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The Elimination of Fast Variables in Complex Chemical Reactions. II. Mesoscopic Level (Reducible Case)

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The master equation for chemical reactions that proceed through a number of steps (complex reactions) is considered. Examples are studied in which the reaction constant of one of the steps is much larger than the others, and a reduced master equation is derived by means of a projection operator formalism. This reduction amounts to an elimination of intermediates. The consistency of the scheme is shown by means of the Ω-expansion.

KEY WORDS: Complex chemical reactions; intrinsic fluctuations; master equation; elimination of fast variables; Ω-expansion.

1. INTRODUCTION

The kinetics of chemical reactions may be studied at two different levels.

At the macroscopic level one is interested in the variation in time of the concentrations of reactants. The concentrations obey certain rate equations, which follow from the reaction mechanism. In order to get insight into the kinetics of the reaction one has to solve the rate equations (this can only be done in special cases; see, e.g., refs. 14 and 15) or reduce their number. This latter approach is appropriate if one or more reaction steps proceeds much faster than the others. The fast stages of the reaction can then be eliminated, and one is left with rate equations that describe only the slow processes (see part I of this work(18)).

The description of a chemical reaction in terms of rate equations is valid if one may consider the chemical substances to be continuously and

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homogeneously distributed in space. The latter condition can be met to any degree of accuracy if the chemical mixture is stirred sufficiently well. The discrete nature of matter, however, implies that the former condition can only be satisfied approximately.

At the mesoscopic level the fact that chemical substances consist of individual molecules is taken into account. The kinetics is described in terms of the numbers of molecules n_i $(i = 1,..., N)$ of the various chemicals involved. It is assumed that the n_i constitute a Markov process, the evolution of which is governed by a master equation. The transition probability is determined by the number of collisions per unit time, which follows from a stosszahlansatz. The resulting fluctuations in the numbers n_i are called intrinsic fluctuations. Basic papers on this kind of fluctuation are, e.g., refs. 1 and 2. Also see ref. 3.

Apart from the *intrinsic* fluctuations, a chemical reaction may also be subjected to *external* noise. Fluctuations that are introduced by the surroundings are, e.g., the nonconstancy of temperature and pressure in the reaction vessel. The effects of external fluctuations have been investigated for the case of explosive reactions.(4,5) In this paper and the following I will deal exclusively with intrinsic fluctuations.

Although intrinsic fluctuations are generally of the order of the square root of the number of particles and therefore relatively small, they still can have a marked effect, as in bistable chemical reactions,(7) reaction-diffusion systems,(8) two-species annihilation,(9) and explosive chemical reactions.(6,16)

The master equation can be solved exactly if all reaction steps are unimolecular, in which case the transition probabilities depend linearly on the n_i.(3) For bimolecular reaction steps (corresponding to nonlinear transition probabilities) no general solution exists, and one has to resort to approximation methods.

A particular powerful approximation scheme for the master equation is the Ω-expansion.(3) Ω is a parameter that measures the size of the system, and it is assumed to be very large. For chemical reactions one usually identifies Ω with the volume of the reaction vessel.[3] The Ω-expansion is based on the insight that fluctuations are of order $\Omega^{1/2}$; the numbers n_i are decomposed into a deterministic and a fluctuating part, $n_i = \Omega\varphi_i + \Omega^{1/2}\xi_i$, and the master equation is expanded in powers of $\Omega^{-1/2}$. The order-$\Omega^{1/2}$ terms yield deterministic equations for the quantities φ_i, which are identical to the macroscopic rate equations. The order-Ω^0 terms produce a linear Fokker–Planck equation for the probability density of the fluctuating

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[3] This is the conventional choice. Recently Burschka(8) introduced a refined version of the Ω-expansion in which Ω is identified with Avogadro's number.

quantities ξ_i. The coefficients in this equation depend on time through the φ_i.

An important consequence of the Ω-expansion is that the fluctuations ξ_i vary on the same time scales as the macroscopic quantities φ_i. Hence the Ω-expansion effectively wipes out all mesoscopic time scales.

Consider now the situation that at the macroscopic level there are a fast and a slow time scale. One may think of a reaction in which X is converted into Z in two steps: first X initiates an intermediate Y, which is subsequently consumed in a fast second reaction to produce Z. At the level of rate equations one may eliminate Y, which is a short-lived intermediate, and derive an equation describing the slow formation of Z. If, at the mesoscopic level, one considers the master equation and performs the Ω-expansion, it turns out that the fluctuations in Y are also rapidly varying. Hence, the fluctuations in Y may be eliminated as well. One ends up with a reduced description that encompasses the rate of conversion of X into Z and fluctuations in it.

