2 The Source of Examples

2.1 The Boltzmann Equation

2.1.1 The Equation

The *Boltzmann equation* is the first and the most celebrated nonlinear kinetic equation introduced by the great Austrian scientist Ludwig Boltzmann in 1872 [111]. This equation describes the dynamics of a moderately rarefied gas, taking into account two processes: the free flight of the particles, and their collisions. In its original version, the Boltzmann equation has been formulated for particles represented by hard spheres. The physical condition of rarefaction means that only pair collisions are taken into account, a mathematical specification of which is given by the *Grad–Boltzmann limit* [200]: If N is the number of particles, and σ is the diameter of the hard sphere, then the Boltzmann equation is expected to hold when N tends to infinity, σ tends to zero, $N\sigma^3$ (the volume occupied by the particles) tends to zero, while $N\sigma^2$ (the total collision cross section) remains constant. The microscopic state of the gas at time t is described by the one-body distribution function $P(\boldsymbol{x}, \boldsymbol{v}, t)$, where $\boldsymbol{x}$ is the position of the center of the particle, and $\boldsymbol{v}$ is the velocity of the particle. The distribution function is the probability density of finding the particle at time t within the infinitesimal phase space volume centered at the phase point $(\boldsymbol{x}, \boldsymbol{v})$. The collision mechanism of two hard spheres is presented by a relation between the velocities of the particles before [$\boldsymbol{v}$ and $\boldsymbol{w}$] and after [$\boldsymbol{v}'$ and $\boldsymbol{w}'$] their impact:

$$\boldsymbol{v}' = \boldsymbol{v} - \boldsymbol{n}(\boldsymbol{n}, \boldsymbol{v} - \boldsymbol{w}) \; ,$$
$$\boldsymbol{w}' = \boldsymbol{w} + \boldsymbol{n}(\boldsymbol{n}, \boldsymbol{v} - \boldsymbol{w}) \; ,$$

where $\boldsymbol{n}$ is the unit vector along $\boldsymbol{v} - \boldsymbol{v}'$. Transformation of the velocities conserves the total momentum of the pair of colliding particles ($\boldsymbol{v}' + \boldsymbol{w}' = \boldsymbol{v} + \boldsymbol{w}$), and the total kinetic energy ($\boldsymbol{v}'^2 + \boldsymbol{w}'^2 = \boldsymbol{v}^2 + \boldsymbol{w}^2$). The Boltzmann equation reads:

$$\begin{aligned}\frac{\partial P}{\partial t} + \left(\boldsymbol{v}, \frac{\partial P}{\partial \boldsymbol{x}}\right) = N\sigma^2 \int_{R^3} \int_{B^-} & (P(\boldsymbol{x}, \boldsymbol{v}', t)P(\boldsymbol{x}, \boldsymbol{w}', t) \\ & -P(\boldsymbol{x}, \boldsymbol{v}, t)P(\boldsymbol{x}, \boldsymbol{w}, t)) \mid (\boldsymbol{w} - \boldsymbol{v}, \boldsymbol{n}) \mid \, \mathrm{d}\boldsymbol{w} \, \mathrm{d}\boldsymbol{n} \; , \quad (2.1)\end{aligned}$$

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where integration in $\boldsymbol{w}$ is carried over the whole space R^3, while integration in $\boldsymbol{n}$ is over a hemisphere $B^- = \{\boldsymbol{n} \in S^2 \mid (\boldsymbol{w}-\boldsymbol{v},\boldsymbol{n}) < 0\}$. This inequality $(\boldsymbol{w}-\boldsymbol{v},\boldsymbol{n}) < 0$ corresponds to the particles entering the collision. The nonlinear integral operator in the right hand side of (2.1) is nonlocal in the velocity variable, and local in space. The Boltzmann equation for arbitrary hard-core interaction is a generalization of the Boltzmann equation for hard spheres under the proviso that the true infinite-range interaction potential between the particles is cut off at some distance. This generalization amounts to a replacement,

$$\sigma^2 \mid (\boldsymbol{w}-\boldsymbol{v},\boldsymbol{n}) \mid \, \mathrm{d}\boldsymbol{n} \to B(\theta, \mid \boldsymbol{w}-\boldsymbol{v} \mid) \, \mathrm{d}\theta \, \mathrm{d}\varepsilon \ , \tag{2.2}$$

where the function B is determined by the interaction potential, and the vector $\boldsymbol{n}$ is identified with two angles, θ and ε. In particular, for potentials proportional to the n-th inverse power of the distance, the function B reads

$$B(\theta, \mid \boldsymbol{v}-\boldsymbol{w} \mid) = \beta(\theta) \mid \boldsymbol{v}-\boldsymbol{w} \mid^{\frac{n-5}{n-1}} \ . \tag{2.3}$$

In the special case $n = 5$, function B is independent of the magnitude of the relative velocity (Maxwell molecules). Maxwell molecules occupy a distinct place in the theory of the Boltzmann equation: they provide exact results. Three most important findings for the Maxwell molecules should be mentioned: (a) The exact spectrum of the linearized Boltzmann collision integral, found by Truesdell and Muncaster [261], (b) Exact transport coefficients found by Maxwell even before the Boltzmann equation was formulated, (c) Exact solutions to the space-free version of the nonlinear Boltzmann equation. Galkin [71] found the general solution to the system of moment equations in a form of a series expansion, Bobylev, Krook and Wu [255,256,262] found an exact solution of a particular elegant closed form, and Bobylev demonstrated the complete integrability of this dynamic system [73]. The review of relaxation of spatially uniform dilute gases for several types of interaction models, of exact solutions and related topics was given in [75].

A broad review of the Boltzmann equation and analysis of analytical solutions to kinetic models is presented in the book of Cercignani [112]. A modern account of rigorous results on the Boltzmann equation is given in the book [113]. Proof of the existence theorem for the Boltzmann equation was given by DiPerna and Lions [119].

It is customary to write the Boltzmann equation using another normalization of the distribution function, $f(\boldsymbol{x},\boldsymbol{v},t)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{v}$, taken in such a way that the function f is compliant with the definition of the hydrodynamic fields: the mass density ρ, the momentum density $\rho\boldsymbol{u}$, and the energy density e:

$$\int f(\boldsymbol{x},\boldsymbol{v},t) m \, \mathrm{d}\boldsymbol{v} = \rho(\boldsymbol{x},t) \ ,$$

$$\int f(\boldsymbol{x},\boldsymbol{v},t) m\boldsymbol{v} \, \mathrm{d}\boldsymbol{v} = \rho\boldsymbol{u}(\boldsymbol{x},t) \ , \tag{2.4}$$

$$\int f(\boldsymbol{x},\boldsymbol{v},t)m\frac{v^2}{2}\,\mathrm{d}\boldsymbol{v} = e(\boldsymbol{x},t)\ .$$

Here m is the particle mass.

The Boltzmann equation for the distribution function f reads,

$$\frac{\partial f}{\partial t} + \left(\boldsymbol{v}, \frac{\partial}{\partial \boldsymbol{x}} f\right) = Q(f,f)\ , \tag{2.5}$$

where the nonlinear integral operator at the right hand side is the Boltzmann collision integral,

$$Q = \int_{R^3}\int_{B^-} (f(\boldsymbol{v}')f(\boldsymbol{w}') - f(\boldsymbol{v})f(\boldsymbol{w}))B(\theta,\boldsymbol{v})\,\mathrm{d}\boldsymbol{w}\,\mathrm{d}\theta\,\mathrm{d}\varepsilon\ . \tag{2.6}$$

Finally, we mention the following form of the Boltzmann collision integral (sometimes referred to as the *scattering* or the *quasi-chemical* representation),

$$Q = \int W(\boldsymbol{v},\boldsymbol{w}\mid \boldsymbol{v}',\boldsymbol{w}')[(f(\boldsymbol{v}')f(\boldsymbol{w}') - f(\boldsymbol{v})f(\boldsymbol{w}))]\,\mathrm{d}\boldsymbol{w}\,\mathrm{d}\boldsymbol{w}'\,\mathrm{d}\boldsymbol{v}'\ , \tag{2.7}$$

where W is a generalized function which is called the probability density of the elementary event,

$$W = w(\boldsymbol{v},\boldsymbol{w}\mid \boldsymbol{v}',\boldsymbol{w}')\delta(\boldsymbol{v}+\boldsymbol{w}-\boldsymbol{v}'-\boldsymbol{w}')\delta(v^2+w^2-v'^2-w'^2)\ . \tag{2.8}$$

2.1.2 The Basic Properties of the Boltzmann Equation

The generalized function W has the following symmetries:

$$\begin{aligned} &W(\boldsymbol{v}',\boldsymbol{w}'\mid \boldsymbol{v},\boldsymbol{w}) \equiv W(\boldsymbol{w}',\boldsymbol{v}'\mid \boldsymbol{v},\boldsymbol{w}) \\ &\equiv W(\boldsymbol{v}',\boldsymbol{w}'\mid \boldsymbol{w},\boldsymbol{v}) \equiv W(\boldsymbol{v},\boldsymbol{w}\mid \boldsymbol{v}',\boldsymbol{w}')\ . \end{aligned} \tag{2.9}$$

The first two identities reflect the symmetry of the collision process with respect to labeling the particles, whereas the last identity is the celebrated *detailed balance* condition which is underpinned by the time-reversal symmetry of the microscopic (Newton's) equations of motion. The basic properties of the Boltzmann equation are:

1. *Additive invariants of the collision operator*:

$$\int Q(f,f)\{1,\boldsymbol{v},v^2\}\,\mathrm{d}\boldsymbol{v} = 0\ , \tag{2.10}$$

for any function f, assuming the integrals exist. Equality (2.10) reflects the fact that the number of particles, the three components of particle's momentum, and the particle's energy are conserved in collisions. Conservation laws (2.10) imply that the local hydrodynamic fields (2.4) can change in time only due to redistribution over space.

2. The zero point of the integral ($Q = 0$) satisfies the equation (which is also called the *detailed balance*): For almost all velocities,

$$f(\boldsymbol{v}', \boldsymbol{x}, t) f(\boldsymbol{w}', \boldsymbol{x}, t) = f(\boldsymbol{v}, \boldsymbol{x}, t) f(\boldsymbol{w}, \boldsymbol{x}, t) \ .$$

3. Boltzmann's *local entropy production inequality*:

$$\sigma(\boldsymbol{x}, t) = -k_{\mathrm{B}} \int Q(f, f) \ln f \, \mathrm{d}\boldsymbol{v} \geq 0 \ , \tag{2.11}$$

for any function f, assuming integrals exist. The dimensional *Boltzmann's constant* ($k_{\mathrm{B}} \approx 1.3806503 \cdot 10^{-23}\mathrm{J/K}$) in this expression serves for a recalculation of the energy units into absolute temperature units. Moreover, equality holds if $\ln f$ is a linear combination of the additive invariants of collision.

Distribution functions f whose logarithm is a linear combination of additive collision invariants with coefficients dependent on $\boldsymbol{x}$, are called *local Maxwell distribution functions* f_{LM},

$$f_{\mathrm{LM}} = \frac{\rho}{m} \left(\frac{2\pi k_{\mathrm{B}} T}{m} \right)^{-3/2} \exp \left(\frac{-m(\boldsymbol{v} - \boldsymbol{u})^2}{2k_{\mathrm{B}} T} \right) \ . \tag{2.12}$$

Local Maxwellians are parametrized by values of five hydrodynamic variables, ρ, $\boldsymbol{u}$ and T. This parametrization is consistent with the definitions of the hydrodynamic fields (2.4), $\int f_{\mathrm{LM}} \{m, m\boldsymbol{v}, mv^2/2\} \, \mathrm{d}\boldsymbol{v} = (\rho, \rho\boldsymbol{u}, e)$, provided the relation between the energy and the kinetic temperature T holds, $e = \frac{3\rho}{2m} k_{\mathrm{B}} T$.

4. Boltzmann's ***H*** *theorem*: The function

$$S[f] = -k_{\mathrm{B}} \int f \ln f \, \mathrm{d}\boldsymbol{v} \ , \tag{2.13}$$

is called the *entropy density*[1]. The *local* ***H*** *theorem* for distribution functions independent of space states that the rate of the entropy density increase is equal to the nonnegative entropy production,

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sigma \geq 0 \ . \tag{2.14}$$

Thus, if no space dependence is considered, the Boltzmann equation describes relaxation to the unique global Maxwellian (whose parameters are fixed by initial conditions), and the entropy density grows monotonically along the solutions. Mathematical specifications of this property has been

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[1] From the physical point of view the value of the function f can be treated as dimensional quantity, but if one changes the scale and multiplies f by a positive number ν then $S[f]$ transforms into $\nu S[f] + \nu \ln \nu \int f \, \mathrm{d}\boldsymbol{v}$. For a closed system the corresponding transformation of the entropy is an inhomogeneous linear transformation with constant coefficients.

initialized by Carleman [259], and many estimations of the entropy growth were obtained over the past two decades. In the case of space-dependent distribution functions, the local entropy density obeys the *entropy balance equation*:

$$\frac{\partial S(\boldsymbol{x},t)}{\partial t} + \left(\frac{\partial}{\partial \boldsymbol{x}}, \boldsymbol{J}_s(\boldsymbol{x},t)\right) = \sigma(\boldsymbol{x},t) \geq 0 \, , \tag{2.15}$$

where $\boldsymbol{J}_s$ is the entropy flux, $\boldsymbol{J}_s(\boldsymbol{x},t) = -k_{\mathrm{B}} \int \ln f(\boldsymbol{x},t) \boldsymbol{v} f(\boldsymbol{x},t) \, \mathrm{d}\boldsymbol{v}$. For suitable boundary conditions, such as specularly reflecting or at infinity, the entropy flux gives no contribution to the equation for the *total entropy*, $S_{tot} = \int S(\boldsymbol{x},t) \, \mathrm{d}\boldsymbol{x}$ and its rate of changes is then equal to the nonnegative total entropy production $\sigma_{tot} = \int \sigma(\boldsymbol{x},t) \, \mathrm{d}\boldsymbol{x}$ (the *global* $\boldsymbol{H}$ *theorem*). For more general boundary conditions which maintain the entropy influx, the global H theorem needs to be modified. A detailed discussion of this question is given by Cercignani [112]. The local Maxwellian is also specified as the maximizer of the Boltzmann entropy function (2.13), subject to fixed hydrodynamic constraints (2.4). For this reason, the local Maxwellian is also termed the local equilibrium distribution function.

2.1.3 Linearized Collision Integral

Linearization of the Boltzmann integral around the local equilibrium results in the linear integral operator,

$$\begin{aligned} Lh(\boldsymbol{v}) = \int & W(\boldsymbol{v},\boldsymbol{w} \mid \boldsymbol{v}',\boldsymbol{w}') f_{\mathrm{LM}}(\boldsymbol{v}) f_{\mathrm{LM}}(\boldsymbol{w}) \\ & \times \left[\frac{h(\boldsymbol{v}')}{f_{\mathrm{LM}}(\boldsymbol{v}')} + \frac{h(\boldsymbol{w}')}{f_{\mathrm{LM}}(\boldsymbol{w}')} - \frac{h(\boldsymbol{v})}{f_{\mathrm{LM}}(\boldsymbol{v})} - \frac{h(\boldsymbol{w})}{f_{\mathrm{LM}}(\boldsymbol{w})}\right] \mathrm{d}\boldsymbol{w}' \, \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{w} \, . \end{aligned} \tag{2.16}$$

The *linearized collision integral* is symmetric with respect to the scalar product defined by the second derivative of the entropy functional,

$$\int f_{\mathrm{LM}}^{-1}(\boldsymbol{v}) g(\boldsymbol{v}) Lh(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} = \int f_{\mathrm{LM}}^{-1}(\boldsymbol{v}) h(\boldsymbol{v}) Lg(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} \, .$$

The operator L is nonpositive definite,

$$\int f_{\mathrm{LM}}^{-1}(\boldsymbol{v}) h(\boldsymbol{v}) Lh(\boldsymbol{v}) \, \mathrm{d}\boldsymbol{v} \leq 0 \, ,$$

where equality holds if the function $h f_{\mathrm{LM}}^{-1}$ is a linear combination of collision invariants which characterize the null-space of the operator L. The spectrum of the linearized collision integral is well studied in the case of the small angle cut-off.

