STOCHASTIC MARKOV MODELS FOR THE PROCESS OF BINARY COMPLEX FORMATION AND DISSOCIATION

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Abstract

We consider the chemical reaction $A + B \leftrightarrow AB$ taking place in a compartment of volume V, which contains M and N, $M \geq N$, particles of species A and B, free or bound. We investigate two stochastic models of the reaction – the quadratic and the linear models. These models are homogeneous birth and death processes with state space $\{0, 1, \cdots, N\}$. We derive inequalities which allow to estimate the accuracy of approximation of the state probability vectors, both transient and stationary, of the quadratic model by the state probability vectors of the linear model as M, $V \to \infty$, $V^{-1}M = \text{const}$. We show that, if N is small, these inequalities give estimates which are of the same order as exact values of the norms of differences of the corresponding state probability vectors.

1. Introduction

We study stochastic mesoscopic models of the reversible chemical reaction of formation of binary complex

$$\mathrm{A+B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{AB}. \qquad (1)$$

Mesoscopic models are used in cases when the number of reacting particles is small, and random deviations of concentrations of the reacting particles from the corresponding mean values should be taken into account [1–5]. Intracellular vesicles and microbiosensors are examples of systems that contain a small number of

particles [6, 7]. The interaction of regulatory proteins with their target sites in a bacterial cell can also be formalized by the reaction (1), and, owing to smallness of the number of interacting particles (units, tens), the deviations of their concentrations from the mean values can be large [8, 9].

The deterministic rate equation for the reaction (1) has the form

$$dn(t)/dt = k_1(a - n(t))(b - n(t)) - k_{-1}n(t), \qquad t \geq 0, \tag{2}$$

where k_1 and k_{-1} are the rate constants for the forward and backward reactions in (1), $n(t)$ is the concentration of species AB, a and b are the overall concentrations of the free and bound forms of species A and B, respectively [10]. It is assumed that, for all $t \geq 0$, the temperature of the chemical system equals some constant T throughout the volume of the system.

If $b << a$, then at all times $n(t) << a$, therefore, the changes in the concentration of free A particles can be neglected. In this case, the forward reaction in (1) is a pseudo-first order reaction with rate constant $k_1 a$, and its rate equation has the form

$$dn(t)/dt = k_1 a(b - n(t)) - k_{-1}n(t). \tag{3}$$

Such an approximation is frequently used by practitioners [1].

We denote by M and N the numbers of A and B particles (free as well as bound) in a compartment of volume V. We assume that $M \geq N$, and that the changes in the number of AB particles can be described by homogeneous birth and death processes $X^{(M,V)} = \{X^{(M,V)}(t),\ t \geq 0\}$ and $Y^{(a)} = \{Y^{(a)}(t),\ t \geq 0\}$, $a = V^{-1}M$, with state space $S_N = \{0, 1, \cdots, N\}$. The processes $X^{(M,V)}$ and $Y^{(a)}$ are the stochastic models of the reaction (1) that correspond to the rate equations (2) and (3) (we shall call these models *the quadratic model* and *the linear model*, respectively). In this paper, expressions are obtained that allow to estimate the accuracy of approximation of the state probability vectors, both transient and stationary, of the process $X^{(M,V)}$ by those of the process $Y^{(a)}$ as $M, V \to \infty$, $V^{-1}M = \text{const}$.

The process $Y^{(a)}$ is a special case of the Prendiville process. For many characteristics of this process (transition probabilities, mathematical expectation, variance), explicit formulae exist [11]. Consequently, by using the linear model instead of the quadratic model, one can substantially simplify the study of the considered chemical system.