In this paper, I will study the effects on the overall reaction of intrinsic fluctuations in short-lived intermediates. The above scenario in which one first takes the limit $\Omega \to \infty$ and subsequently $\varepsilon \to 0$ (ε is a measure of the lifetime of the intermediate) is straightforward, but very cumbersome.

Therefore I will adopt a different strategy and take the limit $\varepsilon \to 0$ immediately (Ω is kept fixed). A projection operator technique is used to perform the elimination of intermediates. This will be illustrated with two examples. For both cases a reduced master equation describing the overall reaction will be obtained.

2. DERIVATION OF A REDUCED MASTER EQUATION

Consider the autocatalytic part of the Schlögl reaction(10):

$$A + 2X \rightleftarrows 3X \tag{1}$$

Only X varies; the amount of substance A is held constant during the reaction.

As (1) involves three-particle interactions, which are highly unprobable, it is expected to be a complex reaction. A plausible reaction mechanism, involving the intermediate Y, is provided by the following two simple reactions(11):

$$2X \underset{k_1}{\overset{k_2}{\rightleftarrows}} Y, \qquad A + Y \underset{k_3}{\overset{k_4}{\rightleftarrows}} X + Y \tag{2}$$

Y is supposed to be a short-lived intermediate. This amounts to the assumption that the reaction step $Y \to 2X$ proceeds much faster than the other ones. Therefore we put $k_2 = 1/\varepsilon$, $\varepsilon \ll 1$. First the intermediate Y is eliminated at the macroscopic and subsequently at the mesoscopic level.

The rate equations associated with (2) read

$$\begin{aligned} \dot{x} &= \frac{2}{\varepsilon} y - 2k_1 x^2 + k_3 a y - k_4 x y \\ \dot{y} &= -\frac{1}{\varepsilon} y + k_1 x^2 \end{aligned} \tag{3}$$

I have denoted the concentrations of A, X, and Y by a, x, and y respectively. If one performs the scaling $y = \varepsilon z$, Eq. (3) are transformed into the standard form,(13)

$$\begin{aligned} \dot{x} &= 2z - 2k_1 x^2 + \varepsilon k_3 a z - \varepsilon k_4 x z \\ \dot{z} &= \frac{1}{\varepsilon} (k_1 x^2 - z) \end{aligned} \tag{4}$$

The fast variable z can now be eliminated straightforwardly. This yields the reduced equation

$$\dot{x} = \varepsilon a k_1 k_3 x^2 - \varepsilon k_1 k_4 x^3 + O(\varepsilon^2) \tag{5}$$

The order-ε^2 corrections in (5) contain a term proportional to x^4; this is a manifestation of the complexity of the reaction.

Let us next consider (2) mesoscopically. The master equation associated with (2) reads

$$\begin{aligned} \dot{p}(n_1, n_2) = {} & k_1 \Omega^{-1} (E_1^2 E_2^{-1} - 1)\, n_1 (n_1 - 1)\, p + \frac{1}{\varepsilon} (E_1^{-2} E_2 - 1)\, n_2 p \\ & + k_3 a (E_1^{-1} - 1)\, n_2 p + k_4 \Omega^{-1} (E_1 - 1)\, n_1 n_2 p \end{aligned} \tag{6}$$

The number of molecules of X and Y are denoted by n_1 and n_2, respectively. The symbol E_i is a step operator: $E_1 f(n_1, n_2) = f(n_1 + 1, n_2)$. Ω is the volume of the vessel in which the reaction takes place.

Equation (6) is a linear evolution equation in which the evolution operator consists of a large part and a remaining one. Its formal structure is given by

$$\dot{\rho} = L\rho, \qquad L = \frac{1}{\varepsilon} L_1 + L_2 \tag{7}$$

The operators L_1 and L_2 refer to fast and slow processes, respectively.