2.2 Phenomenology and Quasi-Chemical Representation of the Boltzmann Equation

Boltzmann's original derivation of his collision integral was based on a phenomenological "bookkeeping" of the gain and loss of probability density in the collision process. This derivation postulates that the rate of gain G^+ equals

$$G^+ = \int W^+(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}') f(\boldsymbol{v}') f(\boldsymbol{w}')\, \mathrm{d}\boldsymbol{v}'\, \mathrm{d}\boldsymbol{w}'\, \mathrm{d}\boldsymbol{w} \ ,$$

while the rate of loss L^- is

$$L^- = \int W^-(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}') f(\boldsymbol{v}) f(\boldsymbol{w})\, \mathrm{d}\boldsymbol{v}'\, \mathrm{d}\boldsymbol{w}'\, \mathrm{d}\boldsymbol{w} \ .$$

The form of the gain and of the loss, containing products of one-body distribution functions in place of the two-body distribution, constitutes the famous Stosszahlansatz. The Boltzmann collision integral follows now as ($Q = G^+ - L^-$), subject to the detailed balance for the rates of individual collisions,

$$W^+(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}') = W^-(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}') \ .$$

This representation $Q = G^+ - L^-$ for interactions different from hard spheres requires also the cut-off of functions β (2.3) at small angles. The gain−loss form of the collision integral makes it evident that the detailed balance for the rates of individual collisions is sufficient to prove the local H theorem. A weaker condition which is also sufficient to establish the H theorem was first derived by Stueckelberg [114] (so-called *semi-detailed balance*), and later generalized *to inequalities of concordance* [115]:

$$\int \mathrm{d}\boldsymbol{v}' \int \mathrm{d}\boldsymbol{w}' (W^+(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}') - W^-(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}')) \geq 0 \ ,$$
$$\int \mathrm{d}\boldsymbol{v} \int \mathrm{d}\boldsymbol{w} (W^+(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}') - W^-(\boldsymbol{v}, \boldsymbol{w} \mid \boldsymbol{v}', \boldsymbol{w}')) \leq 0 \ .$$

The semi-detailed balance follows from these expressions if the inequality signs are replaced by equalities.

The pattern of Boltzmann's phenomenological approach is often used to construct nonlinear kinetic models. In particular, nonlinear *equations of chemical kinetics* are based on this idea: If n chemical species A_i participate in a complex chemical reaction,

$$\sum_i \alpha_{si} A_i \leftrightarrow \sum_i \beta_{si} A_i \ ,$$

where α_{si} and β_{si} are nonnegative integers (*stoichiometric coefficients*) then equations of chemical kinetics for the concentrations of species c_j are written

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \sum_{s=1}^{n} (\beta_{si} - \alpha_{si}) \left[\varphi_s^+ \exp\left(\sum_{j=1}^{n} \frac{\partial G}{\partial c_j} \alpha_{sj} \right) - \varphi_s^- \exp\left(\sum_{j=1}^{n} \frac{\partial G}{\partial c_j} \beta_{sj} \right) \right] .$$

Functions φ_s^+ and φ_s^- are interpreted as constants of the forward and reverse reactions, respectively, while the function G is an analog of the Boltzmann's H-function.

Modern derivations of the Boltzmann equation, initialized by the seminal work of Bogoliubov [2], seek a replacement condition for the Stosszahlansatz which would be more closely related to many-particle dynamics. Different conditions has been formulated by Zubarev [195], Lewis [281] and others. The advantage of these formulations is the possibility to systematically find corrections not included in the Stosszahlansatz.

2.3 Kinetic Models

Mathematical complications caused by the nonlinear Boltzmann collision integral are traced back to the Stosszahlansatz. Several approaches were developed in order to simplify the Boltzmann equation. Such simplifications are termed kinetic models. Various kinetic models preserve only certain features of the Boltzmann equation, while sacrificing the rest of them. The best known kinetic model is the nonlinear Bhatnagar–Gross–Krook model (BGK) [116]. The BGK collision integral reads:

$$Q_{\mathrm{BGK}} = -\frac{1}{\tau}(f - f_{\mathrm{LM}}(f)) .$$

The time parameter $\tau > 0$ is interpreted as a characteristic relaxation time to the local Maxwellian. The BGK collision integral is a nonlinear operator: The parameters of the local Maxwellian (ρ, $\boldsymbol{u}$ and T, see (2.12)) are the values of the corresponding moments of the distribution function f. This nonlinearly is of "lower dimension" than in the Boltzmann collision integral because $f_{\mathrm{LM}}(f)$ is a nonlinear function of only the moments of f whereas the Boltzmann collision integral is nonlinear in the distribution function f itself. This type of simplification introduced by the BGK approach is closely related to the family of the so-called mean-field approximations in statistical mechanics.

By its construction, the BGK collision integral preserves the following three properties of the Boltzmann equation: additive invariants of collision, uniqueness of the equilibrium, and the H theorem.

A class of kinetic models which generalized the BGK model to quasi-equilibrium approximations of a general form is described as follows: The quasiequilibrium f^* for the set of linear functionals $M(f)$ is a distribution function $f^*(M)(\boldsymbol{x}, \boldsymbol{v})$ which maximizes the entropy under fixed values of the functionals M. The quasiequilibrium (QE) models are characterized by the collision integral [117],

$$Q_{\mathrm{QE}}(f) = -\frac{1}{\tau}[f - f^*(M(f))] + Q(f^*(M(f)), f^*(M(f))) \,. \tag{2.17}$$

The first term in (2.17) describes the relaxation *to* the quasiequiulibrium manifold $\{f^*(M)(\boldsymbol{x}, \boldsymbol{v})\}$ (parametrized by the values of the moments M), and the second term is the quasiequilibrium approximation for the Boltzmann collision integral, that is, the value of the Boltzmann collision integral *on* the quasiequilibrium distribution. If the set of moment M is ρ, $\boldsymbol{u}$ and T then the quasiequilibrium model (2.17) turns into the BGK model (2.17)

Same as in the case of the BGK collision integral, operator Q_{QE} is nonlinear in the moments M only. The QE models preserve the following properties of the Boltzmann collision operator: additive invariants, uniqueness of the equilibrium, and the H theorem, provided the relaxation time τ to the quasiequilibrium is sufficiently small [117].

A different nonlinear model was proposed by Lebowitz, Frisch and Helfand [118]:

$$Q_D = D\left(\frac{\partial}{\partial \boldsymbol{v}}\frac{\partial}{\partial \boldsymbol{v}} f + \frac{m}{k_{\mathrm{B}}T}\frac{\partial}{\partial \boldsymbol{v}}(\boldsymbol{v} - \boldsymbol{u}(f))f\right) \,.$$

The collision integral has the form of the self-consistent Fokker–Planck operator, describing diffusion (in the velocity space) in the self-consistent potential. Diffusion coefficient $D > 0$ may depend on the distribution function f. Operator Q_D preserves the same properties of the Boltzmann collision operator as the BGK model.

The kinetic BGK model has been used to obtain exact solutions of gasdynamic problems, especially for stationary problems. The linearized BGK collision model has been extended to model more precisely the linearized Boltzmann collision integral [112].

2.4 Methods of Reduced Description

One of the major issues raised by the Boltzmann equation is the problem of the reduced description. The equations of hydrodynamics constitute a closed set of equations for the hydrodynamic fields (local density, local momentum, and local temperature). From the standpoint of the Boltzmann equation, these quantities are low-order moments of the one-body distribution function, or, in other words, macroscopic variables. The problem of the reduced description consists in the following questions:

1. What are the conditions under which the macroscopic description is valid?
2. What macroscopic variables are relevant for this description?

3. How can we derive equations for the macroscopic variables from the kinetic equations?

The classical methods of reduced description for the Boltzmann equation are the Hilbert method, the Chapman–Enskog method, and the Grad moment method.

2.4.1 The Hilbert Method

In 1911, David Hilbert introduced the notion of normal solutions,

$$f_{\mathrm{H}}(\boldsymbol{v},\, n(\boldsymbol{x},t),\, \boldsymbol{u}(\boldsymbol{x},t),\, T(\boldsymbol{x},t)) \;,$$

that is, solutions to the Boltzmann equation which depend on space and time only through five hydrodynamic fields [16]

$$\int f(\boldsymbol{x},\boldsymbol{v},t)\,\mathrm{d}\boldsymbol{v} = n(\boldsymbol{x},t),\ \int \boldsymbol{v} f(\boldsymbol{x},\boldsymbol{v},t)\,\mathrm{d}\boldsymbol{v} = n(\boldsymbol{x},t)\boldsymbol{u}(\boldsymbol{x},t)\;,$$
$$\int \frac{mv^2}{2} f(\boldsymbol{x},\boldsymbol{v},t)\,\mathrm{d}\boldsymbol{v} = \frac{3}{2} n(\boldsymbol{x},t) k_{\mathrm{B}} T\;.$$

The normal solutions are found from a singularly perturbed Boltzmann equation,

$$D_t f = \frac{1}{\varepsilon} Q(f,f)\;, \tag{2.18}$$

where ε is a small parameter, and

$$D_t f \equiv \frac{\partial}{\partial t} f + \left(\boldsymbol{v}, \frac{\partial}{\partial \boldsymbol{x}}\right) f\;.$$

Physically, parameter ε corresponds to the Knudsen number, the ratio between the mean free path of the molecules between collisions, and the characteristic scale of variation of the hydrodynamic fields. In the Hilbert method, one seeks functions $n(\boldsymbol{x},t)$, $\boldsymbol{u}(\boldsymbol{x},t)$, $T(\boldsymbol{x},t)$, such that the normal solution in the form of the Hilbert expansion,

$$f_{\mathrm{H}} = \sum_{i=0}^{\infty} \varepsilon^i f_{\mathrm{H}}^{(i)} \tag{2.19}$$

satisfies (2.18) order by order. Hilbert was able to demonstrate that this is formally possible. Substituting (2.19) into (2.18), and matching various order in ε, we obtain the sequence of integral equations

$$Q(f_{\mathrm{H}}^{(0)}, f_{\mathrm{H}}^{(0)}) = 0\;, \tag{2.20}$$
$$L f_{\mathrm{H}}^{(1)} = D_t f_{\mathrm{H}}^{(0)}\;, \tag{2.21}$$
$$L f_{\mathrm{H}}^{(2)} = D_t f_{\mathrm{H}}^{(1)} - 2Q(f_{\mathrm{H}}^{(0)}, f_{\mathrm{H}}^{(1)})\;, \tag{2.22}$$

and so on for higher orders. Here L is the linearized collision integral. From (2.20), it follows that $f_{\mathrm{H}}^{(0)}$ is the local Maxwellian with parameters not yet determined. The Fredholm alternative, as applied to (2.21) results in:

(a) Solvability condition,

$$\int D_t f_{\mathrm{H}}^{(0)} \{1, \boldsymbol{v}, v^2\} \, \mathrm{d}\boldsymbol{v} = 0 \, ,$$

which is the set of the compressible Euler equations of the non-viscous hydrodynamics. The solution of the Euler equation determines the parameters of the Maxwellian f_{H}^{0}.

(b) General solution $f_{\mathrm{H}}^{(1)} = f_{\mathrm{H}}^{(1)1} + f_{\mathrm{H}}^{(1)2}$, where $f_{\mathrm{H}}^{(1)1}$ is the special solution to the linear integral equation (2.21), and $f_{\mathrm{H}}^{(1)2}$ is a yet undetermined linear combination of the additive invariants of collision.

(c) Solvability condition to the next equation (2.22) determines coefficients of the function $f_{\mathrm{H}}^{(1)2}$ in terms of solutions to linear hyperbolic differential equations,

$$\int D_t \left(f_{\mathrm{H}}^{(1)1} + f_{\mathrm{H}}^{(1)2}\right) \{1, \boldsymbol{v}, v^2\} \, \mathrm{d}\boldsymbol{v} = 0 \, .$$

Hilbert was able to demonstrate that this procedure of constructing the normal solution can be carried out to arbitrary order n, where the function $f_{\mathrm{H}}^{(n)}$ is determined from the solvability condition at the next, $(n+1)$-th order. In order to summarize, implementation of the Hilbert method requires solutions for the functions $n(\boldsymbol{x}, t)$, $\boldsymbol{u}(\boldsymbol{x}, t)$, and $T(\boldsymbol{x}, t)$ obtained from a sequence of partial differential equations.

2.4.2 The Chapman–Enskog Method

A completely different approach to the reduced description was invented in 1917 by David Enskog [120], and independently by Sidney Chapman [70]. The key idea was to seek an expansion of the time derivatives of the hydrodynamic variables rather than seeking the time-space dependence of these functions, as in the Hilbert method.

The Chapman–Enskog method starts also with the singularly perturbed Boltzmann equation, and with the expansion

$$f_{\mathrm{CE}} = \sum_{n=0}^{\infty} \varepsilon^n f_{\mathrm{CE}}^{(n)} \, .$$

However, the procedure of evaluation of the functions $f_{\mathrm{CE}}^{(n)}$ differs from the Hilbert method:

$$Q\left(f_{\mathrm{CE}}^{(0)}, f_{\mathrm{CE}}^{(0)}\right) = 0 \, , \tag{2.23}$$

$$L f_{\mathrm{CE}}^{(1)} = -Q\left(f_{\mathrm{CE}}^{(0)}, f_{\mathrm{CE}}^{(0)}\right) + \frac{\partial^{(0)}}{\partial t} f_{\mathrm{CE}}^{(0)} + \left(\boldsymbol{v}, \frac{\partial}{\partial \boldsymbol{x}}\right) f_{\mathrm{CE}}^{(0)} \, . \tag{2.24}$$

The operator $\partial^{(0)}/\partial t$ is defined from the expansion of the right hand side of the hydrodynamic equations,

$$\frac{\partial^{(0)}}{\partial t}\{\rho, \rho\boldsymbol{u}, e\} \equiv -\int \left\{m, m\boldsymbol{v}, \frac{mv^2}{2}\right\} \left(\boldsymbol{v}, \frac{\partial}{\partial \boldsymbol{x}}\right) f^{(0)}_{\mathrm{CE}}\, \mathrm{d}\boldsymbol{v} \; . \tag{2.25}$$

From (2.23), function $f^{(0)}_{\mathrm{CE}}$ is again the local Maxwellian, whereas (2.25) are the Euler equations, and $\partial^{(0)}/\partial t$ acts on various functions $g(\rho, \rho\boldsymbol{u}, e)$ according to the chain rule,

$$\frac{\partial^{(0)}}{\partial t} g = \frac{\partial g}{\partial \rho}\frac{\partial^{(0)}}{\partial t}\rho + \frac{\partial g}{\partial(\rho\boldsymbol{u})}\frac{\partial^{(0)}}{\partial t}(\rho\boldsymbol{u}) + \frac{\partial g}{\partial e}\frac{\partial^{(0)}}{\partial t} e \; ,$$

while the time derivatives $\frac{\partial^{(0)}}{\partial t}$ of the hydrodynamic fields are expressed using the right hand side of (2.25).

The result of the Chapman–Enskog definition of the time derivative $\frac{\partial^{(0)}}{\partial t}$, is that the Fredholm alternative is satisfied by the right hand side of (2.24). Finally, the solution to the homogeneous equation is set to zero by the requirement that the hydrodynamic variables as defined by the function $f^{(0)} + \varepsilon f^{(1)}$ coincide with the parameters of the local Maxwellian $f^{(0)}$:

$$\int \{1, \boldsymbol{v}, v^2\} f^{(1)}_{\mathrm{CE}}\, \mathrm{d}\boldsymbol{v} = 0 \; .$$

The first correction $f^{(1)}_{\mathrm{CE}}$ of the Chapman–Enskog method adds the terms

$$\frac{\partial^{(1)}}{\partial t}\{\rho, \rho\boldsymbol{u}, e\} = -\int \left\{m, m\boldsymbol{v}, \frac{mv^2}{2}\right\} \left(\boldsymbol{v}, \frac{\partial}{\partial \boldsymbol{x}}\right) f^{(1)}_{\mathrm{CE}}\, \mathrm{d}\boldsymbol{v}$$

to the time derivatives of the hydrodynamic fields. These terms correspond to the dissipative hydrodynamics where viscous momentum transfer and heat transfer are in the Navier–Stokes and Fourier form. The Chapman–Enskog method was the first true success of the Boltzmann equation since it made it possible to derive macroscopic equations without a priori guessing (the generalization of the Boltzmann equation onto mixtures predicted existence of the thermodiffusion before it has been found experimentally), and to express transport coefficients in terms of microscopic particles interaction.[2]

However, higher-order corrections of the Chapman–Enskog method, resulting in hydrodynamic equations with higher derivatives (Burnett hydrodynamic equations) face severe difficulties both from the theoretical, as well as from the practical point of view. In particular, they result in unphysical instabilities of the equilibrium.

