AUTOCORRELATION AND FLUCTUATION FUNCTIONS IN A SYSTEM WITH A UNIMOLECULAR REACTION

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The relaxation of the autocorrelation and fluctuation functions of the system composition and the autocorrelation function of positions of the system states with respect to the deterministic equilibrium is studied for a stochastic model of a unimolecular reaction $A \rightleftarrows B$ represented by linear birth and death processes. The derived autocorrelation function of the composition is an exponential function of time, and the fluctuation function of the composition approaches with increasing number of particles in the system the fluctuation function of a normal stationary Markovian process. The relaxation times of the fluctuation function of the composition and of the autocorrelation function of the system states positions with respect to the deterministic equilibrium are different (although not by an order of magnitude) from the relaxation time of the autocorrelation function of the system composition; the latter is identical with the chemical relaxation time.

The autocorrelation function[1-3] expresses the degree of the dependence of a time-dependent quantity at a given time on its initial value. A measure of fluctuations around the autocorrelation function is the fluctuation function introduced by Gordon[2]. These functions and their relaxation properties were studied in chemical physics in connection with stochastic models of simple microsystems which can be described by the Smoluchowski equation[3]. It was found that the autocorrelation and fluctuation functions of dynamic variables in these systems relax toward their stationary values generally with different rates and that the time dependence of the autocorrelation function is in all studied cases an exponential one. On the basis of the standard stochastic formulation of chemical processes[4-6], the relaxation of the autocorrelation and fluctuation function of the composition of a system with a chemical reaction can be analysed.

The present work deals with a reversible unimolecular reaction $A \rightleftarrows B$, represented by linear birth and death processes. Besides the autocorrelation and fluctuation functions of the number of particles of reactant A, the autocorrelation function of the system states positions with respect to the deterministic equilibrium is studied.

Stochastic Description of Reaction

We shall consider a system with a constant volume, which is in contact with a large heat reservoir of constant temperature. The system contains N reacting particles, which can exist in two forms, A and B, and an inert constituent M. We assume that the relaxation times of all nonchemical processes in the system are much smaller than the

characteristic time of the chemical change proper (Keizer's third time scale[7]), so that the system can be described by a single random variable — the number of particles of one of the reacting components. The system's state is further characterized by the number of particles A, $N_A(t)$. The probability that the particle A will change to B in the interval $(t, t + \Delta t)$, $\Delta t \to 0$, is according to the assumption of the theory equal to $k_1 \Delta t$, and the probability of change of B to A in the same interval is $k_2 \Delta t$; the constants k_1 and k_2 depend neither on t nor on the system's composition. It can be derived from this postulate that the conditional probability that the system, which is in the state i at a time τ will be in the state j at a time $\tau + t$, $t > 0$, is given by the convolution of binomial distributions[8]:

$$P(j, \tau + t|i, \tau) = P(j, t|i, 0) = \sum_{n=0}^{j} \binom{i}{n} [p_A^{(A)}(t)]^n [p_B^{(A)}(t)]^{i-n} .$$

$$\cdot \binom{N-i}{j-n} [p_A^{(B)}(t)]^{j-n} [p_B^{(B)}(t)]^{N-i-j+n} , \quad 0 \leqq j \leqq N , \tag{1}$$

where

$$p_A^{(A)}(t) = [k_2 + k_1 \exp(-(k_1 + k_2) t)]/(k_1 + k_2) ,$$
$$p_B^{(A)}(t) = 1 - p_A^{(A)}(t) = k_1[1 - \exp(-(k_1 + k_2) t)]/(k_1 + k_2) ,$$
$$p_A^{(B)}(t) = k_2[1 - \exp(-(k_1 + k_2) t)]/(k_1 + k_2) , \tag{1a}$$
$$p_B^{(B)}(t) = 1 - p_A^{(B)}(t) = [k_1 + k_2 \exp(-(k_1 + k_2) t)]/(k_1 + k_2) .$$

The distribution (1) is the solution of a system of differential equations for birth and death processes:

$$dP(j, t|i, 0)/dt = (j + 1) k_1 P(j + 1, t|i, 0) + (N - j + 1) k_2 P(j - 1, t|i, 0) -$$
$$- [jk_1 + (N - j) k_2] P(j, t|i, 0) . \tag{2}$$

The stationary distribution of the number of particles A corresponding to the macroscopic chemical equilibrium is

$$P_e(j) = \lim_{t \to \infty} P(j, t|i, 0) = \binom{N}{j} K^{N-j}/(K + 1)^N , \quad K = k_1/k_2 . \tag{3}$$