2. The quadratic and the linear models

The quadratic model of the reaction (1) is similar to the stochastic model of the reaction $A + B \leftrightarrow C$ considered in [12]. The birth rates of the processes $X^{(M,V)}$ and $Y^{(a)}$ are defined by $\lambda_n^{(X)} = k_1 V^{-1}(M-n)(N-n)$ and $\lambda_n^{(Y)} = k_1 a(N-n)$, and the death rates are given by $\mu_n^{(X)} = \mu_n^{(Y)} = k_{-1} n$, $n \in S_N$. As it is seen from the expressions for the birth rates, $\lambda_n^{(X)} \approx \lambda_n^{(Y)}$ when $M >> N$, and in this case the linear model can be used instead of the quadratic model. Let us introduce the notation: $p_n^{(X)}(t) = P\{X^{(M,V)}(t) = n\}$, $p_n^{(Y)}(t) = P\{Y^{(a)}(t) = n\}$, $p^{(X)}(t) = (p_n^{(X)}(t))$, $p^{(Y)}(t) = (p_n^{(Y)}(t))$, $n = 0, 1, \cdots, N$. We consider the following two types of initial distributions for the processes $X^{(M,V)}$ and $Y^{(a)}$:

1. There exists such $j_0 \in S_N$ that $p_{j_0}^{(X)}(0) = 1$; in this case $p_{j_0}^{(Y)}(0) = 1$,

$$p_n^{(X)}(0) = p_n^{(Y)}(0) = 0, \quad n \in S_N, \quad n \neq j_0; \tag{4}$$

2. $$p^{(X)}(0) = \tilde{\pi}^{(X)}, \quad p^{(Y)}(0) = \tilde{\pi}^{(Y)}, \tag{5}$$

where $\tilde{\pi}^{(X)}$ and $\tilde{\pi}^{(Y)}$ are the stationary distributions of the birth and death processes $\tilde{X}^{(M,V)}$ and $\tilde{Y}^{(a)}$ with state space S_N, birth rates $\tilde{\lambda}_n^{(X)} = \tilde{k}_1 V^{-1}(M-n)(N-n)$, $\tilde{\lambda}_n^{(Y)} = \tilde{k}_1 a(N-n)$ and death rates $\tilde{\mu}_n^{(X)} = \tilde{\mu}_n^{(Y)} = \tilde{k}_{-1} n$, $n \in S_N$. The processes $\tilde{X}^{(M,V)}$ and $\tilde{Y}^{(a)}$ in the stationary state describe the evolution of the considered chemical system in the state of chemical equilibrium at a temperature T_0. It is assumed that the reaction (1) is exothermic, and that $\tilde{k}_1$, $\tilde{k}_{-1}$ satisfy the inequality $\tilde{k}_1 / \tilde{k}_{-1} > k_1 / k_{-1}$. This inequality implies that $T_0 < T$, since the chemical equilibrium shifts to formation of free A and B particles as the tem-

perature of the system increases. It is also assumed that when $t < 0$, the temperature of the system equals T_0, and when $t \geq 0$, it is equal to T, that is at time $t = 0$, a "temperature jump" occurred in the system [10]. The quantities $\widetilde{k}_1$ and $\widetilde{k}_{-1}$ are the rate constants for the reaction (1) before the temperature jump. In this case, it can be assumed that for $t \geq 0$, the evolution of the system is described by the processes $X^{(M,V)}$ and $Y^{(a)}$ with the initial distributions (5).

Let us introduce the notation: $\pi_n^{(X)} = \lim\limits_{t\to\infty} p_n^{(X)}(t)$, $\pi_n^{(Y)} = \lim\limits_{t\to\infty} p_n^{(Y)}(t)$, $\pi^{(X)} = (\pi_n^{(X)})$, $\pi^{(Y)} = (\pi_n^{(Y)})$, $n = 0,1,\cdots,N$. The probabilities $\pi_n^{(X)}$ can be found using the formulae [12]:

$$\pi_n^{(X)} = \pi_0^{(X)} k_1^n M!\, N![(k_{-1}V)^n n!(M-n)!(N-n)!]^{-1},$$

$n = 1,2,\cdots,N$; $\pi_0^{(X)}$ can be obtained from the condition $\pi_n^{(X)} = 1$. The probabilities $\pi_n^{(Y)}$ are given by the expressions [11]:

$$\pi_n^{(Y)} = \binom{N}{n} (k_1 a)^n k_{-1}^{N-n} (k_1 a + k_{-1})^{-N}, \qquad n \in S_N .$$