From (7) a reduced equation, which only contains the slow processes, can be derived if one can find a projection operator P satisfying $PL_1 = L_1 P = 0$ and subject to the condition that L_1 is invertible in its null space.(12, 13) The reduced equation describes the evolution of the projected part of ρ,

$$\dot{P\rho} = L_{\text{red}} P\rho \tag{8}$$

The reduced evolution operator L_{red} is a series in ε; its first two terms are given by(12, 13)

$$L_{\text{red}} = PL_2P - \varepsilon PL_2QL_1^{-1}QL_2P \tag{9}$$

where $Q = 1 - P$. This scheme will now be applied to the master equation (6).

The evolution operator of (6) consists of four terms. We write, in obvious notation,

$$L = \mathbf{W}_1 + \mathbf{W}_2 + \mathbf{W}_3 + \mathbf{W}_4 \tag{10}$$

As $\mathbf{W}_2$ refers to the fast reaction step, a suitable choice to separate L is

$$\frac{1}{\varepsilon} L_1 = \mathbf{W}_2, \qquad L_2 = \mathbf{W}_1 + \mathbf{W}_3 + \mathbf{W}_4 \tag{11}$$

However, a different choice is possible; I will go into this subject in the next section.

The operator L_1 defined in (11) represents the unidirectional reaction $Y \rightarrow 2X$. The combination $m = n_1 + 2n_2$ is constant during this reaction, which proceeds until Y is depleted (see Fig. 1). Hence the projection operator of this reaction is given by

$$Pp(n_1, n_2) = \delta_{n_2,0} \sum_{n'_1 n'_2} \delta_{m, n'_1 + 2n'_2}\, p(n'_1, n'_2) \tag{12}$$

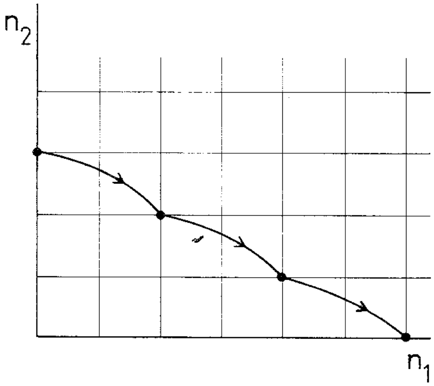

Fig. 1. The reaction $Y \rightarrow 2X$.

With Fig. 1 in mind, its meaning can be easily understood. The quantity

$$q(m) = \sum_{n'_1 n'_2} \delta_{m, n'_1 + 2n'_2} p(n'_1, n'_2) \tag{13}$$

is the total probability along the line $m = n_1 + 2n_2$.

According to (8) and (9), one can deduce a reduced equation for the projected part of the joint probability density [and hence for $q(m)$]. The details of the calculations can be found in ref. 17. To order ε, the result reads

$$\begin{aligned} \dot{q}(m) = {} & \varepsilon a k_1 k_3 \Omega^{-1}(E^{-1} - 1)\, m(m-1)\, q(m) \\ & + \varepsilon k_1 k_4 \Omega^{-2}(E - 1)\, m(m-1)(m-2)\, q(m) \end{aligned} \tag{14}$$

We conclude that $q(m)$ obeys an equation of the master type; (14) is the master equation associated with the overall reaction (1). The effective reaction constants are $\varepsilon k_1 k_3$ and $\varepsilon k_1 k_4$ for the forward and backward reaction, respectively.

Gardiner(11) also arrives at (14), but via a detour. He writes p as a superposition of multivariate uncorrelated Poissonian distributions; the expansion coefficients then obey (at least for bimolecular reactions) a Fokker–Planck-like equation. The elimination of the intermediate Y in his approach is performed at the Fokker–Planck level instead of the master level. However, his function $p_x(v)$ in (7.7.128) is not always normalizable, and hence the P in (7.7.127) may not be a projection operator; this makes his derivation moot.

3. NONUNIQUENESS OF THE PROJECTION OPERATOR

As k_2 is the largest reaction constant, the separation (11) of (10) is suggested. However, one may alternatively include $\mathbf{W}_1$ in L_1. So, now choose

$$\frac{1}{\varepsilon} L_1 = \mathbf{W}_2 + \varepsilon \mathbf{W}_1, \qquad L_2 = \mathbf{W}_3 + \mathbf{W}_4 \tag{15}$$

Consequently, another projection operator is needed,

$$Pp(n_1, n_2) = \frac{(\varepsilon k_1 \Omega^{-1})^{n_2}}{n_1!\, n_2!} A(m)\, q(m) \tag{16}$$

where $q(m)$ is again given by (13), and $A(m)$ follows from a normalization condition;

$$A^{-1}(m) = \sum_{n_1, n_2} \delta_{m, n_1 + 2n_2} \frac{(\varepsilon k_1 \Omega^{-1})^{n_2}}{n_1!\, n_2!} \tag{17}$$

