S the entropy elsewhere below, although it may be a different functional for non-isolated systems.

Thus, we assume that a concave functional S is defined in U, such that it takes maximum in an inner point $x^* \in U$. This point is termed the equilibrium.

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[1] See, e.g. a discussion of this problem for the Tamm–Mott-Smith approximation for the strong shock wave in [9].

For any dissipative system (3.1) under consideration in U, the derivative of S due to equation (3.1) must be nonnegative,

$$\left.\frac{\mathrm{d}S}{\mathrm{d}t}\right|_{x} = (D_x S)(J(x)) \geq 0 \ , \tag{5.4}$$

where $D_x S$ is the linear functional, the differential of the entropy, while the equality in (5.4) is attained only in the equilibrium $x = x^*$.

Most of the works on nonequilibrium thermodynamics deal with quasiequilibrium approximations and corrections to them, or with applications of these approximations (with or without corrections). This viewpoint is not the only possible but it proves very efficient for the construction of a variety of useful models, approximations and equations, as well as methods to solve them. From time to time it is discussed in the literature, who was the first to introduce the quasiequilibrium approximations, and how to interpret them. At least a part of the discussion is due to a different role the quasiequilibrium plays in the entropy-conserving and the dissipative dynamics. The very first use of the entropy maximization dates back to the classical work of G. W. Gibbs [222], but it was first claimed for a principle of informational statistical thermodynamics by E. T. Jaynes [193]. Probably the first explicit and systematic use of quasiequilibria to derive dissipation from entropy-conserving systems was undertaken by D. N. Zubarev. Recent detailed exposition is given in [195]. For dissipative systems, the use of the quasiequilibrium to reduce description can be traced to the works of H. Grad on the Boltzmann equation [201]. A review of the informational statistical thermodynamics was presented in [227]. The connection between entropy maximization and (nonlinear) Onsager relations was also studied [164, 188]. The viewpoint of the present authors was influenced by the papers by L. I. Rozonoer and co-workers, in particular, [223–225]. A detailed exposition of the quasiequilibrium approximation for Markov chains is given in the book [115] (Chap. 3, *Quasiequilibrium and entropy maximum*, pp. 92–122), and for the BBGKY hierarchy in the paper [226]. The maximum entropy principle was applied to the description the universal dependence the three-particle distribution function F_3 on the two-particle distribution function F_2 in classical systems with binary interactions [229]. For a discussion the quasiequilibrium moment closure hierarchies for the Boltzmann equation [224] see the papers [230, 233, 234]. A very general discussion of the maximum entropy principle with applications to dissipative kinetics is given in the review [231]. Recently the quasiequilibrium approximation with some further correction was applied to description of rheology of polymer solutions [254, 266] and of ferrofluids [267, 268]. Quasiequilibrium approximations for quantum systems in the Wigner representation [36, 37] was discussed very recently [232]. We shall now introduce the quasiequilibrium approximation in the most general setting.

A *linear moment parameterization* is a linear operator, $\Pi : E \to L$, where $L = \mathrm{im}\Pi = E/\ker\Pi$, $\ker\Pi$ is a closed linear subspace of space E, and Π is the projection of E onto factor-space L. Let us denote $W = \Pi(U)$. *Quasiequilibrium* (or restricted equilibrium, or conditional equilibrium, or constrained equilibrium) is the embedding, $F^* : W \to U$, which puts into correspondence to each $y \in W$ the solution to the entropy maximization problem:

$$S(x) \to \max,\ \Pi(x) = y\ . \tag{5.5}$$

We assume that, for each $y \in \mathrm{int}W$, there exists the unique solution $F^*(y) \in \mathrm{int}U$ to the problem (5.5). This solution, $F^*(y)$, is called the quasiequilibrium, corresponding to the value y of the macroscopic variables. The set of quasiequilibria $F^*(y)$, $y \in W$, forms a manifold in $\mathrm{int}U$, parameterized by the values of the macroscopic variables $y \in W$.

Let us specify some notations: E^T is the adjoint to the E space. Adjoint spaces and operators will be indicated by ^{T}, whereas notation * is earmarked for equilibria and quasiequilibria.

Furthermore, $[l, x]$ is the result of application of the functional $l \in E^T$ to the vector $x \in E$. We recall that, for an operator $A : E_1 \to E_2$, the adjoint operator, $A^T : E_1^T \to E_2^T$ is defined by the following relation: For any $l \in E_2^T$ and $x \in E_1$,

$$[l, Ax] = [A^T l, x]\ .$$

Next, $D_x S(x) \in E^T$ is the differential of the entropy functional $S(x)$, $D_x^2 S(x)$ is the second differential of the entropy functional $S(x)$. The corresponding quadratic functional $D_x^2 S(x)(z, z)$ on E is defined by the Taylor formula,

$$S(x + z) = S(x) + [D_x S(x), z] + \frac{1}{2} D_x^2 S(x)(z, z) + o(\|z\|^2)\ . \tag{5.6}$$

We keep the same notation for the corresponding symmetric bilinear form, $D_x^2 S(x)(z, p)$, and also for the linear operator, $D_x^2 S(x) : E \to E^T$, defined by the formula,

$$[D_x^2 S(x) z, p] = D_x^2 S(x)(z, p)\ .$$

In the latter formula, on the left hand side, there is the operator, on the right hand side there is the bilinear form. Operator $D_x^2 S(x)$ is symmetric on E, $D_x^2 S(x)^T = D_x^2 S(x)$.

Concavity of the entropy S means that, for any $z \in E$, the inequality holds,

$$D_x^2 S(x)(z, z) \le 0\ ;$$

in the restriction onto the affine subspace parallel to $\ker \Pi$ we assume the strict concavity,

$$D_x^2 S(x)(z, z) < 0,\ \text{if } z \in \ker \Pi,\ \text{and if } z \neq 0\ .$$

In the remainder of this section we are going to construct the important object, the projector onto the tangent space of the quasiequilibrium manifold.

Let us compute the derivative $D_y F^*(y)$. For this purpose, let us apply the method of Lagrange multipliers: There exists such a linear functional $\Lambda(y) \in (L)^T$, that

$$D_x S(x)\big|_{F^*(y)} = \Lambda(y) \cdot \Pi,\ \ \Pi(F^*(y)) = y\ , \tag{5.7}$$

or

$$D_x S(x)\big|_{F^*(y)} = \Pi^T \cdot \Lambda(y),\ \ \Pi(F^*(y)) = y\ . \tag{5.8}$$

From equation (5.8) we get,

$$\Pi(D_y F^*(y)) = 1_L\ , \tag{5.9}$$

where we have indicated the space in which the unit operator acts. Next, using the latter expression, we transform the differential of the equation (5.7),

$$D_y \Lambda = (\Pi (D_x^2 S)^{-1}_{F^*(y)} \Pi^T)^{-1}\ , \tag{5.10}$$

and, consequently,

$$D_y F^*(y) = (D_x^2 S)^{-1}_{F^*(y)} \Pi^T (\Pi (D_x^2 S)^{-1}_{F^*(y)} \Pi^T)^{-1}\ . \tag{5.11}$$

Notice that, elsewhere in equation (5.11), operator $(D_x^2 S)^{-1}$ acts on the linear functionals from L^T. These functionals are precisely those which become zero on $\ker \Pi$ or, that is the same, those which can be represented as linear functionals of macroscopic variables.

The tangent space to the quasiequilibrium manifold at the point $F^*(y)$ is the image of the operator $D_y F^*(y)$:

$$\mathrm{im}\,(D_y F^*(y)) = (D_x^2 S)^{-1}_{F^*(y)} L^T = (D_x^2 S)^{-1}_{F^*(y)} \mathrm{Ann}(\ker \Pi) \tag{5.12}$$

where $\mathrm{Ann}(\ker \Pi)$ is the set of linear functionals which become zero on $\ker \Pi$. Another way to write equation (5.12) is the following:

$$x \in \mathrm{im}\,(D_y F^*(y)) \Leftrightarrow (D_x^2 S)_{F^*(y)}(z, p) = 0,\ \ p \in \ker \Pi\ . \tag{5.13}$$

This means that $\mathrm{im}\,(D_y F^*(y))$ is the orthogonal complement of $\ker \Pi$ in E with respect to the scalar product,

$$\langle z | p \rangle_{F^*(y)} = -(D_x^2 S)_{F^*(y)}(z, p)\ . \tag{5.14}$$

The entropic scalar product (5.14) appears often in the constructions below. (Usually, it becomes the scalar product indeed after the conservation laws are excluded). Let us denote as $T_y = \mathrm{im}(D_y F^*(y))$ the tangent space to the quasiequilibrium manifold at the point $F^*(y)$. Important role in the construction of quasiequilibrium dynamics and its generalizations is played by the quasiequilibrium projector, an operator which projects E on T_y parallel to $\ker \mathit{\Pi}$. This is the orthogonal projector with respect to the entropic scalar product, $P^*_y : E \to T_y$:

$$P^*_y = D_y F^*(y) \cdot \mathit{\Pi} = \left(D^2_x S\big|_{F^*(y)}\right)^{-1} \mathit{\Pi}^T \left(\mathit{\Pi} \left(D^2_x S\big|_{F^*(y)}\right)^{-1} \mathit{\Pi}^T\right)^{-1} \mathit{\Pi} \,. \tag{5.15}$$

It is straightforward to check the equality $P^{*2}_y = P^*_y$, and the self-adjointness of P^*_y with respect to the entropic scalar product (5.14). Thus, we have introduced the basic constructions: the quasiequilibrium manifold, the entropic scalar product, and the quasiequilibrium projector.

Quasiequilibrium entropy $S(y)$ is a functional on W. It is defined as the value of the entropy on the corresponding quasiequilibrium $x = F^*(y)$:

$$S(y) = S(F^*(y)) \tag{5.16}$$

Quasiequilibrium dynamics is a dynamics on W, defined by the equation (5.2) for the quasiequilibrium $F^*(y)$:

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \mathit{\Pi} J(F^*(y)) \,. \tag{5.17}$$

Here $\mathit{\Pi}$ is constant linear operator (in the general case (5.2), it may become nonlinear). The corresponding quasiequilibrium dynamics on the quasiequilibrium manifold $F^*(W)$ is defined using the projector (5.1):

$$\frac{\mathrm{d}x}{\mathrm{d}t} = P^*_y|_{x=F^*(y)} J(x) = (D_y F^*)_{x=F^*(y)} \mathit{\Pi} J(x), \; x \in F^*(W) \,. \tag{5.18}$$

The orthogonal projector P^*_y in the right hand side of equation (5.18) can be explicitly written using the second derivative of S and the operator $\mathit{\Pi}$ (5.15). Let's remind that the only distinguished scalar product in E is the entropic scalar product (5.14):

$$\langle z, p \rangle_x = -(D^2_x S)_x(z, p) \tag{5.19}$$

It depends on the point $x \in U$. This dependence $\langle | \rangle_x$ endows U with the structure of a Riemann space.

The most important property of the quasiequilibrium system (5.17), (5.18) is highlighted by the *conservation of the dynamics type* theorem: if for the original dynamic system (3.1) $\frac{\mathrm{d}S}{\mathrm{d}t} \geq 0$, then for the quasiequilibrium dynamics $\frac{\mathrm{d}S}{\mathrm{d}t} \geq 0$. If for the original dynamic system (3.1) $\frac{\mathrm{d}S}{\mathrm{d}t} = 0$ (conservative system), then for the quasiequilibrium dynamics $\frac{\mathrm{d}S}{\mathrm{d}t} = 0$ as well.

The construction of the quasiequilibrium allows for the following generalization: Almost every manifold can be represented as a set of minimizers of the entropy under linear constraints. However, in contrast to the standard quasiequilibrium, these linear constraints will depend, generally speaking, on the point on the manifold.

So, let the manifold $\varOmega = F(W) \subset U$ be given. However, now macroscopic variables y are not functionals on R or U but just parameters identifying points on the manifold. The problem is how to extend the definitions of y onto a neighborhood of $F(W)$ in such a way that $F(W)$ will become a solution to the variational problem:

$$S(x) \to \max, \ \ \varPi(x) = y \ . \tag{5.20}$$

For each point $F(y)$, we identify $T_y \in E$, the tangent space to the manifold $\varOmega$ in F_y, and the subspace $Y_y \subset E$, which depends smoothly on y, and which has the property, $Y_y \oplus T_y = E$. Let us define $\varPi(x)$ in the neighborhood of $F(W)$ in such a way, that

$$\varPi(x) = y, \ \text{if} \ x - F(y) \in Y_y \ . \tag{5.21}$$

The point $F(y)$ is the solution of the quasiequilibrium problem (5.20) if and only if

$$D_x S(x)\big|_{F(y)} \in \text{Ann}\ Y_y \ . \tag{5.22}$$

That is, if and only if $Y_y \subset \ker D_x S(x)\big|_{F(y)}$. It is always possible to construct subspaces Y_y with the properties just specified, at least locally, if the functional $D_x S\big|_{F(y)}$ is not identically equal to zero on T_y.

The construction just described allows to consider practically any manifold as a quasiequilibrium. This construction is required when one seeks the induced dynamics on a given manifold. Then the vector fields are projected on T_y parallel to Y_y, and this preserves the basic properties of the quasiequilibrium approximations.

5.3 Thermodynamic Projector without a Priori Parameterization

Quasiequilibrium manifolds is a place where the entropy and the moment parameterization "meet each other". The projector P_y for a quasiequilibrium manifold is nothing but the orthogonal with respect to the entropic scalar product $\langle|\rangle_x$ projector (5.15). The quasiequilibrium projector preserves the type of dynamics. Note that in order to preserve the type of dynamics we needed only one condition to be satisfied,

$$\ker P_y \subset \ker (D_x S)_{x=F(y)} \ . \tag{5.23}$$

Let us require that the field of projectors, $P(x, T)$, is defined for any x and T satisfying the following transversality condition holds

$$T \not\subset \ker D_x S \ . \tag{5.24}$$

It follows immediately from the condition (5.23) that in the equilibrium, $P(x^*, T)$ is the orthogonal projector onto T (ortogonality is with respect to the entropic scalar product $\langle | \rangle_{x^*}$).

The field of projectors was constructed in the neighborhood of the equilibrium following the requirement of the maximal smoothness of P as a function of $g_x = D_x S$ and x [22]. It turns out that to the first order in the deviations $x - x^*$ and $g_x - g_{x^*}$, the projector is defined uniquely. Let us first describe the construction of the projector, and next discuss its uniqueness [10].

Let the subspace $T \subset E$, the point x, and the differential of the entropy at this point, $g = D_x S$, be defined in such a way that the transversality condition (5.24) is satisfied. Let us define $T_0 = T \bigcap \ker g_x$. By the condition (5.24), $T_0 \neq T$. Let us denote, $e_g = e_g(T) \in T$ the vector in T, such that e_g is orthogonal to T_0, and is normalized by the condition $g(e_g) = 1$. The vector e_g is defined unambiguously. The projector $P_{S,x} = P(x, T)$ is defined as follows: For any $z \in E$,

$$P_{S,x}(z) = P_0(z) + e_g g_x(z) \ , \tag{5.25}$$

where P_0 is the orthogonal projector on T_0 (orthogonality is with respect to the entropic scalar product $\langle | \rangle_x$). The *thermodynamic projector* (5.25) depends on the point x through the x-dependence of the scalar product $\langle | \rangle_x$, and also through the differential of S in x, the functional g_x. Further we shall often omit the index S in $P_{S,x}$.

Obviously, $P(z) = 0$ implies $g(z) = 0$, that is, the thermodynamicity requirement (5.23) is satisfied. Uniqueness of the thermodynamic projector (5.25) is supported by the requirement of the *maximal smoothness* (analyticity) [22] of the projector as a function of g_x and $\langle | \rangle_x$, and is done in two steps which we sketch here (detailed proof is given in the next section, following the paper [10]):

1. Considering the expansion of the entropy at the equilibrium up to the quadratic terms, one demonstrates that in the equilibrium the thermodynamic projector is the orthogonal projector with respect to the scalar product $\langle | \rangle_{x^*}$.
2. For a given g, one considers auxiliary dissipative dynamic systems (3.1), which satisfy the condition: For every $x' \in U$, it holds, $g_x(J(x')) = 0$, that is, g_x defines an additional linear conservation law for the auxiliary systems. For the auxiliary systems, the point x is the equilibrium. Eliminating the linear conservation law g_x, and using the result of the previous point, we end up with the formula (5.25).

Thus, the entropic structure defines unambiguously the field of projectors (5.25), for which the dynamics of *any* dissipative system (3.1) projected on *any* closure manifold remains dissipative.

5.4 Uniqueness of Thermodynamic Projector

In this section, the uniqueness theorem for thermodynamic projector will be proved.

5.4.1 Projection of Linear Vector Field

Let E be real Hilbert space with the scalar product $\langle \, | \, \rangle$, Q be a set of linear bounded operators in E with negatively definite quadratic form $\langle Ax \mid x\rangle \leq 0$ for every $A \in Q$, $T \subsetneq E$ be a nontrivial ($T \neq \{0\}$) closed subspace. For every projector $P : E \to T$ ($P^2 = P$) and linear operator $A : E \to E$ we define the projected operator $P(A) : T \to T$ in such a way:

$$P(A)x = PAx \equiv PAPx \, \text{for} \, x \in T \; . \tag{5.26}$$

The space T is the Hilbert space with the scalar product $\langle \, | \, \rangle$. Let Q_T be a set of linear bounded operators in T with negatively definite quadratic form $\langle Ax \mid x\rangle \leq 0$.

Proposition 1. *The inclusion $P(Q) \subseteq Q_T$ for a projector $P : E \to T$ holds if and only if P is the orthogonal projector with respect to the scalar product $\langle \, | \, \rangle$.*

Proof. If P is orthogonal (and, hence, selfadjoint) and $\langle Ax \mid x\rangle \leq 0$, then

$$\langle PAPx \mid x\rangle = \langle APx \mid Px\rangle \leq 0 \; .$$

If P is not orthogonal, then $Px \neq 0$ for some vector $x \in T^{\perp}$ in orthogonal complement of T. Let us consider the negatively definite selfadjoint operator

$$A_x = - \mid Px - ax\rangle\langle Px - ax \mid$$

($A_x y = -(Px - ax)\langle Px - ax \mid y\rangle$). The projection of A_x on T is:

$$P(A_x) = (a-1) \mid Px\rangle\langle Px \mid \; .$$

This operator is not negatively definite for $a > 1$. □

Immediately from this proof follows the Corollary 1.

Corollary 1. *Let $Q^{\mathrm{sym}} \subset Q$ be a subset of selfadjoint operators in E. The inclusion $P(Q^{\mathrm{sym}}) \subseteq Q_T$ for a projector $P : E \to T$ holds if and only if P is the orthogonal projector with respect to the scalar product $\langle \, | \, \rangle$.* □

Corollary 2. *Let $Q_T^{\mathrm{sym}} \subset Q_T$ be a subset of selfadjoint operators in T. If $P(Q) \subseteq Q_T$ for a projector $P : E \to T$, then $P(Q^{\mathrm{sym}}) \subseteq Q_T^{\mathrm{sym}}$.*□

It follows from the Proposition 1 and the obvious remark: If operators A and P are selfadjoint, then operator PAP is selfadjoint too.

The Proposition 1 means that a projector which transforms every linear vector field Ax with Lyapunov function $\langle x \mid x \rangle$ into projected vector field $PAPx$ with the same Lyapunov function is orthogonal with respect to the scalar product $\langle \mid \rangle$.

According to the Corollary 1, the conditions of the Proposition 1 can be made weaker: A projector which transforms every *selfadjoint* linear vector field Ax with Lyapunov function $\langle x \mid x \rangle$ into projected vector field $PAPx$ with the same Lyapunov function is orthogonal with respect to the scalar product $\langle \mid \rangle$. In physical applications it means, that we can deal with requirement of dissipation persistence for vector field with Onsager's reciprocity relations. The consequence of such a requirement will be the same, as for the class of all continuous linear vector field: The projector should be orthogonal.

The Corollary 2 is a statement about persistence of the reciprocity relations.

5.4.2 The Uniqueness Theorem

In this subsection we discuss finite-dimensional systems. There are technical details which make the theory of nonlinear infinite-dimensional case too cumbersome: the Hilbert spaces equipped with entropic scalar product $\langle \mid \rangle_x$ (5.14) for different x consist of different functions. Of course, there exists a common dense subspace, and geometrical sense remains the same, as for the finite-dimensional space, but we defer the discussion of all the details till a special mathematical publication.

Let E be n-dimensional real vector space, $U \subset E$ be a domain in E, and a m-dimensional space of parameters L be defined, $m < n$, and let W be a domain in L. We consider differentiable maps, $F: \ W \to U$, such that, for every $y \in W$, the differential of F, $D_yF: \ L \to E$, is an isomorphism of L on a subspace of E. That is, F are the manifolds, immersed in the phase space of the dynamic system (3.1), and parametrized by parameter set W.

Let the twice differentiable function S on U be given (the entropy). We assume that S is strictly concave in the second approximation: The quadratic form defined by second differential of the entropy $D^2_xS(y,y)$ is strictly negative definite in E for every $x \in U$. We will use the entropic scalar product (13.2). Let S have the interior point of maximum in U: $x^{\mathrm{eq}} \in \mathrm{int}U$.