Autocorrelation and Fluctuation Functions of the Number of Particles A

The equilibrium autocorrelation function of the number of particles A, $\varrho(N_A, t)$, is defined as

$$\varrho(N_A, t) = [\langle N_A(0) N_A(t) \rangle_e - \langle N_A \rangle_e^2]/D_e^2(N_A) , \tag{4}$$

where $\langle N_A \rangle_e$ is the mean number of particles A corresponding to the stationary distri-
bution (3), $\langle N_A \rangle_e = \sum_{j=0}^{N} j P_e(j)$, $D^2(N_A)$ denotes variance of the number of particles A
in the equilibrium equal to $\langle N_A^2 \rangle_e - \langle N_A \rangle_e^2$, and $\langle N_A^2 \rangle_e = \sum_{j=0}^{N} j^2 P_e(j)$. The mean
value

$$\langle N_A(0) \, N_A(t) \rangle_e = \sum_{i=0}^{N} \sum_{j=0}^{N} ij P_e(j, t; i, 0) , \qquad (5)$$

where $P_e(j, t; i, 0) = \lim_{\tau \to \infty} P(j, t + \tau; i, \tau)$ is the joint probability that the system,
which at a time $t = 0$ is described by the stationary distribution $P_e(j)$, will be at
$t = 0$ in the state i and at a time t in the state j:

$$P_e(j, t; i, 0) = P_e(i) \, P(j, t | i, 0) . \qquad (6)$$

Eq. (5) represents the mean product of pairs of numbers of particles A observed at
times differing by t under the conditions of macroscopic equilibrium. When these
relations are introduced into (4) we find that the equilibrium autocorrelation function
of the number of particles A is an exponential one:

$$\varrho(N_A, t) = \exp\left(-(k_1 + k_2) t\right) . \qquad (7)$$

This indicates that the random quantity $N_A(t)$ is mean square continuous but not mean
square differentiable $(e.g.,$ ref.[9]$)$.

The quadratic fluctuation function[2,3] of the number of particles A is defined as
the variance of the quantity $[N_A(0) \, N_A(t) - \langle N_A \rangle_e^2]/D_e^2(N_A)$ with respect to the joint
distribution (6):

$$F^2(N_A, t) = [\langle N_A^2(0) \, N_A^2(t) \rangle_e - \langle N_A(0) \, N_A(t) \rangle_e^2]/D^4(N_A) , \qquad (8)$$

where $\langle N_A^2(0) \, N_A^2(t) \rangle_e = \sum_{i=0}^{N} \sum_{j=0}^{N} i^2 j^2 P_e(i) \, P(j, t | i, 0)$. By calculation we find

$$F^2(N_A, t) = 2N[1 + \exp\left(-(k_1 + k_2) t\right)]/K + 1 + \exp\left(-2(k_1 + k_2) t\right) +$$
$$+ 4(K - 1) \exp\left(-(k_1 + k_2) t\right)/K + [(K - 1)^2 \exp\left(-(k_1 + k_2) t\right) -$$
$$- 2K \exp\left(-2(k_1 + k_2) t\right)]/KN . \qquad (9)$$

In a system with a large number of particles, the first term on the right-hand side of
Eq. (9) is dominant, so that

$$F^2(N_A, t) \approx 2N(1 + \exp(-(k_1 + k_2) t))/K . \qquad (10)$$

This dominant term depends on N, whereas $\varrho(N_A, t)$ is independent of N. It is therefore preferable to choose as a variable not $N_A(t)$ but the difference between the number of particles A at a time t and their mean number in the equilibrium, $X_A(t) = N_A(t) - \langle N_A \rangle_e$. The correlation function does not change by this linear transformation,

$$\varrho(X_A, t) = \exp\left(-(k_1 + k_2) t\right), \tag{11}$$

but the fluctuation function changes to

$$F^2(X_A, t) = 1 + \exp\left(-2(k_1 + k_2) t\right) + (K - 1)^2 \exp\left(-(k_1 + k_2) t\right)/KN - 2 \exp\left(-2(k_1 + k_2) t\right)/N. \tag{12}$$