According to our projection formalism, $q(m)$ obeys in lowest order

$$\dot{q}(m) = \bar{P}L_2Pp(n_1, n_2) \tag{18}$$

where $\bar{P} = \sum_{n_1,n_2} \delta_{m,n_1+2n_2}$. In order to find explicit results, one has to perform some calculations,

$$\begin{aligned}\bar{P}L_2Pp = &\sum_{n_1,n_2} \delta_{m,n_1+2n_2} \frac{k_2 a(\varepsilon k_1 \Omega^{-1})^{n_2}}{(n_2-1)!}\\ &\times\left[\frac{A(m-1)\,q(m-1)}{(n_1-1)!} - \frac{A(m)\,q(m)}{n_1!}\right]\\ &+ \sum_{n_1,n_2} \delta_{m,n_1+2n_2} \frac{k_4(\varepsilon k_1 \Omega^{-1})^{n_2}}{\Omega(n_2-1)!}\\ &\times\left[\frac{A(m+1)\,q(m+1)}{n_1!} - \frac{A(m)\,q(m)}{(n_1-1)!}\right]\\ = &\frac{\varepsilon a k_1 k_3}{\Omega}(E^{-1}-1)\frac{A(m)}{A(m-2)}\,q(m)\\ &+\frac{\varepsilon k_1 k_4}{\Omega^2}(E-1)\frac{A(m)}{A(m-3)}\,q(m)\end{aligned} \tag{19}$$

As $\lim_{\varepsilon \to 0} A^{-1}(m) = 1/(m!)$ one thus arrives at

$$\begin{aligned}\dot{q}(m) = &\frac{\varepsilon a k_1 k_3}{\Omega}(E^{-1}-1)\,m(m-1)\,q(m)\\ &+\frac{\varepsilon k_1 k_4}{\Omega^2}(E-1)\,m(m-1)(m-2)\,q(m)\end{aligned} \tag{20}$$

which is identical to (14).

Hence both (11) and (15) yield the same reduced master equation. However, this is not a general feature, but a consequence of the unimolecularity of the fast reaction step $Y \to 2X$. In the next sections it will be shown that, for the case of a bimolecular fast reaction, it is crucial to divide L in the right way.

4. MESOSCOPIC TREATMENT OF THE HBr REACTION

The formation of hydrogen bromide, $H_2 + Br_2 \to 2HBr$, is a complex reaction, which is supposed to proceed according to the following reaction mechanism:

$$\begin{aligned}
&\mathrm{Br}_2+\mathrm{M} \underset{2}{\overset{1}{\rightleftarrows}} 2\mathrm{Br}+\mathrm{M}\\
&\mathrm{H}_2+\mathrm{Br} \underset{4}{\overset{3}{\rightleftarrows}} \mathrm{HBr}+\mathrm{H}\\
&\mathrm{Br}_2+\mathrm{H} \xrightarrow{5} \mathrm{HBr}+\mathrm{Br}
\end{aligned} \tag{21}$$

The rate equations of this reaction have been studied in the preceding paper. It has been shown that, if one assumes that reaction 2 is much faster than the others, the intermediates Br and H can be eliminated successively. Here, it is our aim to perform a similar reduction at the mesoscopic level.

Let us denote the number of molecules of H_2, Br_2, HBr, H, and Br by n_1, n_2, n_3, n_4, and n_5, respectively. The master equation associated with (21) may then be written as

$$\begin{aligned}
\dot{p}(n_1, n_2, n_3, n_4, n_5) = {} & k_1(E_2E_5^{-2}-1)\,n_2\,p\\
&+\frac{k_2}{\Omega}(E_2^{-1}E_5^2-1)\,n_5(n_5-1)\,p\\
&+\frac{k_3}{\Omega}(E_1E_5E_3^{-1}E_4^{-1}-1)\,n_1n_5\,p\\
&+\frac{k_4}{\Omega}(E_1^{-1}E_5^{-1}E_3E_4-1)\,n_3n_4\,p\\
&+\frac{k_5}{\Omega}(E_2E_4E_3^{-1}E_5^{-1}-1)\,n_2n_4\,p
\end{aligned} \tag{22}$$

The numbers $n_1, \ldots, n_5$ are not all independent, as the combinations $2n_1+n_3+n_4$ and $2n_2+n_3+n_5$ remain constant during the reaction. The constant k_2 is assumed to be much larger than the others; $k_2/k_1=1/\varepsilon$, $\varepsilon \ll 1$.