The function S is Lyapunov function for a vector field J in U, if

$$(D_xS)(J(x)) \geq 0 \text{ for every } x \in U \ .$$

First of all, we shall study vector fields with Lyapunov function S in the neighborhood of x^{eq}. Let $0 \in \mathrm{int}W$, $F: \ W \to U$ be an immersion, and $F(0) = x^{\mathrm{eq}}$. Let us define $T_y = \mathrm{im}D_yF(y)$ for each $y \in W$. This T_y is the tangent space to $F(W)$ in the point y. Assume that the mapping F is sufficiently smooth, and $F(W)$ is not tangent to entropy levels:

$$T_y \nsubseteq \ker D_x S|_{x=F(y)}$$

for every $y \neq 0$. The thermodynamic projector for a given F is a projector-valued function $y \mapsto P_y$, where $P_y : E \to T_y$ is a projector. The *thermodynamic conditions* reads: *For every smooth vector field $J(x)$ in U with Lyapunov function S the projected vector field $P_y(J(F(y)))$ on $F(W)$ has the same Lyapunov function $S(F(y))$.*

Proposition 1 and Corollaries 1, 2 make it possible to prove uniqueness of the thermodynamic projector for the weakened thermodynamic conditions too: *For every smooth vector field $J(x)$ in U with Lyapunov function S and selfadjoint Jacobian operator for every equilibrium point (zero of $J(x)$) the projected vector field $P_y(J(F(y)))$ on $F(W)$ has the same Lyapunov function $S(F(y))$.* We shall not discuss it separately.

Proposition 2. *Let the thermodynamic projector P_y be a smooth function of y. Then*

$$P_0 = P_0^{\perp} \text{ and } P_y = P_y^{\perp} + O(y) \ , \tag{5.27}$$

where $P_y^{\perp}$ is orthogonal projector onto T_y with respect to the entropic scalar product $\langle \mid \rangle_{F(y)}$.

Proof. A smooth vector field in the neighborhood of $F(0) = x^{\mathrm{eq}}$ can be presented as $A(x - x^{\mathrm{eq}}) + o(\|x - x^{\mathrm{eq}}\|)$, where A is a linear operator. If S is the Lyapunov function for this vector field, then the quadratic form $\langle Ax \mid x\rangle_{x^{\mathrm{eq}}}$ is negatively definite. $P_y = P_0 + O(y)$, because P_y is a continuous function. Hence, for P_0 we have the problem solved by the Proposition 1, and $P_0 = P_0^{\perp}$. □

Theorem 1. *Let the thermodynamic projector P_y be a smooth function of y. Then*

$$P_y = P_{0y} + e_g D_x S|_{x=F(y)} \ , \tag{5.28}$$

where notations of formula (13.4) are used: T_{0y} is the kernel of linear functional $D_x S|_{x=F(y)}$ in T_y, $P_{0y} : T_{0y} \to E$ is the orthogonal projector with respect to the entropic scalar product $\langle \mid \rangle_{F(y)}$ (5.14). Vector $e_g \in T$ is proportional to the Riesz representation g_y of linear functional $D_x S|_{x=F(y)}$ in T_y with respect to the entropic scalar product:

$$\langle g_y \mid x\rangle_{F(y)} = (D_x S|_{x=F(y)})(x)$$

for every $x \in T_y$, $e_g = g_y / \langle g_y \mid g_y\rangle_{F(y)}$.

Proof. Let $y \neq 0$. Let us consider an auxiliary class of vector fields J on U with additional linear balance $(D_x S)_{x=F(y)})(J) = 0$. If such a vector field has Lyapunov function S, then $x = F(y)$ is its equilibrium point: $J(F(y)) = 0$.

The class of vector fields with this additional linear balance and Lyapunov function S is sufficiently rich and we can use the Propositions 1, 2 for dynamics on the auxiliary phase space

$$\{z \in U | (D_x S|_{x=F(y)})(z - F(y)) = 0\} \ .$$

Hence, the restriction of P_y on the hyperplane $\ker D_x S|_{x=F(y)}$ is P_{0y}. Formula (5.28) gives the unique continuation of this projector on the whole E. □

5.4.3 Orthogonality of the Thermodynamic Projector and Entropic Gradient Models

In Euclidean spaces with the given scalar product, we often identify the differential of a function $f(x)$ with its gradient: in the orthogonal coordinate system $(\mathrm{grad} f(x))_i = \partial f(x)/\partial x_i$. However, when dealing with a more general setting, one can run into problems while making sense out of such a definition. What to do, if there is no distinguished scalar product, no preselected orthogonality?

For a given scalar product $\langle \, | \, \rangle$ the gradient $\mathrm{grad}_x f(x)$ of a function $f(x)$ at a point x is such a vector g that $\langle g | y \rangle = D_x f(y)$ for any vector y, where $D_x f$ is the differential of function f at a point x. The differential of function f is the linear functional that provides the best linear approximation near the given point.

In order to transform a vector into a linear functional one needs a *pairing*, that means a bilinear form $\langle \, | \, \rangle$. This pairing transforms vector g into linear functional $\langle g|$: $\langle g|(x) = \langle g|x \rangle$. Any twice differentiable function $f(x)$ generates a field of pairings: at any point x there exists a second differential of f, a quadratic form $(D_x^2 f)(\Delta x, \Delta x)$. For a convex function these forms are positively definite, and we return to the concept of scalar product. Let us calculate a gradient of f using this scalar product. In coordinate representation the identity $\langle \mathrm{grad} f(x) \mid y \rangle_x = (D_x f)(y)$ (for any vector y) has a form

$$\sum_{i,j} (\mathrm{grad} f(x))_i \frac{\partial^2 f}{\partial x_i \partial x_j} y_j = \sum_i \frac{\partial f}{\partial x_j} y_j \ , \tag{5.29}$$

hence,

$$(\mathrm{grad} f(x))_i = \sum_j (D_x^2 f)^{-1}_{ij} \frac{\partial f}{\partial x_j} \ . \tag{5.30}$$

As we can see, this $\mathrm{grad} f(x)$ is the *Newtonian direction*, and with this gradient the method of steepest descent transforms into the Newton method of optimization.

Entropy is the concave function and we defined the entropic scalar product through negative second differential of entropy (13.2). Let us define the gradient of entropy by means of this scalar product: $\langle \mathrm{grad}_x S | z \rangle_x = (D_x S)(z)$. The *entropic gradient system* is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \varphi(x)\mathrm{grad}_x S \ , \tag{5.31}$$

where $\varphi(x) > 0$ is a positive kinetic multiplier.

The system (5.31) is a representative of a family of *model kinetic equations*. One replaces complicated kinetic equations by model equations for simplicity. The main requirements to such models are: they should be as simple as possible and should not violate the basic physical laws. The most known model equation is the BGK model [116] for the collision integral in the Boltzmann equation. There are different models for simplifying kinetics [117, 118]. The entropic gradient models (5.31) possesses all the required properties (if the entropy Hessian is sufficiently simple). It was invented for the lattice Boltzmann kinetics [166]. In many cases it is simpler than the BGK model, because the gradient model is *local* in the sense that it uses only the entropy function and its derivatives at a current state, and it is not necessary to compute the equilibrium (or quasiequilibrium for quasiequilibrium models 2.92 [22, 117]). The entropic gradient model has a one-point relaxation spectrum, because near the equilibrium x^{eq} the gradient vector field (5.31) has an extremely simple linear approximation: $\mathrm{d}(\Delta x)/\,\mathrm{d}t = -\varphi(x^{\mathrm{eq}})\Delta x$. It corresponds to a well-known fact that the Newton method minimizes a positively defined quadratic form in one step.

A direct computation shows that the thermodynamic projector P (13.4) in a point x onto the tangent space T can be rewritten as

$$P(J) = P^{\perp}(J) + \frac{\mathrm{grad}_x S^{\parallel}}{\langle \mathrm{grad}_x S^{\parallel} | \mathrm{grad}_x S^{\parallel} \rangle_x} \langle \mathrm{grad}_x S^{\perp} | J \rangle_x \ , \tag{5.32}$$

where $P^{\perp}$ is the orthogonal projector onto T with respect the entropic scalar product, and the gradient $\mathrm{grad}_x S$ is splitted onto tangent and orthogonal components:

$$\mathrm{grad}_x S = \mathrm{grad}_x S^{\parallel} + \mathrm{grad}_x S^{\perp} :$$

$$\mathrm{grad}_x S^{\parallel} = P^{\perp}\mathrm{grad}_x S; \ \mathrm{grad}_x S^{\perp} = (1 - P^{\perp})\mathrm{grad}_x S \ .$$

From (5.32) it follows that the two properties of an ansatz manifolds are equivalent: orthogonality of the thermodynamic projector and invariance of the manifold with respect to the entropic gradient system (5.31).

Proposition 3. *The thermodynamic projector for an ansatz manifold Ω is orthogonal at any point $x \in \Omega$ if and only if* $\mathrm{grad}_x S \in T_x(\Omega)$ *at any point* $x \in \Omega$. □

It should be possible to think of gradients as infinitesimal displacements of points x. Usually there are some balances, at least the conservation of the total probability, and the gradient should belong to a given subspace of zero balances change. For example, for the classical Boltzmann-Gibbs-Shannon entropy ($x = \Psi(q)$), $S = -\int \Psi(q)(\ln \Psi(q) - 1)\,\mathrm{d}q$, the entropic scalar product is $\langle g(q)|f(q)\rangle_\Psi = \int g(q)f(q)/\Psi(q)\,\mathrm{d}q$, and $\mathrm{grad}_\Psi S = -\Psi(q)\ln(\Psi(q)) + c(q)$, where function (vector) $c(q)$ is orthogonal to a given subspace of zero balances. This function have to be founded from the conditions of zero balances for the gradient $\mathrm{grad}_\Psi S$. For example, if the only balance is the conservation of the total probability, $\int \Psi(q)\,\mathrm{d}q \equiv 1$, then for the classical Boltzmann-Gibbs-Shannon entropy S

$$\mathrm{grad}_\Psi S = -\Psi(q)\left(\ln(\Psi(q)) - \int \Psi(q')\ln(\Psi(q'))\,\mathrm{d}q'\right) . \tag{5.33}$$

For the Kullback-form entropy (i.e. for the negative free energy or the Massieu-Planck function)

$$S = -F/T = -\int \Psi(q)\left(\ln\left(\frac{\Psi(q)}{\Psi^{\mathrm{eq}}(q)}\right) - 1\right)\mathrm{d}q ,$$

the second differential and the entropic scalar product are the same, as for the classical Boltzmann-Gibbs-Shannon entropy, and

$$\mathrm{grad}_\Psi S = -\Psi(q)\left(\ln\left(\frac{\Psi(q)}{\Psi^{\mathrm{eq}}(q)}\right) - \int \Psi(q')\ln\left(\frac{\Psi(q)}{\Psi^{\mathrm{eq}}(q)}\right)\mathrm{d}q'\right) . \tag{5.34}$$

For more complicated system of balances, linear or non-linear, the system of linear equations for $c(q)$ can also be written explicitly.

5.4.4 Violation of the Transversality Condition, Singularity of Thermodynamic Projection, and Steps of Relaxation

The thermodynamic projector transforms the arbitrary vector field equipped with the given Lyapunov function into a vector field with the same Lyapunov function for a given ansatz manifold which is not tangent to the Lyapunov function levels. Sometimes it is useful to create an ansatz which violates this transversality condition. The point of entropy maximum on such an ansatz is not the equilibrium. The usual examples are: the non-correlated approximation $x = \Psi(q_1, \dots, q_n) = \prod_i f(q_i)$, the Gaussian manifold for a non-quadratic potential, etc. Such manifolds arise often in applications because of simplicity of computations. However, for these manifolds the thermodynamic projector becomes singular in the point of entropy maximum x^* on the ansatz manifold. This is obvious from (5.32): in the neighborhood of x^* it has the form

$$\begin{aligned} P(J) &= P^\perp(J) + \frac{\mathrm{grad}_x S^\parallel}{\langle \mathrm{grad}_x S^\parallel|\mathrm{grad}_x S^\parallel\rangle_x}\langle \mathrm{grad}_x S^\perp|J\rangle_x \\ &= -\frac{\Delta x}{\langle \Delta x|\Delta x\rangle_{x^*}}\sigma(x^*) + O(1) , \end{aligned} \tag{5.35}$$

where $\Delta x = x - x^*$ is the deviation of x from x^*, $\sigma(x^*) = \langle \mathrm{grad}_{x^*} S^{\perp} | J \rangle_{x^*}$ is the entropy production at the point x^*, $\sigma(x^*) \neq 0$, because the point of entropy maximum x^* is not the equilibrium. In this case the projected system in the neighborhood of x^* reaches the point x^* in finite time t^* as $\sqrt{t^* - t}$ goes to zero. The entropy difference $\Delta S = S(x) - S(x^*) = -\frac{1}{2}\langle \Delta x | \Delta x \rangle_{x^*} + o(\langle \Delta x | \Delta x \rangle_{x^*})$ goes to zero as $-\sigma(x^*)(t^* - t)$ $(t \leq t^*)$.

The singularity of projection has a transparent physical sense. The relaxation along the ansatz manifold to the point x^* is not complete, because this point is not the equilibrium. This motion should be considered as a step of relaxation, and after it was completed, the next step should start. In that sense it is obvious that the motion to the point x^* along the ansatz manifold should take the finite time. The results of this step-by-step relaxation can represent the whole process (with smoothing [26], or without it [27]). The experience of such a step-by-step computing of relaxation trajectories in the initial layer problem for the Boltzmann kinetics demonstrated its efficiency (see [26, 27] and Sect. 9.3).

5.4.5 Thermodynamic Projector, Quasiequilibrium, and Entropy Maximum

The thermodynamic projector projects any vector field which satisfies the second law of thermodynamics into the vector field which satisfies the second law too. Other projectors violate the second law. But what does it mean? Each projector P_x onto tangent space of an ansatz manifold in a point x induces the fast-slow motion splitting: Fast motion is the motion parallel to $\ker P_x$ (on the affine subspace $x + \ker P_x$ in the neighborhood of x), slow motion is the motion on the slow manifold and in the first order it is parallel to the tangent space T_x in the point x (in the first order this slow manifold is the affine subspace $x + \mathrm{im} P_x$, $T_x = \mathrm{im} P_x$), and velocity vector of the slow motion in point x belongs to the image of P_x.

If P_x is the thermodynamic projector, then x is the point of entropy maximum on the affine subspace of fast motion $x + \ker P_x$. It gives the solution to the problem

$$S(z) \to \max,\ z \in x + \ker P_x\ . \tag{5.36}$$

This is the most important property of thermodynamic projector. It was introduced in [9] as the main thermodynamic condition for model reduction. Let us call it for nonequilibrium points x *the property* **A**:

$$\mathbf{A}.\quad \ker P_x \subset \ker D_x S\ . \tag{5.37}$$

If the projector P_x with the property **A** can be continued to the equilibrium point, x^{eq}, as a smooth function of x, then in this point $\ker P_x \perp \mathrm{im} P_x$. If this is valid for all systems (including systems with additional linear conservation laws), then the following *property* **B** holds:

$$\mathbf{B}.\quad (\ker P_x \bigcap \ker D_x S) \perp (\mathrm{im} P_x \bigcap \ker D_x S)\ . \tag{5.38}$$

Of course, orthogonality in (5.37, 5.38) is considered with respect to the entropic scalar product in the point x.

The property **A** means that the value of the entropy production persists for all nonequilibrium points. The sense of the property **B** is: each point of the slow manifold can be made an equilibrium point (after a deformation of the system which leads to an additional balance). And for equilibrium points the orthogonality condition (5.38) follows from the property **A**.

If P_x does not have the property **A**, then x is not the point of entropy maximum on the affine subspace of fast motion $x + \ker P_x$, so either the fast motion along this subspace does not leads to x (and, hence, the point x does not belong to the slow manifold), or this motion violates the second law, and the entropy decreases. This is the violation of the second law of thermodynamics during the fast motion. If P_x does not have the property **A**, then such a violation is expected for almost every system.

On the other hand, if P_x is not the thermodynamic projector, then there exists a thermodynamically consistent vector field J, with a nonthermodynamic projection: S is the Lyapunov function for J (it increases), and is not the Lyapunov function for $P_x(J)$ (it decreases in the neighborhood of x). The difference between violation of the second law of thermodynamics in fast and slow motions for a projector without the property **A** is: for the fast motion this violation typically exists, for the slow (projected) motion there exist some thermodynamic systems with such a violation. On the other hand, the violation of thermodynamics in the slow motion is worse for applications, if we use the slow dynamics as the answer (and assume that the fast dynamics is relaxed).

If P_x does not have the property **B**, then there exist systems with violation of the second law of thermodynamics in fast and slow motions. Here we can not claim that the second law is violated for almost every system, but such systems exist.

One particular case of the thermodynamic projector is known during several decades. It is the quasiequilibrium projector (5.15) on the tangent space of the quasiequilibrium (MaxEnt) manifold (5.5) $S(x) \to \max, \Pi(x) = y$. The solution of the problem (5.5) x_y^{qe} parametrized by values of the macroscopic variables y is the quasiequilibrium manifold.

The formula for the quasiequilibrium projector (5.15) was essentially obtained by Robertson [126]. In his dissertation [126] Robertson studied “the equation of motion for the generalized canonical density operator”. The generalized canonical density renders entropy a maximum for given statistical expectations of the thermodynamic coordinates. Robertson considered the Liouville equation for a general quantum system. The first main result of Robertson’s paper is the explicit expression for splitting of the motion in two components: projection of the motion onto generalized canonical density and the motion in the kernel of this projection. The obtained projector operator is a specific case of the quasiequilibrium projector (5.15). The second result is the exclusion of the motion in the kernel of quasiequilibrium projector from the dynamic equation. This operation is similar to the Zwanzig formalism [125]. It leads to the integro-differential equation with delay in time for the generalized canonical density. The quasiequilibrium projector (5.15) is more general than the projector obtained by Robertson [126] in the following sense: It is derived for any functional S with non-degenerate second differential D_x^2S, for the manifold of conditional maxima of S, and for any (nonlinear) evolution equation. Robertson emphasized that this operator is non-Hermitian with respect to standard L^2 scalar product and in that sense is “not a projector at all”. Nevertheless, it is self-adjoint (and, hence, orthogonal), but with respect to another (entropic) scalar product. The general thermodynamic projector (13.4) performs with an arbitrary ansatz manifolds (not obligatory MaxEnt) and in that sense it is much more general.

The thermodynamic projector (5.15) for the quasiequilibrium manifold (5.5) is the orthogonal projector with respect to the entropic scalar product (5.14). In this case both terms in the thermodynamic projector (5.25) are orthogonal projectors with respect to the entropic scalar product (5.14). The first term, P_0, is orthogonal projector by construction. For the second term, $e_g(D_xS)$, it means that the Riesz representation of the linear functional D_xS in the whole space E with respect to the entropic scalar product belongs to the tangent space of the quasiequilibrium manifold. This Riesz representation is the gradient of S with respect to $\langle | \rangle_x$. The following Proposition gives a simple and important condition of orthogonality of the thermodynamic projector (5.25). Let Ω be an ansatz manifold, and let $\boldsymbol{V}$ be some quasiequilibrium manifold, $x \in \Omega \bigcap \boldsymbol{V}$, T_x be the tangent space to the ansatz manifold Ω in the point x. Suppose that there exists a neighborhood of x where $\boldsymbol{V} \subseteq \Omega$. We use the notation $\mathrm{grad}_x S$ for the Riesz representation of the linear functional D_xS in the entropic scalar product $\langle \, | \, \rangle_x$: $\langle \mathrm{grad}_x S | f \rangle_x \equiv (D_xS)(f)$ for $f \in E$.

Proposition 4. *Under given assumptions,* $\mathrm{grad}_x S \in T_x$, *and the thermodynamic projector* P_x *is the orthogonal projector onto* T_x *with respect to the entropic scalar product (5.14).* □

So, if a point x on the ansatz manifold Ω belongs to some quasiequilibrium submanifold $\boldsymbol{V} \subseteq \Omega$, then the thermodynamic projector in this point is simply the orthogonal projector with respect to the entropic scalar product (13.2).

Proposition 4 is useful in the following situation. Let the quasiequilibrium approximation be more or less satisfactory, but the “relevant degrees of freedom” depend on the current state of the system. It means that for some changes of the state we should change the list of relevant macroscopic variables (moments of distribution function for generating the quasiequilibrium, for example). Sometimes it can be described as presence of “hidden” degrees of freedom, which are not moments. In these cases the manifold of reduced description should be extended. We have a family of systems of moments $M_\alpha = m_\alpha(x)$, and a family of corresponding quasiequilibrium manifolds Ω_α: The manifold Ω_α consist of solutions of optimization problem $S(x) \to \max$, $m_\alpha(x) = M$ for given α and all admissible values for M. To create a manifold of reduced description it is possible to join all the moments M_α in one family, and construct the corresponding quasiequilibrium manifold. Points on this manifold are parametrized by the family of moments values $\{M_\alpha\}$ for all possible α. It leads to a huge increase of the quasiequilibrium manifold. Another way of extension of the quasiequlibrium manifold is a union of all the manifolds Ω_α for all α. In accordance with the Proposition 4, the thermodynamic projector for this union is simply the orthogonal projector with respect to the entropic scalar product. This kind of manifolds gives a closest generalization of the quasiequilibrium manifolds. Due to (5.36), the thermodynamic projector gives the presentation of almost arbitrary ansatz as the quasiequilibrium manifold. This property opens the natural field for applications of thermodynamic projector: construction of Galerkin approximations with thermodynamic properties.