Let us establish a correspondence between the stochastic and deterministic models of the reaction (1). The expectation, $x(t)$, of the process $X^{(M,V)}$ satisfies the differential equation

$$dx(t)/dt = \sum_{n=0}^{N} [\lambda_n^{(X)} - \mu_n^{(X)}] p_n^{(X)}(t), \qquad t \geq 0 .$$

Using the expressions for the birth and death rates of the process $X^{(M,V)}$, we get

$$dx(t)/dt = k_1 V^{-1}[(M - x(t))(N - x(t)) + \operatorname{var} X^{(M,V)}(t)] - k_{-1} x(t) .$$

Consequently, the expectation, $c(t)$, of the process $C^{(M,V)} = V^{-1} X^{(M,V)}$ satisfies the differential equation

$$dc(t)/dt = k_1[(a - c(t))(b - c(t)) + \operatorname{var} C^{(M,V)}(t)] - k_{-1} c(t) . \qquad (6)$$

If $(a-c(t))(b-c(t)) >> \operatorname{var} C^{(M,V)}(t)$, then, neglecting the variance $\operatorname{var} C^{(M,V)}(t)$ in (6), we arrive at the equation (2). It can be shown that if $M,\ N,\ V \to \infty$ in such a way that $V^{-1}M = a$, $V^{-1}N = b$, and if $\lim\limits_{M,N,V\to\infty} C^{(M,V)}(0) = n_0$, then

$$\lim_{M,N,V\to\infty} P\left\{\sup_{t\le\tau}\left|C^{(M,V)}(t) - n(t)\right| > \varepsilon\right\} = 0, \qquad t\in[0,\ \tau],$$

for all $\varepsilon > 0$, where $n(t)$ is the solution of the equation (2) for the initial condition $n(0) = n_0$ [12].

It can also be easily shown that the expectation, $y(t)$, of the process $Y^{(a)}$ satisfies the equation

$$dy(t)/dt = k_1 a(N - y(t)) - k_{-1} y(t), \qquad t \ge 0. \tag{7}$$

Dividing this equation by V, we obtain the equation (3).

3. The transient

The vectors $p^{(X)}(t)$ and $p^{(Y)}(t)$, $t \ge 0$, satisfy the differential equations

$$dp^{(X)}(t)/dt = L^{(X)} p^{(X)}(t) \tag{8}$$

and

$$dp^{(Y)}(t)/dt = L^{(Y)} p^{(Y)}(t), \tag{9}$$

where the matrices $L^{(X)}$ and $L^{(Y)}$ are the transposed transition rate matrices of the processes $X^{(M,V)}$ and $Y^{(a)}$.

Proposition. For the matrices $L^{(X)}$, $L^{(Y)}$ the equality

$$L^{(X)} = L^{(Y)} + V^{-1}L \tag{10}$$

holds, where the matrix L does not depend on M, V.

Proof. The systems (8) and (9) are of the form

$$
\begin{aligned}
&dp_0^{(X)}(t)/dt = -k_1V^{-1}MNp_0^{(X)}(t) + k_{-1}p_1^{(X)}(t),\\
&dp_n^{(X)}(t)/dt = k_1V^{-1}(M-n+1)(N-n+1)p_{n-1}^{(X)}(t)\\
&\qquad -[k_1V^{-1}(M-n)(N-n)+k_{-1}n]p_n^{(X)}(t)\\
&\qquad + k_{-1}(n+1)p_{n+1}^{(X)}(t), \qquad n=1,2,\cdots,N-1,\\
&dp_N^{(X)}(t)/dt = k_1V^{-1}(M-N+1)p_{N-1}^{(X)}(t) - k_{-1}Np_N^{(X)}(t),
\end{aligned}
\tag{11}
$$

