

SEMINARIOS LECTURA PAPERS COVID19

Expositor: Jaime Ortega (CMM-DIM, U. de Chile)

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Chapter 4

BOLTZMANN-Like Equations

4.1 Introduction

In the following we will assume to be confronted with systems that consist of N *elements (subsystems)* α . If the dynamics of the system is mainly given by *pair interactions* of the elements (like e.g. in a rarefied gas) it is plausible to use **BOLTZMANN equations** for its description. A typical example of application is a *chemical reaction*



where the different states $x_\alpha \in \{B, C\}$ distinguish whether an atom α is bounded or not (cf. [11, 167]). Apart from pair interactions, the more general ‘**BOLTZMANN-like equations**’ additionally take into account *spontaneous transitions* and are the main topic of [Chaps. 9](#) and [10](#). Interrelations and differences between spontaneous transitions and direct pair interactions will be discussed in detail in [Sect. 4.5](#).

The BOLTZMANN equation, like the master equation, has a structure of the form (3.1). However, the flows of the BOLTZMANN equation are proportional to the probabilities of the states of *both* interacting subsystems. They depend on the *square* of the probability distribution and thus the solution is difficult. In the case of the *gaskinetic BOLTZMANN equation* the *stationary* solution can be found by means of the *H-theorem*. An evaluation of the *time-dependent* solution is usually very complicated and bases, in most cases, on a recursive method.

The derivation of the BOLTZMANN-like equations can be subdivided into the following steps: First, we combine the states

$$x_\alpha = (x_{\alpha 1}, \dots, x_{\alpha i}, \dots, x_{\alpha m})^{\text{tr}} \in \gamma_\alpha \quad (4.2)$$

of all N elements α in the state vector

$$X \equiv (\dots, X_I, \dots)^{\text{tr}} := (x_1, \dots, x_\alpha, \dots, x_N)^{\text{tr}} \quad (4.3)$$

of the total system which has M components ($M := mN$, $I := (\alpha, i)^{\text{tr}}$). γ_α means the set of all possible states x of element α and will be denoted as γ_α -*space*. For

reasons of simplicity we have assumed by (4.2) that the state space γ_α has the same dimension m for each subsystem. This is no restriction since, if a system can be characterized by a *smaller* number $m_\alpha < m$ of variables, the surplus components $x_{\alpha j}$ with $m_\alpha < j \leq m$ can be set to zero.

Next we confine ourselves to spontaneous transitions and pair interactions, i.e. simultaneous interactions between three or more subsystems will be neglected (though a treatment of these is also possible; cf. Sect. 5.4 and [40, 41, 277]). The resulting equations can be reduced to equations for the probability distributions $P_\alpha(x_\alpha, t)$ of the subsystems α but they depend on the *pair distribution functions* $P_{\alpha\beta}(x_\alpha, x_\beta; t)$. In order to obtain *closed* equations we assume the *factorization* of the pair distribution functions (i.e. the *statistical independence* of the elements). Corrections for cases where this assumption is not justified are the topic of Sect. 5.4.

Finally, if we distinguish only a few *types* a of elements, the number of equations reduces drastically. The result are the BOLTZMANN-like equations.

4.2 Derivation

First, for the derivation of the BOLTZMANN-like equations from master equation (3.5) we introduce the vectors

$$X^\alpha := (\mathbf{0}, \dots, \mathbf{0}, x_\alpha, \mathbf{0}, \dots, \mathbf{0})^{\text{tr}}, \quad (4.4)$$

$$X^{\alpha_1 \dots \alpha_k} := \sum_{i=1}^k X^{\alpha_i}, \quad (4.5)$$

and

$$Y_{\alpha_1 \dots \alpha_k} := X - X^{\alpha_1 \dots \alpha_k} + Y^{\alpha_1 \dots \alpha_k}. \quad (4.6)$$

They allow the decomposition of the transition rates

$$w(X'|X; t) := \begin{cases} w_{\alpha_1}(Y^{\alpha_1} | X^{\alpha_1}; t) & \text{if } X' = Y_{\alpha_1} \\ w_{\alpha_1 \alpha_2}(Y^{\alpha_1 \alpha_2} | X^{\alpha_1 \alpha_2}; t) & \text{if } X' = Y_{\alpha_1 \alpha_2} \\ \vdots & \vdots \\ w_{\alpha_1 \dots \alpha_N}(Y^{\alpha_1 \dots \alpha_N} | X^{\alpha_1 \dots \alpha_N}; t) & \text{if } X' = Y_{\alpha_1 \dots \alpha_N} \\ 0 & \text{otherwise} \end{cases} \quad (4.7)$$

into contributions

$$w_{\alpha_1 \dots \alpha_k}(Y^{\alpha_1 \dots \alpha_k} | X^{\alpha_1 \dots \alpha_k}; t) \equiv w_{\alpha_1 \dots \alpha_k}(y_{\alpha_1}, \dots, y_{\alpha_k} | x_{\alpha_1}, \dots, x_{\alpha_k}; t) \quad (4.8)$$

which describe the interactions between k subsystems. In order to exclude self-interactions of an element we set

$$w_{\alpha_1 \dots \alpha_k} \equiv 0 \quad \text{if two subscripts } \alpha_i, \alpha_j \text{ agree.} \quad (4.9)$$