Of course, there is a “law of the difficulty conservation”: for the quasiequilibrium with the moment parameterization the slow manifold is usually not explicitly known, and it can be difficult to calculate it. Thermodynamic projector completely eliminates this difficulty: we can use almost any manifold as appropriate ansatz now. On the other side, on the quasiequilibrium manifold with the moment parameterization (if it is found) it is easy to find the dynamics: simply write $\dot{M} = \Pi(J)$. Building of the thermodynamic projector may require some effort. Finally, if the quasiequilibrium manifold is found, then it is easy to find the projection of any distributions x on the quasiequilibrium manifold: $x \mapsto \Pi(x) \mapsto x^{\mathrm{qe}}_{\Pi(x)}$. It requires just a calculation of the moments $\Pi(x)$. The preimage of the point $x^{\mathrm{qe}}_{\Pi(x)}$ is a set (an affine manifold) of distributions $\{x | \Pi(x - x^{\mathrm{qe}}_{\Pi(x)}) = 0\}$, and $x^{\mathrm{qe}}_{\Pi(x)}$ is the point of entropy maximum on this set. It is possible, but not so easy, to construct such a projector of some neighborhood of the manifold Ω onto Ω for the general thermodynamic projector P_x: for a point z from this neighborhood

$$z \mapsto x \in \Omega, \ \text{if} \ P_x(z - x) = 0 \, . \tag{5.39}$$

A point $x \in \Omega$ is the point of entropy maximum on the preimage of x, i.e. on the affine manifold $\{z | P_x(z - x) = 0\}$. It is necessary to emphasize that the map (5.39) can be defined only in a neighborhood of the manifold Ω, but not in the whole space, because some of affine subspaces $\{z | P_x(z - x) = 0\}$ for different $x \in \Omega$ can intersect. Let us introduce a special notation for the projection of some neighborhood of the manifold Ω onto Ω, associated with the thermodynamic projector P_x (5.39): $\mathbf{P}_\Omega : z \mapsto x$. The preimage of a point $x \in \Omega$ is:

$$\mathbf{P}_\Omega^{-1} x = x + \ker P_x \, , \tag{5.40}$$

(or, strictly speaking, a vicinity of x in this affine manifold). Differential of the operator $\mathbf{P}_{\Omega}$ at a point $x \in \Omega$ from the manifold Ω is simply the projector P_x:

$$\mathbf{P}_{\Omega}(x + \varepsilon z) = x + \varepsilon P_x z + o(\varepsilon) \ . \tag{5.41}$$

Generally, differential of $\mathbf{P}_{\Omega}$ at a point x has not so simple form, if x does not belong Ω.

The "global extension" $\mathbf{P}_{\Omega}$ of a field of "infinitesimal" projectors P_f ($f \in \Omega$) is needed for a discussion of projector operators technique, memory functions and a short memory approximation.

***

Is it necessary to use the thermodynamic projector everywhere? The persistence of dissipation is necessary, because the violation of the second law may lead to non-physical effects. If one creates a very accurate method for solution of the initial equation (3.1), then it may be possible to expect that the persistence of dissipation will hold without additional effort. But this situation does not appear yet. All methods of model reduction need a special tool to control the persistence of dissipation.

In order to summarize, let us give three reasons to use the thermodynamic projector:

1. It guarantees the persistence of dissipation: all the thermodynamic processes which should produce the entropy conserve this property after projecting, moreover, not only the sign of dissipation conserves, but also the value of entropy production and the reciprocity relations are conserved;
2. The coefficients (and, more generally speaking, the right hand part) of kinetic equations are less known than the thermodynamic functionals, so, the *universality* of the thermodynamic projector (it depends only on thermodynamic data) makes the thermodynamic properties of projected system as reliable, as for the initial system;
3. It is easy (much more easy than the spectral projector, for example).

5.5 Example: Quasiequilibrium Projector and Defect of Invariance for the Local Maxwellians Manifold of the Boltzmann Equation

The Boltzmann equation remains the most inspiring source for the model reduction problems. With this subsection we start a series of examples for the Boltzmann equation.

5.5.1 Difficulties of Classical Methods of the Boltzmann Equation Theory

The first systematic and (at least partially) successful method of constructing invariant manifolds for dissipative systems was the celebrated *Chapman-Enskog method* [70] for the Boltzmann kinetic equation (see Chap. 2). The main difficulty of the Chapman-Enskog method [70] are "nonphysical" properties of high-order approximations. This was stated by a number of authors and was discussed in detail in [112]. In particular, as it was noted in [72], the Burnett approximation results in a short-wave instability of the acoustic spectra. This fact contradicts the H-theorem (cf. in [72]). The Hilbert expansion contains secular terms [112]. The latter contradicts the H-theorem.

The other difficulties of both of these methods are: the restriction upon the choice of the initial approximation (the local equilibrium approximation), the requirement for a small parameter, and the usage of slowly converging Taylor expansion. These difficulties never allow a direct transfer of these methods on essentially nonequilibrium situations.

The main difficulty of the Grad method [201] is the uncontrollability of the chosen approximation. An extension of the list of moments can result in a certain success, but it can also give nothing. Difficulties of moment expansion in the problems of shock waves and sound propagation are discussed in [112].

Many attempts were made to refine these methods. For the Chapman-Enskog and Hilbert methods these attempts are based in general on some better rearrangement of expansions (e.g. neglecting high-order derivatives [112], reexpanding [112], Pade approximations and partial summing [43, 221, 233], etc.). This type of work with formal series is wide spread in physics. Sometimes the results are surprisingly good – from the renormalization theory in quantum fields to the Percus-Yevick equation and the ring-operator in statistical mechanics. However, one should realize that success cannot be guaranteed. Moreover, rearrangements never remove the restriction upon the choice of the initial local equilibrium approximation.

Attempts to improve the Grad method are based on quasiequilibrium approximations [223, 224]. It was found in [224] that the Grad distributions are linearized versions of appropriate quasiequilibrium approximations (see also [230, 233, 234]). A method which treats fluxes (e.g. moments with respect to collision integrals) as independent variables in a quasiequilibrium description was introduced in [233, 234, 246, 248], and will be discussed later in Example 5.6.

The important feature of quasiequilibrium approximations is that they are always thermodynamic, i.e. they are consistent with the H-theorem by construction. However, quasiequilibrium approximations do not remove the uncontrollability of the Grad method. Dynamic corrections to Grad's approximation will be addressed later in Chap. 6.

5.5.2 Boltzmann Equation

The phase space E consists of distribution functions $f(\boldsymbol{v},\boldsymbol{x})$ which depend on the spatial variable $\boldsymbol{x}$ and on velocity variable $\boldsymbol{v}$. The variable $\boldsymbol{x}$ spans an open domain $\Omega^3_{\boldsymbol{x}} \subseteq \mathbf{R}_{\boldsymbol{x}}$, and the variable $\boldsymbol{v}$ spans the space $\mathbf{R}^3_{\boldsymbol{v}}$. We require that $f(\boldsymbol{v},\boldsymbol{x}) \in F$ are nonnegative functions, and also that the following integrals are finite for every $\boldsymbol{x} \in \Omega_{\boldsymbol{x}}$ (the existence of the moments and of the entropy):

$$I^{(i_1 i_2 i_3)}_{\boldsymbol{x}}(f) = \int v_1^{i_1} v_2^{i_2} v_3^{i_3} f(\boldsymbol{v},\boldsymbol{x})\,\mathrm{d}^3\boldsymbol{v}, i_1 \geq 0, i_2 \geq 0, i_3 \geq 0\,; \tag{5.42}$$

$$H_{\boldsymbol{x}}(f) = \int f(\boldsymbol{v},\boldsymbol{x})(\ln f(\boldsymbol{v},\boldsymbol{x}) - 1)\,\mathrm{d}^3\boldsymbol{v}, H(f) = \int H_{\boldsymbol{x}}(f)\,\mathrm{d}^3\boldsymbol{x}\,. \tag{5.43}$$

Here and below integration in $\boldsymbol{v}$ is done over $\mathbf{R}^3_{\boldsymbol{v}}$, and it is done over $\Omega_{\boldsymbol{x}}$ in $\boldsymbol{x}$. For every fixed $\boldsymbol{x} \in \Omega_{\boldsymbol{x}}$, $I^{(\dots)}_{\boldsymbol{x}}$ and $H_{\boldsymbol{x}}$ might be treated as functionals defined in F.

We write the Boltzmann equation in the form of (3.1) (in the fixed reference system) using standard notation [112]:

$$\frac{\partial f}{\partial t} = J(f),\;\; J(f) = -v_s \frac{\partial f}{\partial x_s} + Q(f,f)\,. \tag{5.44}$$

Here and further in this Example summation in two repeated indices is assumed, and $Q(f,f)$ stands for the Boltzmann collision integral. The latter represents the dissipative part of the vector field $J(f)$ (5.44).

In this section we consider the case when boundary conditions for equation (5.44) *are relevant to the local with respect to $\boldsymbol{x}$ form of the H-theorem.*

For every fixed $\boldsymbol{x}$, we denote as $H^0_{\boldsymbol{x}}(f)$ the space of linear functionals

$$\sum_{i=0}^{4} a_i(\boldsymbol{x}) \int \psi_i(\boldsymbol{v}) f(\boldsymbol{v},\boldsymbol{x})\,\mathrm{d}^3\boldsymbol{v}\,,$$

where $\psi_i(\boldsymbol{v})$ represent invariants of a collision ($\psi_0 = 1, \psi_i = v_i, i = 1,2,3, \psi_4 = v^2$). We write $(\mathrm{mod} H^0_{\boldsymbol{x}}(f))$ if an expression is valid within the accuracy of adding a functional from $H^0_{\boldsymbol{x}}(f)$. The local H-theorem states: for any functional

$$H_{\boldsymbol{x}}(f) = \int f(\boldsymbol{v},\boldsymbol{x})(\ln f(\boldsymbol{v},\boldsymbol{x}) - 1)\,\mathrm{d}^3\boldsymbol{v}\;\;(\mathrm{mod} H^0_{\boldsymbol{x}}(f)) \tag{5.45}$$

the following inequality is valid:

$$\frac{\mathrm{d}H_{\boldsymbol{x}}(f)}{\mathrm{d}t} \equiv \int Q(f,f)\big|_{f=f(\boldsymbol{v},\boldsymbol{x})} \ln f(\boldsymbol{v},\boldsymbol{x})\,\mathrm{d}^3\boldsymbol{v} \leq 0\,. \tag{5.46}$$

Expression (5.46) is equal to zero if and only if $\ln f = \sum_{i=0}^{4} a_i(\boldsymbol{x})\psi_i(\boldsymbol{v})$.

Although all functionals (5.45) are equivalent in the sense of the H-theorem, it is convenient to work with the functional

$$H_{\boldsymbol{x}}(f) = \int f(\boldsymbol{v}, \boldsymbol{x})(\ln f(\boldsymbol{v}, \boldsymbol{x}) - 1)\, \mathrm{d}^3\boldsymbol{v} \; .$$

All what was said in this chapter can be applied to the Boltzmann equation (5.44). Now we shall discuss some specific points.

5.5.3 Local Manifolds

Although the general description of manifolds $\Omega \subset F$ holds applies also to the Boltzmann equation, a specific class of manifolds can be defined due to the different character of spatial and velocity dependencies in the Boltzmann equation vector field (5.44). These manifolds will be called **local manifolds**, and they are constructed as follows. Denote as F_{loc} the set of functions $f(\boldsymbol{v})$ with finite integrals

$$\begin{aligned} &a) I^{(i_1 i_2 i_3)}(f) = \int v_1^{i_1} v_2^{i_2} v_3^{i_3} f(\boldsymbol{v})\, \mathrm{d}^3\boldsymbol{v}, i_1 \geq 0, i_2 \geq 0, i_3 \geq 0 \; ; \\ &b) H(f) = \int f(\boldsymbol{v}) \ln f(\boldsymbol{v})\, \mathrm{d}^3\boldsymbol{v} \; . \end{aligned} \tag{5.47}$$

In order to construct a local manifold in F, we, first, consider a manifold in F_{loc}. Namely, we define a domain $A \subset B$, where B is a linear space, and consider a smooth immersion $A \to F_{\mathrm{loc}}$: $a \to f(a, \boldsymbol{v})$. The set of functions $f(a, \boldsymbol{v}) \in F_{\mathrm{loc}}$, where a spans a domain A, is a manifold in F_{loc}. Second, we consider *all* bounded and sufficiently smooth functions $a(\boldsymbol{x})$: $\Omega_{\boldsymbol{x}} \to A$, and we define the local manifold in F as the set of functions $f(a(\boldsymbol{x}), \boldsymbol{v})$. Roughly speaking, the local manifold is a set of functions which are parameterized with $\boldsymbol{x}$-dependent functions $a(\boldsymbol{x})$. A local manifold will be called a *locally finite-dimensional* manifold if B is a finite-dimensional linear space.

Locally finite-dimensional manifolds are the natural source of initial approximations for constructing dynamic invariant manifolds in the Boltzmann equation theory. For example, the Tamm–Mott-Smith (TMS) approximation is a locally two-dimensional manifold $\{f(a_-, a_+)\}$ which consists of distributions

$$f(a_-, a_+) = a_- f_- + a_+ f_+ \; . \tag{5.48}$$

Here a_- and a_+ (the coordinates on the manifold $\Omega_{\mathrm{TMS}} = \{f(a_-, a_+)\}$) are non-negative real functions of the position vector $\boldsymbol{x}$, and f_- and f_+ are fixed up- and downstream Maxwellians.

The next example is the locally five-dimensional manifold $\{f(n, \boldsymbol{u}, T)\}$ which consists of local Maxwellians (LM). The LM manifold consists of distributions f_0 which are labeled with parameters $n, \boldsymbol{u}$, and T:

$$f_0(n, \boldsymbol{u}, T) = n \left(\frac{2\pi k_{\mathrm{B}} T}{m}\right)^{-3/2} \exp\left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T}\right) \; . \tag{5.49}$$

Parameters $n, \boldsymbol{u}$, and T in (5.49) are functions of $\boldsymbol{x}$. In this section we shall not indicate this dependency explicitly.

Distribution $f_0(n, \boldsymbol{u}, T)$ is the unique solution of the variational problem:

$$H(f) = \int f \ln f \, \mathrm{d}^3\boldsymbol{v} \to \min$$

for:

$$\begin{aligned} M_0(f) &= \int 1 \cdot f \, \mathrm{d}^3\boldsymbol{v} \; ; \\ M_i(f) &= \int v_i f \, \mathrm{d}^3\boldsymbol{v} = n u_i, i = 1,2,3 \; ; \\ M_4(f) &= \int v^2 f \, \mathrm{d}^3\boldsymbol{v} = \frac{3nk_\mathrm{B}T}{m} + nu^2 \; . \end{aligned} \tag{5.50}$$

Hence, the LM manifold is the quasiequilibrium manifold. Considering $n, \boldsymbol{u}$, and T as five parameters, we see that the LM manifold is parameterized with the values of $M_s(f), s = 0, \ldots, 4$, which are defined in the neighborhood of the LM manifold. It is sometimes convenient to consider the variables $M_s(f_0), s = 0, \ldots, 4$, as a new coordinates on the LM manifold. The relationship between the coordinates $\{M_s(f_0)\}$ and $\{n, \boldsymbol{u}, T\}$ is:

$$n = M_0; u_i = M_0^{-1} M_i, i = 1,2,3; T = \frac{m}{3k_\mathrm{B}} M_0^{-1}(M_4 - M_0^{-1} M_i M_i) \; . \tag{5.51}$$

This is the standard moment parametrization of the quasiequilibrium manifold.

5.5.4 Thermodynamic Quasiequilibrium Projector

Thermodynamic quasiequilibrium projector $P_{f_0(n,\boldsymbol{u},T)}(J)$ onto the tangent space $T_{f_0(n,\boldsymbol{u},T)}$ is defined as:

$$P_{f_0(n,\boldsymbol{u},T)}(J) = \sum_{s=0}^{4} \frac{\partial f_0(n,\boldsymbol{u},T)}{\partial M_s} \int \psi_s J \, \mathrm{d}^3\boldsymbol{v} \; . \tag{5.52}$$

Here we have assumed that $n, \boldsymbol{u}$, and T are functions of $M_0, \ldots, M_4$ (see relationship (5.51)), and

$$\psi_0 = 1, \psi_i = v_i, i = 1,2,3, \psi_4 = v^2 \; . \tag{5.53}$$

Calculating derivatives in (5.52), and next returning to variables $n, \boldsymbol{u}$, and T, we obtain:

$$\begin{aligned} &P_{f_0(n,\boldsymbol{u},T)}(J) = f_0(n,\boldsymbol{u},T) \qquad (5.54) \\ &\times \left\{ \left[\frac{1}{n} - \frac{mu_i}{nk_\mathrm{B}T}(v_i - u_i) + \left(\frac{mu^2}{3nk_\mathrm{B}} - \frac{T}{n} \right) \left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_\mathrm{B}T^2} - \frac{3}{2T} \right) \right] \int J \, \mathrm{d}^3\boldsymbol{v} \right. \end{aligned}$$

$$+\left[\frac{m}{nk_{\mathrm{B}}T}(v_i-u_i)-\frac{2mu_i}{3nk_{\mathrm{B}}}\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T^2}-\frac{3}{2T}\right)\right]\int v_i J\,\mathrm{d}^3\boldsymbol{v}$$
$$\left.+\frac{m}{3nk_{\mathrm{B}}}\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T^2}-\frac{3}{2T}\right)\int \boldsymbol{v}^2 J\,\mathrm{d}^3\boldsymbol{v}\right\} .$$

It is sometimes convenient to rewrite (5.55) as

$$P_{f_0(n,\boldsymbol{u},T)}(J)=f_0(n,\boldsymbol{u},T)\sum_{s=0}^{4}\psi^{(s)}_{f_0(n,\boldsymbol{u},T)}\int\psi^{(s)}_{f_0(n,\boldsymbol{u},T)}J\,\mathrm{d}^3\boldsymbol{v}\,. \tag{5.55}$$

Here

$$\psi^{(0)}_{f_0(n,\boldsymbol{u},T)}=n^{-1/2},\ \psi^{(i)}_{f_0(n,\boldsymbol{u},T)}=(2/n)^{1/2}c_i, \tag{5.56}$$
$$\psi^{(4)}_{f_0(n,\boldsymbol{u},T)}=(2/3n)^{1/2}(c^2-(3/2));\ c_i=(m/2k_{\mathrm{B}}T)^{1/2}(v_i-u_i),\ i=1,2,3\,.$$

It is easy to check that

$$\int f_0(n,\boldsymbol{u},T)\psi^{(k)}_{f_0(n,\boldsymbol{u},T)}\psi^{(l)}_{f_0(n,\boldsymbol{u},T)}\,\mathrm{d}^3\boldsymbol{v}=\delta_{kl}\,. \tag{5.57}$$

Here δ_{kl} is the Kronecker delta.

5.5.5 Defect of Invariance for the LM Manifold

The defect of invariance for the LM manifold at the point $f_0(n,\boldsymbol{u},T)$ for the Boltzmann equation vector field in the co-moving reference system is:

$$\Delta(f_0(n,\boldsymbol{u},T))=P_{f_0(n,\boldsymbol{u},T)}\left(-(v_s-u_s)\frac{\partial f_0(n,\boldsymbol{u},T)}{\partial x_s}+Q(f_0(n,\boldsymbol{u},T))\right)$$
$$-\left(-(v_s-u_s)\frac{\partial f_0(n,\boldsymbol{u},T)}{\partial x_s}+Q(f_0(n,\boldsymbol{u},T))\right)$$
$$=P_{f_0(n,\boldsymbol{u},T)}\left(-(v_s-u_s)\frac{\partial f_0(n,\boldsymbol{u},T)}{\partial x_s}\right)+(v_s-u_s)\frac{\partial f_0(n,\boldsymbol{u},T)}{\partial x_s}\,. \tag{5.58}$$

Substituting (5.55) into (5.58), we obtain:

$$\Delta(f_0(n,\boldsymbol{u},T))=f_0(n,\boldsymbol{u},T)\left\{\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}-\frac{5}{2}\right)(v_i-u_i)\frac{\partial\ln T}{\partial x_i}\right.$$
$$\left.+\frac{m}{k_{\mathrm{B}}T}(((v_i-u_i)(v_s-u_s)-\frac{1}{3}\delta_{is}(\boldsymbol{v}-\boldsymbol{u})^2)\frac{\partial u_s}{\partial x_i}\right\}\,. \tag{5.59}$$

The LM *manifold is not a dynamic invariant manifold of the Boltzmann equation and the defect (5.59) is not equal to zero.* Indeed, inhomogeneity of the temperature and of the flow velocity drives the invariant manifold away from the local equilibrium.

5.6 Example: Quasiequilibrium Closure Hierarchies for the Boltzmann Equation

Explicit method of constructing approximations (the Triangle Entropy Method [233]) is developed for strongly nonequilibrium problems of Boltzmann's–type kinetics, i.e. when the standard moment variables become insufficient. This method enables one to treat any complicated nonlinear functionals that fit best the physics of a problem (such as, for example, rates of processes) as new independent variables.

The method is applied to the problem of derivation of hydrodynamics from the Boltzmann equation. New macroscopic variables are introduced (moments of the Boltzmann collision integral, or scattering rates). They are treated as independent variables rather than as infinite moment series. This approach gives the complete account of rates of scattering processes. Transport equations for scattering rates are obtained (the second hydrodynamic chain), similar to the usual moment chain (the first hydrodynamic chain). Using the triangle entropy method, three different types of the macroscopic description are considered. The first type involves only moments of distribution functions, and results coincide with those of the Grad method in the Maximum Entropy version. The second type of description involves only scattering rates. Finally, the third type involves both the moments and the scattering rates (the mixed description). The second and the mixed hydrodynamics are sensitive to the choice of the collision model. The second hydrodynamics is equivalent to the first hydrodynamics only for Maxwell molecules, and the mixed hydrodynamics exists for all types of collision models excluding Maxwell molecules. Various examples of the closure of the first, of the second, and of the mixed hydrodynamic chains are considered for the hard spheres model. It is shown, in particular, that the complete account of scattering processes leads to a renormalization of transport coefficients.