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[2] For all of the reduction methods many properties of the gas, from the characteristics of the velocity distribution function to the transport coefficients, may be expressed in terms of functions of the collision integral (kinetic integrals). Although the evaluation of these functions is conceptually straightforward, technically it is frequently rather cumbersome. Now the methods for the analytical evaluation of kinetic integrals using computer algebra are developed [121].

2.4.3 The Grad Moment Method

In 1949, Harold Grad extended the basic assumption of the Hilbert and the Chapman–Enskog methods (the space and time dependence of normal solutions is mediated by the five hydrodynamic moments) [201]. A physical rationale behind the Grad moment method is an assumption of the decomposition of motions:

1. During the time of order τ, a set of distinguished moments M' (which include the hydrodynamic moments and a subset of higher-order moments) does not change significantly in comparison to the rest of the moments M'' (the fast dynamics).
2. Towards the end of the fast evolution, the values of the moments M'' become unambiguously determined by the values of the distinguished moments M'.
3. On the time of order $\theta \gg \tau$, dynamics of the distribution function is determined by the dynamics of the distinguished moments while the rest of the moments remain to be determined by the distinguished moments (the slow evolution period).

Implementation of this picture requires an ansatz for the distribution function in order to represent the set of states visited in the course of the slow evolution. In Grad's method, these representative sets are finite-order truncations of an expansion of the distribution functions in terms of Hermite velocity tensors:

$$f_G(M', \boldsymbol{v}) = f_{\mathrm{LM}}(\rho, \boldsymbol{u}, e, \boldsymbol{v}) \left[1 + \sum_{(\alpha)}^{N} a_{(\alpha)}(M') H_{(\alpha)}(\boldsymbol{v} - \boldsymbol{u}) \right] , \qquad (2.26)$$

where $H_{(\alpha)}(\boldsymbol{v} - \boldsymbol{u})$ are Hermite tensor polynomials, orthogonal with the weight f_{LM}, while coefficient $a_{(\alpha)}(M')$ are known functions of the distinguished moments M'. Other moments are assumed to be functions of M': $M'' = M''(f_G(M'))$.

Slow evolution of distinguished moments is found upon substitution of (2.26) into the Boltzmann equation and finding the moments of the resulting expression (*Grad's moment equations*). Following Grad, this very simple approximation can be improved by extending the list of distinguished moments. The best known is Grad's thirteen-moment approximation where the set of distinguished moments consists of the five hydrodynamic moments, the five components of the traceless stress tensor $\sigma_{ij} = \int m[(v_i - u_i)(v_j - u_j) - \delta_{ij}(\boldsymbol{v} - \boldsymbol{u})^2/3] f \, \mathrm{d}\boldsymbol{v}$, and of the three components of the heat flux vector $q_i = \int (v_i - u_i) m (\boldsymbol{v} - \boldsymbol{u})^2 / 2 f \, \mathrm{d}\boldsymbol{v}$.

The decomposition of motions hypothesis cannot be evaluated for its validity within the framework of Grad's approach. It is not surprising therefore that Grad's methods failed to work in situations where it was (unmotivatedly) supposed to, primarily, in phenomena with sharp time-space dependence such as the strong shock waves. On the other hand, Grad's method was quite successful for describing transition between parabolic and hyperbolic propagation, in particular, the second sound effect in massive solids at low temperatures, and, in general, situations slightly deviating from the classical Navier–Stokes–Fourier domain. Finally, the Grad method has been important background for the development of phenomenological nonequilibrium thermodynamics based on a hyperbolic first-order equation, the so-called EIT (extended irreversible thermodynamics [235, 236]).

2.4.4 Special Approximations

Special approximations to the solutions of the Boltzmann equation were found for several problems, which perform better than the results of "regular" procedures. The best known is the Tamm–Mott-Smith ansatz introduced independently by Mott-Smith and Tamm for the strong shock wave problem: The (stationary) distribution function is represented as

$$f_{\mathrm{TMS}}(a(x)) = (1 - a(x))f_+ + a(x)f_- \ , \tag{2.27}$$

where $f_\pm$ are upstream and downstream Maxwell distribution functions, and $a(x)$ is an undetermined scalar function of the coordinate along the shock tube.

Equation for the function $a(x)$ is obtained upon substitution of (2.27) into the Boltzmann equation, and integration with some velocity-dependent function $\varphi(\boldsymbol{v})$. Two general problems arise with the special approximation thus constructed: which function $\varphi(\boldsymbol{v})$ should be taken, and how to find a correction to an ansatz like (2.27)?

2.4.5 The Method of Invariant Manifold

The general problem of reduced description for dissipative system was recognized as the problem of finding stable invariant manifolds in the space of distribution functions [9, 11, 12, 14]. The notion of invariant manifold generalizes the normal solution in the Hilbert and in the Chapman–Enskog method, and the finite-moment sets of distribution function in the Grad method: If Ω is a smooth manifold in the space of distribution functions, and if f_Ω is an element of Ω, then Ω is invariant with respect to the dynamic system,

$$\frac{\mathrm{d}f}{\mathrm{d}t} = J(f) \ , \tag{2.28}$$

$$\text{if } J(f_\Omega) \in T_{f_\Omega}\Omega, \text{ for all } f_\Omega \in \Omega \ , \tag{2.29}$$

where $T_{f_\Omega}\Omega$ is the tangent space of the manifold Ω at the point f_Ω. Application of the invariant manifold idea to dissipative systems is based on iterations, progressively improving the initial approximation, and it involves the following steps: construction of the thermodynamic projector and iterations for the invariance condition

Thermodynamic Projector

Given a manifold Ω (not obligatory invariant), the macroscopic dynamics on this manifold is defined by the *macroscopic vector field*, which is the result of a projection of vectors $J(f_\Omega)$ onto the tangent bundle $T\Omega$. The thermodynamic projector $P^*_{f_\Omega}$ takes advantage of dissipativity:

$$\ker P^*_{f_\Omega} \subseteq \ker D_f S\mid_{f_\Omega} , \tag{2.30}$$

where $D_f S\mid_{f_\Omega}$ is the differential of the entropy evaluated in f_Ω.

This condition of thermodynamicity means that the projector $P^*_{f_\Omega}$ determines a decomposition of motion near Ω: $f_\Omega + \ker P^*_{f_\Omega}$ is the plane of fast motion, and $\mathrm{im} P^*_{f_\Omega}$ is the tangent space to f_Ω, we assume that the motion along Ω is slow. Each state of the manifold Ω can be considered as the result of the fast relaxation. During the fast motion the entropy should grow. Hence, the state f_Ω is the maximum entropy state on the plain of fast motions $f_\Omega + \ker P^*_{f_\Omega}$.

The condition of thermodynamicity (2.30) does not define the projector completely; rather, it is the condition that should be satisfied by any projector used to define the macroscopic vector field, $J'_\Omega = P^*_{f_\Omega} J(f_\Omega)$. For, once the condition (2.30) is met, the macroscopic vector field preserves dissipativity of the original microscopic vector field $J(f)$:

$$D_f S\mid_{f_\Omega} \cdot P^*_{f_\Omega}(J(f_\Omega)) \geq 0 \text{ for all } f_\Omega \in \Omega . \tag{2.31}$$

Nevertheless, the thermodynamic projector is uniquely defined by the requirement dissipativity preservation (2.31) for *all* the dissipative vector field with the given entropy (see Chap. 5 and [10]).

The thermodynamic projector is the formalization of the assumption that Ω is the manifold of slow motion: If a fast relaxation takes place at least in a neighborhood of Ω, then the states visited in this process before arriving at f_Ω belong to $\ker P^*_{f_\Omega}$. In general, $P^*_{f_\Omega}$ depends in a non-trivial way on f_Ω.

Iterations for the Invariance Condition

The invariance condition for the manifold Ω reads,

$$P_\Omega(J(f_\Omega)) - J(f_\Omega) = 0 ,$$

here P_Ω is arbitrary (not obligatory thermodynamic) projector onto the tangent bundle of Ω. The invariance condition is considered as an equation which is solved iteratively, starting with an initial approximation Ω_0. On the

$(n+1)-$st iteration, the correction $f^{(n+1)} = f^{(n)} + \delta f^{(n+1)}$ is found from linear equations,

$$\begin{aligned} D_f J_n^* \delta f^{(n+1)} &= P_n^* J(f^{(n)}) - J(f^{(n)}) \, , \\ P_n^* \delta f^{(n+1)} &= 0 \, , \end{aligned} \tag{2.32}$$

where $D_f J_n^*$ is the linear self-adjoint operator with respect to the scalar product by the second differential of the entropy $D_f^2 S \mid_{f^{(n)}}$.

Together with the above-mentioned principle of thermodynamic projection, the *self-adjoint linearization* implements the assumption about the decomposition of motions around the n'th approximation. The self-adjoint linearization of the Boltzmann collision integral Q (2.7) around a distribution function f is given by the formula,

$$\begin{aligned} D_f Q^{\mathrm{SYM}} \delta f = & \int W(\boldsymbol{v}, \boldsymbol{w}, \mid \boldsymbol{v}', \boldsymbol{w}') \frac{f(\boldsymbol{v}) f(\boldsymbol{w}) + f(\boldsymbol{v}') f(\boldsymbol{w}')}{2} \\ & \times \left[\frac{\delta f(\boldsymbol{v}')}{f(\boldsymbol{v}')} + \frac{\delta f(\boldsymbol{w}')}{f(\boldsymbol{w}')} - \frac{\delta f(\boldsymbol{v})}{f(\boldsymbol{v})} - \frac{\delta f(\boldsymbol{w})}{f(\boldsymbol{w})} \right] \mathrm{d}\boldsymbol{w}' \, \mathrm{d}\boldsymbol{v}' \, \mathrm{d}\boldsymbol{w} \, . \end{aligned} \tag{2.33}$$

If $f = f_{\mathrm{LM}}$, the self-adjoint operator (2.33) becomes the linearized collision integral.

The method of invariant manifold is the iterative process:

$$(f^{(n)}, P_n^*) \to (f^{(n+1)}, P_n^*) \to (f^{(n+1)}, P_{n+1}^*)$$

On the each first step of the iteration, the linear equation (2.32) is solved with the projector known from the previous iteration. On the each second step, the projector is updated, following the thermodynamic construction. The method of invariant manifold can be further simplified if smallness parameters are known.

2.4.6 Quasiequilibrium Approximations

Important generalization of the Grad moment method is the concept of the *quasiequilibrium approximations* already mentioned above (we discuss this approximation in detail in Chap. 5). The quasiequilibrium distribution function for a set of distinguished moments $M = m(f)$ maximizes the entropy density S for fixed M. The quasiequilibrium manifold $\Omega^*(M)$ is the collection of the quasiequilibrium distribution functions for all admissible values of M. The quasiequilibrium approximation is the simplest and extremely useful (not only in the kinetic theory itself) implementation of the hypothesis about a decomposition of motions: If M are considered as slow variables, then states which could be visited in the course of rapid motion in the vicinity of $\Omega^*(M)$ belong to the planes

$$\Gamma_M = \{f \mid m(f - f^*(M)) = 0\} \ .$$

In that respect, the thermodynamic construction in the method of invariant manifold is a generalization of the quasiequilibrium approximation where the given manifold is equipped with a quasiequilibrium structure by choosing appropriately the macroscopic variables of the slow motion. In contrast to the quasiequilibrium, the macroscopic variables thus constructed are not obligatory moments. A textbook example of the quasiequilibrium approximation is the generalized Gaussian function for $M = \{\rho, \rho\boldsymbol{u}, P\}$, where $P_{ij} = \int v_i v_j f \, \mathrm{d}\boldsymbol{v}$ is the pressure tensor.

The thermodynamic projector P^* for a quasiequilibrium approximation was first introduced by B. Robertson [126] (in a different context of conservative dynamics and for a special case of the Gibbs–Shannon entropy). It acts on a function Ψ as follows

$$P^*_M \Psi = \sum_i \frac{\partial f^*}{\partial M_i} \int m_i \Psi \, \mathrm{d}\boldsymbol{v} \ ,$$

where $M = \int m_i f \, \mathrm{d}\boldsymbol{v}$. The quasiequilibrium approximation does not exist if the highest order moment is an odd-order polynomial of velocity (therefore, there exists no quasiequilibrium for thirteen Grad's moments), and a regularization is then required. Otherwise, the Grad moment approximation is the first-order expansion of the quasiequilibrium around the local Maxwellian.

2.5 Discrete Velocity Models

If the number of microscopic velocities is reduced drastically to only a finite set, the resulting discrete velocity models, continuous in time and in space, can still mimic gas-dynamic flows. This idea was introduced in Broadwell's paper in 1963 to mimic the strong shock wave [122].

Further important development of this idea was due to Cabannes and Gatignol in the seventies who introduced a systematic class of discrete velocity models [129]. The structure of the collision operators in the discrete velocity models mimics the polynomial character of the Boltzmann collision integral. Discrete velocity models are implemented numerically by using the natural operator splitting in which each update due to free flight is followed by the collision update, the idea which dates back to Grad. One of the most important recent results is the proof of convergence of the discrete velocity models with pair collisions to the Boltzmann collision integral [124].

2.6 Direct Simulation

Besides the analytical approach, direct numerical simulation of Boltzmann-type nonlinear kinetic equations have been developed since the middle of

1960's, beginning with the seminal works of Bird [127, 128]. The basis of the approach is a representation of the Boltzmann gas by a set of particles whose dynamics is modeled as a sequence of free propagation and collisions. The modeling of collisions uses a random choice of pairs of particles inside the cells of the space, and changing the velocities of these pairs in such a way as to comply with the conservation laws, and in accordance with the kernel of the Boltzmann collision integral. At present, there exists a variety of models based on this scheme known as the Direct Simulation Monte-Carlo method (DSMC) [127, 128]. The DSMC, in particular, provides data to test various analytical theories.

2.7 Lattice Gas and Lattice Boltzmann Models

Since the mid 1980's, the kinetic-theory based approach to simulate complex macroscopic phenomena such as hydrodynamics has been developed. The main idea of the approach is the construction of a minimal kinetic system in such a way that their long-time and large-scale limit matches the desired macroscopic equations. For this purpose, the fully discrete (in time, space, and velocity) nonlinear kinetic equations are considered on sufficiently isotropic lattices, where the links represent the discrete velocities of fictitious particles. In the earlier version of the lattice methods, the particle–based picture has been exploited. These models obey the exclusion rule (one or zero particle per lattice link) (the lattice gas model [130]). Most of the present versions use the distribution function picture, where populations of the links are non-integer (the lattice Boltzmann model [131–135]). Discrete-time dynamics consists of a propagation step where populations are transmitted to adjacent links and collision step where populations of the links at each node of the lattice are equilibrated according a certain simple rule. Many of present versions use the BGK-type equilibration, where the local equilibrium is constructed in such a way as to match desired macroscopic equations. The lattice Boltzmann method is a useful approach for computational fluid dynamics, effectively compliant with parallel architectures. The proof of the H theorem for the Lattice gas models is based on the semi-detailed (or Stueckelberg's) balance principle. The proof of the H theorem in the framework of the lattice Boltzmann method has only very recently been achieved [136–141] (see below).