The evolution operator L in (22) consists of five terms that are to be divided into two groups, corresponding to fast and slow motion, respectively. As in (11), the following separation is suggested:

$$L_1/\varepsilon=\mathbf{W}_2, \qquad L_2=\mathbf{W}_1+\mathbf{W}_3+\mathbf{W}_4+\mathbf{W}_5 \tag{23}$$

However, this choice does not lead to meaningful results, as I will now show.

The projection operator associated with (23) is

$$P=\delta_{n_5, i(m)} \sum_{n_2'n_5'} \delta_{n, 2n_2'+n_5'} \tag{24}$$

where $i(m) = [1-(-1)^m]/2$. This projection operator allows one to eliminate n_5 and to derive a reduced equation for

$$q(n_1, m, n_3, n_4) = \sum_{n_2, n_5} \delta_{m, 2n_2+n_5} p(n_1, n_2, n_3, n_4, n_5)$$

In lowest order one finds

$$\begin{aligned} \dot{q} = {} & \frac{k_3}{\Omega}(E_1 E_3^{-1} E_4^{-1} E_m - 1)\, n_1 i(m) q \\ & + \frac{k_4}{\Omega}(E_1^{-1} E_3 E_4 E_m^{-1} - 1)\, n_3 n_4 q \\ & + \frac{k_5}{\Omega}(E_3^{-1} E_4 E_m - 1)\, n_4 \left(\frac{m - i(m)}{2}\right) q \end{aligned} \tag{25}$$

This equation is independent of ε, and hence a secondary elimination (as at the macroscopic level) is not possible. Moreover, (25) does not refer to a chemical reaction, and one cannot deduce a meaningful rate equation from it.

5. MACROSCOPIC AND MESOSCOPIC TIME SCALES

At the macroscopic level the kinetics of a chemical reaction is described by a master equation. The time scales that are associated with it (mesoscopic time scales) differ from the time scales at the macroscopic level. The macroscopic time scales are only determined by the reaction constants of the individual reaction steps; they are independent of Ω. Mesoscopic time scales, on the other hand, do depend on the size of the system.

Consider, e.g., reaction 1 of (21). According to (22), the time derivative of the probability distribution is proportional to n_2. As n_2 ranges from microscopic values of order 1 to macroscopic values of order Ω, the mesoscopic time scales range from $(k_1\Omega)^{-1}$ to k_1^{-1}. Hence for the unimolecular reaction 1 there are no mesoscopic time scales that are slower than the corresponding macroscopic time scales.

This is no longer true for bimolecular reactions. As one may infer from (22), the mesoscopic time scales of reaction 2 range from $(k_2\Omega)^{-1}$ to Ωk_2^{-1}. Hence the bimolecular reaction 2 contains mesoscopic time scales that are slower than the corresponding macroscopic time scale. This is why (24) is not a good projection operator; (24) implies that all Br molecules (possibly with the expection of one) are depleted. This process proceeds on a slow mesoscopic time scale of order $\varepsilon\Omega$. As (24) also eliminates this slow mesoscopic time scale, one runs into difficulties. In the next section a projection operator will be defined that is free of this complication.

6. PRIMARY ELIMINATION

As one may infer from (22), reaction 2 of (21) becomes very slow for small values of n_5. Reaction 1 keeps n_5 from becoming too small; hence, it is appropriate to include it among the fast terms. So now put

$$L_1/\varepsilon = \mathbf{W}_1 + \mathbf{W}_2, \qquad L_2 = \mathbf{W}_3 + \mathbf{W}_4 + \mathbf{W}_5 \tag{26}$$

The associated projection operator is given by

$$\mathscr{P} = \frac{(\varepsilon\Omega)^{n_5/2}}{n_2!\, n_5!} A(h) \sum_{n'_2, n'_5} \delta_{h, n'_2 + n'_5/2} \tag{27}$$

The function $A(h)$ is determined by a normalization condition,

$$A^{-1}(h) = \sum_{n_1, n_5} \delta_{h, n_2 + n_5/2} \frac{(\varepsilon\Omega)^{n_5/2}}{n_2!\, n_5!} \tag{28}$$

$A^{-1}(h)$ can be expressed in terms of Kummer functions. See ref. 17.