5.6.1 Triangle Entropy Method

In the present subsection, which is of introductory character, we shall refer, to be specific, to the Boltzmann kinetic equation for a one-component gas whose state (in the microscopic sense) is described by the one-particle distribution function $f(\boldsymbol{v}, \boldsymbol{x}, t)$ depending on the velocity vector $\boldsymbol{v} = \{v_k\}_{k=1}^3$, the spatial position $\boldsymbol{x} = \{x_k\}_{k=1}^3$ and time t. The the Boltzmann equation describes the evolution of f and in the absence of external forces is

$$\partial_t f + v_k \partial_k f = Q(f, f) \ , \tag{5.60}$$

where $\partial_t \equiv \partial/\partial t$ is the time partial derivative, $\partial_k \equiv \partial/\partial x_k$ is partial derivative with respect to k-th component of $\boldsymbol{x}$, summation in two repeating indices is assumed, and $Q(f, f)$ is the collision integral (its concrete form is of no importance right now, just note that it is functional-integral operator quadratic with respect to f).

The Boltzmann equation possesses two properties principal for the subsequent reasoning (for the basic properties of the Boltzmann equation see Chap. 2) .

1. There exist five functions $\psi_\alpha(\boldsymbol{v})$ (additive collision invariants),

$$1, \boldsymbol{v}, v^2$$

such that for any their linear combination with coefficients depending on $\boldsymbol{x}, t$ and for arbitrary f the following equality is true:

$$\int \sum_{\alpha=1}^{5} a_\alpha(\boldsymbol{x}, t)\psi_\alpha(\boldsymbol{v})Q(f, f)\,\mathrm{d}\boldsymbol{v} = 0 \ , \tag{5.61}$$

provided the integrals exist.

2. The equation (5.60) possesses global Lyapunov functional: the H-function,

$$H(t) \equiv H[f] = \int f(\boldsymbol{v}, \boldsymbol{x}, t) \ln f(\boldsymbol{v}, \boldsymbol{x}, t)\,\mathrm{d}\boldsymbol{v}\,\mathrm{d}\boldsymbol{x} \ , \tag{5.62}$$

the derivative of which by virtue of the equation (5.60) is non-positive under appropriate boundary conditions:

$$\mathrm{d}H(t)/\mathrm{d}t \le 0 \ . \tag{5.63}$$

Grad's method [201] and its variants construct closed systems of equations for macroscopic variables when the latter are represented by moments (or, more general, linear functionals) of the distribution function f (hence their alternative name is the "moment methods"). The entropy maximum method for the Boltzmann equation is of particular importance for the subsequent reasoning. It consists in the following. A finite set of moments describing the macroscopic state is chosen. The distribution function of the quasiequilibrium state under given values of the chosen moments is determined, i.e. the problem is solved

$$H[f] \to \min, \ \text{for } \hat{M}_i[f] = M_i, \quad i = 1, \dots, k \ , \tag{5.64}$$

where $\hat{M}_i[f]$ are linear functionals with respect to f; M_i are the corresponding values of chosen set of k macroscopic variables. The quasiequilibrium distribution function $f^*(\boldsymbol{v}, M(\boldsymbol{x}, t))$, $M = \{M_1, \dots, M_k\}$, parametrically depends on M_i, its dependence on space $\boldsymbol{x}$ and on time t being represented only by $M(\boldsymbol{x}, t)$. Then the obtained f^* is substituted into the Boltzmann equation (5.60), and operators $\hat{M}_i$ are applied on the latter formal expression.

In the result we have closed systems of equations with respect to $M_i(\boldsymbol{x}, t)$, $i = 1, \dots, k$:

$$\partial_t M_i + \hat{M}_i[\boldsymbol{v}_k \partial_k f^*(\boldsymbol{v}, M)] = \hat{M}_i[Q(f^*(\boldsymbol{v}, M), f^*(\boldsymbol{v}, M))] \ . \tag{5.65}$$

The following heuristic explanation can be given to the entropy method. A state of the gas can be described by a finite set of moments on some time scale θ only if all the other moments ("fast") relax on a shorter time scale time $\tau, \tau \ll \theta$, to their values determined by the chosen set of "slow" moments, while the slow ones almost do not change appreciably on the time scale τ. In the process of the fast relaxation the H-function decreases, and in the end of this fast relaxation process a quasiequilibrium state sets in with the distribution function being the solution of the problem (5.64). Then "slow" moments relax to the equilibrium state by virtue of (5.65).

The entropy method has a number of advantages in comparison with the classical Grad's method. First, being not necessarily restricted to any specific system of orthogonal polynomials, and leading to solving an optimization problem, it is more convenient from the technical point of view. Second, and ever more important, the resulting quasiequilibrium H-function, $H^*(M) = H[f^*(\boldsymbol{v}, M)]$, decreases due of the moment equations (5.65).

Let us note one common disadvantage of all the moment methods, and, in particular, of the entropy method. Macroscopic parameters, for which these methods enable to obtain closed systems, must be moments of the distribution function. On the other hand, it is easy to find examples when the interesting macroscopic parameters are nonlinear functionals of the distribution function. In the case of the one-component gas these are the integrals of velocity polynomials with respect to the collision integral $Q(f, f)$ of (5.60) (scattering rates of moments). For chemically reacting mixtures these are the reaction rates, and so on. If the characteristic relaxation time of such nonlinear macroscopic parameters is comparable with that of the "slow" moments, then they should be also included into the list of "slow" variables on the same footing.

In this Example for constructing closed systems of equations for nonlinear (in a general case) macroscopic variables the *triangle entropy method* is used. Let us outline the scheme of this method.

Let a set of macroscopic variables be chosen: linear functionals $\hat{M}[f]$ and nonlinear functionals (in a general case) $\hat{N}[f]$:

$$\hat{M}[f] = \left\{\hat{M}_1[f], \ldots, \hat{M}_k[f]\right\}, \ \hat{N}[f] = \left\{\hat{N}_1[f], \ldots, \hat{N}_l[f]\right\} .$$

Then, just as for the problem (5.64), the first quasiequilibrium approximation is constructed under fixed values of the linear macroscopic parameters M:

$$H[f] \to \min \ \text{for} \ \hat{M}_i[f] = M_i, \ i = 1, \ldots, k , \tag{5.66}$$

and the resulting distribution function is $f^*(\boldsymbol{v}, M)$. After that, we seek the true quasiequilibrium distribution function in the form,

$$f = f^*(1 + \varphi) , \tag{5.67}$$

where φ is a deviation from the first quasiequilibrium approximation. In order to determine φ, the second quasiequilibrium approximation is constructed.

Let us denote $\Delta H[f^*,\varphi]$ as the quadratic term in the expansion of the H-function into powers of φ in the neighbourhood of the first quasiequilibrium state f^*. The distribution function of the second quasiequilibrium approximation is the solution to the problem,

$$\begin{aligned}&\Delta H[f^*,\varphi] \to \min \text{ for}\\ &\hat{M}_i[f^*\varphi] = 0, \quad i = 1,\dots,k\ ,\\ &\Delta\hat{N}_j[f^*,\varphi] = \Delta N_j, \quad j = 1,\dots,l\ ,\end{aligned} \tag{5.68}$$

where $\Delta\hat{N}_j$ are linear operators characterizing the linear with respect to φ deviation of (nonlinear) macroscopic parameters N_j from their values, $N_j^* = \hat{N}_j[f^*]$, in the first quasiequilibrium state. Note the importance of the homogeneous constraints $\hat{M}_i[f^*\varphi] = 0$ in the problem (5.68). Physically, it means that the variables ΔN_j are "slow" in the same sense, as the variables M_i, at least in the small neighborhood of the first quasiequilibrium f^*. The obtained distribution function,

$$f = f^*(\boldsymbol{v},M)(1+\varphi^{**}(\boldsymbol{v},M,\Delta N)) \tag{5.69}$$

is used to construct the closed system of equations for the macroparameters M, and ΔN. Because the functional in the problem (5.68) is quadratic, and all constraints in this problem are linear, it is always explicitly solvable.

Further in this section some examples of using the triangle entropy method for the one-component gas are considered. Applications to chemically reacting mixtures were discussed in [246, 247].

5.6.2 Linear Macroscopic Variables

Let us consider the simplest example of using the triangle entropy method, when all the macroscopic variables of the first and of the second quasiequilibrium states are the moments of the distribution function.

Quasiequilibrium Projector

Let $\mu_1(\boldsymbol{v}),\dots,\mu_k(\boldsymbol{v})$ be the microscopic densities of the moments

$$M_1(\boldsymbol{x},t),\ \dots\ ,M_k(\boldsymbol{x},t)$$

which determine the first quasiequilibrium state,

$$M_i(\boldsymbol{x},t) = \int \mu_i(\boldsymbol{v}) f(\boldsymbol{v},\boldsymbol{x},t)\,\mathrm{d}\boldsymbol{v}\ , \tag{5.70}$$

and let $\nu_1(\boldsymbol{v}),\dots,\nu_l(\boldsymbol{v})$ be the microscopic densities of the moments

$$N_1(\boldsymbol{x},t),\ \dots\ ,N_l(\boldsymbol{x},t)$$

determining together with (5.60) the second quasiequilibrium state,

$$N_i(\boldsymbol{x},t) = \int \nu_i(\boldsymbol{v}) f(\boldsymbol{v},\boldsymbol{x},t)\,\mathrm{d}\boldsymbol{v}\ . \tag{5.71}$$

The choice of the set of the moments of the first and second quasiequilibrium approximations depends on a specific problem. Further on we assume that the microscopic density $\mu \equiv 1$ corresponding to the normalization condition is always included in the list of microscopic densities of the moments of the first quasiequilibrium state. The distribution function of the first quasiequilibrium state results from solving the optimization problem,

$$H[f] = \int f(\boldsymbol{v}) \ln f(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} \to \min \tag{5.72}$$

for

$$\int \mu_i(\boldsymbol{v}) f(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = M_i, i = 1,\dots,k\ .$$

Let us denote by $M = \{M_1,\dots,M_k\}$ the moments of the first quasiequilibrium state, and by $f^*(\boldsymbol{v},M)$ let us denote the solution of the problem (5.72).

The distribution function of the second quasiequilibrium state is sought in the form,

$$f = f^*(\boldsymbol{v},M)(1+\varphi)\ . \tag{5.73}$$

Expanding the H-function (5.62) in the neighbourhood of $f^*(\boldsymbol{v},M)$ into powers of φ to second order we obtain,

$$\begin{aligned}\varDelta H(\boldsymbol{x},t) \equiv \varDelta H[f^*,\varphi] = H^*(M) &+ \int f^*(\boldsymbol{v},M) \ln f^*(\boldsymbol{v},M)\varphi(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}\\ &+ \frac{1}{2}\int f^*(\boldsymbol{v},M)\varphi^2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}\ ,\end{aligned} \tag{5.74}$$

where $H^*(M) = H[f^*(\boldsymbol{v},M)]$ is the value of the H-function in the first quasiequilibrium state.

When searching for the second quasiequilibrium state, it is necessary that the true values of the moments M coincide with their values in the first quasiequilibrium state, i.e.,

$$\begin{aligned}M_i &= \int \mu_i(\boldsymbol{v}) f^*(\boldsymbol{v},M)(1+\varphi(\boldsymbol{v}))\,\mathrm{d}\boldsymbol{v}\\ &= \int \mu_i(\boldsymbol{v}) f^*(\boldsymbol{v},M)\,\mathrm{d}\boldsymbol{v} = M_i^*,\ i = 1,\dots,k\ .\end{aligned} \tag{5.75}$$

In other words, the set of the homogeneous conditions on φ in the problem (5.68),

$$\int \mu_i(\boldsymbol{v}) f^*(\boldsymbol{v},M)\varphi(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} = 0, i = 1,\dots,k\ , \tag{5.76}$$

ensures a shift (change) of the first quasiequilibrium state only due to the new moments $N_1, \dots, N_l$. In order to take this condition into account automatically, let us introduce the following structure of a Hilbert space:

1. Define the scalar product
$$(\psi_1, \psi_2) = \int f^*(\boldsymbol{v}, M)\psi_1(\boldsymbol{v})\psi_2(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v} \ . \tag{5.77}$$
2. Let E_μ be the linear hull of the set of moment densities
$$\{\mu_1(\boldsymbol{v}), \dots, \mu_k(\boldsymbol{v})\} \ .$$
Let us construct a basis of E_μ $\{e_1(\boldsymbol{v}), \dots, e_r(\boldsymbol{v})\}$ that is orthonormal in the sense of the scalar product (5.77):
$$(e_i, e_j) = \delta_{ij} \ , \tag{5.78}$$
$i, j = 1, \dots, r$; δ_{ij} is the Kronecker delta.
3. Define a projector $\hat{P}^*$ on the first quasiequilibrium state,
$$\hat{P}^*\psi = \sum_{i=1}^{r} e_i(e_i, \psi) \ . \tag{5.79}$$
The projector $\hat{P}^*$ is orthogonal: for any pair of functions ψ_1, ψ_2,
$$(\hat{P}^*\psi_1, (\hat{1} - \hat{P}^*)\psi_2) = 0 \ , \tag{5.80}$$
where $\hat{1}$ is the unit operator. Then the condition (5.76) amounts to
$$\hat{P}^*\varphi = 0 \ , \tag{5.81}$$
and the expression for the quadratic part of the H-function (5.74) takes the form,
$$\Delta H[f^*, \varphi] = H^*(M) + (\ln f^*, \varphi) + (1/2)(\varphi, \varphi) \ . \tag{5.82}$$

Now, let us note that the function $\ln f^*$ is invariant with respect to the action of the projector $\hat{P}^*$:
$$\hat{P}^* \ln f^* = \ln f^* \ . \tag{5.83}$$

This follows directly from the solution of the problem (5.72) using of the method of Lagrange multipliers:
$$f^* = \exp \sum_{i=1}^{k} \lambda_i(M)\mu_i(\boldsymbol{v}) \ ,$$

where $\lambda_i(M)$ are Lagrange multipliers. Thus, if the condition (5.81) is satisfied, then from (5.80) and (5.83) it follows that

$$(\ln f^*, \varphi) = (\hat{P}^* \ln f^*, (\hat{1} - \hat{P}^*)\varphi) = 0 \, .$$

Condition (5.81) is satisfied automatically, if $\varDelta N_i$ are taken as follows:

$$\varDelta N_i = ((\hat{1} - \hat{P}^*)\nu_i, \varphi), i = 1, \dots, l \, . \tag{5.84}$$

Thus, the problem (5.68) of finding the second quasiequilibrium state reduces to

$$\begin{aligned} \varDelta H[f^*, \varphi] - H^*(M) = (1/2)(\varphi, \varphi) \to \min \text{ for} \\ ((\hat{1} - \hat{P}^*)\nu_i, \varphi) = \varDelta N_i, \quad i = 1, \dots, l \, . \end{aligned} \tag{5.85}$$

Note that it is not ultimatively necessary to introduce the structure of the Hilbert space. Moreover that may be impossible, since the “distribution function” and the “microscopic moment densities” are, strictly speaking, elements of different (conjugate one to another) spaces, which may be not reflexive. However, in the examples considered below the mentioned difference is not manifested.

In the remainder of this section we demonstrate how the triangle entropy method is related to Grad’s moment method.

Ten-Moment Grad Approximation

Let us take the five additive collision invariants as moment densities of the first quasiequilibrium state:

$$\mu_0 = 1; \ \mu_k = v_k \ (k = 1, 2, 3); \ \mu_4 = \frac{mv^2}{2} \, , \tag{5.86}$$

where v_k are Cartesian components of the velocity, and m is particle’s mass. Then the solution to the problem (5.72) is the local Maxwell distribution function $f^{(0)}(\boldsymbol{v}, \boldsymbol{x}, t)$:

$$f^{(0)} = n(\boldsymbol{x}, t) \left(\frac{2\pi k_{\mathrm{B}} T(\boldsymbol{x}, t)}{m} \right)^{-3/2} \exp\left\{ -\frac{m(\boldsymbol{v} - \boldsymbol{u}(\boldsymbol{x}, t))^2}{2k_{\mathrm{B}} T(\boldsymbol{x}, t)} \right\} \, , \tag{5.87}$$

where
$n(\boldsymbol{x}, t) = \int f(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v}$ is local number density,
$\boldsymbol{u}(\boldsymbol{x}, t) = n^{-1}(\boldsymbol{x}, t) \int f(\boldsymbol{v}) \boldsymbol{v} \, \mathrm{d}\boldsymbol{v}$ is the local flow density,
$T(\boldsymbol{x}, t) = \int f(\boldsymbol{v}) \frac{m(\boldsymbol{v} - \boldsymbol{u}(\boldsymbol{x}, t))^2}{3k_{\mathrm{B}} n(\boldsymbol{x}, t)} \, \mathrm{d}\boldsymbol{v}$ is the local temperature,
k_{B} is the Boltzmann constant.

Orthonormalization of the set of moment densities (5.86) with the weight (5.87) gives one of the possible orthonormal basis

$$\begin{aligned} e_0 &= \frac{5k_\mathrm{B}T - m(\boldsymbol{v}-\boldsymbol{u})^2}{(10n)^{1/2}k_\mathrm{B}T} , \\ e_k &= \frac{m^{1/2}(v_k - u_k)}{(nk_\mathrm{B}T)^{1/2}}, k = 1,2,3 , \\ e_4 &= \frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{(15n)^{1/2}k_\mathrm{B}T}. \end{aligned} \tag{5.88}$$

For the moment densities of the second quasiequilibrium state let us take,

$$\nu_{ik} = mv_i v_k,\ i,k = 1,2,3 . \tag{5.89}$$

Then

$$(\hat{1} - \hat{P}^{(0)})\nu_{ik} = m(v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}m(\boldsymbol{v}-\boldsymbol{u})^2 , \tag{5.90}$$

and, since $((\hat{1} - \hat{P}^{(0)})\nu_{ik}, (\hat{1} - \hat{P}^{(0)})\nu_{ls}) = (\delta_{il}\delta_{ks} + \delta_{kl}\delta_{is})Pk_\mathrm{B}T/m$, where $P = nk_\mathrm{B}T$ is the pressure, and $\sigma_{ik} = (f, (\hat{1} - \hat{P}^{(0)})\nu_{ik})$ is the traceless part of the stress tensor, then from (5.73), (5.86), (5.87), (5.90) we obtain the distribution function of the second quasiequilibrium state in the form

$$f = f^{(0)}\left(1 + \frac{\sigma_{ik}m}{2Pk_\mathrm{B}T}\left[(v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right]\right) \tag{5.91}$$

This is precisely the distribution function of the ten-moment Grad approximation (let us recall that here summation in two repeated indices is assumed).

Thirteen-Moment Grad Approximation

In addition to (5.86), (5.89), let us extend the list of moment densities of the second quasiequilibrium state with the functions

$$\xi_i = \frac{mv_i v^2}{2},\ i = 1,2,3 . \tag{5.92}$$

The corresponding orthogonal complements to the projection on the first quasiequilibrium state are

$$(\hat{1} - \hat{P}^{(0)})\xi_i = \frac{m}{2}(v_i - u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2 - \frac{5k_\mathrm{B}T}{m}\right) . \tag{5.93}$$

The moments corresponding to the densities $(\hat{1} - \hat{P}^{(0)})\xi_i$ are the components of the heat flux vector q_i:

$$q_i = (\varphi, (\hat{1} - \hat{P}^{(0)})\xi_i) . \tag{5.94}$$

Since

$$((\hat{1}-\hat{P}^{(0)})\xi_i,(\hat{1}-\hat{P}^{(0)})\nu_{lk})=0\ ,$$

for any i,k,l, then the constraints

$$((\hat{1}-\hat{P}^{(0)})\nu_{lk},\varphi)=\sigma_{lk},((\hat{1}-\hat{P}^{(0)})\xi_i,\varphi)=q_i$$

in the problem (5.85) are independent, and Lagrange multipliers corresponding to ξ_i are

$$\frac{1}{5n}\left(\frac{k_{\mathrm{B}}T}{m}\right)^2 q_i\ . \tag{5.95}$$

Finally, taking into account (5.86), (5.91), (5.93), (5.95), we find the distribution function of the second quasiequilibrium state in the form

$$f=f^{(0)}\left(1+\frac{\sigma_{ik}m}{2Pk_{\mathrm{B}}T}\left((v_i-u_i)(v_k-u_k)-\frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right)\right.$$
$$\left.+\frac{q_i m}{Pk_{\mathrm{B}}T}(v_i-u_i)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{5k_{\mathrm{B}}T}-1\right)\right)\ , \tag{5.96}$$

which coincides with the thirteen-moment Grad distribution function [201].

Let us remark on the thirteen-moment approximation. From (5.96) it follows that for large enough negative values of (v_i-u_i) the thirteen-moment distribution function becomes negative. This peculiarity of the thirteen-moment approximation is due to the fact that the moment density ξ_i is odd-order polynomial of v_i. In order to eliminate this difficulty, one may consider from the very beginning that in a finite volume the square of velocity of a particle does not exceed a certain value $v^2_{\max}$, which is finite owing to the finiteness of the total energy, and q_i is such that when changing to infinite volume $q_i\to 0, v^2_{\max}\to\infty$ and $q_i(v_i-u_i)(\boldsymbol{v}-\boldsymbol{u})^2$ remains finite.

On the other hand, the solution to the optimization problem (5.64) does not exist (is not normalizable), if the highest-order velocity polynomial is odd, as it is for the full 13-moment quasiequilibrium.

Approximation (5.91) yields ΔH (5.82) as follows:

$$\Delta H=H^{(0)}+n\frac{\sigma_{ik}\sigma_{ik}}{4P^2}\ , \tag{5.97}$$

while ΔH corresponding to (5.96) is,

$$\Delta H=H^{(0)}+n\frac{\sigma_{ik}\sigma_{ik}}{4P^2}+n\frac{q_k q_k\rho}{5P^3}\ , \tag{5.98}$$

where $\rho=mn$, and $H^{(0)}$ is the local equilibrium value of the H-function

$$H^{(0)}=\frac{5}{2}n\ln n-\frac{3}{2}n\ln P-\frac{3}{2}n\left(1+\ln\frac{2\pi}{m}\right)\ . \tag{5.99}$$

These expressions coincide with the corresponding expansions of the quasiequilibrium H-functions obtained by the entropy method, if microscopic moment densities of the first quasiequilibrium approximation are chosen as $1, v_i$, and $v_i v_j$, or as $1, v_i$, $v_i v_j$, and $v_i v^2$. As it was noted in [224], they differs from the H-functions obtained by the Grad method (without the maximum entropy hypothesis), and in contrast to the latter they give proper entropy balance equations.