For most *chemical reactions* [11, 167] and many other cases the contributions with $k \leq 2$ are the most important ones because simultaneous interactions between three or more elements are rare. Hence the terms with $k > 2$ will be neglected in the following. Then master equation (3.5a) obtains the form

$$\begin{aligned} \frac{d}{dt} P(X, t) &= \sum_{\beta} \sum_{Y_{\beta}} \left[w_{\beta}(X^{\beta} | Y^{\beta}; t) P(Y_{\beta}, t) - w_{\beta}(Y^{\beta} | X^{\beta}; t) P(X, t) \right] \\ &\quad + \frac{1}{2} \sum_{\beta, \gamma} \sum_{Y_{\beta\gamma}} \left[w_{\beta\gamma}(X^{\beta\gamma} | Y^{\beta\gamma}; t) P(Y_{\beta\gamma}, t) - w_{\beta\gamma}(Y^{\beta\gamma} | X^{\beta\gamma}; t) P(X, t) \right] \\ &= \sum_{\beta} \sum_{y_{\beta}} \left[w_{\beta}(x_{\beta} | y_{\beta}; t) P(Y_{\beta}, t) - w_{\beta}(y_{\beta} | x_{\beta}; t) P(X, t) \right] \\ &\quad + \frac{1}{2} \sum_{\beta, \gamma} \sum_{y_{\beta}, y_{\gamma}} \left[w_{\beta\gamma}(x_{\beta}, x_{\gamma} | y_{\beta}, y_{\gamma}; t) P(Y_{\beta\gamma}, t) \right. \\ &\quad \left. - w_{\beta\gamma}(y_{\beta}, y_{\gamma} | x_{\beta}, x_{\gamma}; t) P(X, t) \right]. \end{aligned} \quad (4.10)$$

The factor $1/2$ results from

$$\sum_{\substack{\alpha_1, \dots, \alpha_k \\ (\alpha_1 < \dots < \alpha_k)}} = \frac{1}{k!} \sum_{\substack{\alpha_1, \dots, \alpha_k \\ (\alpha_i \neq \alpha_j)}} \quad (4.11)$$

and ensures that identical transitions will not be counted twice. (There exist $k!$ *permutations (interchanges)* $(\beta_1, \dots, \beta_k)$ of the k elements $\alpha_i \in \{\alpha_1, \dots, \alpha_k\}$).

Now let us introduce the *multi-particle distribution functions*

$$P_{\alpha_1 \dots \alpha_k}(x_{\alpha_1}, \dots, x_{\alpha_k}; t) := \sum_{x_{\beta}} P_{\alpha_1 \dots \beta \dots \alpha_k}(x_{\alpha_1}, \dots, x_{\beta}, \dots, x_{\alpha_k}; t) \quad (4.12a)$$

for the k particles $\alpha_1, \dots, \alpha_k$ and introduce the notation

$$P_{1 \dots N}(x_1, \dots, x_N; t) \equiv P(x_1, \dots, x_N; t). \quad (4.12b)$$

The summation of (4.10) over all $x_{\beta} \in \gamma_{\beta}$ with $\beta \neq \alpha$ (using relations which are analogous to (3.94)) leads to

$$\begin{aligned}
\frac{d}{dt}P_\alpha(x_\alpha, t) = & \sum_{y_\alpha} \left[w_\alpha(x_\alpha|y_\alpha; t)P_\alpha(y_\alpha, t) - w_\alpha(y_\alpha|x_\alpha; t)P_\alpha(x_\alpha, t) \right] \\
& + \sum_{y_\alpha} \left[\sum_{\beta} \sum_{y_\beta} \sum_{x_\beta} w_{\alpha\beta}(x_\alpha, x_\beta|y_\alpha, y_\beta; t)P_{\alpha\beta}(y_\alpha, y_\beta; t) \right. \\
& \left. - \sum_{\beta} \sum_{y_\beta} \sum_{x_\beta} w_{\alpha\beta}(y_\alpha, y_\beta|x_\alpha, x_\beta; t)P_{\alpha\beta}(x_\alpha, x_\beta; t) \right] \quad (4.13)
\end{aligned}$$

with

$$\sum_{x_\alpha} P_\alpha(x_\alpha, t) = 1. \quad (4.14)$$

Due to the dependence on the *pair distribution functions* $P_{\alpha\beta}(x_\alpha, x_\beta; t)$ Eq. (4.13) are *not closed*. The equations for the pair distribution functions which can be derived from (4.10), however, depend on the three-particle distribution functions $P_{\alpha\beta\gamma}(x_\alpha, x_\beta, x_\gamma; t)$ etc. As a consequence, a *hierarchy of non-closed equations* (cf. [170], pp. 74ff.) results so that an approximation becomes necessary. Assuming a *factorization* of the pair distribution functions of the form