With the help of the projection operator (27), one can effectively eliminate the variable n_5 and derive a reduced equation for the quantity q,

$$q(n_1, h, n_3, n_4) = \sum_{n'_2, n'_5} \delta_{h, n'_2 + n'_5/2}\, p(n_1, n'_2, n_3, n_4, n'_5) \tag{29}$$

The role of n_2 is taken over by the half-integer h. In lowest order one finds

$$\begin{aligned} \dot{q} = {} & \varepsilon^{1/2}\Omega^{-1/2}k_3(E_1 E_h^{1/2} E_3^{-1} E_4^{-1} - 1) n_1 \frac{A(h)}{A(h-1/2)} q \\ & + \Omega^{-1}k_4(E_1^{-1} E_h^{-1/2} E_3 E_4 - 1)\, n_3 n_4 q \\ & + \Omega^{-1}k_5(E_h^{1/2} E_3^{-1} E_4 - 1) n_4 \frac{A(h)}{A(h-1)} q \end{aligned} \tag{30}$$

where $E_h^{1/2} f(h) = f(h+1/2)$.

One of the terms in (30) is of order $\sqrt{\varepsilon}$. This is a consequence of the ε dependence of the projection operator (27). The first-order correction to (30) is given by [see (9)] $-\varepsilon\mathscr{P}L_2\mathscr{Q}L_1^{-1}\mathscr{Q}L_2\mathscr{P}p$. This term is of order ε, as L_1^{-1} does not introduce negative powers of ε. See ref. 17.

The result (30) may be interpreted in terms of a virtual reaction. As $A(h+1/2)/A(h) \simeq \sqrt{h}$ for large h,[17] one may associate the following reactions with (30):

$$\begin{aligned} X_1 + \tfrac{1}{2}X_h &\rightleftarrows X_3 + X_4 \\ X_4 + X_h &\rightarrow X_3 + \tfrac{1}{2}X_h \end{aligned} \tag{31}$$

Hence on a slower time scale the complex reaction (21), which consists of five steps, may be viewed as a virtual reaction that proceeds through three steps.

Equation (30) is the result of the elimination of the intermediate Br. As one of the effective reaction constants of the virtual reactions in (30) is much smaller than the other two, a second elimination (as at the macroscopic level) is possible. In the next section the elimination of H will be performed.

7. SECONDARY ELIMINATION

Equation (30) is of the form

$$\dot{q} = (\hat{\mathbf{W}}_3 + \hat{\mathbf{W}}_4 + \hat{\mathbf{W}}_5)q \tag{32}$$

$\hat{\mathbf{W}}_4$ and $\hat{\mathbf{W}}_5$ are faster than $\hat{\mathbf{W}}_3$; one should therefore look for a projection operator that obeys $\mathscr{P}(\hat{\mathbf{W}}_4 + \hat{\mathbf{W}}_5) = (\hat{\mathbf{W}}_4 + \hat{\mathbf{W}}_5)\mathscr{P} = 0$.

First note that q depends only on two variables, as $2h + n_3$ and $2n_1 + n_3 + n_4$ remain constant during the reaction (31). If one chooses n_3 and n_4 as the independent variables, one can write (30) in the simplified form

$$\begin{aligned} \dot{q} = {} & \varepsilon^{1/2}\Omega^{-1/2}k_3(E_3^{-1}E_4^{-1} - 1)n_1 \frac{A(h)}{A(h-1/2)} q \\ & + \Omega^{-1}k_4(E_3E_4 - 1)\, n_3 n_4 q \\ & + \Omega^{-1}k_5(E_3^{-1}E_4 - 1)n_4 \frac{A(h)}{A(h-1)} q \end{aligned} \tag{33}$$

It is understood that $2n_1 = C_1 - n_3 - n_4$ and $h = C_2 - \frac{1}{2}n_3$.