The transition to the closed system of equations for the moments of the first and of the second quasiequilibrium approximations is accomplished by proceeding from the chain of the Maxwell moment equations, which is equivalent to the Boltzmann equation. Substituting f in the form of $f^{(0)}(1+\varphi)$ into equation (5.60), and multiplying by $\mu_i(\boldsymbol{v})$, and integrating over $\boldsymbol{v}$, we obtain

$$\begin{aligned}&\partial_t(1, \hat{P}^{(0)}\mu_i(\boldsymbol{v})) + \partial_t(\varphi(\boldsymbol{v}), \mu_i(\boldsymbol{v})) + \partial_k(v_k\varphi(\boldsymbol{v}), \mu_i(\boldsymbol{v}))\\ &+\partial_k(v_k, \mu_i(\boldsymbol{v})) = M_Q[\mu_i, \varphi]\ .\end{aligned} \tag{5.100}$$

Here

$$M_Q[\mu_i, \varphi] = \int Q(f^{(0)}(1+\varphi), f^{(0)}(1+\varphi))\mu_i(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}$$

is a “moment” (corresponding to the microscopic density) $\mu_i(\boldsymbol{v})$ with respect to the collision integral (further we term M_Q the collision moment or the scattering rate). Now, if one uses f given by equations (5.91), and (5.96) as a closure assumption, then the system (5.100) gives the ten- and thirteen-moment Grad equations, respectively, whereas only linear terms in φ should be kept when calculating M_Q.

Let us note some limitations of truncating the moment hierarchy (5.100) by means of the quasiequilibrium distribution functions (5.91) and (5.96) (or for any other closure which depends on the moments of the distribution functions only). When such closure is used, it is assumed implicitly that the scattering rates in the right hand side of (5.100) “rapidly” relax to their values determined by “slow” (quasiequilibrium) moments. Scattering rates are, generally speaking, independent variables. This peculiarity of the chain (5.100), resulting from the nonlinear character of the Boltzmann equation, distinct it essentially from the other hierarchy equations of statistical mechanics (for example, from the BBGKY chain which follows from the linear Liouville equation). Thus, equations (5.100) are not closed twice: into the left hand side of the equation for the i-th moment enters the $(i+1)$-th moment, and the right hand side contains additional variables – scattering rates.

A consequent way of closure of (5.100) should address both sets of variables (moments and scattering rates) as independent variables. The triangle entropy method enables to do this.

5.6.3 Transport Equations for Scattering Rates in the Neighbourhood of Local Equilibrium. Second and Mixed Hydrodynamic Chains

In this section we derive equations of motion for the scattering rates. It proves convenient to use the following form of the collision integral $Q(f,f)$:

$$Q(f,f)(\boldsymbol{v}) = \int w(\boldsymbol{v}'_1, v'|\boldsymbol{v}, v_1)\,(f(\boldsymbol{v}')f(\boldsymbol{v}'_1) - f(\boldsymbol{v})f(\boldsymbol{v}_1))\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}'_1\,\mathrm{d}\boldsymbol{v}_1\;, \tag{5.101}$$

where $\boldsymbol{v}$ and $\boldsymbol{v}_1$ are velocities of the two colliding particles before the collision, $\boldsymbol{v}'$ and $\boldsymbol{v}'_1$ are their velocities after the collision, w is a kernel responsible for the post-collision relations $\boldsymbol{v}'(\boldsymbol{v},\boldsymbol{v}_1)$ and $\boldsymbol{v}'_1(\boldsymbol{v},\boldsymbol{v}_1)$, momentum and energy conservation laws are taken into account in w by means of corresponding δ-functions. The kernel w has the following symmetry property with respect to its arguments:

$$w(\boldsymbol{v}'_1,\boldsymbol{v}'|\boldsymbol{v},\boldsymbol{v}_1) = w(\boldsymbol{v}'_1,\boldsymbol{v}'|\boldsymbol{v}_1,\boldsymbol{v}) = w(\boldsymbol{v}',\boldsymbol{v}'_1 \mid \boldsymbol{v}_1,\boldsymbol{v}) = w(\boldsymbol{v},\boldsymbol{v}_1 \mid \boldsymbol{v}',\boldsymbol{v}'_1)\;. \tag{5.102}$$

Let $\mu(\boldsymbol{v})$ be the microscopic density of a moment M. The corresponding scattering rate $M_Q[f,\mu]$ is defined as follows:

$$M_Q[f,\mu] = \int Q(f,f)(\boldsymbol{v})\mu(\boldsymbol{v})\,\mathrm{d}\boldsymbol{v}\;. \tag{5.103}$$

First, we should obtain transport equations for scattering rates (5.103), analogous to the moment's transport equations. Let us restrict ourselves to the case when f is represented in the form,

$$f = f^{(0)}(1+\varphi)\;, \tag{5.104}$$

where $f^{(0)}$ is local Maxwell distribution function (5.87), and all the quadratic with respect to φ terms will be neglected below. It is the linear approximation around the local equilibrium.

Since, by detailed balance,

$$f^{(0)}(\boldsymbol{v})f^{(0)}(\boldsymbol{v}_1) = f^{(0)}(\boldsymbol{v}')f^{(0)}(\boldsymbol{v}'_1) \tag{5.105}$$

for all such $(\boldsymbol{v},\,\boldsymbol{v}_1)$, $(\boldsymbol{v}',\,\boldsymbol{v}'_1)$ which are related to each other by conservation laws, we have,

$$M_Q[f^{(0)},\mu] = 0, \quad \text{for any } \mu\;. \tag{5.106}$$

Further, by virtue of conservation laws,

$$M_Q[f,\hat{P}^{(0)}\mu] = 0, \quad \text{for any } f\;. \tag{5.107}$$

From (5.105)–(5.107) it follows,

$$\begin{aligned} &M_Q[f^{(0)}(1+\varphi),\mu] = M_Q[\varphi,(\hat{1}-\hat{P}^{(0)})\mu] \\ &= -\int w(\boldsymbol{v}',\boldsymbol{v}'_1 \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) f^{(0)}(\boldsymbol{v}_1) \left\{(1-\hat{P}^{(0)})\mu(\boldsymbol{v})\right\} \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}'_1 \, \mathrm{d}\boldsymbol{v}_1 \, \mathrm{d}\boldsymbol{v} \, . \end{aligned} \tag{5.108}$$

We used notation,

$$\{\psi(\boldsymbol{v})\} = \psi(\boldsymbol{v}) + \psi(\boldsymbol{v}_1) - \psi(\boldsymbol{v}') - \psi(\boldsymbol{v}'_1) \, . \tag{5.109}$$

Also, it proves convenient to introduce the microscopic density of the scattering rate, $\mu_Q(\boldsymbol{v})$:

$$\mu_Q(\boldsymbol{v}) = \int w(\boldsymbol{v}',\boldsymbol{v}'_1 \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) \left\{(1-\hat{P}^{(0)})\mu(\boldsymbol{v})\right\} \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}'_1 \, \mathrm{d}\boldsymbol{v}_1 \, . \tag{5.110}$$

Then,

$$M_Q[\varphi,\mu] = -(\varphi,\mu_Q) \, , \tag{5.111}$$

where $(\cdot,\cdot)$ is the L_2 scalar product with the weight $f^{(0)}$ (5.87). This is a natural scalar product in the space of functions φ (5.104) (multipliers), and it is obviously related to the entropic scalar product in the space of distribution functions at the local equilibrium $f^{(0)}$, which is the L_2 scalar product with the weight $(f^{(0)})^{-1}$.

Now, we obtain transport equations for the scattering rates (5.111). We write down the time derivative of the collision integral due to the Boltzmann equation,

$$\partial_t Q(f,f)(\boldsymbol{v}) = \hat{T}Q(f,f)(\boldsymbol{v}) + \hat{R}Q(f,f)(\boldsymbol{v}) \, , \tag{5.112}$$

where

$$\begin{aligned} \hat{T}Q(f,f)(\boldsymbol{v}) &= \int w(\boldsymbol{v}',\boldsymbol{v}'_1 \mid \boldsymbol{v},\boldsymbol{v}_1) \, [f(\boldsymbol{v}) v_{1k} \partial_k f(\boldsymbol{v}_1) + f(\boldsymbol{v}_1) v_k \partial_k f(\boldsymbol{v}) \\ &\quad - f(\boldsymbol{v}') v'_{1k} \partial_k f(\boldsymbol{v}'_1) - f(\boldsymbol{v}'_1) v'_k \partial_k f(\boldsymbol{v}')] \, \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}'_1 \, \mathrm{d}\boldsymbol{v}_1 \, \mathrm{d}\boldsymbol{v} \, ; \quad (5.113) \\ \hat{R}Q(f,f)(\boldsymbol{v}) &= \int w(\boldsymbol{v}',\boldsymbol{v}'_1 \mid \boldsymbol{v},\boldsymbol{v}_1) \, [Q(f,f)(\boldsymbol{v}') f(\boldsymbol{v}'_1) + Q(f,f)(\boldsymbol{v}'_1) f(\boldsymbol{v}') \\ &\quad - Q(f,f)(\boldsymbol{v}_1) f(\boldsymbol{v}) - Q(f,f)(\boldsymbol{v}) f(\boldsymbol{v}_1)] \, \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}'_1 \, \mathrm{d}\boldsymbol{v}_1 \, \mathrm{d}\boldsymbol{v} \, . \quad (5.114) \end{aligned}$$

Using the representation,

$$\begin{aligned} &\partial_k f^{(0)}(\boldsymbol{v}) = A_k(\boldsymbol{v}) f^{(0)}(\boldsymbol{v}) \, ; \\ &A_k(\boldsymbol{v}) = \partial_k \ln(nT^{-3/2}) + \frac{m}{k_{\mathrm{B}}T}(v_i - u_i)\partial_k u_i + \frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T} \partial_k \ln T \, , \end{aligned} \tag{5.115}$$

and after some simple transformations using the relation

$$\{A_k(\boldsymbol{v})\} = 0 \, , \tag{5.116}$$

in linear with respect to φ deviation from $f^{(0)}$ (5.104), we obtain in (5.112):

$$\begin{aligned}
\hat{T}Q(f,f)(\boldsymbol{v}) &= \partial_k \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) \left\{ v_k \varphi(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1 \\
&\quad + \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) \left\{ v_k A_k(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}_1 \\
&\quad + \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) f^{(0)}(\boldsymbol{v}_1) \left[\varphi(\boldsymbol{v}) A_k(\boldsymbol{v}_1)(v_{1k} - v_k) \right. \\
&\quad + \varphi(\boldsymbol{v}_1) A_k(\boldsymbol{v})(v_k - v_{1k}) + \varphi(\boldsymbol{v}') A_k(\boldsymbol{v}_1')(v_k' - v_{1k}') \\
&\quad \left. + \varphi(\boldsymbol{v}_1') A_k(\boldsymbol{v}')(v_{1k}' - v_k') \right] \mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1 \; ; \qquad (5.117) \\
\hat{R}Q(f,f)(\boldsymbol{v}) &= \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) f^{(0)}(\boldsymbol{v}_1) \left\{ \xi(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1 \; ; \\
\xi(\boldsymbol{v}) &= \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) \left\{ \varphi(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1 \; ; \qquad (5.118) \\
\partial_t Q(f,f)(\boldsymbol{v}) & \qquad (5.119) \\
&= -\partial_t \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) f^{(0)}(\boldsymbol{v}_1) \left\{ \varphi(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}_1 \; .
\end{aligned}$$

Let us use two identities:

1. From the conservation laws it follows

$$\left\{ \varphi(\boldsymbol{v}) \right\} = \left\{ (\hat{1} - \hat{P}^{(0)}) \varphi(\boldsymbol{v}) \right\} \; . \qquad (5.120)$$

2. The symmetry property of the kernel w (5.102) which follows from (5.102), (5.105)

$$\begin{aligned}
&\int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) g_1(\boldsymbol{v}) \left\{ g_2(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}_1 \,\mathrm{d}\boldsymbol{v} \qquad (5.121) \\
&= \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) g_2(\boldsymbol{v}) \left\{ g_1(\boldsymbol{v}) \right\} \mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}_1 \,\mathrm{d}\boldsymbol{v} \; .
\end{aligned}$$

It is valid for any two functions g_1, g_2 ensuring existence of the integrals, and also using the first identity.

Now, multiplying (5.117)–(5.120) by the microscopic moment density $\mu(\boldsymbol{v})$, performing integration over $\boldsymbol{v}$ (and using identities (5.120), (5.122)) we obtain the required transport equation for the scattering rate in the linear neighborhood of the local equilibrium:

$$\begin{aligned}
&-\partial_t \Delta M_Q[\varphi,\mu] \equiv -\partial_t(\varphi,\mu_Q) \\
&= (v_k A_k(\boldsymbol{v}), \mu_Q((\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v}))) \\
&+ \partial_k(\varphi(\boldsymbol{v}) v_k, \mu_Q((\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v}))) + \int w(\boldsymbol{v}',\boldsymbol{v}_1' \mid \boldsymbol{v},\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}) \\
&\times \left\{ (\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v}) \right\} A_k(\boldsymbol{v}_1)(v_{1k} - v_k) \varphi(\boldsymbol{v}) \,\mathrm{d}\boldsymbol{v}' \,\mathrm{d}\boldsymbol{v}_1' \,\mathrm{d}\boldsymbol{v}_1 d\boldsymbol{v} \\
&+ \left(\xi(\boldsymbol{v}), \mu_Q \left((\hat{1} - \hat{P}^{(0)})\mu(\boldsymbol{v}) \right) \right) \; . \qquad (5.122)
\end{aligned}$$

The chain of equations (5.122) for scattering rates is a counterpart of the hydrodynamic moment chain (5.100). Below we call (5.122) the *second chain*, and (5.100) – the *first chain*. Equations of the second chain are coupled in the same way as the first one: the last term in the right part of (5.91) $(\xi, \mu_Q((\hat{1}-\hat{P}^{(0)})\mu))$ depends on the whole totality of moments and scattering rates and may be treated as a new variable. Therefore, generally speaking, we have an infinite sequence of chains of increasingly higher orders. Only in the case of a special choice of the collision model – Maxwell potential $U = -\kappa r^{-4}$ – this sequence degenerates: the second and the higher-order chains are equivalent to the first (see below).

Let us restrict our consideration to the first and second hydrodynamic chains. Then a deviation from the local equilibrium state and transition to a closed macroscopic description may be performed in three different ways for the microscopic moment density $\mu(\boldsymbol{v})$. First, one can specify the moment $\hat{M}[\mu]$ and perform a closure of the chain (5.100) by the triangle method given in previous subsections. This leads to Grad's moment method. Second, one can specify scattering rate $\hat{M}_Q[\mu]$ and perform a closure of the second hydrodynamic chain (5.91). Finally, one can consider simultaneously both $\hat{M}[\mu]$ and $\hat{M}_Q[\mu]$ (mixed chain). Quasiequilibrium distribution functions corresponding to the last two variants will be constructed in the following subsection. The hard spheres model (H.S.) and Maxwell's molecules (M.M.) will be considered.

5.6.4 Distribution Functions of the Second Quasiequilibrium Approximation for Scattering Rates

First Five Moments and Collision Stress Tensor

Elsewhere below the local equilibrium $f^{(0)}$(5.87) is chosen as the first quasi-equilibrium approximation.

Let us choose $\nu_{ik} = m v_i v_k$(5.89) as the microscopic density $\mu(\boldsymbol{v})$ of the second quasiequilibrium state. Let us write down the corresponding scattering rate (collision stress tensor) Δ_{ik} in the form,

$$\Delta_{ik} = -(\varphi, \nu_{Qik}) \,, \tag{5.123}$$

where

$$\nu_{Qik}(\boldsymbol{v}) = m \int w(\boldsymbol{v}', \boldsymbol{v}_1' \mid \boldsymbol{v}_1, \boldsymbol{v}) f^{(0)}(\boldsymbol{v}_1) \times \left\{ (v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2 \right\} \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}_1' \, \mathrm{d}\boldsymbol{v}_1 \tag{5.124}$$

is the microscopic density of the scattering rate Δ_{ik}.

The quasiequilibrium distribution function of the second quasiequilibrium approximation for fixed scattering rates (5.123) is determined as the solution to the problem

$$\begin{aligned} &(\varphi, \varphi) \to \min \ \text{ for} \\ &(\varphi, \nu_{Qik}) = -\Delta_{ik} \ . \end{aligned} \tag{5.125}$$

The method of Lagrange multipliers yields

$$\begin{aligned} &\varphi(\boldsymbol{v}) = \lambda_{ik} \nu_{Qik}(\boldsymbol{v}) \ , \\ &\lambda_{ik}(\nu_{Qik}, \nu_{Qls}) = \Delta_{ls} \ , \end{aligned} \tag{5.126}$$

where λ_{ik} are the Lagrange multipliers.

In the examples of collision models considered below (and in general, for centrally symmetric interactions) ν_{Qik} is of the form

$$\nu_{Qik}(\boldsymbol{v}) = (\hat{1} - \hat{P}^{(0)}) \nu_{ik}(\boldsymbol{v}) \Phi((\boldsymbol{v} - \boldsymbol{u})^2) \ , \tag{5.127}$$

where $(\hat{1} - \hat{P}^{(0)})\nu_{ik}$ is determined by relationship (5.90) only, and function Φ depends only on the absolute value of the peculiar velocity $(\boldsymbol{v} - \boldsymbol{u})$. Then

$$\begin{aligned} \lambda_{ik} &= r \Delta_{ik} \ ; \\ r^{-1} &= (2/15) \left(\Phi^2((\boldsymbol{v} - \boldsymbol{u})^2), (\boldsymbol{v} - \boldsymbol{u})^4 \right) \ , \end{aligned} \tag{5.128}$$

and the distribution function of the second quasiequilibrium approximation for scattering rates (5.123) is given by the expression

$$f = f^{(0)}(1 + r \Delta_{ik} \mu_{Qik}) \ . \tag{5.129}$$

The form of the function $\Phi((\boldsymbol{v} - \boldsymbol{u})^2)$, and the value of the parameter r are determined by the model of particle's interaction. In the Appendix to this example, they are found for hard spheres and Maxwell molecules models (see (5.187)–(5.192)). The distribution function (5.129) is given by the following expressions:

For Maxwell molecules:

$$\begin{aligned} f &= f^{(0)} \\ &\times \left\{ 1 + \mu_0^{\text{M.M.}} m (2P^2 k_{\text{B}} T)^{-1} \Delta_{ik} \left((v_i - u_i)(v_k - u_k) - \frac{1}{3} \delta_{ik} (\boldsymbol{v} - \boldsymbol{u})^2 \right) \right\} \ , \\ \mu_0^{\text{M.M.}} &= \frac{k_{\text{B}} T \sqrt{2m}}{3\pi A_2(5) \sqrt{\kappa}} \ , \end{aligned} \tag{5.130}$$

where $\mu_0^{\text{M.M.}}$ is viscosity coefficient in the first approximation of the Chapman-Enskog method (it is exact in the case of Maxwell molecules), κ is a force constant, $A_2(5)$ is a number, $A_2(5) \approx 0.436$ (see [70]);

For the hard spheres model:

$$\begin{aligned} f &= f^{(0)} \\ &\times \left\{ 1 + \frac{2\sqrt{2}\tilde{r} m \mu_0^{\mathrm{H.S.}}}{5P^2 k_{\mathrm{B}} T} \Delta_{ik} \int_{+1}^{-1} \exp\left\{ -\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T} y^2 \right\} (1-y^2)(1+y^2) \right. \\ &\times \left. \left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}(1-y^2) + 2 \right) \mathrm{d}y \left((v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2 \right) \right\} , \\ \mu_0^{\mathrm{H.S.}} &= (5\sqrt{k_{\mathrm{B}} T m})/(16\sqrt{\pi}\sigma^2) , \end{aligned} \tag{5.131}$$

where $\tilde{r}$ is a number represented as follows:

$$\begin{aligned} \tilde{r}^{-1} &= \frac{1}{16} \int_{-1}^{+1} \int_{-1}^{+1} \alpha^{-11/2} \beta(y)\beta(z)\gamma(y)\gamma(z) \\ &\times (16\alpha^2 + 28\alpha(\gamma(y)+\gamma(z)) + 63\gamma(y)\gamma(z)) \,\mathrm{d}y\,\mathrm{d}z , \\ \alpha &= 1 + y^2 + z^2, \qquad \beta(y) = 1 + y^2, \qquad \gamma(y) = 1 - y^2 . \end{aligned} \tag{5.132}$$

Numerical value of $\tilde{r}^{-1}$ is 5.212, to third decimal point accuracy.