$$P_{\alpha\beta}(x_\alpha, x_\beta; t) \approx P_\alpha(x_\alpha, t)P_\beta(x_\beta, t) \quad (4.15)$$

we arrive at the *closed equations*

$$\begin{aligned}
\frac{d}{dt}P_\alpha(x_\alpha, t) = & \sum_{y_\alpha} \left[w_\alpha(x_\alpha|y_\alpha; t)P_\alpha(y_\alpha, t) - w_\alpha(y_\alpha|x_\alpha; t)P_\alpha(x_\alpha, t) \right] \\
& + \sum_{y_\alpha} \left[\left(\sum_{\beta} \sum_{y_\beta} \sum_{x_\beta} w_{\alpha\beta}(x_\alpha, x_\beta|y_\alpha, y_\beta; t)P_\beta(y_\beta, t) \right) P_\alpha(y_\alpha, t) \right. \\
& \left. - \left(\sum_{\beta} \sum_{y_\beta} \sum_{x_\beta} w_{\alpha\beta}(y_\alpha, y_\beta|x_\alpha, x_\beta; t)P_\beta(x_\beta, t) \right) P_\alpha(x_\alpha, t) \right] \quad (4.16)
\end{aligned}$$

(cf. [170], pp. 72ff., and [25, 93, 94, 162, 224, 240]). $w_\alpha(y_\alpha|x_\alpha; t)$ describes *spontaneous* or *externally induced transitions* of element α from state x_α to state y_α . $w_{\alpha\beta}(y_\alpha, y_\beta|x_\alpha, x_\beta; t)$ reflects *pair interactions* between two systems α and β due to which their states change from x_α and x_β to y_α and y_β respectively. Introducing the *effective transition rates*

$$w^\alpha(x'|x; t) := w_\alpha(x'|x; t) + \sum_{\beta} \sum_{y'} \sum_y w_{\alpha\beta}(x', y'|x, y; t)P_\beta(y, t), \quad (4.17a)$$

Eq. (4.16) can be cast into the simple form

$$\frac{d}{dt}P_\alpha(x, t) = \sum_{x'} \left[w^\alpha(x|x'; t)P_\alpha(x', t) - w^\alpha(x'|x; t)P_\alpha(x, t) \right]. \quad (4.17b)$$

Factorization assumption (4.15) is *exactly* valid only if two arbitrary subsystems α and β are *statistically independent*. It is *approximately* justified if the interactions are *weak* ($w_{\alpha\beta} \approx 0$) or if the correlations between two subsystems α and β due to pair interactions are soon destroyed (cf. also (5.20)). Equation (4.15) is often substantiated by the assumption of ‘*molecular chaos*’ [154] (cf. Sect. 10.3.4). For the case that (4.15) is violated there exist methods for the calculation of corrections (cf. [25, 54]). Moreover, a generalization of the above equations to simultaneous interactions of arbitrarily many elements is possible (cf. Sect. 5.4).

4.3 Subdivision into Several Types of Subsystems

Usually the immense number N of subsystems α can be divided into A types a which are characterized by certain properties, e.g. by the kind of interaction. In example (4.1) one type of subsystems would consist of the molecules of sort B and a second one of the molecules of sort C .

Now let N_a be the number of elements $\alpha \in a$ (i.e. of type a). Then we have

$$\sum_{a=1}^A N_a = N. \quad (4.18)$$

If subsystems $\alpha \in a$ of the same type a are not further distinguished this implies

$$\gamma_\alpha \equiv \gamma_a \quad \text{if } \alpha \in a, \quad (4.19a)$$

$$P_\alpha \equiv P_a \quad \text{if } \alpha \in a, \quad (4.19b)$$

$$w_\alpha \equiv \widehat{w}_a \quad \text{if } \alpha \in a, \quad (4.19c)$$

and

$$w_{\alpha\beta} \equiv \begin{cases} \widehat{w}_{ab} & \text{if } \alpha \neq \beta, \alpha \in a, \beta \in b \\ 0 & \text{if } \alpha = \beta \end{cases} \quad (4.19d)$$

where $\widehat{w}_{..}$ are the *individual transition rates*. Furthermore, after introducing the notations

$$w_a := \widehat{w}_a \quad (4.20a)$$

and

$$w_{ab} := \begin{cases} N_b \cdot \widehat{w}_{ab} & \text{if } b \neq a \\ (N_a - 1) \cdot \widehat{w}_{ab} & \text{if } b = a, \end{cases} \quad (4.20b)$$

from (4.14) and (4.17) we gain

$$\sum_x P_a(x, t) = 1 \quad (4.21)$$

and

$$\frac{d}{dt} P_a(x, t) = \sum_{x'} \left[w^a(x|x'; t) P_a(x', t) - w^a(x'|x; t) P_a(x, t) \right] \quad (4.22a)$$

with the *effective transition rates*

$$w^a(x'|x; t) := w_a(x'|x; t) + \sum_b \sum_{y'} \sum_y w_{ab}(x', y'|x, y; t) P_b(y, t). \quad (4.22b)$$

By distinguishing only a few types of subsystems the number of variables is considerably reduced if $A \ll N$ or $N_a \gg 1$. Thus (4.22) becomes accessible to a treatment by computers.