Consider an operator K with

$$Kq = \sum_{n_3', n_4'} K(n_3, n_4 \mid n_3', n_4')\, q(n_3', n_4') \tag{34}$$

If one requires $K(\hat{\mathbf{W}}_4+\hat{\mathbf{W}}_5)=0$, it is found that K must obey the equation

$$\begin{aligned} & k_4 n_3' n_4' [K(n_3, n_4 \mid n_3'-1, n_4'-1) - K(n_3, n_4 \mid n_3', n_4')] \\ & \quad = k_5 n_4' \frac{A(h')}{A(h'-1)} [K(n_3, n_4 \mid n_3'+1, n_4'-1) - K(n_3, n_4 \mid n_3', n_4')] \end{aligned} \tag{35}$$

Or alternatively

$$\begin{aligned} K(n_3, n_4 \mid n_3', n_4') = {} & \frac{k_4 n_3'}{k_4 n_3' + k_5 A(h')/A(h'-1)} K(n_3, n_4 \mid n_3'-1, n_4'-1) \\ & + \frac{k_5 A(h')/A(h'-1)}{k_4 n_3' + k_5 A(h')/A(h'-1)} K(n_3, n_4 \mid n_3'+1, n_4'-1) \end{aligned} \tag{36}$$

This equation may be interpreted in terms of a branching process.(3) $K(n_3, n_4 \mid n_3', n_4')$ is the probability that if one starts in the point n_3', n_4' one ends up in n_3, n_4 after $n_4'-n_4$ steps (see Fig. 2). Here

$$\pi_+ = k_5 A(h')\, A(h'-1)^{-1}\, [k_4 n_3' + k_5 A(h')\, A(h'-1)^{-1}]^{-1}$$

is the probability to make a transition $(n_3', n_4') \to (n_3'+1, n_4'-1)$, and

$$\pi_- = k_4 n_3' [k_4 n_3' + k_5 A(h')\, A(h'-1)^{-1}]^{-1}$$

is the probability to go from (n_3', n_4') to $(n_3'-1, n_4'-1)$.

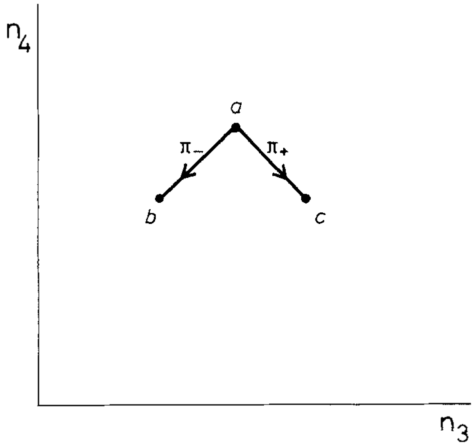

Fig. 2. Branching process.

As projection operator choose

$$\mathscr{P} = \delta_{n_4,0} \sum_{n'_3,n'_4} K(n_3, n_4 = 0 \,|\, n'_3, n'_4) \tag{37}$$

With this $\mathscr{P}$ the condition $\mathscr{P}(\hat{\mathbf{W}}_4 + \hat{\mathbf{W}}_5)$ is also satisfied.

It is unnecessary to solve the branching process (36) in all detail (although it is possible). The only quantities that are needed are

$$K_0 = K(n_3, n_4 = 0 \,|\, n'_3, n'_4 = 0) = \delta_{n_3,n'_3} \tag{38}$$

and

$$K_1 = K(n_3, n_4 = 0 \,|\, n'_3, n'_4 = 1) = \pi_- \;\delta_{n_3,n'_3-1} + \pi_+ \;\delta_{n_3,n'_3+1} \tag{39}$$

With the help of the projection operator (37) one may obtain a reduced equation for the quantity $r = Kq$. The calculation is straightforward. The lowest is $K\hat{\mathbf{W}}_3 \mathscr{P} q$ [cf. (9)],

$$\begin{aligned} K\hat{\mathbf{W}}_3 \mathscr{P} q = & \sum_{n'_3,n'_4} K(n_3, n_4 = 0 \,|\, n'_3, n'_4)(n'_1 + 1) \\ & \times \frac{A(h'+1/2)}{A(h')} \,\delta_{n'_4,1}\, q(n'_3 - 1) \\ & - \sum_{n'_3,n'_4} K(n_3, n_4 = 0 \,|\, n'_3, n'_4) n'_1 \,\frac{A(h')}{A(h'-1/2)} \,\delta_{n'_4,0}\, q(n_3) \end{aligned} \tag{40}$$