2.7.1 Discrete Velocity Models for Hydrodynamics

We start with a generic discrete velocity kinetic model. Let $f_i(\boldsymbol{x}, t)$ be the population of D-dimensional discrete velocities $\boldsymbol{c}_i$, $i = 1, \dots, n_{\mathrm{d}}$, at position $\boldsymbol{x}$ and time t. The hydrodynamic fields are the first few moments of the populations, namely

$$\sum_{i=1}^{n_\mathrm{d}} \{1,\, \boldsymbol{c}_i,\, c_i^2\} f_i = \{\rho,\, \rho \boldsymbol{u},\, \rho D T + \rho u^2\} \,, \tag{2.34}$$

where ρ is the mass density of the fluid, $\rho \boldsymbol{u}$ is the D-dimensional momentum density vector, and $e = \rho D T + \rho u^2$ is the energy density. Below, the index $\alpha = 1, \dots, D$, denotes the spatial components. In the case of athermal hydrodynamics, the set of independent hydrodynamic fields contains only the mass and momentum densities. It is convenient to introduce n_d-dimensional population vectors $\boldsymbol{f}$, and the standard scalar product, $\langle \boldsymbol{f} | \boldsymbol{g} \rangle = \sum_{i=1}^{n_\mathrm{d}} x_i y_i$. We will describe here the construction of the discrete velocity models for the incompressible hydrodynamics (the most important field of applications), and will present the results for a weakly compressible case below. So, let the locally conserved fields be density and momentum density,

$$\langle \boldsymbol{1} | \boldsymbol{f} \rangle = \rho,\ \langle \boldsymbol{c}_\alpha | \boldsymbol{f} \rangle = \rho u_\alpha \,. \tag{2.35}$$

Here $\boldsymbol{1} = \{1\}_{i=1}^{n_\mathrm{d}}$, $\boldsymbol{v}_\alpha = \{c_{i\alpha}\}_{i=1}^{n_\mathrm{d}}$, $\alpha = 1, \dots, D$. In this case, the construction of the kinetic simulation scheme begins with finding a convex function of populations H (entropy function), which satisfies the following condition: If $\boldsymbol{f}^\mathrm{eq}(\rho, \boldsymbol{u})$ (local equilibrium) minimizes H subject to the hydrodynamic constraints (2.35), then $\boldsymbol{f}^\mathrm{eq}$ also satisfies certain restrictions on the higher-order moments. For example, the equilibrium stress tensor must respect the Galilean invariance,

$$\sum_{i=1}^{n_\mathrm{d}} c_{i\alpha} c_{i\beta} f_i^\mathrm{eq}(\rho, \boldsymbol{u}) = \rho c_\mathrm{s}^2 \delta_{\alpha\beta} + \rho u_\alpha u_\beta \,. \tag{2.36}$$

Here c_s is the speed of sound. The corresponding entropy functions for the athermal and thermal cases are given below (see Table 2.1 and Table 2.2). For the time being, assume the convex function H is fixed.

The next step is to write down the set of kinetic equations,

$$\partial_t f_i + c_{i\alpha} \partial_\alpha f_i = \varDelta_i \,. \tag{2.37}$$

Table 2.1. Reconstruction of macroscopic dynamics with the increase of the order of the Hermite polynomial

Order of Polynomial	Independent Variables	Discrete Velocities (1D)	Weights	Target Equation
2	ρ	± 1	$\frac{1}{2}$	Diffusion
3	$\rho,\, \rho\boldsymbol{u}$	$0,\, \pm\sqrt{3T_0}$	$\frac{2}{3},\, \frac{1}{6}$	Athermal Navier–Stokes, $O(u^2)$
4	$\rho,\, \rho\boldsymbol{u},\, e$	$\pm a,\ \pm b$	$\frac{T_0}{4a^2},\ \frac{T_0}{4b^2}$	Thermal Navier–Stokes, $O(\theta^2)$ Athermal Navier–Stokes, $O(u^3)$

Table 2.2. Reconstruction of higher-order moments, in comparison to the continuous case. Symbol $\varDelta$ denotes the difference from the continuous case

	$\varDelta P^{\text{eq}}_{\alpha\beta}$	$\varDelta Q^{\text{eq}}_{\alpha\beta\gamma}$	$\varDelta R^{\text{eq}}_{\alpha\beta}$
Athermal case	$O(u^4)$	$O(u^3)$	
Thermal case*	$O(u^8)$	$O(u\theta^2)$, $O(u^3\theta)$, and $O(u^5)$	$O(\theta^2)$, $O(u^2\theta^2)$, and $O(u^4)$

*$\theta = (T_0 - T)/T_0$ is the deviation of the temperature from the reference value.

For a generic case of n_{c} locally conserved fields $M_i = \langle \boldsymbol{m}_i | \boldsymbol{f} \rangle$, $i = 1, \dots, n_{\text{c}}$, $n_{\text{c}} < n_{\text{d}}$, the n_{d}-dimensional vector function $\boldsymbol{\varDelta}$ (collision integral), must satisfy the conditions:

$$\langle \boldsymbol{m}_i | \boldsymbol{\varDelta} \rangle = 0 \text{ (local conservation laws)} \; ,$$

$$\sigma = \langle \boldsymbol{\nabla} H | \boldsymbol{\varDelta} \rangle \leq 0 \text{ (entropy production inequality)} \; .$$

Here $\boldsymbol{\nabla} H$ is the row-vector of partial derivatives $\partial H / \partial f_i$. Moreover, the local equilibrium vector $\boldsymbol{f}^{\text{eq}}$ must be the only zero point of $\boldsymbol{\varDelta}$, that is, $\boldsymbol{\varDelta}(\boldsymbol{f}^{\text{eq}}) = \boldsymbol{0}$, and, finally, $\boldsymbol{f}^{\text{eq}}$ must be the only zero point of the local entropy production, $\sigma(\boldsymbol{f}^{\text{eq}}) = 0$. Collision integral which satisfies all these requirements is called admissible. Let us discuss several possibilities of constructing admissible collision integrals.

BGK Model

Suppose the entropy function H known. If, in addition, the local equilibrium is also known as an explicit function of locally conserved variables (or some reliable approximation of this function is known), the simplest option is to use the Bhatnagar-Gross-Krook (BGK) model. In the case of athermal hydrodynamics, for example, we write

$$\boldsymbol{\varDelta} = -\frac{1}{\tau}(\boldsymbol{f} - \boldsymbol{f}^{\text{eq}}(\rho(\boldsymbol{f}), \boldsymbol{u}(\boldsymbol{f}))) \; . \tag{2.38}$$

The BGK collision operator is sufficient for many applications. However, it becomes advantageous only if the local equilibrium is known in a closed form. In other cases only the entropy function is known but not its minimizer. For those cases one should construct collision integrals based solely on the knowledge of the entropy function. We here present two particular realizations of the collision integral based on the knowledge of the entropy only.

Quasi-Chemical Model

Let $\boldsymbol{m}_1, \dots, \boldsymbol{m}_{n_{\text{c}}}$ be the n_{d}-dimensional vectors of locally conserved fields, $M_i = \langle \boldsymbol{m}_i | \boldsymbol{f} \rangle$, $i = 1, \dots, n_{\text{c}}$, and let $\boldsymbol{g}_s$, $s = 1, \dots, n_{\text{d}} - n_{\text{c}}$, be a basis of the subspace orthogonal (in the standard scalar product) to vectors of conservation laws. For each vector $\boldsymbol{g}_s$, we define a decomposition $\boldsymbol{g}_s = \boldsymbol{g}_s^+ - \boldsymbol{g}_s^-$, where all components of vectors $\boldsymbol{g}_s^\pm$ are nonnegative, and if $g_{si}^\pm \neq 0$, then $g_{si}^\mp = 0$. Let us consider the collision integral of the form:

$$\boldsymbol{\Delta} = \sum_{s=1}^{n_\mathrm{d}-n_\mathrm{c}} \gamma_s \boldsymbol{g}_s \left\{ \exp\left[\langle \boldsymbol{\nabla} H | \boldsymbol{g}_s^- \rangle\right] - \exp\left[\langle \boldsymbol{\nabla} H | \boldsymbol{g}_s^+ \rangle\right] \right\} \ . \tag{2.39}$$

Here $\gamma_s > 0$. By the construction, the collision integral (2.39) is admissible. If the entropy function is Boltzmann–like, and the components of vectors $\boldsymbol{g}_s$ are integers, the collision integral assumes the familiar Boltzmann–like (or mass action law) form.

Single Relaxation Time Gradient Model

The BGK collision model (2.38) has the important property: linearization of the operator (2.38) at the local equilibrium point has a very simple spectrum $\{0, -1/\tau\}$, where 0 is the n_c-times degenerated eigenvalue corresponding to the conservation laws, while the eigenvalue $-1/\tau$ corresponds to all the rest of the (kinetic) eigenvectors. Nonlinear collision operators which have this property of their linearizations at equilibrium are called single relaxation time models (SRTM). They play an important role in modelling because they allow for the simplest identification of transport coefficients.

The SRTM, based on the given entropy function H, is constructed as follows (single relaxation time gradient model, SRTGM). For the system with n_c local conservation laws, let $\boldsymbol{e}_s$, $s = 1, \ldots, n_\mathrm{d} - n_\mathrm{c}$, be an orthonormal basis in the kinetic subspace, $\langle \boldsymbol{m}_i | \boldsymbol{e}_s \rangle = 0$, and $\langle \boldsymbol{e}_s | \boldsymbol{e}_p \rangle = \delta_{sp}$. Then the single relaxation time gradient model is

$$\boldsymbol{\Delta} = -\frac{1}{\tau} \sum_{s,p=1}^{n_\mathrm{d}-n_\mathrm{c}} \boldsymbol{e}_s K_{sp}(\boldsymbol{f}) \langle \boldsymbol{e}_p | \boldsymbol{\nabla} H \rangle \ , \tag{2.40}$$

where K_{sp} are elements of a positive definite $(n_\mathrm{d} - n_\mathrm{c}) \times (n_\mathrm{d} - n_\mathrm{c})$ matrix $\mathbf{K}$,

$$\begin{aligned} \mathbf{K}(\boldsymbol{f}) &= \boldsymbol{C}^{-1}(\boldsymbol{f}) \ , \\ C_{sp}(\boldsymbol{f}) &= \langle \boldsymbol{e}_s | \boldsymbol{\nabla\nabla} H(\boldsymbol{f}) | \boldsymbol{e}_p \rangle \ . \end{aligned} \tag{2.41}$$

Here $\boldsymbol{\nabla\nabla} H(\boldsymbol{f})$ is the $n_\mathrm{d} \times n_\mathrm{d}$ matrix of second derivatives, $\partial^2 H / \partial f_i \partial f_j$. Linearization of the collision integral at equilibrium results in the form,

$$\boldsymbol{L} = -\frac{1}{\tau} \sum_{s=1}^{n_\mathrm{d}-n_\mathrm{c}} \boldsymbol{e}_s \boldsymbol{e}_s \ , \tag{2.42}$$

and is obviously single relaxation time. Use of the SRTGM instead of the BGK model results in the equivalent hydrodynamics even when the local equilibrium is not known in a closed form.

H-Functions of Minimal Kinetic Models

The Boltzmann H-function written in terms of the one-particle distribution function $F(\boldsymbol{x}, \boldsymbol{c})$ is $H = \int F \ln F \, d\boldsymbol{c}$, where $\boldsymbol{c}$ is the continuous velocity. Close to the local equilibrium, this integral can be approximated by using the Gauss–Hermite quadrature. This gives the entropy functions of the discrete-velocity models,

$$H_{\{w_i, \boldsymbol{c}_i\}} = \sum_{i=1}^{n_{\mathrm{d}}} f_i \ln \left(\frac{f_i}{w_i} \right) . \qquad (2.43)$$

Here w_i is the weight associated with the i-th discrete velocity $\boldsymbol{c}_i$, while the particles mass and Boltzmann‘s constant k_{B} are set equal to one. The discrete-velocity distribution functions (populations) $f_i(\boldsymbol{x})$ are related to the values of the continuous distribution function at the nodes of the quadrature by the formula,

$$f_i(\boldsymbol{x}) = w_i (2\,\pi\, T_0)^{(D/2)} \exp(c_i^2/(2\,T_0)) F(\boldsymbol{x}, \boldsymbol{c}_i) .$$

The discrete-velocity entropy functions (2.43) for various $\{w_i, \boldsymbol{c}_i\}$ is the single input for all the constructions of the minimal kinetic models. The set of discrete velocities corresponds to zeroes of the Hermite polynomials.

As the order of the Hermite polynomials used in the quadrature is increased (this corresponds to increasing the number of discrete velocities), the discrete H-functions $H_{\{w_i, \boldsymbol{c}_i\}}$ (2.43) become a better approximation. Thus, with the increase of the order of the Hermite polynomials, a better approximation to the hydrodynamics is obtained as demonstrated in Table 2.1, where $a = \sqrt{3 - \sqrt{6}}(T_0)^{1/2}$, and $b = \sqrt{3 + \sqrt{6}}(T_0)^{1/2}$ are the absolute values of the roots of the fourth-order Hermite polynomial. In higher dimensions, the discrete velocities are products of the discrete velocities in one dimension, and the weights are constructed by multiplying the weights associated with each component direction.

Athermal Hydrodynamics

If the discrete velocities are formed using the roots of the third-order Hermite polynomials (see Table 2.1), the Navier–Stokes equation is reproduced up to the order $O(u^2)$, and which is sufficient for many hydrodynamic applications.

As the higher-order moments of the local equilibrium are not enforced by the construction, we need to check their behavior. Relevant higher-order moments of the equilibrium distribution, required to reproduce the hydrodynamics in the long-time large-scale limit are the equilibrium pressure tensor, $P^{\mathrm{eq}}_{\alpha\beta} = \sum_i f_i^{\mathrm{eq}} c_{i\alpha} c_{i\beta}$, the equilibrium third-order moments, $Q^{\mathrm{eq}}_{\alpha\beta\gamma} = \sum_i f_i^{\mathrm{eq}} c_{i\alpha} c_{i\beta} c_{i\gamma}$, and the equilibrium fourth order moment $R^{\mathrm{eq}}_{\alpha\beta} = \sum_i c_{i\,\alpha} c_{i\,\beta} c^2 f_i^{\mathrm{eq}}$. For the athermal hydrodynamics, only the equilibrium pressure tensor and the equilibrium third-order moments are required to be correctly reproduced in order to recover the Navier–Stokes equations. The deviation of these higher-order moments from the expression for the continuous case is reported in Table 2.2.

2.7.2 Entropic Lattice Boltzmann Method

If the set of discrete velocities forms the links of a Bravais lattice (with possibly several sub-lattices), then the discretization in time and space of the discrete velocity kinetic equations is particularly simple, and it leads to the entropic lattice Boltzmann scheme. This happens in the most important case of the athermal hydrodynamics. The equation of the entropic lattice Boltzmann scheme reads

$$f_i(\boldsymbol{x}+\boldsymbol{v}_i\delta t, t+\delta t) - f_i(\boldsymbol{x}, t) = \beta\alpha(\boldsymbol{f}(\boldsymbol{x}, t))\Delta_i(\boldsymbol{f}(\boldsymbol{x}, t)) \ . \tag{2.44}$$

Here δt is the discretization time step, $\beta \in [0,1]$ is a fixed parameter which matches the viscosity coefficient in the long-time large-scale dynamics of the kinetic scheme (2.44), while the function of the population vector α defines the maximal over-relaxation of the scheme, and is found from the entropy condition,

$$H(\boldsymbol{f}(\boldsymbol{x}, t) + \alpha\boldsymbol{\Delta}(\boldsymbol{f}(\boldsymbol{x}, t)) = H(\boldsymbol{f}(\boldsymbol{x}, t)) \ . \tag{2.45}$$

The nontrivial root of this equation is found for populations at each lattice site at each moment of discrete time. Equation (2.45) ensures the discrete-time H-theorem, and is required in order to stabilize the scheme if the relaxation parameter β is close to 1. The latter limit is of particular importance in the applications of the entropic lattice Boltzmann method because it corresponds to the vanishing viscosity, and hence to simulations of high Reynolds number flows. The geometrical sense of the over-relaxation is illustrated in Fig. 2.1.

2.7.3 Entropic Lattice BGK Method (ELBGK)

An important further simplifications happens in the case of athermal hydrodynamics when the entropy function is constructed using third-order Hermite polynomials (see Table 2.1). In this case the local equilibrium populations vector can be found in a closed form [141]. This enables the simplest entropic scheme – the entropic lattice BGK model – for simulation of athermal hydrodynamics. We present this model in the dimensionless lattice units.