4.4 Properties

4.4.1 Non-negativity and Normalization

If the condition $P_a(x, t_0) \geq 0$ is fulfilled at a certain time t_0 for all states x , the *non-negativity* defined by $P_a(x, t) \geq 0$ will be guaranteed for all later times $t > t_0$. Moreover, despite the applied factorization assumption (4.15) we can derive

$$\frac{d}{dt} \left(\sum_x P_a(x, t) \right) = 0, \quad \text{i.e.} \quad \sum_x P_a(x, t) = \text{const.} \quad (4.23)$$

which allows the *normalization* of distribution $P_a(x, t)$. The corresponding proofs are analogous to those in Sects. 3.3.1 and 3.3.2.

4.4.2 The Gaskinetic BOLTZMANN Equation

The BOLTZMANN equation for *fairly rare gases* is a special case of Eqs. (4.22a.). It results, if one combines in the state

$$x := (r, v) \quad (\text{or } y := (s, w)) \quad (4.24)$$

the *place* r (or s) and the *velocity* v (or w) of a gas particle. By types a we distinguish different *sorts* of particles. The *spontaneous state changes* are given by the *motion*

$$\frac{dr}{dt} = v \quad (4.25)$$

and the *acceleration*

$$\frac{dv}{dt} = \frac{d^2r}{dt^2} := \frac{F_a(t)}{m_a} \quad (4.26)$$

where $F_a(t)$ is the *force* exerted on a particle of *mass* m_a . They are described by the transition rates

$$\widehat{w}_a(r', v' | r, v; t) := \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \delta\left(r' - \left(r + v\Delta t\right)\right) \delta\left(v' - \left(v + \frac{F_a(t)}{m_a}\Delta t\right)\right). \quad (4.27)$$

In the **KRAMERS-MOYAL** *representation* (cf. [Sect. 6.2](#)) they contribute to Eq. (4.22) with the *divergence terms*

$$- \nabla_r \left[v P_a(r, v; t) \right] - \nabla_v \left[\frac{F_a(t)}{m_a} P_a(r, v; t) \right]. \quad (4.28)$$

Additionally, state changes result from *scattering processes* of particles (from *direct pair interactions*). These are described by the transition rates

$$\widehat{w}_{ab}(x', y' | x, y; t) := \widehat{w}'_{ab}(v', w' | v, w) \delta(r' - r) \delta(s' - s) \delta(r - s) \quad (4.29)$$

which reflect the *collisions* of two particles at location $r = s$ and the resulting velocity changes.

With respect to the *densities*

$$\rho(a, r, v; t) := N_a P_a(r, v; t) \quad (4.30)$$

where N_a denotes the number of particles of sort a within the considered volume V , we have the *gaskinetic BOLTZMANN equation* [[26](#), [154](#), [163](#)]

$$\begin{aligned} & \frac{\partial}{\partial t} \rho(a, r, v; t) \\ &= - \nabla_r \left[v \rho(a, r, v; t) \right] - \nabla_v \left[\frac{F_a(t)}{m_a} \rho(a, r, v; t) \right] \\ &+ \sum_b \int d^3 v' \int d^3 w \int d^3 w' \widehat{w}'_{ab}(v, w | v', w') \rho(a, r, v'; t) \rho(b, r, w'; t) \\ &- \sum_b \int d^3 v' \int d^3 w \int d^3 w' \widehat{w}_{ab}(v', w' | v, w) \rho(a, r, v; t) \rho(b, r, w; t). \end{aligned} \quad (4.31)$$

In most cases the pair interaction rates $\widehat{w}'_{ab}$ are expressed by the *differential scattering cross section*

$$d^6\sigma'_{ab} \equiv d^6\sigma'_{ab}(v', w'|v, w) := \frac{\widehat{w}'_{ab}(v', w'|v, w)d^3v'd^3w'}{\|v - w\|}. \quad (4.32)$$