and

$$
\begin{aligned}
&dp_0^{(Y)}(t)/dt = -k_1aNp_0^{(Y)}(t) + k_{-1}p_1^{(Y)}(t),\\
&dp_n^{(Y)}(t)/dt = k_1a(N-n+1)p_{n-1}^{(Y)}(t) - [k_1a(N-n)+k_{-1}n]p_n^{(Y)}(t)\\
&\qquad + k_{-1}(n+1)p_{n+1}^{(Y)}(t), \qquad n=1,2,\cdots,N-1,\\
&dp_N^{(Y)}(t)/dt = k_1ap_{N-1}^{(Y)}(t) - k_{-1}Np_N^{(Y)}(t).
\end{aligned}
\tag{12}
$$

Write (11) in the following form:

$$
\begin{aligned}
&dp_0^{(X)}(t)/dt = \{-k_1V^{-1}MNp_0^{(X)}(t) + k_{-1}p_1^{(X)}(t)\},\\
&dp_n^{(X)}(t)/dt = \{k_1V^{-1}M(N-n+1)p_{n-1}^{(X)}(t)\\
&\qquad -[k_1V^{-1}M(N-n)+k_{-1}n]p_n^{(X)}(t) + k_{-1}(n+1)p_{n+1}^{(X)}(t)\}\\
&\qquad + V^{-1}k_1\{(1-n)(N-n+1)p_{n-1}^{(X)}(t) + n(N-n)p_n^{(X)}(t)\},\\
&\qquad\qquad\qquad\qquad\qquad\qquad n=1,2,\cdots,N-1,\\
&dp_N^{(X)}(t)/dt = \{k_1V^{-1}Mp_{N-1}^{(X)}(t) - k_{-1}Np_N^{(X)}(t)\} + V^{-1}k_1\{(1-N)p_{N-1}^{(X)}(t)\}.
\end{aligned}
$$

Using this representation of (11) and the system (12), we obtain (10). □

Remark 1. $L=0$ *when* $N=1$.

Further we assume that $N>1$.

By $\|\cdot\|$ we denote the 1-norm for vectors and matrices. Using the expressions (8)–(10) and the identity $\left\|p^{(X)}(t)\right\| \equiv 1$, one can obtain the estimate

$$
\begin{aligned}
\left\|p^{(X)}(t)-p^{(Y)}(t)\right\| &\le \left\|p^{(X)}(0)-p^{(Y)}(0)\right\| \exp(l^{(Y)}\tau)\\
&\quad + l(l^{(Y)}V)^{-1}[\exp(l^{(Y)}\tau)-1],
\end{aligned}
\tag{13}
$$

where $t \in [0,\ \tau]$, $l^{(Y)} = \left\| L^{(Y)} \right\|$, $l = \|L\|$ [13]. We shall show that this estimate can be improved.

Theorem 1. *The inequality*

$$\left\| p^{(X)}(t) - p^{(Y)}(t) \right\| \le \left\| p^{(X)}(0) - p^{(Y)}(0) \right\| + V^{-1} l \tau, \qquad t \in [0,\ \tau], \tag{14}$$

holds.

Proof. Consider the vector $z(t) = p^{(X)}(t) - p^{(Y)}(t)$. It follows from (8)–(10) that this vector satisfies the differential equation

$$dz(t)/dt = L^{(Y)} z(t) + V^{-1} L p^{(X)}(t), \qquad t \ge 0,$$

and the initial condition $z(0) = p^{(X)}(0) - p^{(Y)}(0)$. Using Cauchy's formula, we obtain

$$z(t) = \exp(L^{(Y)} t) z(0) + V^{-1} \int_0^t \exp(L^{(Y)}(t-u)) L p^{(X)}(u) du .$$

This implies the inequality

$$\|z(t)\| \le \left\| \exp(L^{(Y)} t) \right\| \|z(0)\| + V^{-1} \int_0^t \left\| \exp(L^{(Y)}(t-u)) \right\| \|L\| \left\| p^{(X)}(u) \right\| du .$$