Let D be the spatial dimension. For $D = 1$, the three discrete velocities are

$$\boldsymbol{c} = \{-1, 0, 1\} \ . \tag{2.46}$$

For $D > 1$, the discrete velocities are tensor products of the discrete velocities of the one-dimensional velocities (2.46). Thus, we have the 9-velocity model for $D = 2$ and the 27-velocity model for $D = 3$. The H function is Boltzmann-like,

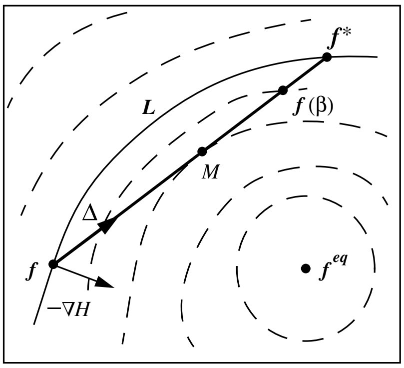

Fig. 2.1. Entropic stabilization of the lattice Boltzmann scheme with over-relaxation. Curves represent entropy levels, surrounding the local equilibrium $\boldsymbol{f}^{\mathrm{eq}}$. The solid curve L is the entropy level with the value $H(\boldsymbol{f}) = H(\boldsymbol{f}^*)$, where $\boldsymbol{f}$ is the initial, and $\boldsymbol{f}^*$ is the maximally over-relaxed population $\boldsymbol{f} + \alpha\boldsymbol{\Delta}$. The vector $\boldsymbol{\Delta}$ represents the collision integral, the sharp angle between $\boldsymbol{\Delta}$ and the vector $-\boldsymbol{\nabla} H$ reflects the entropy production inequality, while $\boldsymbol{M}$ is the point of minimum of H on the segment between $\boldsymbol{f}$ and $\boldsymbol{f}^*$. The point $\boldsymbol{f}^*$ $\boldsymbol{M}$ is the solution to (2.45). The result of the collision update is represented by the point $\boldsymbol{f}(\beta)$. The choice of β shown corresponds to the over-relaxation: $H(\boldsymbol{f}(\beta)) > H(\boldsymbol{M})$ but $H(\boldsymbol{f}(\beta)) < H(\boldsymbol{f})$. The particular case of the BGK collision (not shown) would be represented by a vector $\boldsymbol{\Delta}_{\mathrm{BGK}}$, pointing from $\boldsymbol{f}$ towards $\boldsymbol{f}^{\mathrm{eq}}$, in which case $\boldsymbol{M} = \boldsymbol{f}^{\mathrm{eq}}$

$$H = \sum_{i=1}^{3^D} f_i \ln\left(\frac{f_i}{w_i}\right) \; . \tag{2.47}$$

The weights w_i are associated with the each of the ith discrete velocity $\boldsymbol{c}_i$. For $D = 1$, the three-dimensional vector of the weights corresponding to the velocities (2.46) is

$$\boldsymbol{w} = \left\{\frac{1}{6}, \frac{2}{3}, \frac{1}{6}\right\} \; . \tag{2.48}$$

For $D > 1$, the weights are constructed by multiplying the weights associated with each component direction.

The local equilibrium minimizes the H-function (2.43) subject to the fixed density and momentum,

$$\sum_{i=1}^{3^D} f_i = \rho, \; \sum_{i=1}^{3^D} f_i c_{i\alpha} = \rho u_\alpha, \; \alpha = 1, \ldots, D \; . \tag{2.49}$$

The explicit solution to this minimization problem reads,

$$f_i^{\mathrm{eq}} = \rho w_i \prod_{\alpha=1}^{D} \left(2 - \sqrt{1 + 3u_\alpha^2}\right) \left(\frac{2\,u_\alpha + \sqrt{1 + 3\,u_\alpha^2}}{1 - u_\alpha}\right)^{c_{i\alpha}} \; . \tag{2.50}$$

Note that the exponent, $c_{i\alpha}$, in (2.50) takes the values ±1, and 0 only. The speed of sound, c_{s}, in this model is equal to $1/\sqrt{3}$. The factorization of the local equilibrium (2.50) over spatial components is quite remarkable, and resembles the familiar property of the local Maxwellians.

The entropic lattice BGK model for the local equilibrium (2.50) reads,

$$f_i(\boldsymbol{x}+\boldsymbol{c}_i\delta t, t+\delta t) - f_i(\boldsymbol{x},t) = -\beta\alpha(f_i(\boldsymbol{x},t) - f_i^{\mathrm{eq}}(\rho(\boldsymbol{f}(\boldsymbol{x},t)), \boldsymbol{u}(\boldsymbol{f}(\boldsymbol{x},t))) \ . \tag{2.51}$$

The parameter β is related to the relaxation time τ of the BGK model (2.38) by the formula,

$$\beta = \frac{\delta t}{2\tau + \delta t} \ . \tag{2.52}$$

Note that β depends on the discretization interval δt nonlinearly. The value of the over-relaxation parameter α is computed on each lattice site at every time from the entropy estimate,

$$H(\boldsymbol{f} - \alpha(\boldsymbol{f} - \boldsymbol{f}^{\mathrm{eq}}(\boldsymbol{f}))) = H(\boldsymbol{f}) \ . \tag{2.53}$$

In the hydrodynamic limit, the model (2.51) reconstructs the Navier-Stokes equations with the viscosity

$$\mu = \rho c_{\mathrm{s}}^2 \tau = \rho c_{\mathrm{s}}^2 \delta t \left(\frac{1}{2\beta} - \frac{1}{2} \right) \ . \tag{2.54}$$

The zero-viscosity limit corresponds to $\beta \to 1$. It is the maximal over-relaxation (see Fig. 2.1).

Thermal Hydrodynamics

The minimal entropic kinetic model for the thermal case requires zeroes of fourth-order Hermite polynomials (see Table 2.1). This is an off-lattice model (discrete velocities at zeroes of the fourth-order Hermit polynomials do not form links of any lattice). Therefore, a discretization in space should use other methods familiar from the discretization of hyperbolic equations. However, the theory of the entropy estimate for the discretization in the time presented above is fully applicable in this case too. We here present the local equilibrium of the thermal model.

In order to evaluate Lagrange multipliers in the formal solution to the minimization problem,

$$f_i^{\mathrm{eq}} = w_i \exp\left(A + B_\alpha c_{i\alpha} + C\, c_i^2 \right) ,$$

we note that they can be computed exactly for $\mathbf{u} = 0$ and any temperature T within the positivity interval, $a^2 < T < b^2$:

$$
\begin{aligned}
B_\alpha = 0, \quad C_0 &= \frac{1}{(b^2-a^2)} \log\left(\frac{w_a\,(T-a^2)}{w_b\,(b^2-T)}\right) , \\
A_0 &= \log\left(\frac{\rho\,(b^2-T)^D}{(2w_a)^D(b^2-a^2)^D}\right) - D\,a^2 C_0 \; .
\end{aligned}
\tag{2.55}
$$

With this, the equilibrium at the zero value of the average velocity and the arbitrary temperature reads

$$
f_i^{\mathrm{eq}} = \frac{\rho\, w_i}{2^D (b^2-a^2)^D} \prod_{\alpha=1}^{D} \left(\frac{b^2-T}{w_a}\right)^{\left(\frac{b^2-c_{i\alpha}^2}{b^2-a^2}\right)} \left(\frac{T-a^2}{w_b}\right)^{\left(\frac{c_{i\alpha}^2-a^2}{b^2-a^2}\right)} \; . \tag{2.56}
$$

The factorization over spatial components is again clearly visible. Once the exact solution for the zero velocity is found, the extension to $\mathbf{u} \neq 0$ is obtained perturbatively. The first few terms of the expansion of the Lagrange multipliers are:

$$
\begin{aligned}
A &= A_0 - \frac{T}{(T-a^2)(b^2-T)} u^2 + O(u^4) \; , \\
B_\alpha &= \frac{u_\alpha}{T} + \frac{(T-T_0)^2}{2DT^4} \left(D\, u_\beta u_\theta u_\gamma \delta_{\alpha\beta\gamma\theta} - 3u^2\, u_\alpha\right) + O(u^5) \; , \\
C &= C_0 + \frac{a^2(b^2-T) - T(b^2-3T)}{2DT^2(T-a^2)(b^2-T)} u^2 + O(u^4) \; .
\end{aligned}
$$

For the numerical implementation, the equilibrium distribution function can be calculated analytically up to any order of accuracy required. The accuracy of the relevant higher-order moments in this case is shown in the Table 2.2. Once the errors in these terms are small, the minimal kinetic models reconstruct the full thermal hydrodynamic equations.

While in the athermal case the closeness of the resulting macroscopic equations to the Navier–Stokes equations is controlled solely by the deviations from zero of the average velocity (low Mach number flows), in the thermal regime deviations are also due to variations of the temperature away from the reference value. This means that not only the actual velocity should be much less than the heat velocity, but also that the temperature deviation from T_0 should be small, $|T-T_0|/T_0 \ll 1$. However, by increasing the reference temperature, one gets a wider range of validity of the present model. Another important remark is about the use of the thermal model for the Navier–Stokes equation. If the temperature is fixed at the reference value $T = T_0$, the pressure tensor becomes exact to any purposes of simulation, while the third moment $Q^{\mathrm{eq}}_{\alpha\beta\gamma}$ becomes exact to the order $O(u^5)$.

In the construction of the discrete velocity model, the focus is on achieving a good approximation of the Boltzmann H-function. Thus, one can expect that the correct thermodynamics will be also preserved (within the accuracy of the discretization) even in the discrete case. Indeed, the local equilibrium entropy, $S = -k_{\mathrm{B}} H_{\{w_i,\boldsymbol{c}\}}(f^{\mathrm{eq}})$, for the thermal model satisfies the usual expression for the entropy of the ideal monatomic gas to the overall order of approximation of the method,

$$S = \rho\, k_{\mathrm{B}} \ln\left(T^{D/2}/\rho\right) + O(u^4, \theta^2)\ . \tag{2.57}$$

2.7.4 Boundary Conditions

The boundary (a solid wall) ∂R is specified at any point $\boldsymbol{x} \in \partial R$ by the inward unit normal $\boldsymbol{n}$, the wall temperature T_{w} and the wall velocity $\boldsymbol{u}_{\mathrm{w}}$. The simplest boundary condition for the minimal kinetic models is obtained upon evaluation of the diffusive wall boundary condition for the Boltzmann equation [112] with the help of the Gauss-Hermite quadrature [142]. The explicit expression for the diffusive wall boundary condition in the discrete velocity models is

$$f_i = \frac{\sum_{\boldsymbol{\xi}_{i'}\cdot \boldsymbol{n}\,<0} |(\boldsymbol{\xi}_{i'}\cdot \boldsymbol{n})| f_{i'}}{\sum_{\boldsymbol{\xi}_{i'}\cdot \boldsymbol{n}\,<0} |(\boldsymbol{\xi}_{i'}\cdot \boldsymbol{n})| f_{i'}^{\mathrm{eq}}(\rho_{\mathrm{w}}, \boldsymbol{u}_{\mathrm{w}})} f_i^{\mathrm{eq}}(\rho_{\mathrm{w}}, \boldsymbol{u}_{\mathrm{w}}), \qquad (\boldsymbol{\xi}_i \cdot \boldsymbol{n} > 0)\ , \tag{2.58}$$

Here $\boldsymbol{\xi}_i$ is the discrete velocity in the wall reference frame, $\boldsymbol{\xi}_i = \boldsymbol{c}_i - \boldsymbol{u}_{\mathrm{w}}$. Implementation of the diffusive wall boundary condition (2.58) in the context of the fully discrete entropic lattice Boltzmann method is given in the paper [143].

2.7.5 Numerical Illustrations of the ELBGK

The Kramers problem [112] is a limiting case of the plane Couette flow, where one of the plates is moved to infinity, while keeping a fixed shear rate. The analytical solution for the slip-velocity at the wall calculated for the linearized BGK collision model [112] are compared with the simulation of the entropic lattice BGK model in Fig. 2.2. This shows that the important feature of the original Boltzmann equation, the Knudsen number dependent slip at the wall is retained in the present model.

In another numerical experiment, the ELBGK method was tested in the setup of the two-dimensional Poiseuille flow. The time evolution of the computed profile as compared to the analytical result obtained from the incompressible Navier–Stokes equations is demonstrated in Fig. 2.3.

2.8 Other Kinetic Equations

2.8.1 The Enskog Equation for Hard Spheres

The Enskog equation for hard spheres is an extension of the Boltzmann equation to moderately dense gases. The Enskog equation explicitly takes into

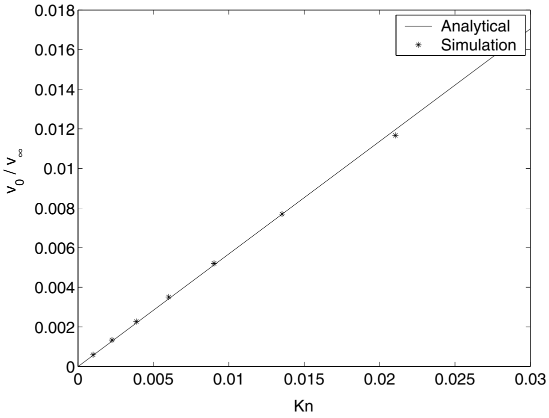

Fig. 2.2. Relative slip at the wall in the simulation of the Kramers problem for shear rate $a = 0.001$, box length $L = 32$, $v_\infty = a \times L = 0.032$ (See for details the paper [142])

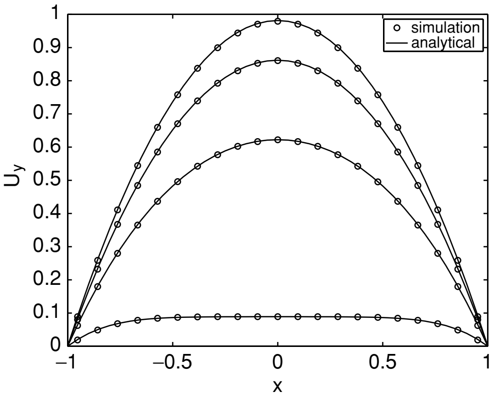

Fig. 2.3. Development of the velocity profile in the Poiseuille flow. Reduced velocity $U_y(x) = u_y/u_{y_{\max}}$ is shown versus the reduced coordinate across the channel x. Solid line: Analytical solution. Different lines correspond to different instants of the reduced time $T = (\mu t)/(4R^2)$, increasing from bottom to top, R is the half-width of the channel. Symbol: simulation with the ELBGK algorithm. Parameters used are: viscosity $\mu = 5.0015 \times 10^{-5}(\beta = 0.9997)$, steady state maximal velocity $u_{y_{\max}} = 1.10217 \times 10^{-2}$. Reynolds number $Re = 1157$. (See for details the paper [140])

account the nonlocality of collisions through a two-fold modification of the Boltzmann collision integral: First, the one-particle distribution functions are evaluated at the locations of the centers of spheres, separated by the nonzero distance at the impact. This makes the collision integral nonlocal in space. Second, the equilibrium pair distribution function at the contact of the spheres enhances the scattering probability.

Enskog's collision integral for hard spheres of radius r_0 is written in the following form [70]:

$$\begin{aligned} Q = \int_{R^3} \int_{B^-} & [(\boldsymbol{v} - \boldsymbol{w}) \cdot \boldsymbol{n}]\, [\chi(\boldsymbol{x}, \boldsymbol{x} + r_0\boldsymbol{n}) f(\boldsymbol{x}, \boldsymbol{v}') f(\boldsymbol{x} + 2r_0\boldsymbol{n}, \boldsymbol{w}') \\ & - \chi(\boldsymbol{x}, \boldsymbol{x} - r_0\boldsymbol{n}) f(\boldsymbol{x}, \boldsymbol{v}) f(\boldsymbol{x} - 2r_0\boldsymbol{n}, \boldsymbol{w})]\, \mathrm{d}\boldsymbol{w}\, \mathrm{d}\boldsymbol{n}\ , \end{aligned} \tag{2.59}$$

where $\chi(\boldsymbol{x}, \boldsymbol{y})$ is the equilibrium pair-correlation function for given temperature and density, and integration in $\boldsymbol{w}$ is carried over the whole space R^3, while integration in $\boldsymbol{n}$ is over a hemisphere $B^- = \{\boldsymbol{n} \in S^2 \mid (\boldsymbol{w} - \boldsymbol{v}, \boldsymbol{n}) < 0\}$.

The proof of the H theorem for the Enskog equation has posed certain difficulties, and has led to a modification of the collision integral [145].

Methods of solution of the Enskog equation are immediate generalizations of those developed for the Boltzmann equation, but there is one additional difficulty. The Enskog collision integral is nonlocal in space. The Chapman–Enskog method, when applied to the Enskog equation, is supplemented with a gradient expansion around the homogeneous equilibrium state.