Furthermore we have

$$\widehat{w}'_{ab}(v, w|v', w') = \widehat{w}'_{ab}(v', w'|v, w) \quad (4.33)$$

since the pair interaction rates $\widehat{w}_{ab}$ are *symmetrical* (cf. (3.88)):

$$\widehat{w}_{ab}(x, y|x', y') = \widehat{w}_{ab}(x', y'|x, y). \quad (4.34)$$

(This symmetry is a consequence of the *time reversal invariance* and the *isotropy of space*; cf. [154], pp. 69ff.) Consequently, the gaskinetic BOLTZMANN equation (4.31) can be written in the form

$$\begin{aligned} \frac{d}{dt}\rho(a, r, v; t) = \sum_b \int d^3w \int d^6\sigma'_{ab} \|v - w\| & \left[\rho(a, r, v'; t)\rho(b, r, w'; t) \right. \\ & \left. - \rho(a, r, v; t)\rho(b, r, w; t) \right]. \end{aligned} \quad (4.35)$$

Here

$$\begin{aligned} \frac{d}{dt}\rho(a, r, v; t) &:= \frac{\partial}{\partial t}\rho(a, r, v; t) + \nabla_r \cdot \left[v\rho(a, r, v; t) \right] + \nabla_v \cdot \left[\frac{F_a(t)}{m_a}\rho(a, r, v; t) \right] \\ &= \frac{\partial}{\partial t}\rho(a, r, v; t) + v \cdot \nabla_r \rho(a, r, v; t) + \frac{F_a(t)}{m_a} \cdot \nabla_v \rho(a, r, v; t) \end{aligned} \quad (4.36)$$

is the *total (substantial) time derivative* which describes the temporal change of the density $\rho(a, r, v; t)$ in a *transformed coordinate system* which moves *along* with velocity $(v, F_a/m_a)^{\text{tr}}$. Obviously, $d\rho(a, r, v; t)/dt$ is only given by the scattering processes. In this sense, BOLTZMANN equation (4.35) is already determined by *pair interactions*. In contrast to this, the terms due to *spontaneous transitions* usually *cannot* be eliminated from the general Eq. (4.22): In the case of *non-deterministic* transition rates $w_a(x'|x; t)$ the KRAMERS-MOYAL expansion leads not only to divergence terms but also to further contributions which cannot be eliminated by a transformation.

In the following, Eq. (4.22) will be called ‘BOLTZMANN equations’ if these are solely given by *pair interactions*. If, in addition to pair interactions, *spontaneous transitions* play a role, it is reasonable to speak of ‘BOLTZMANN-like equations’.

4.4.3 The *H*-Theorem for the Gaskinetic BOLTZMANN Equation

For the gaskinetic BOLTZMANN equation (4.31) there exists, analogous to Sect. 3.3.5, a LIAPUNOV function

$$H(t) := \sum_a \int d^6x \rho(a, x; t) \ln \rho(a, x; t) \quad (4.37)$$

with the property

$$\frac{dH}{dt} \leq 0. \quad (4.38)$$

Again, this causes the system to approach an *equilibrium*. Except for an *affine transformation*, $H(t)$ is identical with BOLTZMANN's *entropy function*

$$S(t) := -k \sum_a \int d^6x P(a, x; t) \log_2 P(a, x; t) \quad (4.39)$$

with

$$P(a, x; t) := \frac{N_a}{N} P_a(x, t) = \frac{\rho(a, x; t)}{N}. \quad (4.40)$$

For the proof of (4.38) we first show

$$\begin{aligned} \frac{dH}{dt} &= \sum_a \int d^6x \left[\frac{\partial \rho(a, x; t)}{\partial t} \ln \rho(a, x; t) + \frac{\partial \rho(a, x; t)}{\partial t} \right] \\ &= - \sum_a \int d^6x \ln \rho(a, x; t) \left\{ \nabla_r [v \rho(a, x; t)] + \nabla_v \left[\frac{F_a(t)}{m_a} \rho(a, x; t) \right] \right\} \\ &\quad + \sum_{a,b} \iiint \ln \rho(a, x; t) \left[\widehat{w}_{ab}(x, y|x', y') \rho(a, x'; t) \rho(b, y'; t) \right. \\ &\quad \left. - \widehat{w}_{ab}(x', y'|x, y) \rho(a, x; t) \rho(b, y; t) \right] d^6x d^6x' d^6y d^6y' \end{aligned} \quad (4.41)$$

$$\begin{aligned} &= - \sum_a \int d^6x \left\{ \nabla_r \left[v \left(\rho(a, x; t) \ln \rho(a, x; t) - \rho(a, x; t) \right) \right] \right. \\ &\quad \left. + \nabla_v \left[\frac{F_a(t)}{m_a} \left(\rho(a, x; t) \ln \rho(a, x; t) - \rho(a, x; t) \right) \right] \right\} \\ &\quad + \sum_{a,b} \iiint \ln \rho(a, x; t) \left[\widehat{w}_{ab}(x, y|x', y') \rho(a, x'; t) \rho(b, y'; t) \right. \\ &\quad \left. - \widehat{w}_{ab}(x', y'|x, y) \rho(a, x; t) \rho(b, y; t) \right] d^6x d^6x' d^6y d^6y'. \end{aligned} \quad (4.42)$$