Since $p^{(X)}(t)$ is a probability vector, $\left\| p^{(X)}(t) \right\| \equiv 1$. The matrix $\exp(L^{(Y)}(t-u))$, $u \le t$, is the transposed transition probability matrix of the process $Y^{(a)}$, hence its columns are probability vectors, whence it follows that $\left\| \exp(L^{(Y)}(t-u)) \right\| = 1$. □

Remark 2. *The function* $f_t(\alpha) = \alpha^{-1}[\exp(\alpha t) - 1]$, $t > 0$, *is increasing when* $\alpha \in (0, \infty)$, *and* $\lim\limits_{\alpha \to 0} f_t(\alpha) = t$, *hence* $t < f_t(\alpha)$. *From this it follows that the estimate* (14) *is more accurate than the estimate* (13).

4. The stationary state

The vectors $\pi^{(X)}$ and $\pi^{(Y)}$ satisfy the equations

$$L^{(X)} \pi^{(X)} = 0, \tag{15}$$

$$L^{(Y)}\pi^{(Y)} = 0. \qquad (16)$$

The quantities $k_1 V^{-1}$ and k_{-1} have the dimension of inverse time; $L^{(X)}$ and $L^{(Y)}$ also have this dimension. Since the equations (15) and (16) are homogeneous, they possess one and the same set of solutions under any units used. Consequently, these equations can be reduced to an equivalent dimensionless form by dividing by a unity factor of the same dimension. By replacing one of the equations in (15) and (16) with the dimensionless equations $\sum_{n=0}^{N} \pi_n^{(X)} = 1$ and $\sum_{n=0}^{N} \pi_n^{(Y)} = 1$, respectively, we obtain systems of equations whose unique solutions are the vectors $\pi^{(X)}$ and $\pi^{(Y)}$.

Let us introduce the notation: $L_i^{(X)}$ and $L_i^{(Y)}$ are the matrices obtained from $L^{(X)}$ and $L^{(Y)}$, respectively, by replacing all the elements of the i th row with ones, $i \in S_N$; L_i is the matrix obtained from L by replacing all the elements of the i th row with zeros; e_i is a column vector of dimension $N+1$ whose i th component is equal to unity, and all other components are equal to zero.

Theorem 2. *The inequality*

$$\left\| \pi^{(X)} - \pi^{(Y)} \right\| \le V^{-1} \left\| (L_i^{(Y)})^{-1} \right\| \left\| L_i \right\| \qquad (17)$$

holds.

Proof. The vectors $\pi^{(X)}$ and $\pi^{(Y)}$ satisfy the equations (15) and (16), respectively, and the conditions $\sum_{n=0}^{N} \pi_n^{(X)} = \sum_{n=0}^{N} \pi_n^{(Y)} = 1$. Therefore, the equalities $L_i^{(X)}\pi^{(X)} = L_i^{(Y)}\pi^{(Y)} = e_i$ hold. It follows from (10) that $L_i^{(X)} = L_i^{(Y)} + V^{-1}L_i$. We have $(L_i^{(Y)} + V^{-1}L_i)\pi^{(X)} = L_i^{(Y)}\pi^{(Y)}$ and $L_i^{(Y)}(\pi^{(Y)} - \pi^{(X)}) = V^{-1}L_i\pi^{(X)}$. This gives the inequality

$$\left\| L_i^{(Y)}(\pi^{(X)} - \pi^{(Y)}) \right\| \le V^{-1} \left\| L_i \right\|. \qquad (18)$$

Since $\left\| (L_i^{(Y)})^{-1} \right\|^{-1} = \inf_{\substack{x \in R^{N+1} \\ \|x\|=1}} \left\| L_i^{(Y)} x \right\|$ (it is evident that $(L_i^{(Y)})^{-1}$ exists), $\left\| L_i^{(Y)} x \right\| \ge \left\| (L_i^{(Y)})^{-1} \right\|^{-1} \|x\|$, $x \in R^{N+1}$ [14]. This inequality, together with (18), proves the theorem. □