2.8.2 The Vlasov Equation

The Vlasov equation (or kinetic equation for a self-consistent force) is the nonlinear equation for the one-body distribution function, which takes into account a long-range interaction between particles:

$$\frac{\partial}{\partial t} f + \left(\boldsymbol{v}, \frac{\partial}{\partial \boldsymbol{x}} f\right) + \left(\boldsymbol{F}, \frac{\partial}{\partial \boldsymbol{v}} f\right) = 0\ ,$$

where $\boldsymbol{F} = \int \Phi(|\ \boldsymbol{x} - \boldsymbol{x}'\ |) \frac{\boldsymbol{x}-\boldsymbol{x}'}{|\boldsymbol{x}-\boldsymbol{x}'|} n(\boldsymbol{x}')\, \mathrm{d}\boldsymbol{x}'$ is the self-consistent force. In this expression $\Phi(|\ \boldsymbol{x} - \boldsymbol{x}'\ |) \frac{\boldsymbol{x}-\boldsymbol{x}'}{|\boldsymbol{x}-\boldsymbol{x}'|}$ is the microscopic force between the two particles, and $n(\boldsymbol{x}')$ is the density of particles, defined self-consistently, $n(\boldsymbol{x}') = \int f(\boldsymbol{x}', \boldsymbol{v})\, \mathrm{d}\boldsymbol{v}$.

The Vlasov equation is used for the description of collisionless plasmas in which case it is complemented by the set of Maxwell equations for the electromagnetic field [172]. It is also used for the description of gravitating gas.

The Vlasov equation is an infinite-dimensional Hamiltonian system [146]. Many special and approximate (wave-like) solutions to the Vlasov equation are known and they describe important physical effects [147]. One of the best known effects is the Landau damping [172]: The energy of a volume element dissipates with the rate

$$Q \approx -\mid E \mid^2 \frac{\omega(k)}{k^2} \left.\frac{\mathrm{d}f_0}{\mathrm{d}v}\right|_{v=\frac{\omega}{k}}\ ,$$

where f_0 is the Maxwell distribution function, $\mid E \mid$ is the amplitude of the applied monochromatic electric field with the frequency $\omega(k)$, k is the wave vector. The Landau damping is thermodynamically reversible, and it is not accompanied with an entropy increase. Thermodynamically reversed to the Landau damping is the plasma echo effect.

2.8.3 The Fokker–Planck Equation

The Fokker–Planck equation (FPE) is a familiar model in various problems of nonequilibrium statistical physics [148–150]. We consider the FPE of the form

$$\frac{\partial W(\boldsymbol{x},t)}{\partial t} = \frac{\partial}{\partial \boldsymbol{x}} \left\{ D \left[W \frac{\partial}{\partial \boldsymbol{x}} U + \frac{\partial}{\partial \boldsymbol{x}} W \right] \right\} . \tag{2.60}$$

Here, $W(\boldsymbol{x},t)$ is the probability density over the configuration space x at time t, while $U(\boldsymbol{x})$ and $D(\boldsymbol{x})$ are the potential and the positively semi-definite $((\boldsymbol{y}, D\boldsymbol{y}) \geq 0)$ diffusion matrix.

The FPE (2.60) is particularly important in studies of polymer solutions [151–153].

Let us recall the three properties of the FPE (2.60):

1. Conservation of the total probability:
$$\int W(\boldsymbol{x},t)\, \mathrm{d}x \equiv 1 .$$
2. The equilibrium distribution,
$$W_{\mathrm{eq}} \propto \exp(-U) ,$$
is the unique stationary solution to the FPE (2.60) for the given total probability.
3. The entropy,
$$S[W] = -\int W(\boldsymbol{x},t) \ln \left[\frac{W(\boldsymbol{x},t)}{W_{\mathrm{eq}}(\boldsymbol{x})} \right] \mathrm{d}x , \tag{2.61}$$
is a monotonically growing function due to the FPE (2.60), and it attaines the global maximum at equilibrium.

These properties become more elicit when the FPE (2.60) is rewritten as follows:

$$\partial_t W(\boldsymbol{x},t) = \hat{M}_W \frac{\delta S[W]}{\delta W(\boldsymbol{x},t)} , \tag{2.62}$$

where

$$\hat{M}_W = -\frac{\partial}{\partial \boldsymbol{x}} \left[W(\boldsymbol{x},t) D(\boldsymbol{x}) \frac{\partial}{\partial \boldsymbol{x}} \right]$$

is a positive semi-definite symmetric operator. The form (2.62) is the dissipative part of a structure termed GENERIC (the dissipative vector field is a metric transform of the entropy gradient) [154, 155].

Entropy does not depend on kinetic constants. It is the same for different details of kinetics, and depends only on the equilibrium data. Let us call this property *"universality"*. It is known that for the Boltzmann equation there exists only one universal Lyapunov functional: the entropy (we do not distinguish functionals which are related to each other by monotonic transformations). For the FPE there exists a whole family of universal Lyapunov functionals. Let $h(a)$ be a convex function of one variable $a \geq 0$, $h''(a) > 0$,

$$S_h[W] = -\int W_{\mathrm{eq}}(\boldsymbol{x}) h\left[\frac{W(\boldsymbol{x},t)}{W_{\mathrm{eq}}(\boldsymbol{x})}\right] \mathrm{d}x \ . \tag{2.63}$$

The density of production of the generalized entropy S_h, σ_h, is nonnegative:

$$\sigma_h(\boldsymbol{x}) = W_{\mathrm{eq}}(\boldsymbol{x}) h''\left[\frac{W(\boldsymbol{x},t)}{W_{\mathrm{eq}}(\boldsymbol{x})}\right]\left(\frac{\partial}{\partial \boldsymbol{x}}\frac{W(\boldsymbol{x},t)}{W_{\mathrm{eq}}(\boldsymbol{x})}, D\frac{\partial}{\partial \boldsymbol{x}}\frac{W(\boldsymbol{x},t)}{W_{\mathrm{eq}}(\boldsymbol{x})}\right) \geq 0 \ . \tag{2.64}$$

The most important variants for the choice of h are:

- $h(a) = a \ln a$, and S_h is the Boltzmann–Gibbs–Shannon entropy (in the Kullback form [156, 157]),
- $h(a) = a \ln a - \epsilon \ln a$, $\epsilon > 0$, and S_h^{ϵ} is the maximal family of *additive* entropies [158–160] (these entropies are additive for the composition of independent subsystems).
- $h(a) = \frac{1-a^q}{1-q}$, and S_h^q is the family of Tsallis entropies [161, 162]. These entropies are not additive, but become additive after a nonlinear monotonous transformation. This property can serve as a definition of the Tsallis entropies in the class of generalized entropies (2.63) [160].

2.9 Equations of Chemical Kinetics and Their Reduction

2.9.1 Dissipative Reaction Kinetics

We begin with an outline of reaction kinetics (for details see, for example, the book [81]). Let us consider a closed system with n chemical species $\mathrm{A}_1, \dots, \mathrm{A}_n$, participating in a complex reaction. The mechanism of complex reaction is represented by the following stoichiometric equations:

$$\alpha_{s1}\mathrm{A}_1 + \ldots + \alpha_{sn}\mathrm{A}_n \rightleftharpoons \beta_{s1}\mathrm{A}_1 + \ldots + \beta_{sn}\mathrm{A}_n \ , \tag{2.65}$$

where the index $s = 1, \dots, r$ enumerates the reaction steps, and the integers, α_{si} and β_{si}, are the stoichiometric coefficients. For each reaction step s, we introduce n-dimensional vectors $\boldsymbol{\alpha}_s$ and $\boldsymbol{\beta}_s$ with components α_{si} and β_{si}. The *stoichiometric vector*, $\boldsymbol{\gamma}_s$, has integer components $\gamma_{si} = \beta_{si} - \alpha_{si}$.

For every A_i, an *extensive variable* N_i, "the number of particles of the i-th specie", is introduced. The concentration of A_i is then $c_i = N_i/V$, where V is the volume of the system.

Given the reaction mechanism (2.65), the kinetic equations read:

$$\dot{\boldsymbol{N}} = V\boldsymbol{J}(\boldsymbol{c}),\ \ \boldsymbol{J}(\boldsymbol{c}) = \sum_{s=1}^{r} \boldsymbol{\gamma}_s W_s(\boldsymbol{c}) \ , \tag{2.66}$$

where dot denotes the time derivative, and W_s is the reaction rate function of the sth reaction step. In particular, the *mass action law* suggests a polynomial form for the reaction rates:

$$W_s(\boldsymbol{c}) = W_s^+(\boldsymbol{c}) - W_s^-(\boldsymbol{c}) = k_s^+(T)\prod_{i=1}^{n} c_i^{\alpha_{si}} - k_s^-(T)\prod_{i=1}^{n} c_i^{\beta_{si}} \ , \tag{2.67}$$

where $k_s^+(T)$ and $k_s^-(T)$ are the constants of the forward and reverse reactions, respectively, of the sth reaction step, and T is the temperature. The (generalized) Arrhenius equation is the most popular expression for $k_s^{\pm}(T)$:

$$k_s^{\pm}(T) = a_s^{\pm} T^{b_s^{\pm}} \exp(S_s^{\pm}/k_{\mathrm{B}}) \exp(-H_s^{\pm}/k_{\mathrm{B}}T) \ , \tag{2.68}$$

where $a_s^{\pm}$, $b_s^{\pm}$ are constants, $H_s^{\pm}$ are activation enthalpies, and $S_s^{\pm}$ are activation entropies.

If the stoichiometric vectors $\{\boldsymbol{\gamma}_s\}$ are linearly dependent then the rate constants are not independent, but related through the *principle of detailed balance* gives the following connection between these constants: There exists a positive vector, $\boldsymbol{c}^{\mathrm{eq}}(T)$, such that

$$W_s^+(\boldsymbol{c}^{\mathrm{eq}}) = W_s^-(\boldsymbol{c}^{\mathrm{eq}}) \ \text{for all}\ s = 1, \ldots, r \ . \tag{2.69}$$

The necessary and sufficient conditions for the existence of such a $\boldsymbol{c}^{\mathrm{eq}}$ can be formulated as the system of polynomial equalities for $\{k_s^{\pm}\}$, (see, for example, [81]).

The reaction kinetics equations (2.66) do not form a closed system, because the dynamics of the volume V is not yet defined. Four classical conditions for closure of this system are well studied: U, V = const (isolated system, U is the internal energy); H, P = const (thermal isolated isobaric system, P is the pressure, $H = U + PV$ is the enthalpy), V, T = const (isochoric isothermal conditions); P, T = const (isobaric isothermal conditions). For V, T = const no additional equations and data are needed. Equation (2.66) can be divided by the constant volume to obtain

$$\dot{\boldsymbol{c}} = \sum_{s=1}^{r} \boldsymbol{\gamma}_s W_s(\boldsymbol{c}) \ . \tag{2.70}$$

For non-isothermal and non-isochoric conditions addition formulae are needed to derive T and V. For all four classical conditions, the thermodynamic Lyapunov functions $G_\bullet$ for kinetic equations are known:

$$\begin{aligned}
&U,\ V = \text{const},\ G_{U,V} = -S/k_{\text{B}}\ ;\\
&V,\ T = \text{const},\ G_{V,T} = F/k_{\text{B}}T = U/k_{\text{B}}T - S/k_{\text{B}}\ ;\\
&H,\ P = \text{const},\ G_{H,P} = -S/k_{\text{B}}\ ;\\
&P,\ T = \text{const},\ G_{P,T} = G/k_{\text{B}}T = H/k_{\text{B}}T - S/k_{\text{B}}\ ,
\end{aligned} \tag{2.71}$$

where $F = U - TS$ is the free energy (Helmholtz free energy), and $G = H - TS$ is the free enthalpy (Gibbs free energy). All the thermodynamic Lyapunov functions are normalized to the dimensionless scale (if the number of particles is expressed in moles, it is necessary to change k_{B} to R). All these functions decrease with time. For the classical conditions, the corresponding thermodynamic Lyapunov functions can be written in the form: $G_\bullet(\text{const}, \boldsymbol{N})$. The derivatives $\partial G_\bullet(\text{const}, \boldsymbol{N})/\partial N_i$ are the same functions of $\boldsymbol{c}$ and T for all classical conditions:

$$\mu_i(\boldsymbol{c}, T) = \frac{\partial G_\bullet(\text{const}, \boldsymbol{N})}{\partial N_i} = \frac{\mu_i^{\text{chem}}(\boldsymbol{c}, T)}{k_{\text{B}}T}\ , \tag{2.72}$$

where $\mu_i^{\text{chem}}(\boldsymbol{c}, T)$ is the chemical potential of species A_i.

Usual $G_\bullet(\text{const}, \boldsymbol{N})$ are strictly convex functions of $\boldsymbol{N}$, and the matrix $\partial\mu_i/\partial c_j$ is positively definite. The dissipation inequality

$$\frac{1}{V}\frac{\mathrm{d}G_\bullet}{\mathrm{d}t} = (\boldsymbol{\mu}, \boldsymbol{J}) \leq 0 \tag{2.73}$$

holds. This inequality poses a restriction on possible kinetic laws and on possible values of the kinetic constants.

One of the most important generalizations of the mass action law (2.67) is the Marcelin–De Donder kinetic function. This generalization [243, 244] is based on ideas from the thermodynamic theory of affinity [245]. Within this approach, the functions W_s are constructed as follows [244]: For a given $\boldsymbol{\mu}(\boldsymbol{c}, T)$ (2.72), and for a given reaction mechanism (2.65), we define the gain $(+)$ and the loss $(-)$ rates of the sth reaction step as,

$$W_s^+ = \varphi_s^+ \exp(\boldsymbol{\mu}, \boldsymbol{\alpha}_s), \quad W_s^- = \varphi_s^- \exp(\boldsymbol{\mu}, \boldsymbol{\beta}_s)\ , \tag{2.74}$$

where $\varphi_s^\pm > 0$ are kinetic factors, $(\ ,\ )$ is the standard inner product (the sum of coordinates products).

The Marcelin–De Donder kinetic function reads: $W_s = W_s^+ - W_s^-$, and the right hand side of the kinetic equation (2.66) becomes,

$$\boldsymbol{J} = \sum_{s=1}^{r} \gamma_s \{\varphi_s^+ \exp(\boldsymbol{\mu}, \boldsymbol{\alpha}_s) - \varphi_s^- \exp(\boldsymbol{\mu}, \boldsymbol{\beta}_s)\}\ . \tag{2.75}$$

For the Marcelin–De Donder reaction rate (2.74), the dissipation inequality (2.73) is particularly elegant:

$$\dot{G} = \sum_{s=1}^{r} [(\boldsymbol{\mu}, \boldsymbol{\beta}_s) - (\boldsymbol{\mu}, \boldsymbol{\alpha}_s)] \left\{ \varphi_s^{+} e^{(\boldsymbol{\mu}, \boldsymbol{\alpha}_s)} - \varphi_s^{-} e^{(\boldsymbol{\mu}, \boldsymbol{\beta}_s)} \right\} \leq 0 \, . \tag{2.76}$$

The kinetic factors $\varphi_s^{\pm}$ should satisfy certain conditions in order to satisfy the dissipation inequality (2.76). A well known sufficient condition is the detailed balance:

$$\varphi_s^{+} = \varphi_s^{-} \, . \tag{2.77}$$

Other sufficient conditions are discussed in detail elsewhere [81, 115, 163].

For ideal systems, the function $G_{\bullet}$ is constructed from the thermodynamic data of individual species. It is convenient to start from the isochoric isothermal conditions. The Helmholtz free energy for an ideal system is

$$F = k_{\mathrm{B}} T \sum_{i} N_i [\ln c_i - 1 + \mu_{0i}] + \mathrm{const}_{T,V} \, , \tag{2.78}$$

where the internal energy is assumed to be a linear function of N in a given interval of $\boldsymbol{c}$, T:

$$U = \sum_{i} N_i u_i(T) = \sum_{i} N_i (u_{0i} + C_{Vi} T) \, ,$$

where $u_i(T)$ is the internal energy of species A_i per particle. It is well known that $S = -(\partial F / \partial T)_{V,N=\mathrm{const}}$, $U = F + TS = F - T(\partial F / \partial T)_{V,N=\mathrm{const}}$, hence, $u_i(T) = -k_{\mathrm{B}} T^2 d\mu_{0i}/dT$ and

$$\mu_{0i} = \delta_i + u_{0i}/k_{\mathrm{B}}T - (C_{Vi}/k_{\mathrm{B}}) \ln T \, , \tag{2.79}$$

where $\delta_i = \mathrm{const}$, C_{Vi} is the heat capacity at constant volume (per particle) of species A_i.