With the help of (38) and (39) one easily finds

$$\begin{aligned} K\hat{\mathbf{W}}_3 \mathscr{P} q = & \;\varepsilon^{1/2} \Omega^{-1/2} k_3 k_5 (n_1 + 1) \frac{A(h+1)}{A(h+1/2)} \\ & \times \left[1 + \frac{k_4}{k_5} \frac{n_3 - 1}{A(h+1/2)/A(h-1/2)} \right] r(n_3 - 2) \\ & - \varepsilon^{1/2} \Omega^{1/2} k_3 k_5 n_1 \frac{A(h)}{A(h-1/2)} \\ & \times \left[1 + \frac{k_4}{k_5} \frac{n_3 + 1}{A(h-1/2)/A(h-3/2)} \right] r(n_3) \end{aligned} \tag{41}$$

Hence for the reduced equation one obtains

$$\begin{aligned} \dot{r}(n_1, n_3, h) = & \;\varepsilon^{1/2} \Omega^{-1/2} k_3 (E_1 E_h E_3^{-2} - 1) n_1 \\ & \times \frac{A(h)}{A(h-1/2)} \left[1 + \frac{k_4}{k_5} \frac{(n_3 + 1)\, A(h-3/2)}{A(h-1/2)} \right]^{-1} r \end{aligned} \tag{42}$$

This equation may be interpreted as the effective master equation of the overall reaction $H_2 + Br_2 \rightarrow 2HBr$.

8. Ω-EXPANSION

Equation (42) describes the reaction $H_2 + Br_2 \rightarrow 2HBr$ at the mesoscopic level. An approximate solution of this equation can be found by the Ω-expansion.(3) Put $n_3 = \Omega\phi_3 + \Omega^{1/2}\xi$, $n_1 = \Omega\phi_1 - \frac{1}{2}\Omega^{1/2}\xi$, and expand the step operator,

$$(E_1 E_2 E_3^{-2} - 1) = -2\Omega^{-1/2}\frac{\partial}{\partial\xi} + 2\Omega^{-1}\frac{\partial^2}{\partial\xi^2} + \cdots \tag{43}$$

If one furthermore uses the asymptotic behavior of the function $A(h)$,(17) the order-$\Omega^{1/2}$ terms yield

$$\dot{\phi} = 2\varepsilon^{1/2}k_3\phi_1\phi_2^{1/2}\left(1 + \frac{k_4}{k_5}\frac{\phi_3}{\phi_2}\right)^{-1} \tag{44}$$

This equation is equivalent to the reduced equation that was obtained at the macroscopic level. This shows that our elimination scheme is consistent.

The order-Ω^0 terms yield a Fokker–Planck equation for the probability density $\Pi(\xi)$,

$$\begin{aligned}\frac{\partial\Pi}{\partial t} &= \frac{1}{2}\varepsilon^{1/2}k_3k_5\phi_2^{1/2}(3\phi_1 + 2\phi_2)\frac{\partial}{\partial\xi}\xi\Pi \\ &\quad + \varepsilon^{1/2}k_3k_5\frac{(2k_4 - k_5)\,\phi_1\phi_2^{3/2}}{(k_4\phi_3 + k_5\phi_2)^2}\frac{\partial}{\partial\xi}\xi\Pi \\ &\quad + 2\varepsilon^{1/2}k_3k_5\frac{\phi_1\phi_2^{3/2}}{(k_4\phi_3 + k_5\phi_2)^2}\frac{\partial^2}{\partial\xi^2}\Pi\end{aligned} \tag{45}$$

This Fokker–Planck equation is linear, and hence its solution is a Gaussian.(3) For the fluctuations in the number of HBr molecules, (45) yields

$$\begin{aligned}\frac{\partial}{\partial t}\langle\!\langle\xi^2\rangle\!\rangle &= -\varepsilon^{1/2}k_3k_5\left[\phi_2^{1/2}(3\phi_1 + 2\phi_2) + \frac{2(2k_4 - k_5)\,\phi_1\phi_2^{1/2}}{(k_4\phi_3 + k_5)\phi_2)^2}\right]\langle\!\langle\xi^2\rangle\!\rangle \\ &\quad + 4\varepsilon^{1/2}k_3k_5\frac{\phi_1\phi_2^{3/2}}{(k_4\phi_3 + k_5\phi_2)^2}\end{aligned} \tag{46}$$

This result could also have been obtained by first performing the Ω-expansion of the original master equation (22) and subsequently eliminating the intermediates Br and H and their fluctuations.

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