Let α be a positive number. Consider the matrices $L^{(Y)}_{\alpha,i}$ and $L_{\alpha,i}$ obtained from the matrices $\alpha L^{(Y)}$ and αL by replacing all the elements of the i th row with ones and zeros, respectively. Multiplying the matrices $L^{(X)}$ and $L^{(Y)}$ by α does not change the corresponding stationary distributions. We shall determine now how the function $\varphi_i(\alpha) = \left\|(L^{(Y)}_{\alpha,i})^{-1}\right\|\left\|L_{\alpha,i}\right\|$ depends on α.

Let us introduce the notation: $a^{(kl)}_{\alpha,i}$ is the element of $(L^{(Y)}_{\alpha,i})^{-1}$ located at the intersection of the k th row and the l th column, $k, l \in S_N$; $a^{(l)}_{\alpha,i}$ and $a^{(l)}_i$ are the l th columns of $(L^{(Y)}_{\alpha,i})^{-1}$ and $(L^{(Y)}_i)^{-1}$, respectively; $C_i = \|L_i\| \max\limits_{l \neq i} \left\|a^{(l)}_i\right\|$; $S^{(lk)}_{\alpha,i}$ and $S^{(lk)}_i$ are the matrices obtained from $L^{(Y)}_{\alpha,i}$ and $L^{(Y)}_i$, respectively, by removing the l th row and the k th column; $A^{(lk)}_{\alpha,i} = (-1)^{l+k} \det S^{(lk)}_{\alpha,i}$; $A^{(lk)}_i = (-1)^{l+k} \det S^{(lk)}_i$; $d_{\alpha,i} = \det L^{(Y)}_{\alpha,i}$; $d_i = \det L^{(Y)}_i$.

Theorem 3. $\varphi_i(\alpha) = \max\left(C_i, \alpha\|L_i\|\left\|a^{(i)}_i\right\|\right)$.

Proof. Expand the determinant of the matrix $L^{(Y)}_{\alpha,i}$ by the elements of the i th row: $d_{\alpha,i} = \sum\limits_{k=0}^{N} A^{(ik)}_{\alpha,i}$. It is easily seen that $A^{(ik)}_{\alpha,i} = \alpha^N A^{(ik)}_i$. From this equality and the equality $a^{(kl)}_{\alpha,i} = d^{-1}_{\alpha,i} A^{(lk)}_{\alpha,i}$, $k, l \in S_N$, it follows that the elements of the i th column of the matrix $(L^{(Y)}_{\alpha,i})^{-1}$ do not depend on α; consequently, $\left\|a^{(i)}_{\alpha,i}\right\| \equiv \left\|a^{(i)}_i\right\|$.

Consider the matrix $S^{(lk)}_{\alpha,i}$, $l, k \in S_N$, $l \neq i$. One of its rows is a vector of ones; let m be the number of this row. By expanding $\det S^{(lk)}_{\alpha,i}$ by the elements of the m th row, we obtain $\det S^{(lk)}_{\alpha,i} = \sum\limits_{j=1}^{N} D^{(lk),\,j}_{\alpha,i}$, where $D^{(lk),\,j}_{\alpha,i}$ are the cofactors of the elements of the m th row. In a similar manner, by expanding $\det S^{(lk)}_i$ by the elements of the m th row, we get $\det S^{(lk)}_i = \sum\limits_{j=1}^{N} D^{(lk),\,j}_i$.