The term

$$\sum_a \int d^6x \frac{\partial \rho(a, x; t)}{\partial t} = \sum_a \frac{\partial}{\partial t} \int d^6x \rho(a, x; t) = \sum_a \frac{\partial N_a}{\partial t} = \frac{\partial N}{\partial t} \quad (4.43)$$

vanishes on the condition that the considered system is a *closed system* which implies a *conservation of the number of particles*. The divergence terms can be transformed into surface integrals by using *GAUSS' divergence theorem* (cf. (6.16)). Due to

$$\lim_{\|v\| \rightarrow \infty} \rho(a, r, v; t) = 0, \quad (4.44)$$

however, these provide no contributions. Thus the following remains:

$$\begin{aligned} \frac{dH}{dt} &= \sum_{a,b} \iiint \ln \rho(a, x; t) \left[\widehat{w}_{ab}(x, y|x', y') \rho(a, x'; t) \rho(b, y'; t) \right. \\ &\quad \left. - \widehat{w}_{ab}(x', y'|x, y) \rho(a, x; t) \rho(b, y; t) \right] d^6x d^6x' d^6y d^6y' \end{aligned} \quad (4.45)$$

$$\begin{aligned} &= \sum_{a,b} \iiint \left[\ln \rho(a, x; t) - \ln \rho(a, x'; t) \right] \\ &\quad \times \widehat{w}_{ab}(x, y|x', y') \rho(a, x'; t) \rho(b, y'; t) d^6x d^6x' d^6y d^6y' \end{aligned} \quad (4.46)$$

$$\begin{aligned} &= \frac{1}{2} \sum_{a,b} \iiint \left[\ln \rho(a, x; t) - \ln \rho(a, x'; t) + \ln \rho(b, y; t) - \ln \rho(b, y'; t) \right] \\ &\quad \times \widehat{w}_{ab}(x, y|x', y') \rho(a, x'; t) \rho(b, y'; t) d^6x d^6x' d^6y d^6y'. \end{aligned} \quad (4.47)$$

From (4.45) we come to (4.46) by renaming the variables of the second term in accordance with $x \leftrightarrow x'$ and $y \leftrightarrow y'$. The identity of (4.46) and (4.47) results by interchanging the variables of two interacting particles α, β and taking into account

$$\widehat{w}_{ba}(y, x|y', x') = w_{\beta\alpha}(y, x|y', x') = w_{\alpha\beta}(x, y|x', y') = \widehat{w}_{ab}(x, y|x', y'). \quad (4.48)$$

On the condition

$$\int d^6x' \int d^6y' \widehat{w}_{ab}(x, y|x', y') = \int d^6x' \int d^6y' \widehat{w}_{ab}(x', y'|x, y) \quad (4.49)$$

which is fulfilled due to (4.34) we further have

$$\begin{aligned}
& \frac{1}{2} \sum_b \iiint \int \widehat{w}_{ab}(x, y|x', y') \left[\rho(a, x'; t) \rho(b, y; t) \right. \\
& \quad \left. - \rho(a, x; t) \rho(b, y; t) \right] d^6 x d^6 x' d^6 y d^6 y' \\
&= \frac{1}{2} \sum_b \iiint \int \left[\widehat{w}_{ab}(x, y|x', y') \rho(a, x'; t) \rho(b, y'; t) \right. \\
& \quad \left. - \widehat{w}_{ab}(x', y'|x, y) \rho(a, x; t) \rho(b, y; t) \right] d^6 x d^6 x' d^6 y d^6 y' \\
&= 0.
\end{aligned} \tag{4.50}$$

This can immediately be seen by renaming the variables in the second term in accordance with $x \leftrightarrow x'$ and $y \leftrightarrow y'$.

Now, formally adding in the vanishing term (4.50) to (4.47) and introducing the abbreviations

$$z_{ab} \equiv z_{ab}(x, y; x', y'; t) := \frac{\rho(a, x'; t) \rho(b, y'; t)}{\rho(a, x; t) \rho(b, y; t)}, \tag{4.51a}$$

$$z'_{ab} \equiv z'_{ab}(v, w; v', w'; t) := \frac{\rho(a, r, v'; t) \rho(b, r, w'; t)}{\rho(a, r, v; t) \rho(b, r, w; t)}, \tag{4.51b}$$

we find the relation

$$\begin{aligned}
\frac{dH}{dt} &= -\frac{1}{2} \sum_{a,b} \iiint \int \rho(a, x; t) \rho(b, y; t) \left(z_{ab} \ln z_{ab} - z_{ab} + 1 \right) \\
& \quad \times \widehat{w}_{ab}(x, y|x', y') d^6 x d^6 x' d^6 y d^6 y' \\
&= -\frac{1}{2} \sum_{a,b} \iiint \int \int \rho(a, r, v; t) \rho(b, r, w; t) \left(z'_{ab} \ln z'_{ab} - z'_{ab} + 1 \right) \\
& \quad \times \widehat{w}'_{ab}(v, w|v', w') d^3 v d^3 v' d^3 w d^3 w' d^3 r \\
&\leq 0
\end{aligned} \tag{4.52}$$

because of

$$z'_{ab} \ln z'_{ab} - z'_{ab} + 1 \geq 0 \quad \text{for} \quad z'_{ab} > 0. \tag{4.53}$$

Consequently, a system described by the gaskinetic BOLTZMANN equation (4.35) moves towards an *equilibrium*. However, without the validity of relation (4.49) a BOLTZMANN equation can also show an *oscillatory* or *chaotic* behaviour (cf. Sects. 10.3.2 and 10.3.4).

