SIMULATION STUDY OF A STOCHASTIC MODEL
OF REVERSIBLE FIRST-ORDER REACTION EQUILIBRIUM

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Fluctuations of the composition of a system close to equilibrium of a reversible first order reaction were studied by the simulation method. Returns into the state corresponding to the deterministic equilibrium and the frequency of fluctuations on one side of the equilibrium were examined.

It was shown in preceding communications[1,2] how the stochastic model of a reversible first-order reaction can be used in studying the statistic and dynamic characters of the equilibrium and fluctuations of the number of particles both of the reactant and the product in the system. In the special case of a reaction with unit equilibrium constant, the short-time fluctuations of the system composition close to equilibrium can be represented approximately by the mathematic model of ideal coin tossings[1]; in the study of long-time fluctuations it must be kept in mind that the reaction represents a finite periodic Markov chain[2]. In the present work, certain results of the study of fluctuations are illustrated on the basis of the previously described simulation method[3]. In contrast to the orginal version of the method, where the life times of all particles of the system were generated and the least of them was sought, this smallest life time was now generated directly with the use of the expression for the probability density of the smallest number from a set of N random numbers, $X_{\min}^{(N)}$. If we assign to this random quantity another random quantity Y by the equation

$$Y = 1 - (1 - X_{\min}^{(N)})^N, \qquad (1)$$

then

$$\text{Prob} \left\{ x < X_{\min}^{(N)} < x + dx \right\} = N(1-x)^{N-1} dx = \text{Prob} \left\{ y < Y < y + dy \right\} = dy, \qquad (2)$$

where $y = 1 - (1 - x)^N$. If a random number (strickly speaking, pseudorandom number), Y, is generated, to which the number $X_{\min}^{(N)}$ is assigned according to (1) then the numbers $X_{\min}^{(N)}$ thus obtained have the same distribution as those generated by the previous method (by selection from a set of N generated random numbers).

The reaction is modelled as follows. In a closed system there is a constant total number, N, of particles of the type A and B, their numbers being N_A and N_B. A particle A can be transformed to B during a time interval $(t, t + \Delta t)$, where $\Delta t \to 0$, is $k_1 \Delta t$, and the probability of the reverse case B $\to$ A during the same time interval is $k_2 \Delta t$. We assume for the sake of simplicity that $k_1 = k_2$, hence a unit equilibrium constant of the reaction $K = k_1/k_2$. The state of the system is characterized by the number of particles A, N_A.

In the study of fluctuations, it is advantageous to replace the time scale of the reaction by the number of reaction events scale[2] (a reaction event will be understood as an elementary change of particle A to B or B to A). For this purpose, transition probabilities can be derived from the model. If the system is in the state $N_A = i$ then the probability that it will pass into the state j by a subsequent reaction event is

$$p_{ij} = \begin{cases} (N-i)/N & \text{for } j = i+1, \\ i/N & \text{for } j = i-1, \\ 0 & \text{in other cases.} \end{cases} \quad (3)$$

The reaction is fully characterized by the stochastic matrix $\|p_{ij}\|$ as a Markov chain in the number of reaction events scale. In this scale the course of the reaction can be simulated in a still more simple manner on the basis of the relation (3): if a generated pseudorandom number, X, is larger than i/N then B is converted to A; if $X < i/N$ then A is converted to B. With this method, however, a return to the time scale is not possible. We proved that all the mentioned methods of simulation of the reaction are equivalent and correspond to a finite periodic Markov chain reaction model (in the time scale to the model of linear birth and death processes[4]).

It follows[4] from the properties of the stochastic matrix $\|p_{ij}\|$ that the system, which was initially in the state i, returns into this state after a certain number of reaction events, the mean number of events between repeated returns into the state i, μ_i, being characteristic for this state. As deduced earlier[2], the smallest mean number of events between the returns characterizes the state $N/2$ (we assume N even for simplicity), which corresponds to the deterministic equilibrium composition $N_A = N_B = N/2$: $\mu_{N/2} \approx (\pi N/2)^{1/2}$.