The equalities $D_{\alpha,i}^{(lk),j} = \alpha^{N-1} D_i^{(lk),j}$, $d_{\alpha,i} = \alpha^N d_i$ hold. Consequently, $a_{\alpha,i}^{(kl)} = (\alpha d_i)^{-1} A_i^{(lk)}$, $k, l \in S_N$, $l \neq i$. This gives $\left\| a_{\alpha,i}^{(l)} \right\| = \alpha^{-1} \left\| a_i^{(l)} \right\|$, $l \neq i$, and $\left\| (L_{\alpha,i}^{(Y)})^{-1} \right\| = \max\left(\alpha^{-1} \max\limits_{l \neq i} \left\| a_i^{(l)} \right\|, \left\| a_i^{(i)} \right\| \right)$. Since $\left\| L_{\alpha,i} \right\| = \alpha \left\| L_i \right\|$, the theorem follows.

□

Corollary. *The function* $\varphi_i(\alpha)$ *reaches its minimum in the interval* $(0, \infty)$, *and* $\min\limits_{\alpha>0} \varphi_i(\alpha) = C_i$, $C_i > 0$.

Proof. The norms $\left\| a_i^{(l)} \right\|$, $l \in S_N$, cannot be equal to zero, since in this case we would have $\det(L_i^{(Y)})^{-1} = 0$, which is impossible. It follows from the definition of the matrix L that $\left\| L_i \right\| > 0$ if $N > 1$. These statements, together with Theorem 3, prove the corollary. □

As it follows from (17), for every $\alpha > 0$

$$\left\| \pi^{(X)} - \pi^{(Y)} \right\| \leq V^{-1} \varphi_i(\alpha)$$

holds. This, together with the corollary to Theorem 3, gives

$$\left\| \pi^{(X)} - \pi^{(Y)} \right\| \leq V^{-1} C_i . \tag{19}$$

Using (14) and (19), for the processes $X^{(M,V)}$ и $Y^{(a)}$ with initial conditions (5) we obtain the inequality

$$\left\| p^{(X)}(t) - p^{(Y)}(t) \right\| \leq V^{-1} \left(\widetilde{C}_i + l\tau \right), \qquad t \in [0,\ \tau], \tag{20}$$

where $\widetilde{C}_i$ is defined for the process $\widetilde{X}^{(M,V)}$ in the same manner as C_i.

5. Numerical experiments

In order to investigate the accuracy of the estimates (14), (19) and (20), a series of computer experiments was carried out, in which exact values of the expressions $\nu_{tr}(t_r) = (N+1)^{-1} \left\| p^{(X)}(t_r) - p^{(Y)}(t_r) \right\|$ and $\nu_{st} = (N+1)^{-1} \left\| \pi^{(X)} - \pi^{(Y)} \right\|$

(mean absolute error of approximation of the state probabilities) were compared with their estimates obtained by using the inequalities (14), (19) and (20). The times t_r were defined as follows. By making the substitution $\Delta y(t) = y(t) - Nk_1a/(k_1a + k_{-1})$ in (7), we obtain $d(\Delta y(t))/dt = -(k_1a + k_{-1})\Delta y(t)$ and $\Delta y(t) = \Delta y(0)\exp(-(k_1a + k_{-1})t)$. Define $t_r = 1/(k_1a + k_{-1})$. Thus, t_r is the relaxation time for $\Delta y(t)$ which tends to $Nk_1a/(k_1a + k_{-1})$ as $t \to \infty$.

We used the following parameters: k_1, k_{-1}, N, $k = N^{-1}M$, $a = V^{-1}M$, i, j_0. We put $k_1 = 1.1\widetilde{k}_1$, $k_{-1} = 1.2\widetilde{k}_{-1}$. For the same values of k_1, k_{-1}, N, k and a, we considered both types of initial conditions ((4) with initial state j_0 and (5) with rate constants $\widetilde{k}_1$, $\widetilde{k}_{-1}$). Parameter values for the computer experiments are given in Table 1.

For each of the ten sets of parameter values, we calculated t_r, E_1, the estimate of $\nu_{tr}(t_r)$ for the initial conditions (4) (the inequality (14)), E_2, the estimate of $\nu_{tr}(t_r)$ for the initial conditions (5) (the inequality (20)), E_3, the estimate of ν_{st} (the inequality (19)), and their ratios, r_1, r_2, r_3, to the corresponding exact values. For the computations, the program package MATLAB was used.