4.4.4 Solution of the Gaskinetic BOLTZMANN Equation

According to (4.52), the relation $dH/dt = 0$ presupposes that the *equilibrium condition* $z'_{ab} \stackrel{!}{=} 1$ is fulfilled. This implies the condition

$$\psi_a(v) + \psi_b(w) \stackrel{!}{=} \psi_a(v') + \psi_b(w') \quad (4.54a)$$

with

$$\psi_a(v) := \ln \rho(a, r, v). \quad (4.54b)$$

Obviously, (4.54) is satisfied by the *collisional invariants*

$$\text{mass } m_a, \quad (4.55a)$$

$$\text{momentum } m_a v_i, \quad (4.55b)$$

$$\text{energy } \frac{m_a}{2} \|v\|^2 = \frac{m_a}{2} \sum_i (v_i)^2, \quad (4.55c)$$

and *linear combinations* of these. Inserting

$$\psi_a(v) := c_a^1 m_a + \sum_i c_{a,i}^2 m_a v_i + c_a^3 \frac{m_a}{2} \sum_i (v_i)^2 \quad (4.56)$$

into (4.54) and representing the density of particles of sort a at location r by $\rho(a, r)$ we obtain

$$\rho(a, r, v) = \rho(a, r) P_a(v) \quad (4.57a)$$

with the MAXWELL-BOLTZMANN *distribution*

$$P_a(v) := \prod_i \left(\frac{1}{\sqrt{2\pi}\sigma_a} e^{-(v_i - \langle v_i \rangle_a)^2 / (2\sigma_a)} \right) = \frac{1}{(2\pi\sigma_a)^{3/2}} e^{-(v - \langle v \rangle_a)^2 / (2\sigma_a)}. \quad (4.57b)$$

Here $\langle v \rangle_a$ has the meaning of the mean velocity of the particles of sort a . σ_a is related to their *absolute temperature* T'_a via the BOLTZMANN *constant* k :

$$\sigma_a = kT'_a. \quad (4.58)$$

For the determination of the *time-dependent* solution of the gaskinetic BOLTZMANN equation there exists a (rather complicated) recursive method which was developed by CHAPMAN [38] and ENSKOG [64] (cf. [170], pp. 187ff.).

4.5 Comparison of Spontaneous Transitions and Direct Interactions

In the following we will elaborate the interrelations and differences between spontaneous transitions and direct interactions.

4.5.1 Transitions Induced by Interactions

Let us assume that we have $A' \equiv A + B$ types a of elements and that the elements of all types are able to change their states only by *pair interactions*. Provided the dynamics of all A' types is known, it is described by the BOLTZMANN equations

$$\begin{aligned} \frac{d}{dt} P_a(x, t) = & \sum_{b=1}^{A'} \sum_{x'} \sum_y \sum_{y'} w_{ab}(x, y|x', y'; t) P_b(y', t) P_a(x', t) \\ & - \sum_{b=1}^{A'} \sum_{x'} \sum_y \sum_{y'} w_{ab}(x', y'|x, y; t) P_b(y, t) P_a(x, t) \quad (4.59) \end{aligned}$$

($a \in \{1, \dots, A + B\}$). If, however, only the dynamics of the A types $a \in \{1, \dots, A\}$ is known, it obeys the BOLTZMANN-like equations

$$\frac{d}{dt} P_a(x, t) = \sum_{x'} \left[w^a(x|x'; t) P_a(x', t) - w^a(x'|x; t) P_a(x, t) \right] \quad (4.60a)$$

with

$$w^a(x'|x; t) := w_a(x'|x; t) + \sum_{b=1}^A \sum_y \sum_{y'} w_{ab}(x', y'|x, y; t) P_b(y, t). \quad (4.60b)$$

The connection with (4.59) is given by

$$w_a(x'|x; t) := \sum_{b=A+1}^{A+B} \sum_y \sum_{y'} w_{ab}(x', y'|x, y; t) P_b(y, t). \quad (4.60c)$$

So the transition rates w_a may describe transitions which are *induced* by unknown pair interactions.