In concordance with the form of ideal free energy (2.78) the expression for $\boldsymbol{\mu}$ is:

$$\mu_i = \ln c_i + \delta_i + u_{0i}/k_{\mathrm{B}}T - (C_{Vi}/k_{\mathrm{B}}) \ln T \, . \tag{2.80}$$

For the function $\boldsymbol{\mu}$ of the form (2.80), the Marcelin–De Donder equation obtains the more familiar mass action law form (2.67). Taking into account the principle of detailed balance (2.77) we get the ideal rate functions:

$$\begin{aligned} W_s(\boldsymbol{c}) &= W_s^{+}(\boldsymbol{c}) - W_s^{-}(\boldsymbol{c}) \, , \\ W_s^{+}(\boldsymbol{c}) &= \varphi_s(\boldsymbol{c}, T) T^{-\sum_i \alpha_{si} C_{Vi}/k_{\mathrm{B}}} e^{\sum_i \alpha_{si}(\delta_i + u_{0i}/k_{\mathrm{B}}T)} \prod_{i=1}^{n} c_i^{\alpha_{si}} \, , \\ W_s^{-}(\boldsymbol{c}) &= \varphi_s(\boldsymbol{c}, T) T^{-\sum_i \beta_{si} C_{Vi}/k_{\mathrm{B}}} e^{\sum_i \beta_{si}(\delta_i + u_{0i}/k_{\mathrm{B}}T)} \prod_{i=1}^{n} c_i^{\beta_{si}} \, . \end{aligned} \tag{2.81}$$

where $\varphi_s(\boldsymbol{c}, T)$ is an arbitrary positive function (from the thermodynamic point of view).

Let us discuss further the vector field $\boldsymbol{J}(\boldsymbol{c})$ in the concentration space (2.70). Conservation laws (balances) impose linear constraints on admissible vectors $\mathrm{d}\boldsymbol{c}/\mathrm{d}t$:

$$(\boldsymbol{b}_i, \boldsymbol{c}) = B_i = \mathrm{const}, \ \left(\boldsymbol{b}_i, \frac{\mathrm{d}\boldsymbol{c}}{\mathrm{d}t}\right) = 0, \ i = 1, \dots, l \ , \tag{2.82}$$

where $\boldsymbol{b}_i$ are fixed and linearly independent vectors. Let us denote as $\boldsymbol{B}$ the set of vectors which satisfy the conservation laws (2.82) for given B_i:

$$\boldsymbol{B} = \{\boldsymbol{c} | (\boldsymbol{b}_1, \boldsymbol{c}) = B_1, \dots, (\boldsymbol{b}_l, \boldsymbol{c}) = B_l\} \ .$$

The natural phase space $\boldsymbol{X}$ of the system (2.70) is the intersection of the cone of n-dimensional vectors with nonnegative components, with the set $\boldsymbol{B}$, and $\dim \boldsymbol{X} = d = n - l$. In the sequel, we term a vector $\boldsymbol{c} \in \boldsymbol{X}$ the state of the system. In addition, we assume that each of the conservation laws is supported by each elementary reaction step, that is

$$(\boldsymbol{\gamma}_s, \boldsymbol{b}_i) = 0 \ , \tag{2.83}$$

for each pair of vectors $\boldsymbol{\gamma}_s$ and $\boldsymbol{b}_i$.

Reaction kinetic equations describe variations of the states in time. The phase space $\boldsymbol{X}$ is positive-invariant for system (2.70): If $\boldsymbol{c}(0) \in \boldsymbol{X}$, then $\boldsymbol{c}(t) \in \boldsymbol{X}$ for all times $t > 0$.

In the sequel, we assume that the kinetic equations (2.70) describe evolution towards the unique equilibrium state, $\boldsymbol{c}^{\mathrm{eq}}$, in the interior of the phase space $\boldsymbol{X}$. Furthermore, we assume that there exists a strictly convex function $G(\boldsymbol{c})$ which decreases monotonically in time due to (2.70), $\boldsymbol{\nabla} G$ is the vector of partial derivatives $\partial G/\partial c_i$, and the convexity means that the $n \times n$ matrix

$$\boldsymbol{H}_{\boldsymbol{c}} = \|\partial^2 G(\boldsymbol{c})/\partial c_i \partial c_j\| \ , \tag{2.84}$$

is positive definite for all $\boldsymbol{c} \in \boldsymbol{X}$. In addition, we assume that the matrix (2.84) is invertible if $\boldsymbol{c}$ is taken in the interior of the phase space.

Function G is the Lyapunov function for the system (2.66), and $\boldsymbol{c}^{\mathrm{eq}}$ is the point of global minimum of G in the phase space $\boldsymbol{X}$. Otherwise stated, the manifold of equilibrium states $\boldsymbol{c}^{\mathrm{eq}}(B_1, \dots, B_l)$ is the solution to the variational problem,

$$G \to \min \text{ for } (\boldsymbol{b}_i, \boldsymbol{c}) = B_i, \ i = 1, \dots, l \ . \tag{2.85}$$

For each fixed value of the conserved quantities B_i, the solution is unique. In many cases, however, it is convenient to consider the whole equilibrium manifold, keeping the conserved quantities as parameters.

For example, for perfect systems in a constant volume system at constant temperature, the Lyapunov function G reads:

$$G = \sum_{i=1}^{n} c_i [\ln(c_i/c_i^{\mathrm{eq}}) - 1] \ . \tag{2.86}$$

It is important to stress that $\boldsymbol{c}^{\mathrm{eq}}$ in (2.86) is an *arbitrary* equilibrium of the system, under arbitrary values of the balances. In order to compute $G(\boldsymbol{c})$, it is unnecessary to calculate the specific equilibrium $\boldsymbol{c}^{\mathrm{eq}}$ which corresponds to the initial state $\boldsymbol{c}$. Let us compare the Lyapunov function G (2.86) with the classical formula for the free energy (2.78). This comparison gives a possible choice for $\boldsymbol{c}^{\mathrm{eq}}$:

$$\ln c_i^{\mathrm{eq}} = -\delta_i - u_{0i}/k_{\mathrm{B}}T + (C_{Vi}/k_{\mathrm{B}}) \ln T \ . \tag{2.87}$$

2.9.2 The Problem of Reduced Description in Chemical Kinetics

Reduction of a description of a chemical system means the following:

1. Reduce the number of species. This, in turn, can be achieved in two ways:
   - eliminate inessential species, or
   - lump some of the species into integrated components.
2. Reduce the number of reactions. This can also be done in several ways:
   - eliminate inessential reactions, those which do not significantly influence the reaction progress;
   - assume that some of the reactions "have already been completed", and that the equilibrium has been reached along their paths (this leads to dimensional reduction because the rate constants of the "completed" reactions are not used thereafter, what one needs are equilibrium constants only).
3. Decompose the motions into fast and slow, into independent (almost-independent) and slaved etc. As a result of such a decomposition, the system admits a study "in parts". At the end, the results are combined into a joint picture. There are several approaches which fall into this category. The famous method of the *quasi-steady state* (QSS), pioneered by Bodenstein and Semenov, follows the Chapman–Enskog method. The *partial equilibrium approximations* are predecessors of Grad's method and quasiequilibrium approximations in physical kinetics. These two family of methods have different physical backgrounds and mathematical forms.

2.9.3 Partial Equilibrium Approximations

Quasiequilibrium with respect to reactions is constructed as follows: From the list of reactions (2.65), one selects those which are assumed to equilibrate first. Let these reactions be indexed with the integers $s_1, \dots, s_k$. The quasiequilibrium manifold is defined by the system of equations,

$$W_{s_i}^{+} = W_{s_i}^{-}, \ i = 1, \dots, k \ . \tag{2.88}$$

This system looks particularly elegant when written in terms of conjugated (dual) variables, $\boldsymbol{\mu} = \boldsymbol{\nabla} G$:

$$(\boldsymbol{\gamma}_{s_i}, \boldsymbol{\mu}) = 0,\ i = 1, \dots, k \ . \tag{2.89}$$

In terms of the conjugated variables, the quasiequilibrium manifold forms a linear subspace. This subspace, $L^{\perp}$, is the orthogonal completement to the linear envelope of vectors, $L = \mathrm{lin}\{\boldsymbol{\gamma}_{s_1}, \dots, \boldsymbol{\gamma}_{s_k}\}$.

Quasiequilibrium with respect to species is constructed practically in the same way but without selecting the subset of reactions. For a given set of species, $A_{i_1}, \dots, A_{i_k}$, one assumes that their concentrations evolve fast to equilibrium and remain there. Formally, this means that in the k-dimensional subspace of the space of concentrations with coordinates $c_{i_1}, \dots, c_{i_k}$, one constructs the subspace L which is defined by the balance equations, $(\boldsymbol{b}_i, \boldsymbol{c}) = 0$. In terms of the conjugated variables, the quasiequilibrium manifold, $L^{\perp}$, is defined by the equations,

$$\boldsymbol{\mu} \in L^{\perp},\ (\boldsymbol{\mu} = (\mu_1, \dots, \mu_n)) \ . \tag{2.90}$$

The same quasiequilibrium manifold can also be defined with the help of fictitious reactions: Let $\boldsymbol{g}_1, \dots, \boldsymbol{g}_q$ be a basis in L. Then (2.90) may be rewritten as follows:

$$(\boldsymbol{g}_i, \boldsymbol{\mu}) = 0,\ i = 1, \dots, q \ . \tag{2.91}$$

Illustration: Quasiequilibrium with respect to reactions in hydrogen oxidation: Let us assume equilibrium with respect to the dissociation reactions, $H_2 \rightleftharpoons 2H$, and, $O_2 \rightleftharpoons 2O$, in some subdomain of reaction conditions. This gives:

$$k_1^+ c_{H_2} = k_1^- c_H^2,\ k_2^+ c_{O_2} = k_2^- c_O^2 \ .$$

Quasiequilibrium with respect to species: For the same reactions, let us assume equilibrium over H, O, OH, and H_2O_2, in a subdomain of reaction conditions. The subspace L is defined by the balance constraints:

$$c_H + c_{OH} + 2c_{H_2O_2} = 0,\ c_O + c_{OH} + 2c_{H_2O_2} = 0 \ .$$

The subspace L is twodimensional. Its basis, $\{\boldsymbol{g}_1, \boldsymbol{g}_2\}$, in the coordinates c_H, c_O, c_{OH}, and $c_{H_2O_2}$ reads:

$$\boldsymbol{g}_1 = (1, 1, -1, 0), \quad \boldsymbol{g}_2 = (2, 2, 0, -1) \ .$$

Correspondingly (2.91) becomes:

$$\mu_H + \mu_O = \mu_{OH},\ 2\mu_H + 2\mu_O = \mu_{H_2O_2} \ .$$

General construction of the quasiequilibrium manifold: In the space of concentrations, one defines a subspace L which satisfies the balance constraints:

$$(\boldsymbol{b}_i, L) \equiv 0 \ .$$

The orthogonal complement of L in the space with coordinates $\boldsymbol{\mu} = \boldsymbol{\nabla} G$ defines then the quasiequilibrium manifold $\boldsymbol{\Omega}_L$. For the actual computations, one requires the inversion from $\boldsymbol{\mu}$ to $\boldsymbol{c}$. The duality structure $\boldsymbol{\mu} \leftrightarrow \boldsymbol{c}$ is well studied by many authors [163, 164].

Quasiequilibrium projector. It is not sufficient to just derive the manifold, it is also required to define a *projector* which transforms the vector field defined on the space of concentrations into a vector field on the manifold. The quasiequilibrium manifold consists of points which minimize G in affine spaces of the form $\boldsymbol{c} + L$. These affine planes are hypothetical planes of fast motions (G is decreasing in the course of the fast motions). Therefore, the quasiequilibrium projector maps the whole space of concentrations on $\boldsymbol{\Omega}_L$ parallel to L. The vector field is also projected onto the tangent space of $\boldsymbol{\Omega}_L$ parallel to L.

Thus, the quasiequilibrium approximation assumes the decomposition of motions into fast – parallel to L, and slow – along the quasiequilibrium manifold. In order to construct the quasiequilibrium approximation, the knowledge of reaction rate constants of "fast" reactions is not required (stoichiometric vectors of all these fast reaction are in L, $\boldsymbol{\gamma}_{\text{fast}} \in L$, thus, the knowledge of L suffices), one only needs some confidence in that they all are sufficiently fast [165]. The quasiequilibrium manifold itself is constructed based on the knowledge of L and G. The dynamics on the quasiequilibrium manifold is defined as the quasiequilibrium projection of the "slow component" of the kinetic equations (2.66).

2.9.4 Model Equations

The assumption behind quasiequilibrium is the hypothesis of the decomposition of motions into fast and slow. The quasiequilibrium approximation itself describes slow motions. However, sometimes it becomes necessary to restore the state of the whole system, and take into account the fast motions as well. With this, it is desirable to keep intact one of the important advantages of the quasiequilibrium approximation – its independence from the rate constants of the fast reactions. For this purpose, the detailed fast kinetics is replaced by a model equation (*single relaxation time approximation*).

Quasiequilibrium models (QEM) are constructed as follows: For each concentration vector $\boldsymbol{c}$, consider the affine manifold, $\boldsymbol{c} + L$. It intersects the quasiequilibrium manifold $\boldsymbol{\Omega}_L$ at a single point. This point delivers the minimum to G on $\boldsymbol{c} + L$. Let us denote this point as $\boldsymbol{c}_L^*(\boldsymbol{c})$. The equation of the quasiequilibrium model reads:

$$\dot{\boldsymbol{c}} = -\frac{1}{\tau}[\boldsymbol{c} - \boldsymbol{c}_L^*(\boldsymbol{c})] + \sum_{\text{slow}} \boldsymbol{\gamma}_s W_s(\boldsymbol{c}_L^*(\boldsymbol{c})) \,, \tag{2.92}$$

where $\tau > 0$ is the relaxation time of the fast subsystem. Rates of slow reactions are computed at the points $\boldsymbol{c}_L^*(\boldsymbol{c})$ (the second term in the right hand side of (2.92), whereas the rapid motion is taken into account by a simple relaxational term (the first term in the right hand side of (2.92). The most famous model kinetic equation is the BGK equation in the theory of the Boltzmann equation [116]. The general theory of the quasiequilibrium models, including proofs of their thermodynamic consistency, was constructed in the paper [117].

Single relaxation time gradient models (SRTGM) were introduced in the context of the lattice Boltzmann method for hydrodynamics [140,166]. These models are aimed at improving the obvious drawback of the quasiequilibrium model (2.92): In order to construct the QEM, one needs to compute the function,

$$\boldsymbol{c}_L^*(\boldsymbol{c}) = \arg \min_{\boldsymbol{x}\in \boldsymbol{c}+L,\ \boldsymbol{x}>0} G(\boldsymbol{x}) \,. \tag{2.93}$$

This is a convex programming problem, which does not always have a closed-form solution.

Let $\boldsymbol{g}_1, \dots, \boldsymbol{g}_k$ be some orthonormal basis of L. We denote as $\boldsymbol{D}(\boldsymbol{c})$ the $k \times k$ matrix with elements $(\boldsymbol{g}_i, \boldsymbol{H}_{\boldsymbol{c}}\boldsymbol{g}_j)$, where $\boldsymbol{H}_{\boldsymbol{c}}$ is the matrix of second derivatives of G (2.84). Let $\boldsymbol{C}(\boldsymbol{c})$ be the inverse of $\boldsymbol{D}(\boldsymbol{c})$. The single relaxation time gradient model has the form:

$$\dot{\boldsymbol{c}} = -\frac{1}{\tau}\sum_{i,j=1}^{k} \boldsymbol{g}_i \boldsymbol{C}(\boldsymbol{c})_{ij}(\boldsymbol{g}_j, \boldsymbol{\nabla} G) + \sum_{\text{slow}} \boldsymbol{\gamma}_s W_s(\boldsymbol{c}) \,. \tag{2.94}$$

The first term drives the system to the minimum of G on $\boldsymbol{c} + L$, does not require solving problem (2.93), and its spectrum at quasiequilibrium is the same as in the quasiequilibrium model (2.92). Note that the slow component is evaluated at the "current" state $\boldsymbol{c}$.