For large N values $(N \gg (K - 1)^2/K)$, only two terms can be considered on the right-hand side of Eq. (12):

$$F^2(X_A, t) \approx 1 + \exp\left(-2(k_1 + k_2) t\right). \tag{13}$$

A calculation shows that the scaled fluctuation function (defined in ref.[3])

$$U(X_A, t) = \left[F(X_A, t) - F(X_A, \infty)\right]/\left[F(X_A, 0) - F(X_A, \infty)\right] \tag{14}$$

decreases with time much faster than $\varrho(X_A, t)$. If we define the relaxation time τ_1 of the autocorrelation function by $\varrho(X_A, \tau_1) = 1/e$ and the relaxation time τ_2 of the scaled fluctuation function $U(X_A, \tau_2) = 1/e$, then (for large N values) $\tau_1 = 1/(k_1 + k_2)$, $\tau_2 = -(1/2(k_1 + k_2)) \ln\left[((\sqrt{2} - 1)/e + 1)^2 - 1\right]$ and $\tau_2/\tau_1 \approx 0{\cdot}56$.
    The time dependence of the mean value of the variable $X_A(t)$ is given (with the initial condition $N_A(0) = i$) as

$$\langle X_A(t) \rangle = X_A(0) \exp\left(-(k_1 + k_2) t\right), \tag{15}$$

where $\langle X_A(t) \rangle = \langle N_A(t) \rangle - \langle N_A \rangle_e$ and $X_A(0) = i - \langle N_A \rangle_e$ (averaging both sides of Eq. (15) with respect to the stationary distribution $P_e^*(i)$ corresponding to a value of the external state parameter, such as temperature, other than $P_e(j)$ leads to the relaxation formula known from the theory of the perturbation of chemical equilibrium[10,11]). The ratio $\langle X_A(t) \rangle/X_A(0)$ relaxes to the equilibrium zero value as rapidly as the correlation of the system states expressed by the autocorrelation function $\varrho(X_A, t)$. The time dependence of the autocorrelation function can be derived directly from Eq. (15), which is rewritten in the form

$$\sum_{j=0}^{N} jP(j, t|i,0) - \sum_{j=0}^{N} jP_e(j) = \left[i - \sum_{j=0}^{N} jP_e(j)\right] \exp\left(-(k_1 + k_2) t\right), \tag{16}$$

multiplied by $iP_e(i)$ and summed from $i = 0$ to N. We thus obtain an equation for the covariance of the number of particles A, which is equivalent to the above derived equation for the autocorrelation function. The states of the system can be therefore considered noncorrelated only on the time scale whose characteristic time is substantially lower than the chemical relaxation time, $1/(k_1 + k_2)$. Since on this time scale the reaction in a large system represents a normal (Gaussian) stationary Markovian process[7], the states of the system differing by a time, t, much larger than $1/(k_1 + k_2)$ can be considered independent.

It is known that the autocorrelation function of a stationary Markovian process is an exponential one if this process is at the same time normal[12,13]. The equilibrium autocorrelation function $\varrho(X_A, t)$, however, has an exponential form also when the reaction is not a normal process (the exponential form of the autocorrelation function was found also with other stochastic models that do not represent a normal process[14,15]). In contrast, $F^2(X_A, t)$ approaches a quadratic fluctuation function of a normal process only in the limit for a large number of particles: for a normal process we have $F^2 = \varrho^2 + 1$, which corresponds to the limiting relation (13).

Correlation of State Positions with Respect to Mean Equilibrium Value

We shall consider a function of the random variable $X_A(t)$ equal to the Heaviside unit function, $H(X_A(t))$. This random quantity can acquire only two values, namely $H(X_A(t)) = 1$ for $X_A(t) > 0$ and $H(X_A(t)) = 0$ for $X_A(t) < 0$, hence it indicates the position of the system's state with respect to the equilibrium mean value $\langle X_A \rangle_e = = 0$ (which is identical with the position with respect to the deterministic equilibrium). We shall further concentrate for simplicity on the special case $k_1 = k_2 = k$ (which corresponds in the discrete time scale to the Ehrenfest model of diffusion[16]), so that if we choose N odd then the case $X_A(t) = 0$ cannot occur (for N even, however, it is possible to define additionally $H(0) = \frac{1}{2}$).