In the mixed description, the distribution function of the second quasiequilibrium approximation under fixed values of the moments and of the scattering rates corresponding to the microscopic density (5.89) is determined as a solution of the problem

$$\begin{aligned} &(\varphi, \varphi) \to \min \quad \text{for} \\ &((\hat{1} - \hat{P}^{(0)})\nu_{ik}, \varphi) = \sigma_{ik} , \\ &(\nu_{Qik}, \varphi) = \Delta_{ik} . \end{aligned} \tag{5.133}$$

Taking into account the relation (5.127), we obtain the solution of the problem (5.133) in the form,

$$\varphi(\boldsymbol{v}) = (\lambda_{ik}\Phi((\boldsymbol{v}-\boldsymbol{u})^2) + \beta_{ik})((v_i - u_i)(v_k - u_k) - (1/3)\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2) . \tag{5.134}$$

Lagrange multipliers λ_{ik}, β_{ik} are determined from the system of linear equations,

$$\begin{aligned} m s^{-1} \lambda_{ik} + 2P k_{\mathrm{B}} T m^{-1} \beta_{ik} &= \sigma_{ik} , \\ m r^{-1} \lambda_{ik} + m s^{-1} \beta_{ik} &= \Delta_{ik} , \end{aligned} \tag{5.135}$$

where

$$s^{-1} = (2/15)(\Phi((\boldsymbol{v}-\boldsymbol{u})^2), (\boldsymbol{v}-\boldsymbol{u})^4) . \tag{5.136}$$

If the solvability condition of the system (5.135) is satisfied,

$$D = m^2 s^{-2} - 2P k_{\mathrm{B}} T r^{-1} \neq 0 , \tag{5.137}$$

then the distribution function of the second quasiequilibrium approximation exists and takes the form

$$\begin{aligned} f = f^{(0)} \{&1 + (m^2 s^{-2} - 2Pk_{\mathrm{B}}Tr^{-1})^{-1} \\ &\times[(ms^{-1}\sigma_{ik} - 2Pk_{\mathrm{B}}Tm^{-1}\mathit{\Delta}_{ik})\mathit{\Phi}((\boldsymbol{v}-\boldsymbol{u})^2) \\ &+ (ms^{-1}\mathit{\Delta}_{ik} - mr^{-1}\sigma_{ik})]((v_i-u_i)(v_k-u_k) - (1/3)\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2)\} \ . \end{aligned} \tag{5.138}$$

The condition (5.137) means independence of the set of moments σ_{ik} from the scattering rates $\mathit{\Delta}_{ik}$. If this condition is not satisfied, then the scattering rates $\mathit{\Delta}_{ik}$ can be represented in the form of linear combinations of σ_{ik} (with coefficients depending on the hydrodynamic moments). Then the closed by means of (5.129) equations of the second chain are equivalent to the ten moment Grad equations, while the mixed chain does not exist. This happens only in the case of Maxwell molecules. Indeed, in this case

$$s^{-1} = 2P^2 k_{\mathrm{B}}T(m^2\mu_0^{\mathrm{M.M.}})^{-1}; D = 0 \ .$$

The transformation changing $\mathit{\Delta}_{ik}$ to σ_{ik} is

$$\mu_0^{\mathrm{M.M.}}\mathit{\Delta}_{ik}P^{-1} = \sigma_{ik} \ . \tag{5.139}$$

For hard spheres:

$$s^{-1} = \frac{5P^2k_{\mathrm{B}}T}{4\sqrt{2}\mu_0^{\mathrm{H.S.}}m^2}\cdot\tilde{s}^{-1}, \ \tilde{s}^{-1} = \int_{-1}^{+1}\gamma(y)(\beta(y))^{-7/2}\left(\beta(y)+\frac{7}{4}\gamma(y)\right)\mathrm{d}y \ . \tag{5.140}$$

The numerical value of $\tilde{s}^{-1}$ is 1.115 to third decimal point. The condition (5.136) takes the form,

$$D = \frac{25}{32}\left(\frac{P^2k_{\mathrm{B}}T}{m\mu_0^{\mathrm{H.S.}}}\right)^2(\tilde{s}^{-2} - \tilde{r}^{-1}) \neq 0 \ . \tag{5.141}$$

Consequently, for the hard spheres model the distribution function of the second quasiequilibrium approximation of the mixed chain exists and is determined by the expression

$$\begin{aligned} f = f^{(0)}\{&1 + m(4Pk_{\mathrm{B}}T(\tilde{s}^{-2}-\tilde{r}^{-1}))^{-1} \\ &\times\left[\left(\sigma_{ik}\tilde{s}^{-1} - \frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\mathit{\Delta}_{ik}\right)\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\right. \\ &\times(1-y^2)(1+y^2)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}(1-y^2)+2\right)\mathrm{d}y \\ &\left.+2\left(\tilde{s}^{-1}\cdot\frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\mathit{\Delta}_{ik} - \tilde{r}^{-1}\sigma_{ik}\right)\right] \\ &\left.\times((v_i-u_i)(v_k-u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2)\right\} \ . \end{aligned} \tag{5.142}$$

First Five Moments, Collision Stress Tensor, and Collision Heat Flux Vector

Distribution function of the second quasiequilibrium approximation which takes into account the collision heat flux vector Q is constructed in a similar way. The microscopic density ξ_{Qi} is

$$\xi_{Qi}(\boldsymbol{v}) = \int w(\boldsymbol{v}', \boldsymbol{v}_1' \mid \boldsymbol{v}, \boldsymbol{v}_1) f^{(0)}(\boldsymbol{v}_1) \left\{ (\hat{1} - \hat{P}^{(0)}) \frac{v_i^2 v}{2} \right\} \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{v}_1' \, \mathrm{d}\boldsymbol{v}_1 \; . \tag{5.143}$$

The desired distribution functions are the solutions to the following optimization problems: for the second chain it is the solution to the problem (5.125) with the additional constraints,

$$m(\varphi, \xi_{Qi}) = Q_i \; . \tag{5.144}$$

For the mixed chain, the distribution functions is the solution to the problem (5.133) with additional conditions,

$$m(\varphi, \xi_{Qi}) = Q_i \; , \tag{5.145}$$

$$m(\varphi, (\hat{1} - \hat{P}^{(0)})\xi_i) = q_i \; . \tag{5.146}$$

Here $\xi_i = v_i v^2/2$ (see (5.92)). In the Appendix functions ξ_{Qi} are found for Maxwell molecules and hard spheres (see (5.192)–(5.197)). Since

$$\begin{aligned} &(\xi_{Qi}, \nu_{Qkj}) = ((\hat{1} - \hat{P}^{(0)})\xi_i, \nu_{Qkj}) \\ &= (\xi_{Qi}, (\hat{1} - \hat{P}^{(0)})\nu_{kj}) = ((\hat{1} - \hat{P}^{(0)})\xi_i, (\hat{1} - \hat{P}^{(0)})\nu_{kj}) = 0 \; , \end{aligned} \tag{5.147}$$

the conditions (5.144) are linearly independent from the constraints of the problem (5.125), and the conditions (5.146) do not depend on the constraints of the problem (5.133).

Distribution function of the second quasiequilibrium approximation of the second chain for fixed $\mathit{\Delta}_{ik}, Q_i$ is of the form,

$$f = f^{(0)}(1 + r\mathit{\Delta}_{ik}\nu_{Qik} + \eta Q_i \xi_{Qi}) \; . \tag{5.148}$$

The parameter η is determined by the relation

$$\eta^{-1} = (1/3)(\xi_{Qi}, \xi_{Qi}) \; . \tag{5.149}$$

According to (5.196), for Maxwell molecules

$$\eta = \frac{9m^3(\mu_0^{\mathrm{M.M.}})^2}{10P^3(k_{\mathrm{B}}T)^2} \; , \tag{5.150}$$

and the distribution function (5.148) is

$$
\begin{aligned}
f &= f^{(0)} \\
&\quad\times \left\{1 + \mu_0^{\mathrm{M.M.}} m (2P^2 k_{\mathrm{B}} T)^{-1} \varDelta_{ik} ((v_i - u_i)(v_k - u_k) - (1/3)\delta_{ik} (\boldsymbol{v} - \boldsymbol{u})^2)\right. \\
&\quad\left. + \mu_0^{\mathrm{M.M.}} m (P^2 k_{\mathrm{B}} T)^{-1} (v_i - u_i) \left(\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{5 k_{\mathrm{B}} T} - 1 \right) \right\} . \qquad (5.151)
\end{aligned}
$$

For hard spheres (see Appendix)

$$
\eta = \tilde{\eta} \frac{64 m^3 (\mu_0^{\mathrm{H.S.}})^2}{125 P^3 (k_{\mathrm{B}} T)^2} , \qquad (5.152)
$$

where η is a number equal to 16.077 to third decimal point accuracy.

The distribution function (5.148) for hard spheres takes the form

$$
\begin{aligned}
f = f^{(0)} &\left\{ 1 + \frac{2\sqrt{2} \tilde{r} m \mu_0^{\mathrm{H.S.}}}{5 P^2 k_{\mathrm{B}} T} \varDelta_{ik} \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} y^2 \right) \beta(y) \gamma(y) \right. \\
&\times \left(\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} \gamma(y) + 2 \right) \mathrm{d}y \left((v_i - u_i)(v_k - u_k) - \frac{1}{3} \delta_{ik} (\boldsymbol{v} - \boldsymbol{u})^2 \right) \\
&+ \frac{2\sqrt{2} \tilde{\eta} m^3 \mu_0^{\mathrm{H.S.}}}{25 P^2 (k_{\mathrm{B}} T)^2} Q_i \left[(v_i - u_i) \left((\boldsymbol{v} - \boldsymbol{u})^2 - \frac{5 k_{\mathrm{B}} T}{m} \right) \right. \\
&\times \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} y^2 \right) \beta(y) \gamma(y) \left(\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} \gamma(y) + 2 \right) \mathrm{d}y \\
&+ (v_i - u_i)(\boldsymbol{v} - \boldsymbol{u})^2 \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} y^2 \right) \beta(y) \gamma(y) \\
&\left.\left. \times \left(\sigma(y) \frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2 k_{\mathrm{B}} T} + \delta(y) \right) \mathrm{d}y \right] \right\} . \qquad (5.153)
\end{aligned}
$$

The functions $\beta(y), \gamma(y), \sigma(y)$ and $\delta(y)$ are

$$
\beta(y) = 1 + y^2 ,\ \gamma(y) = 1 - y^2 ,\ \sigma(y) = y^2 (1 - y^2) ,\ \delta(y) = 3y^2 - 1 . \qquad (5.154)
$$

The condition of existence of the second quasiequilibrium approximation of the mixed chain (5.137) should be supplemented with the requirement

$$
R = m^2 \tau^{-2} - \frac{5 P (k_{\mathrm{B}} T)^2}{2m} \eta^{-1} \neq 0 . \qquad (5.155)
$$

Here

$$
\tau^{-1} = \frac{1}{3} \left((\hat{1} - \hat{P}^{(0)}) \frac{v_i^2 v}{2}, \xi_{Qi}(\boldsymbol{v}) \right) . \qquad (5.156)
$$

For Maxwell molecules

$$
\tau^{-1} = \left(5 P^2 k_B^2 T^2 \right) / \left(3 \mu_0^{\mathrm{M.M.}} m^3 \right) ,
$$

and the solvability condition (5.155) is not satisfied. Distribution function of the second quasiequilibrium approximation of mixed chain does not exist for Maxwell molecules. The variables Q_i are changed to q_i by the transformation

$$3\mu_0^{\mathrm{M.M.}} Q_i = 2Pq_i \ . \tag{5.157}$$

For hard spheres,

$$\tau^{-1} = \tilde{\tau}^{-1} = \frac{25(Pk_{\mathrm{B}}T)^2}{8\sqrt{2}m^3\mu_0^{\mathrm{H.S.}}} \ , \tag{5.158}$$

where

$$\begin{aligned}\tilde{\tau}^{-1} = \frac{1}{8}\int_{-1}^{+1} & \beta^{-9/2}(y)\gamma(y)\{63(\gamma(y)+\sigma(y)) \\ & +7\beta(y)(4-10\gamma(y)+2\delta(y)-5\sigma(y)) \\ & +\beta^2(y)(25\gamma(y)-10\delta(y)-40)+20\beta^3(y)\}\,\mathrm{d}y \ .\end{aligned} \tag{5.159}$$

The numerical value of $\tilde{\tau}^{-1}$ is about 4.322. Then the condition (5.155) is verified:

$$R \approx 66m^{-4}(Pk_{\mathrm{B}}T)^4(\mu_0^{\mathrm{H.S.}})^2 \ .$$

Finally, for the fixed values of $\sigma_{ik}, \Delta_{ik}, q_i$ and Q_i the distribution function of the second quasiequilibrium approximation of the second chain for hard spheres is of the form,

$$\begin{aligned} f = f^{(0)} \Bigg\{ & 1 + \frac{m}{4Pk_{\mathrm{B}}T}(\tilde{s}^{-2}-\tilde{r}^{-1})^{-1} \\ & \times \left[\left(\tilde{s}^{-1}\sigma_{ik} - \frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\Delta_{ik} \right) \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2 \right) \right. \\ & \left. \times\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2 \right)\mathrm{d}y + 2\left(\tilde{s}^{-1}\frac{8\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\Delta_{ik} - \tilde{r}^{-1}\sigma_{ik} \right) \right] \\ & \times \left((v_i-u_i)(v_k-u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2 \right) \\ & + \frac{m^2}{10(Pk_{\mathrm{B}}T)^2}(\tilde{\tau}^{-2}-\tilde{\eta}^{-1})^{-1} \left[\left(\tilde{\tau}^{-1}q_i - \frac{4\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}Q_i \right) \right. \\ & \times \left((v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2 - \frac{5k_{\mathrm{B}}T}{m} \right) \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2 \right) \right. \\ & \times\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y)+2 \right)\mathrm{d}y + (v_i-u_i)(\boldsymbol{v}-\boldsymbol{u})^2 \\ & \left. \times \int_{-1}^{+1} \exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2 \right)\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}\sigma(y)+\delta(y) \right)\mathrm{d}y \right) \\ & \left. + \ 2\left(\frac{4\sqrt{2}}{5P}\mu_0^{\mathrm{H.S.}}\tilde{\tau}^{-1}Q_i - \tilde{\eta}^{-1}q_i \right)(v_i-u_i)\left((\boldsymbol{v}-\boldsymbol{u})^2 - \frac{5k_{\mathrm{B}}T}{m} \right) \right] \Bigg\} \ . \end{aligned} \tag{5.160}$$

Thus, the expressions (5.130), (5.131), (5.142), (5.151), (5.153) and (5.160) give distribution functions of the second quasiequilibrium approximation of the second and mixed hydrodynamic chains for Maxwell molecules and hard spheres. They are analogues of ten- and thirteen-moment Grad approximations (5.91), (5.95).

The next step is to close the second and mixed hydrodynamic chains by means of the found distribution functions.

5.6.5 Closure of the Second and Mixed Hydrodynamic Chains

Second Chain, Maxwell Molecules

The distribution function of the second quasiequilibrium approximation under fixed $\varDelta_{ik}$ for Maxwell molecules (5.130) presents the simplest example of the closure of the first (5.99) and second (5.122) hydrodynamic chains. With the help of it, we obtain from (5.99) the following transport equations for the moments of the first (local equilibrium) approximation:

$$\begin{aligned}
&\partial_t\rho + \partial_i(u_i\rho) = 0\ ;\\
&\rho(\partial_t u_k + u_i\partial_i u_k) + \partial_k P + \partial_i(P^{-1}\mu_0^{\mathrm{M.M.}}\varDelta_{ik}) = 0\ ;\\
&\frac{3}{2}(\partial_t P + u_i\partial_i P) + \frac{5}{2}P\partial_i u_i + P^{-1}\mu_0^{\mathrm{M.M.}}\varDelta_{ik}\partial_i u_k = 0\ . \qquad (5.161)
\end{aligned}$$

Now, let us from the scattering rate transport chain (5.122) find an equation for $\varDelta_{ik}$ which closes the system (5.123). Substituting (5.130) into (5.122), we obtain after some computation:

$$\begin{aligned}
&\partial_t\varDelta_{ik} + \partial_s(u_s\varDelta_{ik}) + \varDelta_{is}\partial_s u_k + \varDelta_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\varDelta_{ls}\partial_s u_l\\
&+P^2(\mu_0^{\mathrm{M.M.}})^{-1}\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right)\\
&+P(\mu_0^{\mathrm{M.M.}})^{-1}\varDelta_{ik} + \varDelta_{ik}\partial_s u_s = 0\ . \qquad (5.162)
\end{aligned}$$

For comparison, let us give ten-moment Grad equations obtained when closing the chain (5.99) by the distribution functions (5.91):

$$\begin{aligned}
&\partial_t\rho + \partial_i(u_i\rho) = 0\ ;\\
&\rho(\partial_t u_k + u_i\partial_i u_k) + \partial_k P + \partial_i\sigma_{ik} = 0\ ;\\
&\frac{3}{2}(\partial_t P + u_i\partial_i P) + \frac{5}{2}P\partial_i u_i + \sigma_{ik}\partial_i u_k = 0\ ; \qquad (5.163)\\
&\partial_t\sigma_{ik} + \partial_s(u_s\sigma_{ik}) + P\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right)\\
&+\sigma_{is}\partial_s u_k + \sigma_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\sigma_{ls}\partial_s u_l + P(\mu_0^{\mathrm{M.M.}})^{-1}\sigma_{ik} = 0\ . \qquad (5.164)
\end{aligned}$$

Using the explicit form of $\mu_0^{\text{M.M.}}$ (5.130), it is easy to verify that the transformation (5.139) maps the systems (5.161), (5.162) and (5.163) into one another. This is a consequence of the degeneration of the mixed hydrodynamic chain which was already discussed. The systems (5.161), (5.162) and (5.163) are essentially equivalent. These specific properties of Maxwell molecules result from the fact that for them the microscopic densities $(\hat{1}-\hat{P}^{(0)})v_i v_k$ and $(\hat{1}-\hat{P}^{(0)})v_i v^2$ are eigen functions of the linearized collision integral.

Second Chain, Hard Spheres

We now turn our attention to the closure of the second and of the mixed hydrodynamic chains for the hard spheres model. Substituting the distribution function (5.131) into (5.99) and (5.122), we obtain an analogue of the systems (5.161) and (5.162) (second chain, hard spheres):

$$
\begin{aligned}
&\partial_t \rho + \partial_i (u_i \rho) = 0\,; \qquad\qquad (5.165)\\
&\rho(\partial_t u_k + u_i \partial_i u_k) + \partial_k P + \tilde{r}\tilde{s}^{-1}\cdot\frac{8\sqrt{2}}{5}\partial_i(\mu_0^{\text{H.S.}} P^{-1}\Delta_{ik}) = 0\,;\\
&\frac{3}{2}(\partial_t P + u_i\partial_i P) + \frac{5}{2}P\partial_i u_i + \tilde{r}\tilde{s}^{-1}\cdot\frac{8\sqrt{2}}{5}\mu_0^{\text{H.S.}} P^{-1}\Delta_{ik}\partial_i u_k = 0\,;\\
&\partial_t \Delta_{ik} + \partial_s(u_s\Delta_{ik}) + \tilde{r}\tilde{a}_1(\partial_s u_s)\Delta_{ik} + \frac{5\tilde{s}^{-1}P^2}{8\sqrt{2}\mu_0^{\text{H.S.}}}\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right)\\
&+\tilde{r}(\tilde{a}_1+\tilde{a}_2)\left(\Delta_{is}\partial_s u_k + \Delta_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\Delta_{ls}\partial_s u_l\right)\\
&+\tilde{r}(\tilde{a}_1+\tilde{a}_3)\left(\Delta_{is}\partial_k u_s + \Delta_{ks}\partial_i u_s - \frac{2}{3}\delta_{ik}\Delta_{ls}\partial_s u_l\right) + (P\hat{r}\tilde{a}_0/\mu_0^{\text{H.S.}})\Delta_{ik} = 0\,.
\end{aligned}
$$

The dimensionless parameters $\tilde{a}_0, \tilde{a}_1, \tilde{a}_2$ and $\tilde{a}_3$ are determined by the quadratures

$$
\begin{aligned}
\tilde{a}_1 = {} & \frac{1}{16}\int_{-1}^{+1}\int_{-1}^{+1}\beta(y)\beta(z)\gamma^2(z)\gamma(y)\alpha^{-13/2}(y,z)\\
&\times\{99\gamma(y)\gamma(z)(\gamma(z)-1) + 18\alpha(y,z)(2\gamma(z)(\gamma(z)-1)\\
&+4\gamma(y)(4\gamma(z)-3)) + 8\alpha^2(y,z)(4\gamma(z)-3)\}\,\mathrm{d}y\,\mathrm{d}z\,;\\
\tilde{a}_2 = {} & \frac{1}{16}\int_{-1}^{+1}\int_{-1}^{+1}\beta(y)\beta(z)\gamma(y)\gamma^2(z)\alpha^{-11/2}(y,z)\{63\gamma(y)\gamma(z)\\
&+14\alpha(y,z)(3\gamma(y)+2\gamma(z)) + 24\alpha^2(y,z)\}\,\mathrm{d}y\,\mathrm{d}z\,;\\
\tilde{a}_3 = {} & \frac{1}{16}\int_{-1}^{+1}\int_{-1}^{+1}\alpha^{-11/2}(y,z)\beta(y)\beta(z)\gamma(y)\gamma(z)\\
&\times\{63\gamma(y)\gamma(z)(\gamma(z)-1) + 14(2\gamma(z)(\gamma(z)-1)\\
&+\gamma(y)(3\gamma(z)-2))\alpha(y,z) + 8\alpha^2(y,z)(3\gamma(z)-2)\}dydz\,; \qquad (5.166)
\end{aligned}
$$

$$
\begin{aligned}
\tilde{a}_0 \approx\ & \frac{1}{1536\sqrt{2}} \int_{-1}^{+1} \int_{-1}^{+1} \int_{-1}^{+1} (\psi(x,y,z))^{-13/2} \beta(x)\beta(y)\beta(z) \\
& \times \gamma(x)\gamma(y)\gamma(z)\{10395\gamma(x)\gamma(y)\gamma(z) + 3780\psi(x,y,z) \\
& \times (\gamma(x)\gamma(y) + \gamma(x)\gamma(z) + \gamma(y)\gamma(z)) + 1680\psi^2(x,y,z) \\
& \times (\gamma(x) + \gamma(y) + \gamma(z)) + 960\psi^3(x,y,z)\}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\ ; \\
& \psi(x,y,z) = 1 + x^2 + y^2 + z^2\ .
\end{aligned}
\tag{5.167}
$$

Their numerical values are $\tilde{a}_1 \approx 0.36$, $\tilde{a}_2 \approx 5.59$, $\tilde{a}_3 \approx 0.38$, $\tilde{a}_0 \approx 2.92$ to second decimal point.