4.5.2 Exponential Function and Logistic Equation

Let us consider the case of one type a of subsystems ($A = 1$) which can change between $S = 2$ states $x \equiv x \in \{1, 2\}$. Then there is

$$P(2, t) = 1 - P(1, t) \quad (4.61)$$

where subscript a was omitted. If only *spontaneous transitions* occur and the transition rates are time-independent, the corresponding BOLTZMANN-like equation is the *master equation*

$$\begin{aligned} \frac{d}{dt}P(1, t) &= w(1|2)P(2, t) - w(2|1)P(1, t) \\ &= w(1|2) - [w(1|2) + w(2|1)]P(1, t). \end{aligned} \quad (4.62)$$

Its solution is the *exponential function*

$$P(1, t) = P^0(1) + [P(1, t_0) - P^0(1)]e^{-\lambda(t-t_0)} \quad (4.63a)$$

with

$$P^0(1) := \frac{w(1|2)}{w(1|2) + w(2|1)} \leq 1 \quad (4.63b)$$

and

$$\lambda := w(1|2) + w(2|1). \quad (4.63c)$$

If, in contrast to this, only *direct pair interactions* take place and if the transition rates are again time-independent, the corresponding BOLTZMANN-like equation is the *BOLTZMANN equation*

$$\begin{aligned} \frac{d}{dt}P(1, t) &= [w(1, 1|2, 2)P(2, t)P(2, t) + w(1, 2|2, 2)P(2, t)P(2, t)] \\ &\quad - [w(2, 1|1, 2)P(2, t)P(1, t) + w(2, 2|1, 2)P(2, t)P(1, t)] \\ &\quad + [w(1, 1|2, 1)P(1, t)P(2, t) + w(1, 2|2, 1)P(1, t)P(2, t)] \\ &\quad - [w(2, 1|1, 1)P(1, t)P(1, t) + w(2, 2|1, 1)P(1, t)P(1, t)] \\ &\equiv -C_1[P(1, t)]^2 + C_2P(1, t) + C_3 \end{aligned} \quad (4.64)$$

where C_1 , C_2 , and C_3 are constants that are determined by the pair interaction rates w together with (4.61). After introducing

$$Q(1, t) := P(1, t) - C \quad \text{and} \quad C := \frac{C_2 - \sqrt{(C_2)^2 + 4C_1C_3}}{2C_1} \quad (4.65)$$

we can transform (4.64) into the *logistic equation*

$$\frac{d}{dt} Q(1, t) = r Q(1, t) \left(1 - \frac{Q(1, t)}{Q^0(1)} \right) \quad (4.66)$$

with

$$r := C_2 - 2C_1 C = \sqrt{(C_2)^2 + 4C_1 C_3} \quad (4.67a)$$

and

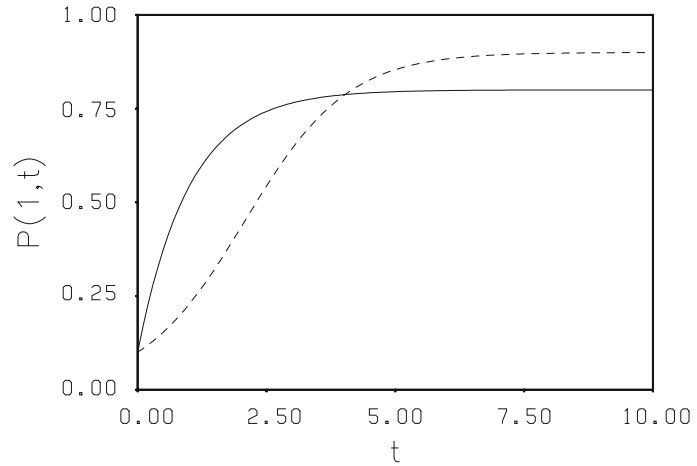
$$Q^0(1) := \frac{r}{C_1} = \frac{\sqrt{(C_2)^2 + 4C_1 C_3}}{C_1}. \quad (4.67b)$$

(4.66) has the solution

$$Q(1, t) = \frac{Q^0(1)}{1 + \frac{Q^0(1) - Q(1, t_0)}{Q(1, t_0)} e^{-r(t-t_0)}}. \quad (4.68)$$

The exponential solution of (4.62) and the logistic solution of (4.64) are compared with each other in Fig. 4.1.

Fig. 4.1 Comparison of an exponential solution (—) and a solution of the *logistic equation* (---)



4.5.3 Stationary and Oscillatory Solutions

In the case of exclusively spontaneous transitions with time-independent transition rates ($w^a(x'|x; t) \equiv w_a(x'|x)$) the BOLTZMANN-like equations for the temporal evolution of the distributions $P_a(x, t)$ have the form of master equations (cf. (4.62)). According to the discussion in Sect. 3.3.5, $P_a(x, t)$ converges in the course of time to a *unique stationary equilibrium distribution* $P_a^0(x)$.

In contrast to this, there exist BOLTZMANN equations for pair interactions which have *various* stationary solutions, *oscillatory solutions*, or *chaotic solutions* even in the case of time-independent pair interaction rates (cf. [Sects. 10.3.2](#) and [10.3.4](#)). However, this presupposes that condition (4.49) is violated so that the *H-theorem* does not hold.