The first term of equation (2.94) has a simple form

$$\dot{\boldsymbol{c}} = -\frac{1}{\tau}\mathrm{grad} G + \sum_{\text{slow}} \boldsymbol{\gamma}_s W_s(\boldsymbol{c}) \,, \tag{2.95}$$

if one calculates the gradient $\mathrm{grad}G \in L$ on the plane of fast motions $\boldsymbol{c} + L$ with the entropic scalar product[3] $\langle \boldsymbol{x}, \boldsymbol{y}\rangle = (\boldsymbol{x}, \boldsymbol{H}_{\boldsymbol{c}}\boldsymbol{y})$.

The models (2.92) and (2.94) lift the quasiequilibrium approximation to a kinetic equation by approximating the fast dynamics with a single "reaction rate constant" – the relaxation time τ.

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[3] Let us remind that grad$G$ is the Riesz representation of the differential of G in the phase space $\boldsymbol{X}$: $G(\boldsymbol{c}+\Delta\boldsymbol{c}) = G(\boldsymbol{c})+\langle \mathrm{grad}G(\boldsymbol{c}), \Delta\boldsymbol{c}\rangle + o(\Delta\boldsymbol{c})$. It belongs to the tangent space of $\boldsymbol{X}$ and depends on the scalar product. From the thermodynamic point of view, there is only one distinguished scalar product in the concentration space, the entropic scalar product. The usual definition of grad$G$ as the vector of partial derivatives ($\boldsymbol{\nabla} G$) corresponds to the standard scalar product $(\bullet, \bullet)$ and to the choice $\boldsymbol{X}$ being the whole concentration space. In equation (2.95), $\boldsymbol{X} = \boldsymbol{c} + L$ and we use the entropic scalar product.

2.9.5 Quasi-Steady State Approximation

The quasi-steady state approximation (QSS) is a tool used in a large number of works. Let us split the species in two groups: The basic and the intermediate (radicals etc). Concentration vectors are denoted accordingly, $\boldsymbol{c}^{\mathrm{s}}$ (slow, basic species), and $\boldsymbol{c}^{\mathrm{f}}$ (fast, intermediate species). The concentration vector $\boldsymbol{c}$ is the direct sum, $\boldsymbol{c} = \boldsymbol{c}^{\mathrm{s}} \oplus \boldsymbol{c}^{\mathrm{f}}$. The fast subsystem is (2.66) for the concentrations $\boldsymbol{c}^{\mathrm{f}}$ at fixed values of $\boldsymbol{c}^{\mathrm{s}}$. If it happens that the so-defined fast subsystem relaxes to a stationary state, $\boldsymbol{c}^{\mathrm{f}} \to \boldsymbol{c}^{\mathrm{f}}_{\mathrm{qss}}(\boldsymbol{c}^{\mathrm{s}})$, then the assumption that $\boldsymbol{c}^{\mathrm{f}} = \boldsymbol{c}^{\mathrm{f}}_{\mathrm{qss}}(\boldsymbol{c})$ is precisely the QSS assumption. The slow subsystem is the part of system (2.66) for $\boldsymbol{c}^{\mathrm{s}}$, in the right hand side of which the component $\boldsymbol{c}^{\mathrm{f}}$ is replaced with $\boldsymbol{c}^{\mathrm{f}}_{\mathrm{qss}}(\boldsymbol{c})$. Thus, $\boldsymbol{J} = \boldsymbol{J}_{\mathrm{s}} \oplus \boldsymbol{J}_{\mathrm{f}}$, where

$$\dot{\boldsymbol{c}}^{\mathrm{f}} = \boldsymbol{J}_{\mathrm{f}}(\boldsymbol{c}^{\mathrm{s}} \oplus \boldsymbol{c}^{\mathrm{f}}),\ \ \boldsymbol{c}^{\mathrm{s}} = \mathrm{const}; \quad \boldsymbol{c}^{\mathrm{f}} \to \boldsymbol{c}^{\mathrm{f}}_{\mathrm{qss}}(\boldsymbol{c}^{\mathrm{s}})\ ; \tag{2.96}$$

$$\dot{\boldsymbol{c}}^{\mathrm{s}} = \boldsymbol{J}_{\mathrm{s}}(\boldsymbol{c}^{\mathrm{s}} \oplus \boldsymbol{c}^{\mathrm{f}}_{\mathrm{qss}}(\boldsymbol{c}^{\mathrm{s}}))\ . \tag{2.97}$$

Bifurcations of the system (2.96) under variation of $\boldsymbol{c}^{\mathrm{s}}$ correspond to kinetic critical phenomena. Studies of more complicated dynamic phenomena in the fast subsystem (2.96) require various techniques of averaging, stability analysis of the averaged quantities etc.

Various versions of the QSS method are possible, and are actually used widely, for example, the hierarchical QSS method. There, one defines not a single fast subsystem but a hierarchy of them, $\boldsymbol{c}^{\mathrm{f}_1}, \dots, \boldsymbol{c}^{\mathrm{f}_k}$. Each subsystem $\boldsymbol{c}^{\mathrm{f}_i}$ is regarded as a slow system for all the foregoing subsystems, and it is regarded as a fast subsystem for the following members of the hierarchy. Instead of one system of equations (2.96), a hierarchy of systems of lower-dimensional equations is considered, each of these subsystem being easier to study analytically.

The theory of singularly perturbed systems of ordinary differential equations provides the mathematical background and refinements of the QSS approximation. In spite of a broad literature on this subject, it remains, in general, unclear, what is the smallness parameter that separates the intermediate (fast) species from the basic (slow). Reaction rate constants cannot be such a parameter (unlike in the case of quasiequilibrium). Indeed, intermediate species participate in the *same* reactions, as the basic species (for example, $\mathrm{H}_2 \rightleftharpoons 2\mathrm{H}$, $\mathrm{H} + \mathrm{O}_2 \rightleftharpoons \mathrm{OH} + \mathrm{O}$). It is therefore incorrect to state that $\boldsymbol{c}^{\mathrm{f}}$ evolves faster than $\boldsymbol{c}^{\mathrm{s}}$. In the sense of reaction rate constants, $\boldsymbol{c}^{\mathrm{f}}$ is not faster.

For catalytic reactions, it is not difficult to figure out what is the smallness parameter that separates the intermediate species from the basic, and which allows to upgrade the QSS assumption to a singular perturbation theory rigorously [81]. This smallness parameter is the ratio of balances: Intermediate species include a catalyst, and their total amount is simply significantly smaler than the amount of all the $\boldsymbol{c}_i$'s. After renormalizing to the variables of one order of magnitude, the small parameter appears explicitly. The simplest example is provided by the catalytic reaction $A + Z \rightleftharpoons AZ \rightleftharpoons P + Z$ (here Z is a catalyst, A and P are an initial substrate and a product). The kinetic equations are (in obvious notations):

$$\begin{aligned}
\dot{c}_A &= -k_1^+ c_A c_Z + k_1^- c_{AZ} \ , \\
\dot{c}_Z &= -k_1^+ c_A c_Z + k_1^- c_{AZ} + k_2^+ c_{AZ} - k_2^- c_Z c_P \ , \\
\dot{c}_{AZ} &= k_1^+ c_A c_Z - k_1^- c_{AZ} - k_2^+ c_{AZ} + k_2^- c_Z c_P \ , \\
\dot{c}_P &= k_2^+ c_{AZ} - k_2^- c_Z c_P \ .
\end{aligned} \tag{2.98}$$

The constants and the reactions rates are the same for concentrations c_A, c_P, and for c_Z, c_{AZ}, and they cannot be a reason for the relative slowness of c_A, c_P in comparison with c_Z, c_{AZ}. However, there may be another source of slowness. There are two balances for this kinetics: $c_A + c_P + c_{AZ} = B_A$, $c_Z + c_{AZ} = B_Z$. Let us switch to the dimensionless variables:

$$\varsigma_A = c_A/B_A, \ \varsigma_P = c_P/B_A, \ \varsigma_Z = c_Z/B_Z, \ \varsigma_{AZ} = c_{AZ}/B_Z \ .$$

The kinetic system (2.98) is then rewritten as

$$\begin{aligned}
\dot{\varsigma}_A &= B_Z \left[-k_1^+ \varsigma_A \varsigma_Z + \frac{k_1^-}{B_A} \varsigma_{AZ} \right] , \\
\dot{\varsigma}_Z &= B_A \left[-k_1^+ \varsigma_A \varsigma_Z + \frac{k_1^-}{B_A} \varsigma_{AZ} + \frac{k_2^+}{B_A} \varsigma_{AZ} - k_2^- \varsigma_Z \varsigma_P \right] \ , \\
& \varsigma_A + \varsigma_P + \frac{B_Z}{B_A} \varsigma_{AZ} = 1, \ \varsigma_Z + \varsigma_{AZ} = 1; \ \varsigma_\bullet \geq 0 \ .
\end{aligned} \tag{2.99}$$

For $B_Z \ll B_A$ (the total amount of the catalyst is much smaller than the total amount of the substrate) the slowness of ς_A, ς_P is evident from these equations (2.99).

For usual radicals, the origin of the smallness parameter is quite similar. There are much less radicals than basic species (otherwise, the QSS assumption is inapplicable). In the case of radicals, however, the smallness parameter cannot be extracted directly from the balances B_i (2.82). Instead, one can come up with a thermodynamic estimate: Function G decreases in the course of reactions, whereupon we obtain the limiting estimate of concentrations of any species:

$$c_i \leq \max_{G(\boldsymbol{c}) \leq G(\boldsymbol{c}(0))} c_i \ , \tag{2.100}$$

where $\boldsymbol{c}(0)$ is the initial composition. If the concentration c_{R} of the radical R is small both initially and at equilibrium, then it should also remain small along the path to equilibrium. For example, in the case of ideal G (2.86) under relevant conditions, for any $t > 0$, the following inequality is valid:

$$c_{\mathrm{R}} [\ln(c_{\mathrm{R}}(t)/c_{\mathrm{R}}^{\mathrm{eq}}) - 1] \leq G(\boldsymbol{c}(0)) \ . \tag{2.101}$$

Inequality (2.101) provides the simplest (but rather crude) thermodynamic estimate of $c_{\mathrm{R}}(t)$ in terms of $G(\boldsymbol{c}(0))$ and $c_{\mathrm{R}}^{\mathrm{eq}}$ *uniformly for* $t > 0$. The complete theory of thermodynamic estimates of reaction kinetics has been developed in the book [115].

One can also do computations without a priori estimations, if one accepts the QSS assumption as long as the values $\boldsymbol{c}^{\mathrm{f}}$ stay sufficiently small. It is the simplest way to operate with QSS: Just use it *as long as* $\boldsymbol{c}^{\mathrm{f}}$ are small!

Let us assume that an a priori estimate has been found, $c_i(t) \leq c_{i\ \max}$, for each c_i. These estimates may depend on the initial conditions, thermodynamic data etc. With these estimates, we are able to renormalize the variables in the kinetic equations (2.66) in such a way that the renormalized variables take their values from the unit interval $[0, 1]$: $\tilde{c}_i = c_i/c_{i\ \max}$. Then the system (2.66) can be written as follows:

$$\frac{\mathrm{d}\tilde{c}_i}{\mathrm{d}t} = \frac{1}{c_{i\ \max}} J_i(\boldsymbol{c}) \ . \tag{2.102}$$

The system of dimensionless parameters, $\epsilon_i = c_{i\ \max}/\max_i c_{i\ \max}$ defines a hierarchy of relaxation times, and with its help one can establish various realizations of the QSS approximation. The simplest version is the standard QSS assumption: Parameters ϵ_i are separated in two groups, the smaller ones, and those of order 1. Accordingly, the concentration vector is split into $\boldsymbol{c}^{\mathrm{s}} \oplus \boldsymbol{c}^{\mathrm{f}}$. Various hierarchical QSS are possible, rendering the problem more tractable analytically.

There exists a variety of ways to introduce the smallness parameter into kinetic equations, and one can find applications to each of the realizations. However, two particular realizations remain basic for chemical kinetics:

- Fast reactions (under a given thermodynamic data);
- Small concentrations.

In the first case, one is led to the quasiequilibrium approximation, in the second, to the classical QSS assumption. Both of these approximations allow for hierarchical realizations, those which include not just two but many relaxation time scales. Such a *multi-scale approach* essentially simplifies analytical studies of the problem.

2.9.6 Thermodynamic Criteria for the Selection of Important Reactions

One of the problems addressed by sensitivity analysis is the selection of the important and unimportant reactions. In the paper [167] a simple idea was suggested to compare the importance of different reactions according to their contribution to the entropy production (or, which is the same, according to their contribution to $\mathrm{d}G/\mathrm{d}t$). Based on this principle, Dimitrov [170] described domains of parameters in which the reaction of hydrogen oxidation,

H_2+O_2+M, proceeds due to different mechanisms. For each elementary reaction, he has derived the domain inside which the contribution of this reaction cannot be neglected. Due to its simplicity, this entropy production principle is especially well suited for the analysis of complex problems. In particular, recently, a version of the entropy production principle was used in the problem of selection of boundary conditions for Grad's moment equations [168, 169]. For ideal systems (2.86), as well, as for the Marcelin–De Donder kinetics (2.76) the contribution of the sth reaction to $\dot{G}$ has a particularly simple form:

$$\dot{G}_s = -W_s \ln\left(\frac{W_s^+}{W_s^-}\right), \quad \dot{G} = \sum_{s=1}^{r} \dot{G}_s \ . \tag{2.103}$$

2.9.7 Opening

One of the problems to focus on when studying closed systems is to extend the result for open or driven by flows systems. External flows are usually taken into account by additional terms in the kinetic equations (2.66):

$$\dot{\boldsymbol{N}} = V\boldsymbol{J}(\boldsymbol{c}) + \boldsymbol{\Pi}(\boldsymbol{c},t) \ . \tag{2.104}$$

It is important to stress here that the vector field $\boldsymbol{J}(\boldsymbol{c})$ in equations (2.104) is the same as for the closed system, with thermodynamic restrictions, Lyapunov functions, etc. The thermodynamic structures are important for the analysis of open systems (2.104), if the external flow $\boldsymbol{\Pi}$ is small in some sense, for example, if it is a linear function of $\boldsymbol{c}$, has small time derivatives, etc. There are some general results for such "weakly open" systems, for example, the Prigogine minimum entropy production theorem [171] and the estimations of possible steady states and limit sets for open systems, based on thermodynamic functions and stoihiometric equations [115].

There are general results for another limiting case: for very intensive flows the dynamics becomes very simple again [81]. Let the flow have a natural structure: $\boldsymbol{\Pi}(\boldsymbol{c},t) = v_{in}(t)\boldsymbol{c}_{in}(t) - v_{out}(t)\boldsymbol{c}(t)$, where v_{in} and v_{out} are the rates of inflow and outflow, $\boldsymbol{c}_{in}(t)$ is the concentration vector for inflow. If v_{out} is sufficiently large, $v_{out}(t) > v_0$ for some critical value v_0 and all $t > 0$, then for the open system (2.104) the Lyapunov norm exists: for any two solutions $\boldsymbol{c}^1(t)$ and $\boldsymbol{c}^2(t)$ the function $\|\boldsymbol{c}^1(t) - \boldsymbol{c}^2(t)\|$ monotonically decreases in time. Such a critical value v_0 exists for any norm, for example, for usual Euclidian norm $\| \bullet \|^2 = (\bullet, \bullet)$.

For an arbitrary form of $\boldsymbol{\Pi}$, the system (2.104) can loose all signs of being a thermodynamic one. Nevertheless, thermodynamic structures can often help in the study of open systems.

The crucial questions are: What happens with slow/fast motion separation after opening? Which slow invariant manifolds for the closed system can be deformed to the slow invariant manifolds of the open system? Which slow invariant manifold for the closed system can be used as approximate slow invariant manifold for the open system? There exists a more or less useful technique to seek answers for specific systems under consideration. We shall return to this question in Chap. 13.

The way to study an open system as the result of opening a closed system may be fruitful. Out of this way we have a general dynamical system (2.104) and no hints what to do with it.

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The basic introductory textbook on physical kinetics of the Landau and Lifshitz Course of Theoretical Physics [172] contains many further examples and their applications.

Modern development of kinetics follows the route of specific numerical methods, such as direct simulations. An opposite tendency is also clearly observed, and kinetic theory based schemes are increasingly often used for the development of numerical methods and models in mechanics of continuous media.