Mixed Chain

The closure of the mixed hydrodynamic chain with the functions (5.142) gives the following modification of the system of equations (5.166):

$$
\begin{aligned}
& \partial_t \rho + \partial_i(u_i \rho) = 0\ ; \\
& \rho(\partial_t u_k + u_i \partial_i u_k) + \partial_k P + \partial_i \sigma_{ik} = 0\ ; \\
& \frac{3}{2}(\partial_t P + u_i \partial_i P) + \frac{5}{2} P \partial_i u_i + \sigma_{ik} \partial_i u_k = 0\ ; \\
& \partial_t \sigma_{ik} + \partial_s(u_s \sigma_{ik}) + P\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right) \\
& + \sigma_{is}\partial_s u_k + \sigma_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\sigma_{ls}\partial_s u_l + \mathit{\Delta}_{ik} = 0\ ; \\
& \partial_t \mathit{\Delta}_{ik} + \partial_s(u_s \mathit{\Delta}_{ik}) + \frac{5P^2}{\tilde{s}8\sqrt{2}\mu_0^{\text{H.S.}}}\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right) \\
& + \frac{5P}{4\sqrt{2}\mu_0^{\text{H.S.}}(\tilde{s}^{-2} - \tilde{r}^{-1})}\left\{\frac{\tilde{a}_1}{2}(\partial_s u_s)\alpha_{ik}\right. \\
& + \frac{1}{2}(\tilde{a}_1 + \tilde{a}_2)\left(\alpha_{is}\partial_s u_k + \alpha_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\alpha_{ls}\partial_s u_l\right) \\
& + \frac{1}{2}(\tilde{a}_1 + \tilde{a}_3)\left(\alpha_{is}\partial_k u_s + \alpha_{ks}\partial_i u_s - \frac{2}{3}\delta_{ik}\alpha_{ls}\partial_s u_l\right) \\
& + \tilde{b}_1(\partial_s u_s)\beta_{ik} + (\tilde{b}_1 + \tilde{b}_2)\left(\beta_{is}\partial_s u_k + \beta_{ks}\partial_s u_i - \frac{2}{3}\delta_{ik}\beta_{ls}\partial_s u_l\right) \\
& \left. + (\tilde{b}_1 + \tilde{b}_3)\left(\beta_{is}\partial_k u_s + \beta_{ks}\partial_i u_s - \frac{2}{3}\delta_{ik}\beta_{ls}\partial_s u_l\right)\right\} \\
& + \frac{5P^2}{8\sqrt{2}(\mu_0^{\text{H.S.}})^2(\tilde{s}^{-2} - \tilde{r}^{-1})}\left\{\frac{5}{8\sqrt{2}\tilde{r}}\beta_{ik} + \tilde{a}_0\alpha_{ik}\right\} = 0\ ;
\end{aligned}
\tag{5.168}
$$

$$
\begin{aligned}
& \alpha_{ik} = \tilde{s}^{-1}\sigma_{ik} - \frac{8\sqrt{2}}{5P} \cdot \mu_0^{\text{H.S.}} \mathit{\Delta}_{ik}\ ; \\
& \beta_{ik} = \tilde{s}^{-1}\frac{8\sqrt{2}}{5P} \cdot \mu_0^{\text{H.S.}} \mathit{\Delta}_{ik} - \tilde{r}^{-1}\sigma_{ik}\ .
\end{aligned}
\tag{5.169}
$$

It is clear from the analysis of distribution functions of the second quasiequilibrium approximations of the second hydrodynamic chain that in the Grad moment method the function $\varPhi(c^2)$ is substituted by a constant. Finally, let us note the simplest consequence of the variability of function $\varPhi(c^2)$. If μ_0 is multiplied with a small parameter (Knudsen number Kn equal to the ratio of the main free path the to characteristic spatial scale of variations of hydrodynamic values), then the first with respect to Kn approximation of collision stress tensor $\varDelta_{ik}^{(0)}$ has the form,

$$\varDelta_{ik}^{(0)} = P\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u\right) \tag{5.170}$$

for Maxwell molecules, and

$$\varDelta_{ik}^{(0)} = \frac{5\tilde{r}}{8\sqrt{2}\tilde{s}\tilde{a}_0} P\left(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s\right) \tag{5.171}$$

for hard spheres. Substitution of these expressions into the momentum equations results in the Navier-Stokes equations with effective viscosity coefficients μ_{eff},

$$\mu_{\text{eff}} = \mu_0^{\text{M.M.}} \tag{5.172}$$

for Maxwell molecules and

$$\mu_{\text{eff}} = \tilde{a}_0^{-1}\mu_0^{\text{H.S.}} \tag{5.173}$$

for hard spheres. When using ten-moment Grad approximation which does not distinguish Maxwell molecules and hard spheres, we obtain $\mu_{\text{eff}} = \mu_0^{\text{H.S.}}$. Some consequences of this fact are studied below in Sect. 5.7.

5.6.6 Appendix: Formulas of the Second Quasiequilibrium Approximation of the Second and Mixed Hydrodynamic Chains for Maxwell Molecules and Hard Spheres

Write ν_{Qik} (5.124) in the standard form:

$$\nu_{Qik} = \int f^{(0)} \mid \boldsymbol{v}_1 - \boldsymbol{v} \mid \left\{(v_i - u_i)(v_k - u_k) - \frac{1}{3}\delta_{ik}(\boldsymbol{v} - \boldsymbol{u})^2\right\} b\,\mathrm{d}b\,\mathrm{d}\epsilon\,\mathrm{d}\boldsymbol{v}_1 \,, \tag{5.174}$$

where b is the impact parameter, ϵ is the angle between the plane containing the trajectory of the particle being scattered in the system of the center of mass and the plane containing the entering asymptote, the trajectory, and a certain fixed direction. It is convenient to switch to the dimensionless velocity $\mathbf{c}$:

$$c_i = \left(\frac{m}{2k_{\mathrm{B}}T}\right)^{1/2}(v_i - u_i) \tag{5.175}$$

and to the dimensionless relative velocity $\mathbf{g}$:

$$g_i = \frac{1}{2}\left(\frac{m}{k_{\mathrm{B}}T}\right)^{1/2}(v_{1i} - u_i) \tag{5.176}$$

After standard transformations and integration with respect to ϵ (see [70]) we obtain in (5.174)

$$\begin{aligned}\nu_{Qik} &= \frac{3P}{m}\pi^{-1/2} \\ &\times \int \exp(-c_1^2)\varphi_1^{(2)}(g)\left((c_{1i} - c_i)(c_{1k} - c_k) - \frac{1}{3}\delta_{ik}(\mathbf{c}_1 - \mathbf{c})^2\right)\mathrm{d}\mathbf{c_1}\ .\end{aligned} \tag{5.177}$$

Here

$$\varphi_1^{(2)} = \int (1 - \cos^2\chi)\mid \boldsymbol{v}_1 - \boldsymbol{v} \mid b(\chi)\left|\frac{\mathrm{d}b}{\mathrm{d}\chi}\right| d\chi\ , \tag{5.178}$$

and χ is an angle between the vectors g and g'.

The dependence of $\varphi_1^{(2)}$ on the vector g is determined by the choice of the model of particle's interaction.

For Maxwell molecules,

$$\varphi_1^{(2)} = \left(\frac{2\kappa}{m}\right)^{1/2} A_2(5)\ , \tag{5.179}$$

where κ is a force constant, $A_2(5)$ is a number, $A_2(5) \approx 0.436$.

For the model of hard spheres

$$\varphi_1^{(2)} = \frac{\sqrt{2}\sigma^2}{3}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2} \mid \mathbf{c_1} - \mathbf{c} \mid\ , \tag{5.180}$$

where σ is diameter of the sphere modelling the particle.

Substituting (5.179) and (5.180) into (5.178), we transform the latter to the form:
for Maxwell molecules

$$\begin{aligned}\nu_{Qik} &= \frac{3P}{4m}\left(\frac{2\kappa}{\pi m}\right)^{1/2} A_2(5)\exp(-c^2)\left(\frac{\partial}{\partial c_i}\frac{\partial}{\partial c_k} - \frac{1}{3}\delta_{ik}\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_s}\right)T^{\mathrm{M.M.}}(c^2)\ ; \\ T^{\mathrm{M.M.}}(c^2) &= \int \exp(-x^2 - 2x_k c_k)\,\mathrm{d}\boldsymbol{x}\ ;\end{aligned} \tag{5.181}$$

for hard spheres

$$\begin{aligned}\nu_{Qik} &= \frac{P\sigma^2}{2\sqrt{2}m}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2}\exp(-c^2)\left(\frac{\partial}{\partial c_i}\frac{\partial}{\partial c_k} - \frac{1}{3}\delta_{ik}\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_s}\right)T^{\mathrm{H.S.}}(c^2)\ ; \\ T^{\mathrm{H.S.}}(c^2) &= \int \mid \boldsymbol{x} \mid \exp(-x^2 - 2x_k c_k)\,\mathrm{d}\boldsymbol{x}\ .\end{aligned} \tag{5.182}$$

It is an easy matter to perform integration in (5.181), the integral is equal to $\pi^{3/2}e^{c^2}$.
Therefore for Maxwell molecules,

$$\nu_{Qik} = \frac{3}{2}n\pi\left(\frac{2\kappa}{m}\right)^{1/2} A_2(5)\left((v_i-u_i)(v_k-u_k)-\frac{1}{3}\delta_{ik}(\boldsymbol{v}-\boldsymbol{u})^2\right) . \quad (5.183)$$

The integral $T^{\text{H.S.}}$ in (5.182) can be transformed as follows:

$$T^{\text{H.S.}}(c^2) = 2\pi + \pi\int_{-1}^{+1}\exp(c^2(1-y^2))c^2(1+y^2)\,\mathrm{d}y . \quad (5.184)$$

Then for the model of hard spheres,

$$\nu_{Qik} = \sqrt{2\pi}n\sigma^2\left(\frac{k_{\mathrm{B}}T}{m}\right)^{3/2}\left(c_ic_k-\frac{1}{3}\delta_{ik}c^2\right) \\ \times\int_{-1}^{+1}\exp(-c^2y^2)(1+y^2)(1-y^2)(c^2(1-y^2)+2)\,\mathrm{d}y . \quad (5.185)$$

Let us note a useful relationship:

$$d^nT^{\text{H.S.}}/d(c^2)^n = \pi\int_{-1}^{+1}\exp(c^2(1-y^2)) \\ \times(1+y^2)(1-y^2)^{n-1}(c^2(1-y^2)+n)\,\mathrm{d}y, n\geq 1 . \quad (5.186)$$

Use the expressions for the viscosity coefficient μ_0 which are obtained in the first approximation of the Chapman-Enskog method:
for Maxwell molecules,

$$\mu_0^{\text{M.M.}} = \left(\frac{2m}{\kappa}\right)^{1/2}\frac{k_{\mathrm{B}}T}{3\pi A_2(5)} ; \quad (5.187)$$

for hard spheres,

$$\mu_0^{\text{H.S.}} = \frac{5(k_{\mathrm{B}}Tm)^{1/2}}{16\pi^{1/2}\sigma^2} . \quad (5.188)$$

Transformation of (5.183), (5.185) to the form of (5.127) gives the following functions $\Phi((\boldsymbol{v}-\boldsymbol{u})^2)$:
for Maxwell molecules,

$$\Phi = P/\mu_0^{\text{M.M.}} ; \quad (5.189)$$

for hard spheres

$$\Phi = \frac{5P}{16\sqrt{2}\mu_0^{\text{H.S.}}}\int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right) \\ \times(1+y^2)(1-y^2)\left(\frac{m(\boldsymbol{v}-\boldsymbol{u})^2}{2k_{\mathrm{B}}T}(1-y^2)+2\right)dy . \quad (5.190)$$

The parameter r from (5.128) is:
for Maxwell molecules:

$$r = \left(m\mu_0^{\mathrm{M.M.}}\right)^2 / (2P^3 k_{\mathrm{B}} T) \; ; \tag{5.191}$$

for hard spheres:

$$r = \tilde{r} \frac{64 \left(m\mu_0^{\mathrm{M.M.}}\right)^2}{25 P^3 k_{\mathrm{B}} T} \; . \tag{5.192}$$

The dimensionless parameter $\tilde{r}$ is represented as follows:

$$\begin{aligned} \tilde{r}^{-1} = & \frac{1}{16} \int_{-1}^{+1} \int_{-1}^{+1} \alpha^{-11/2} \beta(y) \beta(z) \gamma(y) \gamma(z) \\ & \times (16\alpha^2 + 28\alpha(\gamma(y) + \gamma(z)) + 63\gamma(y)\gamma(z))\, \mathrm{d}y\, \mathrm{d}z \; . \end{aligned} \tag{5.193}$$

Here and below the following notations are used:

$$\beta(y) = 1 + y^2 \; , \qquad \gamma(y) = 1 - y^2 \; , \qquad \alpha = 1 + y^2 + z^2 \; . \tag{5.194}$$

Numerical value of $\tilde{r}^{-1}$ is 5.212 to third decimal point.

The parameter (5.136) is:
for Maxwell molecules

$$s^{-1} = (2P^2 k_{\mathrm{B}} T) / \left(m^2 \mu_0^{\mathrm{M.M.}}\right) \; ; \tag{5.195}$$

for hard spheres

$$s^{-1} = \tilde{s}^{-1} \frac{5\sqrt{2} P^2 k_{\mathrm{B}} T}{8 m^2 \mu_0^{\mathrm{H.S.}}} \; . \tag{5.196}$$

The dimensionless parameter $\tilde{s}^{-1}$ is of the form

$$\tilde{s}^{-1} = \int_{-1}^{+1} \gamma(y) \beta^{-7/2}(y) \left(\beta(y) + \frac{7}{4}\gamma(y)\right) \mathrm{d}y \; . \tag{5.197}$$

Numerical value of $\tilde{s}^{-1}$ is 1.115 to third decimal point.

The scattering rate density (5.143) is of the form,

$$\xi_{Qi} = \sqrt{2} \left(\frac{k_{\mathrm{B}} T}{m}\right)^{3/2} \int f^{(0)}(\boldsymbol{v}_1) \mid \boldsymbol{v}_1 - \boldsymbol{v} \mid \left\{ c_i \left(c^2 - \frac{5}{2}\right) \right\} b\, \mathrm{d}b\, \mathrm{d}\epsilon d\boldsymbol{v}_1 \; . \tag{5.198}$$

Standard transformation of the expression $\left\{c_i(c^2 - 5/2)\right\}$ and integration with respect to ϵ change (5.198) to the form,

$$\xi_{Qi} = \frac{P}{\sqrt{2\pi m}} \int \exp(-c_1^2) \varphi_1^{(2)} (3(c_1^2 - c^2)(c_{1i} - c_i) - (\mathbf{c}_1 - \mathbf{c})^2 (c_{1i} + c_i))\, \mathrm{d}\mathbf{c_1} \; . \tag{5.199}$$

Further, using the expressions (5.179) and (5.180) for $\varphi_1^{(2)}$, we obtain:

for Maxwell molecules:

$$\xi_{Qi} = \frac{P}{m^2}\left(\frac{\kappa k_{\mathrm{B}}T}{\pi}\right)^{1/2} A_2(5)\exp\left(-c^2\right)\hat{D}_i T^{\mathrm{M.M.}}(c^2)\ ; \tag{5.200}$$

for hard spheres:

$$\xi_{Qi} = \frac{P k_{\mathrm{B}} T \sigma^2}{\sqrt{\pi} m^2}\exp(-c^2)\hat{D}_i T^{\mathrm{H.S.}}(c^2)\ . \tag{5.201}$$

The operator $\hat{D}_i$ is of the form

$$\frac{1}{4}\frac{\partial}{\partial c_i}\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_s} + \frac{3}{2}c_s\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_i} - \frac{1}{2}c_i\frac{\partial}{\partial c_s}\frac{\partial}{\partial c_s}\ . \tag{5.202}$$

The operator $\hat{D}_i$ acts on the function $\psi(c^2)$ as follows:

$$\frac{d^2\psi}{d(c^2)^2}2c_i\left(c^2 - \frac{5}{2}\right) + c_i c^2\left(\frac{d^2\psi}{d(c^2)^2} - \frac{d^3\psi}{d(c^2)^3}\right)\ . \tag{5.203}$$

From (5.200), (5.201) we obtain:
for Maxwell molecules:

$$\xi_{Qi} = \frac{P}{3\mu_0^{\mathrm{M.M.}}}(v_i - u_i)\left((\boldsymbol{v} - \boldsymbol{u})^2 - \frac{5k_{\mathrm{B}}T}{m}\right)\ ; \tag{5.204}$$

for hard spheres:

$$\begin{aligned} \xi_{Qi} = {} & \frac{5P}{16\sqrt{2}\mu_0^{\mathrm{H.S.}}}\left\{(v_i - u_i)\left((\boldsymbol{v} - \boldsymbol{u})^2 - \frac{5k_{\mathrm{B}}T}{m}\right)\right. \\ & \times \int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y)\left(\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2k_{\mathrm{B}}T}\gamma(y) + 2\right)dy \\ & + (v_i - u_i)(\boldsymbol{v} - \boldsymbol{u})^2 \\ & \left.\times \int_{-1}^{+1}\exp\left(-\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2k_{\mathrm{B}}T}y^2\right)\beta(y)\gamma(y)\left(\sigma(y)\frac{m(\boldsymbol{v} - \boldsymbol{u})^2}{2k_{\mathrm{B}}T} + \delta(y)\right)\mathrm{d}y\right\}\ . \end{aligned} \tag{5.205}$$

The functions $\sigma(y), \delta(y)$ are of the form

$$\sigma(y) = y^2(1 - y^2)\ , \qquad \delta(y) = 3y^2 - 1\ . \tag{5.206}$$

The parameter η from (5.149) is:
for Maxwell molecules:

$$\eta = \frac{9m^3\left(\mu_0^{\mathrm{M.M.}}\right)^2}{10P^3(k_{\mathrm{B}}T)^2}\ ; \tag{5.207}$$

for hard spheres:

$$\eta = \tilde{\eta}\frac{64m^3\left(\mu_0^{\mathrm{H.S.}}\right)^2}{125P^3(k_{\mathrm{B}}T)^2}\ . \tag{5.208}$$

The dimensionless parameter $\tilde{\eta}$ is of the form

$$\begin{aligned}
\tilde{\eta}^{-1} = \int_{-1}^{+1}\int_{-1}^{+1} & \beta(y)\beta(z)\gamma(y)\gamma(z)\alpha^{-13/2}\left\{\frac{639}{32}(\gamma(y)\gamma(z) + \sigma(y)\sigma(z)\right. \\
& + \sigma(y)\gamma(z) + \sigma(z)\gamma(y)) + \frac{63}{16}\alpha(2\gamma(y) + 2\gamma(z) - 5\gamma(y)\gamma(z) \\
& + 2(\sigma(y) + \sigma(z)) + \gamma(z)\delta(y) + \gamma(y)\delta(z) + \sigma(y)\delta(z) + \sigma(z)\delta(y)) \\
& + \frac{7}{8}\alpha^2(4 - 10\gamma(y) - 10\gamma(z)) + \frac{25}{4}\gamma(y)\gamma(z) + 2\delta(y) \\
& + 2\delta(z) - 5\sigma(y) - 5\sigma(z) - \frac{5}{2}(\gamma(z)\delta(y) + \gamma(y)\delta(z) + \delta(y)\delta(z)) \\
& \left. + \frac{1}{4}\alpha^3\left(-20 + \frac{25}{4}(\gamma(y) + \gamma(z)) - 5(\delta(y) + \delta(z))\right) + \frac{5}{2}\alpha^4\right\}\,\mathrm{d}y\,\mathrm{d}z\ .
\end{aligned} \tag{5.209}$$

Numerical value of $\tilde{\eta}^{-1}$ is 0.622 to second decimal point.

Finally, from (5.204), (5.206) we obtain τ^{-1}(5.156):
for Maxwell molecules

$$\tau^{-1} = \frac{5(Pk_{\mathrm{B}}T)^2}{3\mu_0^{\mathrm{M.M.}}m^3}\ ; \tag{5.210}$$

for hard spheres

$$\begin{aligned}
\tau^{-1} &= \tilde{\tau}^{-1}\frac{25P^2(k_{\mathrm{B}}T)^2}{8\sqrt{2}m^3\mu_0^{\mathrm{H.S.}}}\ ; \\
\tilde{\tau}^{-1} &= \frac{1}{8}\int_{-1}^{+1}\beta^{-9/2}(y)\gamma(y)\{63(\gamma(y) + \sigma(y)) \\
&\quad + 7\beta(y)(4 - 10\gamma(y) + 2\delta(y) - 5\sigma(y)) + 20\beta^3(y) \\
&\quad + \beta^2(y)(25\gamma(y) - 10\delta(y) - 40)\}\,\mathrm{d}y \approx 4.322\ .
\end{aligned} \tag{5.211}$$

5.7 Example: Alternative Grad Equations and a "New Determination of Molecular Dimensions" (Revisited)

Here we apply the method developed in the previous section to a classical problem: determination of molecular dimensions (as diameters of equivalent hard spheres) from experimental viscosity data. Scattering rates (moments of collision integral) are treated as new independent variables, and as an alternative to moments of the distribution function, to describe the rarefied gas near local equilibrium. A version of entropy maximum principle is used to derive the Grad-like description in terms of a finite number of scattering rates. New equations are compared to the Grad moment system in the heat non-conductive case. Estimations for hard spheres demonstrate, in particular, some 10% excess of the viscosity coefficient resulting from the scattering rate description, as compared to the Grad moment estimation. All necessary details of the second chain formalism are explained below.