It is seen from the results of the experiments (Table 2) that, when N is small, the inequalities (14), (19) and (20) give estimates which are of the same order as the corresponding exact values. This is true for (19) and (20), if the quantities k_1a and k_{-1}, $\widetilde{k}_1a$ and $\widetilde{k}_{-1}$ are of the same order. The influence of the magnitude of the ratio k_1a/k_{-1} on the accuracy of the estimate (14) in the case of initial conditions (4) depends on j_0. As N increases, the accuracy of the estimates (19) and (20) decreases faster than that of (14). The accuracy of the estimates (19) and (20) depends on i, the estimates being more accurate if i is close to $(N+1)/2$.

6. Conclusion

Using the inequalities (14) and (17), one can show that the error of approximation of the probabilities

$$P\{X^{(M,V)}(t_1) = i_{t_1}, X^{(M,V)}(t_2) = i_{t_2}, \cdots, X^{(M,V)}(t_m) = i_{t_m}\},$$

where $t_k \geq 0$, $i_{t_k} \in S_N$, $k = 1, 2, \cdots, m$, by the corresponding probabilities for the process $Y^{(a)}$ is of order $O(V^{-1})$ as M, $V \to \infty$, $V^{-1}M = a$. Consequently, the finite-dimensional distributions of the processes $X^{(N,V_0)}$, $X^{(N+1,V_1)}, \cdots$, $X^{(N+n,V_n)}, \cdots$, where $V_n^{-1}(N+n) = a$, $n = 0, 1, \cdots$, weakly converge to those of the process $Y^{(a)}$.

The limit $M, V \to \infty$, $V^{-1}M = \text{const}$, can be called one-species thermodynamic limit by analogy with the thermodynamic limit (the volume and numbers of particles of all species tend to infinity, the concentrations stay constant [15]). The thermodynamic limit gives the deterministic rate equations, whereas the one-species thermodynamic limit gives the limiting stochastic process. In the case of the reaction (1), the use of the limiting process simplifies the model substantially. This suggests that considering such limits will be useful for analysis of stochastic models of more complex reacting particle systems.

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T a b l e 1

Parameter values for the experiments

No.	k_1	k_{-1}	N	k	a	i	j_0
1	0.9	0.5	3	30	0.3333	2	1
2	0.9	0.5	3	300	0.3333	2	1
3	0.9	0.05	3	30	0.3333	2	3
4	0.9	0.005	3	30	0.3333	2	1
5	0.009	0.5	3	30	0.3333	2	2
6	0.9	0.5	3	30	0.003	2	0
7	0.9	0.5	8	30	0.3333	4	4
8	0.9	0.5	20	300	0.3333	9	14
9	0.9	0.5	20	300	0.3333	2	2
10	0.9	0.5	20	300	0.3333	18	18

T a b l e 2

Results of the experiments

No.	t_r	E_1	r_1	E_2	r_2	E_3	r_3
1	1.2500	0.0042	3.1900	0.0083	5.0522	0.0039	2.4335
2	1.2500	0.0004	3.1953	0.0008	5.0617	0.0004	2.4376
3	2.8574	0.0095	10.7593	0.0186	6.8272	0.0090	3.1997
4	3.2790	0.0109	2.7437	0.0217	43.7594	0.0108	20.4005
5	1.9881	0.0001	3.3927	0.0002	262.537	0.0001	166.489
6	1.9893	0.0001	311.673	0.0002	291.089	0.0001	184.988
7	1.2500	0.0056	5.5003	0.0184	12.9264	0.0123	8.9853
8	1.2500	0.0006	8.7886	0.0024	23.7910	0.0017	17.3794
9	1.2500	0.0006	12.1351	0.0032	31.7705	0.0024	24.7988
10	1.2500	0.0006	10.4912	0.0032	31.7605	0.0025	25.2021