First we shall discuss the relaxation of the mean value $\langle H(X_A(t)) \rangle = \sum_{j=0}^{N} H(j - N/2) P(j, t|i, 0)$ in a system which is at $t = 0$ in the state $N_A(0) = i$, i.e., $X_A(0) = = i - N/2$. It can be shown that the time dependence of $\langle H(X_A(t)) \rangle$ is given (for large N values) by

$$\langle H(X_A(t)) \rangle \approx \tfrac{1}{2}(1 + \operatorname{erf} z), \tag{17}$$

where $\operatorname{erf} z = (2/\sqrt{\pi}) \int_0^z \exp(-u^2)\, du$ and $z = (i - N/2) \exp(-2kt)/[N(1 - \exp(-4kt))/2]^{1/2}$. The relaxation rate of the quantity $\langle H(X_A(t)) \rangle$ depends on N. If we define the relaxation time, τ_3, of the function $[\langle H(X_A(t)) \rangle - \langle H(X_A) \rangle_e]/\langle H(X_A) \rangle_e = = \operatorname{erf} z$, where $\langle H(X_A) \rangle_e = \sum_{i=0}^{N} H(i - N/2) P_e(i)$, again by $\operatorname{erf} z_0 = 1/e$, where $z_0 = $

$$= (i - N/2) \exp{(2k\tau_3)}/[N(1 - \exp{(-4k\tau_3)})/2]^{1/2} \approx 0.34, \text{ then}$$

$$\tau_3 = (1/4k) \ln{[(z_0^2 + N/2 + 2i(i/N - 1))/z_0^2]}. \tag{18}$$

Particularly for $i = N$ we have

$$\tau_3 = (1/4k) \ln{[(z_0^2 + N/2)/z_0^2]} \approx (1/4k)(\ln N + 1.46), \tag{19}$$

a quantity much larger than the chemical relaxation time $1/2k$. At a time $t = \tau_3$, the composition of the system (expressed by the mean value $\langle N_A(t) \rangle$) differs from the mean equilibrium value $\langle N_A \rangle_e$ by a quantity of the order of $D_e(N_A) (\langle X_A(\tau_3) \rangle \approx \approx \sqrt{N/4})$, i.e., by a quantity characterizing the equilibrium fluctuations of the composition. The relaxation time τ_3 can be therefore considered in a certain sense as a quantity characterizing the time necessary for the attainment of the equilibrium composition of the system (although $\langle N_A(t) \rangle = \langle N_A \rangle_e$ only in the limit for $t \to \infty$).

Since for large N values the conditional probability $P(X_A(t) = x | X_A(0) = y)$ and the stationary probability $P_e(X_A)$ can be approximated by the normal distribution[7], we can write

$$\langle H(X_A(0)) H(X_A(t)) \rangle_e = (1/2\pi D(X_A(t)) D_e(X_A)) \cdot$$

$$\cdot \int_0^\infty \int_0^\infty \exp{[-(x - \langle X_A(t) \rangle)^2/2D^2(X_A(t))]} \exp{(-y^2/2D_e^2(X_A))} \, dx \, dy =$$

$$= 1/4 + (1/2\pi) \arcsin{(\exp{(-2kt)})}, \tag{20}$$

where $\langle X_A(t) \rangle = y \exp{(-2kt)}$, $D^2(X_A(t)) = (N/4)(1 - \exp{(-4kt)})$ and $D_e^2(X_A) = = N/4$. Since the stationary singlet probability $P_e(H(X_A) = 1)$ is equal to $\frac{1}{2}$, we have $\langle H(X_A) \rangle_e = \langle H^2(X_A) \rangle_e = \frac{1}{2}$ and $D_e^2(H(X_A)) = \frac{1}{4}$. From Eq. (20) follows the equilibrium autocorrelation function $\varrho(H(X_A), t) = [\langle H(X_A(0)) H(X_A(t)) \rangle_e - \langle H(X_A) \rangle_e^2/ /D_e^2(H(X_A))$ in the form

$$\varrho(H(X_A), t) = (2/\pi) \arcsin{(\exp{(-2kt)})}. \tag{21}$$

If we introduce the relaxation time, τ_4, of this function as $\varrho(H(X_A), \tau_4) = 1/e$, then $\tau_4 = -(1/2k) \ln{(\sin{(\pi/2e)})}$ and $\tau_4/\tau_1 \approx 0.60$.