The classical Grad moment method provides an approximate solution to the Boltzmann equation, and leads to a closed system of equations where hydrodynamic variables ρ, $\boldsymbol{u}$, and P (density, mean flux, and pressure) are coupled to a finite set of non-hydrodynamic variables. The latter are usually the stress tensor σ and the heat flux $\boldsymbol{q}$ constituting 10 and 13 moment Grad systems. The Grad method was originally introduced for diluted gases to describe regimes beyond the normal solutions [70], but later it was used, in particular, as a prototype of certain phenomenological schemes in nonequilibrium thermodynamics [235].

However, the moments do not constitute the unique system of non-hydrodynamic variables, and the exact dynamics might be equally expressed in terms of other infinite sets of variables (possibly, of a non-moment nature). Moreover, as long as one shortens the description to only a finite subset of variables, the advantage of the moment description above other systems is not obvious. As we have seen it above, the two sets of variables

5.7.1 Nonlinear Functionals Instead of Moments in the Closure Problem

Here we consider a new system of non-hydrodynamic variables, *scattering rates* $M_Q(f)$:

$$M_{Q\,i_1i_2i_3}(f) = \int \mu_{i_1i_2i_3} Q(f,f)\,\mathrm{d}\boldsymbol{v}\;; \tag{5.212}$$
$$\mu_{i_1i_2i_3} = m v_1^{i_1} v_2^{i_2} v_3^{i_3}\;,$$

which, by definition, are the moments of the Boltzmann collision integral $Q(f,f)$:

$$Q(f,f) = \int w(\boldsymbol{v}', \boldsymbol{v}_1', \boldsymbol{v}, \boldsymbol{v}_1)\,\{f(\boldsymbol{v}')f(\boldsymbol{v}_1') - f(\boldsymbol{v})f(\boldsymbol{v}_1)\}\,\mathrm{d}\boldsymbol{v}'\,\mathrm{d}\boldsymbol{v}_1'\,\mathrm{d}\boldsymbol{v}_1\;.$$

Here w is the probability density of a change of the velocities, $(\boldsymbol{v}, \boldsymbol{v}_1) \to (\boldsymbol{v}', \boldsymbol{v}_1')$, of the two particles after their encounter, and w is defined by a model of pair interactions. The description in terms of the scattering rates M_Q (5.212) is alternative to the usually treated description in terms of the moments M: $M_{i_1i_2i_3}(f) = \int \mu_{i_1i_2i_3} f\,\mathrm{d}\boldsymbol{v}$.

A reason to consider scattering rates instead of the moments is that M_Q (5.212) reflect features of the interactions because of the w incorporated in their definition, while the moments do not. For this reason we can expect that, in general, a description with a *finite* number of scattering rates will be more informative than a description provided by the same number of their moment counterparts.

To come to the Grad-like equations in terms of the scattering rates, we have to complete the following two steps:

(i) To derive a hierarchy of transport equations for ρ, $\boldsymbol{u}$, P, and $M_{Q\,i_1 i_2 i_3}$ in a neighborhood of the local Maxwell states $f_0(\rho, \boldsymbol{u}, P)$.
(ii) To truncate this hierarchy, and to come to a closed set of equations with respect to ρ, $\boldsymbol{u}$, P, and a finite number of scattering rates.

In the step (i), we derive a description with infinite number of variables, which is formally equivalent both to the Boltzmann equation near the local equilibrium, and to the description with an infinite number of moments. The approximation comes into play in the step (ii) where we reduce the description to a finite number of variables. The difference between the moment and the alternative description occurs at this point.

The program (i) and (ii) is similar to what is done in the Grad method [201], with the only exception (and this is important) that we should always use scattering rates as independent variables and not to expand them into series in moments. Consequently, we use a method of a closure in the step (ii) that does not refer to the moment expansions. Major steps of the computation will be presented below.

5.7.2 Linearization

To complete the step (i), we represent f as $f_0(1+\varphi)$, where f_0 is the local Maxwellian, and we linearize the scattering rates (5.212) with respect to φ:

$$\begin{aligned} \varDelta M_{Q\,i_1 i_2 i_3}(\varphi) &= \int \varDelta\mu_{Q\,i_1 i_2 i_3} f_0 \varphi \, \mathrm{d}\boldsymbol{v} \; ; \\ \varDelta\mu_{Q\,i_1 i_2 i_3} &= L_Q(\mu_{i_1 i_2 i_3}) \; . \end{aligned} \tag{5.213}$$

Here L_Q is the usual linearized collision integral, divided by f_0. Though $\varDelta M_Q$ are linear in φ, they are not moments because their microscopic densities, $\varDelta\mu_Q$, are not velocity polynomials for a general case of w.

It is not difficult to derive the corresponding hierarchy of transport equations for variables $\varDelta M_{Q\,i_1 i_2 i_3}$, ρ, $\boldsymbol{u}$, and P (we refer further to this hierarchy as to the alternative chain): one has to calculate the time derivative of the scattering rates (5.212) due to the Boltzmann equation, in the linear approximation (5.213), and to complete the system with the five known balance equations for the hydrodynamic moments (scattering rates of the hydrodynamic moments are equal to zero due to conservation laws). The structure of the alternative chain is quite similar to that of the usual moment transport chain, and for this reason we do not reproduce it here (details of calculations can be found in [237]). One should only keep in mind that the stress tensor and the heat flux vector in the balance equations for $\boldsymbol{u}$ and P are no more independent variables, and they are expressed in terms of $\Delta M_{Q\,i_1i_2i_3}$, ρ, $\boldsymbol{u}$, and P.

5.7.3 Truncating the Chain

To truncate the alternative chain (step (ii)), we have, first, to choose a finite set of "essential" scattering rates (5.213), and, second, to obtain the distribution functions which depend parametrically only on ρ, $\boldsymbol{u}$, P, and on the chosen set of scattering rates. We will restrict our consideration to a single non-hydrodynamic variable, $\sigma_{Q\,ij}$, which is the counterpart of the stress tensor σ_{ij}. This choice corresponds to the polynomial mv_iv_j in the expressions (5.212) and (5.213), and the resulting equations will be alternative to the 10 moment Grad system[2]. For a spherically symmetric interaction, the expression for $\sigma_{Q\,ij}$ may be written:

$$\sigma_{Q\,ij}(\varphi) = \int \Delta\mu_{Q\,ij} f_0 \varphi \, \mathrm{d}\boldsymbol{v} \; ; \tag{5.214}$$

$$\Delta\mu_{Q\,ij} = L_Q(mv_iv_j) = \frac{P}{\eta_{Q\,0}(T)} S_Q(c^2) \left\{ c_ic_j - \frac{1}{3}\delta_{ij}c^2 \right\} \; .$$

Here $\eta_{Q\,0}(T)$ is the first Sonine polynomial approximation of the Chapman-Enskog viscosity coefficient (VC) [70], and, as usual, $\mathbf{c} = \sqrt{\frac{m}{2kT}}(\boldsymbol{v} - \boldsymbol{u})$. The scalar dimensionless function S_Q depends only on c^2, and its form depends on the choice of interaction w.

5.7.4 Entropy Maximization

Next, we find the functions

$$f^*(\rho, \boldsymbol{u}, P, \sigma_{Q\,ij}) = f_0(\rho, \boldsymbol{u}, P)(1 + \varphi^*(\rho, \boldsymbol{u}, P, \sigma_{Q\,ij}))$$

which maximize the Boltzmann entropy $S(f)$ in a neighborhood of f_0 (the quadratic approximation to the entropy is valid within the accuracy of our consideration), for fixed values of $\sigma_{Q\,ij}$. That is, φ^* is a solution to the following conditional variational problem:

$$\Delta S(\varphi) = -\frac{k_{\mathrm{B}}}{2} \int f_0 \varphi^2 \, \mathrm{d}\boldsymbol{v} \to \max \; , \tag{5.215}$$

$$\text{i)} \int \Delta\mu_{Q\,ij} f_0 \varphi \, \mathrm{d}\boldsymbol{v} = \sigma_{Q\,ij}; \quad \text{ii)} \int \left\{1, \boldsymbol{v}, v^2\right\} f_0 \varphi \, \mathrm{d}\boldsymbol{v} = 0 \; .$$

---

[2] To get the alternative to the 13 moment Grad equations, one should take into account the scattering counterpart of the heat flux, $q_{Q\,i} = m \int v_i \frac{v^2}{2} Q(f,f) \, \mathrm{d}\boldsymbol{v}$.

The second (homogeneous) condition in (5.215) reflects that a deviation φ from the state f_0 is due only to non-hydrodynamic degrees of freedom, and it is straightforwardly satisfied for $\Delta\mu_{Q\,ij}$ (5.214).

Notice, that if we turn to the usual moment description, then condition (i) in (5.215) would fix the stress tensor σ_{ij} instead of its scattering counterpart $\sigma_{Q\,ij}$. Then the resulting function $f^*(\rho, \boldsymbol{u}, P, \sigma_{ij})$ will be exactly the 10 moment Grad approximation. It can be shown that a choice of any finite set of higher moments as the constraint (i) in (5.215) results in the corresponding Grad approximation. In that sense our method of constructing f^* is a direct generalization of the Grad method onto the alternative description.

The Lagrange multipliers method gives straightforwardly the solution to the problem (5.215). After the alternative chain is closed with the functions $f^*(\rho, \boldsymbol{u}, P, \sigma_{Q\,ij})$, the step (ii) is completed, and we arrive at a set of equations with respect to the variables ρ, $\boldsymbol{u}$, P, and $\sigma_{Q\,ij}$. Switching to the variables $\zeta_{ij} = n^{-1}\sigma_{Q\,ij}$, we have:

$$\partial_t n + \partial_i(nu_i) = 0\,; \tag{5.216}$$

$$\rho(\partial_t u_k + u_i\partial_i u_k) + \partial_k P + \partial_i\left\{\frac{\eta_{Q\,0}(T)n}{2r_Q P}\zeta_{ik}\right\} = 0\,; \tag{5.217}$$

$$\frac{3}{2}(\partial_t P + u_i\partial_i P) + \frac{5}{2}P\partial_i u_i + \left\{\frac{\eta_{Q\,0}(T)n}{2r_Q P}\zeta_{ik}\right\}\partial_i u_k = 0\,; \tag{5.218}$$

$$\begin{aligned}&\partial_t\zeta_{ik} + \partial_s(u_s\zeta_{ik}) + \{\zeta_{ks}\partial_s u_i + \zeta_{is}\partial_s u_k - \frac{2}{3}\delta_{ik}\zeta_{rs}\partial_s u_r\}\\ &+\left\{\gamma_Q - \frac{2\beta_Q}{r_Q}\right\}\zeta_{ik}\partial_s u_s - \frac{P^2}{\eta_{Q\,0}(T)n}(\partial_i u_k + \partial_k u_i - \frac{2}{3}\delta_{ik}\partial_s u_s)\\ &-\frac{\alpha_Q P}{r_Q\eta_{Q\,0}(T)}\zeta_{ik} = 0\,.\end{aligned} \tag{5.219}$$

Here $\partial_t = \partial/\partial t, \partial_i = \partial/\partial x_i$, summation in two repeated indices is assumed, and the coefficients r_Q, β_Q, and α_Q are defined with the help of the function S_Q (5.214) as follows:

$$\begin{aligned}r_Q &= \frac{8}{15\sqrt{\pi}}\int_0^\infty \mathrm{e}^{-c^2}c^6\left(S_Q(c^2)\right)^2\,\mathrm{d}c\,;\\ \beta_Q &= \frac{8}{15\sqrt{\pi}}\int_0^\infty \mathrm{e}^{-c^2}c^6 S_Q(c^2)\frac{\mathrm{d}S_Q(c^2)}{\mathrm{d}(c^2)}\,\mathrm{d}c\,;\\ \alpha_Q &= \frac{8}{15\sqrt{\pi}}\int_0^\infty \mathrm{e}^{-c^2}c^6 S_Q(c^2)R_Q(c^2)\,\mathrm{d}c\,.\end{aligned} \tag{5.220}$$

The function $R_Q(c^2)$ in the last expression is defined due to the action of the operator L_Q on the function $S_Q(c^2)(c_ic_j - \frac{1}{3}\delta_{ij}c^2)$:

$$\frac{P}{\eta_{Q\,0}}R_Q(c^2)(c_ic_j - \frac{1}{3}\delta_{ij}c^2) = L_Q(S_Q(c^2)(c_ic_j - \frac{1}{3}\delta_{ij}c^2))\,. \tag{5.221}$$

Finally, the parameter γ_Q in (5.216–5.220) reflects the temperature dependence of the VC:

$$\gamma_Q = \frac{2}{3}\left(1 - \frac{T}{\eta_{Q\,0}(T)}\left(\frac{\mathrm{d}\eta_{Q\,0}(T)}{\mathrm{d}T}\right)\right) .$$

The set of ten equations (5.216–5.220) is alternative to the 10 moment Grad equations.

5.7.5 A New Determination of Molecular Dimensions (Revisited)

The observation already made is that for Maxwell molecules we have: $S^{\text{M.M.}} \equiv 1$, and $\eta_0^{\text{M.M.}} \propto T$; thus $\gamma^{\text{M.M.}} = \beta^{\text{M.M.}} = 0$, $r^{\text{M.M.}} = \alpha^{\text{M.M.}} = \frac{1}{2}$, and (5.216–5.220) becomes the 10 moment Grad system under a simple change of variables $\lambda\zeta_{ij} = \sigma_{ij}$, where λ is the proportionality coefficient in the temperature dependence of $\eta_0^{\text{M.M.}}$.

These properties (the function S_Q is a constant, and the VC is proportional to T) are true only for Maxwell molecules. For all other interactions, the function S_Q is not identical to one, and the VC $\eta_{Q\,0}(T)$ is not proportional to T. Thus, the shortened alternative description is not equivalent indeed to the Grad moment description. In particular, for hard spheres, the exact expression for the function $S^{\text{H.S.}}$ (5.214) reads:

$$S^{\text{H.S.}} = \frac{5\sqrt{2}}{16}\int_0^1 \exp(-c^2t^2)(1-t^4)\left(c^2(1-t^2)+2\right)\,\mathrm{d}t\,; \qquad (5.222)$$
$$\eta_0^{\text{H.S.}} \propto \sqrt{T}\,.$$

Thus, $\gamma^{\text{H.S.}} = \frac{1}{3}$, and $\frac{\beta^{\text{H.S.}}}{r^{\text{H.S.}}} \approx 0.07$, and the equation for the function ζ_{ik} (5.220) contains a nonlinear term,

$$\theta^{\text{H.S.}}\zeta_{ik}\partial_s u_s\,, \qquad (5.223)$$

where $\theta^{\text{H.S.}} \approx 0.19$. This term is missing in the Grad 10 moment equation.

Finally, let us evaluate the VC which results from the alternative description (5.216–5.220). Following Grad's arguments [201], we see that, if the relaxation of ζ_{ik} is fast compared to the hydrodynamic variables, then the two last terms in the equation for ζ_{ik} (5.216–5.220) become dominant, and the equation for $\boldsymbol{u}$ casts into the standard Navier-Stokes form with an effective VC $\eta_{Q\,\text{eff}}$:

$$\eta_{Q\,\text{eff}} = \frac{1}{2\alpha_Q}\eta_{Q\,0}\,. \qquad (5.224)$$

For Maxwell molecules, we easily derive that the coefficient α_Q in (5.224) is equal to $\frac{1}{2}$. Thus, as one expects, the effective VC (5.224) is equal to the Grad value, which, in turn, is equal to the exact value in the frames of the Chapman-Enskog method for this model.

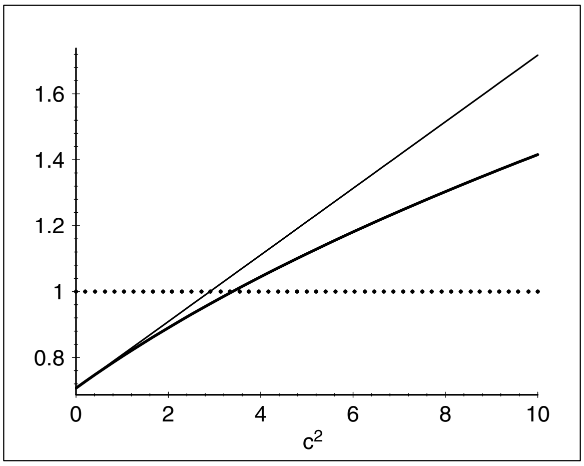

Fig. 5.1. Approximations for hard spheres: *bold* line – function $S^{\mathrm{H.S.}}$, *solid* line – approximation $S_a^{\mathrm{H.S.}}$, *dotted* line – Grad moment approximation

For all interactions different from the Maxwell molecules, the VC $\eta_{Q\,\mathrm{eff}}$ (5.224) is not equal to $\eta_{Q\,0}$. For hard spheres, in particular, a computation of the VC (5.224) requires information about the function $R^{\mathrm{H.S.}}$ (5.221). This is achieved upon a substitution of the function $S^{\mathrm{H.S.}}$ (5.222) into (5.221). Further, we have to compute the action of the operator $L^{\mathrm{H.S.}}$ on the function $S^{\mathrm{H.S.}}(c_i c_j - \frac{1}{3}\delta_{ij}c^2)$, which is rather complicated. However, the VC $\eta_{\mathrm{eff}}^{\mathrm{H.S.}}$ can be relatively easily estimated by using a function $S_a^{\mathrm{H.S.}} = \frac{1}{\sqrt{2}}(1+\frac{1}{7}c^2)$, instead of the function $S^{\mathrm{H.S.}}$, in (5.221). Indeed, the function $S_a^{\mathrm{H.S.}}$ is tangent to the function $S^{\mathrm{H.S.}}$ at $c^2 = 0$, and is its majorant (see Fig. 5.1). Substituting $S_a^{\mathrm{H.S.}}$ into (5.221), and computing the action of the collision integral, we find the approximation $R_a^{\mathrm{H.S.}}$; thereafter we evaluate the integral $\alpha^{\mathrm{H.S.}}$ (5.220), and finally come to the following expression:

$$\eta_{\mathrm{eff}}^{\mathrm{H.S.}} \geq \frac{75264}{67237}\eta_0^{\mathrm{H.S.}} \approx 1.12\eta_0^{\mathrm{H.S.}}\ . \tag{5.225}$$

Thus, for hard spheres, the description in terms of scattering rates results in the VC of more than 10% higher than in the Grad moment description.

A discussion of the results concerns the following two items.

1. Having two not equivalent descriptions which were obtained within one method, we may ask: which is more relevant? A simple test is to compare characteristic times of an approach to hydrodynamic regime. We have $\tau_G \sim \eta_0^{\mathrm{H.S.}}/P$ for 10-moment description, and $\tau_a \sim \eta_{\mathrm{eff}}^{\mathrm{H.S.}}/P$ for alternative description. As $\tau_a > \tau_G$, we see that scattering rate decay slower than corresponding moment, hence, at least for rigid spheres, the alternative description is more relevant. For Maxwell molecules both the descriptions are, of course, equivalent.

2. The VC $\eta_{\text{eff}}^{\text{H.S.}}$ (5.225) has the same temperature dependence as $\eta_0^{\text{H.S.}}$, and also the same dependence on a scaling parameter (a diameter of the sphere). In the classical book [70] (pp. 228–229), "sizes" of molecules are presented, assuming that a molecule is represented with an equivalent sphere and VC is estimated as $\eta_0^{\text{H.S.}}$. Since our estimation of VC differs only by a dimensionless factor from $\eta_0^{\text{H.S.}}$, it is straightforward to conclude that effective sizes of molecules will be reduced by the factor b, where

$$b = \sqrt{\eta_0^{\text{H.S.}}/\eta_{\text{eff}}^{\text{H.S.}}} \approx 0.94\ .$$

Further, it is well known that sizes of molecules estimated via viscosity in [70] disagree with the estimation via the virial expansion of the equation of state. In particular, in book [238], p. 5, the measured second virial coefficient B_{exp} was compared with the calculated B_0, in which the diameter of the sphere was taken from the viscosity data. The reduction of the diameter by factor b gives $B_{\text{eff}} = b^3 B_0$. The values B_{exp} and B_0 [238] are compared with B_{eff} in the Table 5.1 for three gases at $T = 500\,K$. The results for argon and helium are better for B_{eff}, while for nitrogen B_{eff} is worth than B_0. However, both B_0 and B_{eff} are far from the experimental values.

Table 5.1. Three virial coefficients: experimental B_{exp}, classical B_0 [238], and reduced B_{eff} for three gases at $T = 500\,K$

	B_{exp}	B_0	B_{eff}
Argon	8.4	60.9	50.5
Helium	10.8	21.9	18.2
Nitrogen	168	66.5	55.2

Hard spheres is, of course, an oversimplified model of interaction, and the comparison presented does not allow for a decision between $\eta_0^{\text{H.S.}}$ and $\eta_{\text{eff}}^{\text{H.S.}}$. However, this simple example illustrates to what extend the correction to the VC can affect a comparison with experiment. Indeed, as it is well known, the first-order Sonine polynomial computation for the Lennard-Jones (LJ) potential gives a very good fit of the temperature dependence of the VC for all noble gases [239], subject to a proper choice of the two unknown scaling parameters of the LJ potential[3]. We may expect that a dimensionless correction of the VC for the LJ potential might be of the same order as above for rigid spheres. However, the functional character of the temperature dependence will not be affected, and a fit will be obtained subject to a different choice of the molecular parameters of the LJ potential.

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[3] A comparison of molecular parameters of the LJ potential, as derived from the viscosity data, to those obtained from independent sources, can be found elsewhere, e.g. in [70], p. 237.