Based on the mentioned reaction model and modes of simulation, fluctuations of the composition of a system were studied, in which a chemical reaction A $\rightleftarrows$ B with a unit equilibrium constant proceeds. The state $N_A = N/2$ was always chosen as initial. In a system with $N = 100$,
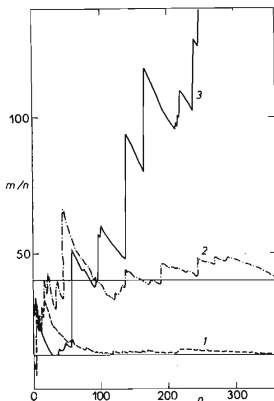

FIG. 1

Mean Number of Reaction Events between Returns to Equilibrium

The ratio of the number of events realized up to the n-th return to the total number of returns into the state $N_A = N/2$ is denoted as m/n. The points were connected with a broken line for illustration. 1 $N = 100$ ($\mu_{50} \approx 12 \cdot 5$); 2 $N = 1000$ ($\mu_{500} \approx 39 \cdot 6$); 3 $N = \infty$.

13210 reaction events were simulated, during which 1 000 returns into the equilibrium occurred (*i.e.* into the state $N_A = 50$). In a system with $N = 1\,000$, 23444 reaction events were simulated, during which 500 returns into the state $N_A = 500$ occurred. With the model of ideal coin tossings (corresponding to a system with $N = \infty$), 44868 events (tossings) were simulated, during which an equalization of the number of heads and tails occurred 250 times.

First the frequency of returns into the state $N_A = N/2$ was studied. The ratios of the number, of realized events, m, up to the n-th return, to the number of returns, n, in systems with $N = 100$ 1 000 and ∞ are plotted in Fig. 1. In the latter case a finite mean value of the number of events between returns to equilibrium (*i.e.* to the state where the numbers of simulated heads and tails are equal) does not exist and the number of returns increases not with the first power but with the square root of the number of events (*cf.* discussion of the model of ideal coin tossing in ref.[4]) For finite N the Fig. 1 illustrates how the ratio m/n approaches $\mu_{N/2}$ with increasing number of returns.

For $N = 100$, the number of returns after two reaction events was 511, after four 137 from the total number of 1 000 returns in accord with the theoretical probabilities of return after two (0·510) and four (0·130) events. The longest fluctuation beyond the equilibrium lasted for 262 reaction events. For $N = 1\,000$, the number of returns after two reaction events was 229, after four 84 of the total of 500 simulated returns. Theoretical probabilities of return after two and four events are 0·501 and 0·1255, which would correspond on the average to 250 and 63 returns after two and four events of the total of 500 returns. The longest fluctuation beyond equilibrium lasted for 1 804 reaction events. During simulation of the ideal coin tossing model, the number of returns into the initial state after two events (tossings) was 125 (theoretical mean: 125) and after four 35 (theoretically 31) of the total of 250 returns. The longest fluctuation lasted for 13 705 events (hence about 30% of the total number of simulated events).

Further, the number of intervals between neighbouring events was studied, in which the system persisted on one side of equilibrium. (In this case we use the following definition: The system is
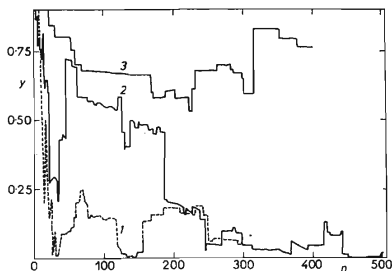

Fig. 2

Fraction of Fluctuations on one Side of Equilibrium

$y = |\,x_+ - x_-\,|/(x_- + x_+)$, n denotes number of returns into the state $N_A = N/2$ (for x_+ and x_- see text). The points were connected with a broken line for illustration. *1* $N = 100$; *2* = 1000; *3* $N = \infty$ (theoretical mean value of y is for this case and $m \to \infty$ about 0·64).

between the m-th and $(m + 1)$-st reaction event in a state above equilibrium if $N_A > N/2$ after the m-th and/or $(m + 1)$ st reaction event; analogously, the system is in the same interval below equilibrium if $N_A < N/2$ after the m-th and/or $(m + 1)$-st reaction event.) Fig. 2 shows how in a system of a finite number of particles the ratio $|x_+ - x_-|/(x_+ + x_-)$, where x_+ and x_- denote numbers of intervals, during which the system persisted above and below equilibrium, respectively, decreases to zero with increasing number of returns. Fig. 2 illustrates the fact that the finite system studied for a sufficiently long time persists on both sides of equilibrium approximately for an equal number of intervals. In the case of the ideal coin tossings model, however, the system persists prevailingly on one side of the original state (*cf.* the Chung–Feller theorem and the first arcsine law[4]) even when the probability that the ratio of the numbers of heads and tails is arbitrarily close to one approaches unity with increasing number of events.

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