Eq. (20) is a satisfactory approximation for $t \gg 1/kN$, however for t comparable with $1/kN$ the normal approximation cannot be used. The calculation of the quantity $\langle H(X_A(0)) H(X_A(t)) \rangle_e$ in the limit for $t = \Delta t \to 0$ can be done as follows: If we consider only the terms not higher than of the first order with respect to Δt, then

$$P(j, \Delta t | i, 0) = \begin{cases} 1 - kN \Delta t \text{ for } j = i; & k(N - i) \Delta t \text{ for } j = i + 1; \\ ki \Delta t \text{ for } j = i - 1; & 0 \text{ for other cases}; \end{cases} \tag{22}$$

$$\langle H(X_A(0))\, H(X_A(\Delta t))\rangle_e = \sum_{i=(N+1)/2}^{N} \sum_{j=(N+1)/2}^{N} P_e(i)\, P(j, \Delta t|i, 0) =$$

$$= \sum_{i=(N+1)/2}^{N} P_e(i) - P_e((N+1)/2)\, k(N+1)\, \Delta t/2 \approx \tfrac{1}{2}(1 - k(2N/\pi)^{1/2}\, \Delta t)\,. \quad (23)$$

The expression $k(2N/\pi)^{1/2}\, \Delta t$ represents the probability that in a system that is characterized at $t = 0$ by a stationary distribution $P_e(i)$ the value of the function $H(X_A(t))$ will change during the interval $(0, \Delta t)$, $\Delta t \to 0$. The probability that during the same interval this value will not change is $1 - k(2N/\pi)^{1/2}\, \Delta t$. The probability that the value of $H(X_A(t))$ will not change in the interval $(0, t)$ can be therefore approximated as $[1 - k(2N/\pi)^{1/2}\, \Delta t]^{t/\Delta t} \approx \exp(-k(2N/\pi)^{1/2}t)$. The mean time during which the value of $H(X_A(t))$ does not change is

$$\bar{t} \approx k(2N/\pi)^{1/2} \int_0^\infty \exp(-k(2N/\pi)^{1/2}\, t)\, t\, \mathrm{d}t = (\pi/2N)^{1/2}/k\,, \quad (24)$$

an expression identical with the previously derived[17] mean time of persisting of the fluctuation on one side of the deterministic equilibrium.

From Eq. (23) it follows that the autocorrelation function $\varrho(H(X_A), t)$ depends in the region of small t values $(t = \Delta t \to 0)$ on N in the form

$$\varrho(H(X_A), \Delta t) \approx 1 - 2k(2N/\pi)^{1\,2}\, \Delta t \quad (25)$$

and decreases in large systems with time much faster than $\varrho(X_A, \Delta t) \approx 1 - 2k\, \Delta t$. In the range of large t values $(t > 1/2k)$, the autocorrelation function $\varrho(H(X_A), t)$ is proportional to $\varrho(X_A, t)$:

$$\varrho(H(X_A), t) \approx (2/\pi)\, \varrho(X_A, t)\,. \quad (26)$$

REFERENCES

1. Bartlett M. S.: *An Introduction to Stochastic Processes*, p. 160. Cambridge Univ. Press, Cambridge 1960.
2. Gordon R. G.: J. Chem. Phys. *47*, 1 (1967).
3. Verdier P. H.: Advan. Chem. Phys. *15*, 137 (1969).
4. Bharucha-Reid A. T.: *Elements of the Theory of Markov Processes and their Applications*. McGraw-Hill, New York 1960.
5. McQuarrie D. A.: J. Appl. Prob. *4*, 413 (1967).
6. McQuarrie D. A.: Advan. Chem. Phys. *15*, 149 (1969).
7. Keizer J.. J. Chem. Phys. *56*, 5775 (1972).
8. Šolc M.: This Journal *39*, 1055 (1974).
9. Ramakrishnan A. in the book: *Handbuch der Physik* (S. Flügge, Ed.), Vol. III/2, p. 576. Springer, Berlin 1959.

10. Eigen M., de Mayer L. in the book: *Technique of Organic Chemistry* (A. Weissberger, Ed.), Vol. VIII, Part 2, Chapter 18. Interscience, New York 1963.
11. Ishida K.: Bull. Chem. Soc. Jap. *43*, 314 (1970).
12. Feller W.: *An Introduction to Probability Theory and its Applications,* Vol. II, p. 97. Wiley, New York 1971.
13. Doob J. L.: Ann. Math. *43*, 351 (1942).
14. Bak T. A.: *Contributions to the Theory of Chemical Kinetics*, p. 88. Munksgaard, Copenhagen 1963.
15. Cooper R. D., Hoare M. R.: Chem. Phys. Lett. *12*, 123 (1971).
16. Ehrenfest P., Ehrenfest T.: Physik. Z. *8*, 311 (1907).
17. Šolc M.: Z. Phys. Chem. (Frankfurt am Main) *83*, 64 (1973).