FIRST PASSAGE TIME FOR THE STATE OF EXACT CHEMICAL EQUILIBRIUM

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Received December 14th, 1978

The establishment of chemical equilibrium in a system with a reversible first order reaction is characterized in terms of the distribution of first passage times for the state of exact chemical equilibrium. The mean first passage time of this state is a linear function of the logarithm of the total number of particles in the system. The equilibrium fluctuations of composition in the system are characterized by the distribution of the recurrence times for the state of exact chemical equilibrium. The mean recurrence time is inversely proportional to the square root of the total number of particles in the system.

The composition of a closed isothermal system in which an elementary chemical reaction takes place is described by an integer-valued random variable – the number of particles (atoms, molecules, radicals) of one of reacting components and the change in composition can be modelled as the Markov stochastic process[1,2]. Chemical equilibrium in a set of systems with the same initial number of reactant particles is characterized by the stationary distribution of the number of reactant or product particles. This distribution determines not only the limiting average equilibrium composition of the system (denoted here as the state of exact chemical equilibrium) which the actual average composition approaches asymptotically in time but also the equilibrium fluctuations reflecting the dynamics of reaction in the vicinity of equilibrium. As equilibrium system we can consider such a system whose composition lies in the band of equilibrium fluctuations surrounding symmetrically the state of exact chemical equilibrium, and the time interval in which the system reaches the boundary of this band can be considered as the time necessary to establish chemical equilibrium[3]. The recently studied calculation procedure of this time starts from the definition of width of this band of fluctuations (in terms of: *1*) the standard deviation in composition in a stationary state, *2*) the relaxation of the mean value of the state position indicator and *3*) the standard deviation of the reaction entropy in the vicinity of equilibrium) and from the calculation of the time in which the mean number of particles in the system reaches the boundary of this band[3,4].

The time necessary for establishing the chemical equilibrium can be, however, defined more exactly as the mean first passage time for the state of exact chemical equilibrium. In this work, an approximate calculation of this quantity is proposed for the simplest chemical reaction – a reversible first order reaction with the unit equilibrium constant. Moreover, the distribution of the recurrence times for the state of exact chemical equilibrium is derived; this characterizes the equilibrium fluctuations of composition. The treatment is based on the usual postulates of stochastic theory of chemical reactions[2] which represents the reaction as a birth-and death process homogeneous in time.

The First Entry to the State of Exact Chemical Equilibrium

Let us consider a reversible first order reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B} \tag{1}$$

with the unit equilibrium constant. The probability that the particle A will be converted to B in a time interval $(t, t + \Delta t)$, $\Delta t \to 0$ is $k\,\Delta t$ and the probability of the conversion B to A in the same interval is $k\,\Delta t$ as well, where k is the constant identical with the deterministic rate constant of the isolated reactions A → B and B → A. Let us have N particles A and no particle B in the system at time $t = 0$. We shall assume that N is even and large (in laboratory conditions of reaction on macroscopic scale, N is of the order of 10^{20}). The composition of the system at a time $t > 0$ is determined by the number of particles A at the time t, $N_A(t)$. This quantity is an integer-valued random variable whose distribution is $\mathrm{Prob}\{N_A(t) = j \mid N_A(0) = N\} = P_{N,j}(t)$. Let us denote the probability density of the first passage times from the state N to the state of exact chemical equilibrium by the symbol $f_{N,N/2}(t)$; the probability that the system which was in the state $N_A(0) = N$ at time $t = 0$ will reach the state $N_A(t) = N/2$ at time t to $t + \Delta t$, $\Delta t \to 0$, for the first time is $f_{N,N/2}(t)\,\Delta t$. Obviously it holds

$$P_{N,N/2}(t) = \int_0^t f_{N,N/2}(x)\, P_{N/2,N/2}(t - x)\, \mathrm{d}x\,, \tag{2}$$

where $P_{N/2,N/2}(t - x) = \mathrm{Prob}\,\{N_A(t - x) = N/2 \mid N_A(0) = N/2\}$. The distribution $P_{N,N/2}(t)$ for the reaction (*1*) is given by the relation[5]:

$$P_{N,N/2}(t) = \binom{N}{N/2} [1 - \exp(-2\alpha t)]^{N/2}/2^N \approx (2/\pi N)^{1/2} [1 - \exp(-2\alpha t)]^{N/2}\,, \tag{3}$$

where $1/\alpha = 1/2k$ is the relaxation time of the reaction[6]. The exact form of distribution $P_{N/2,N/2}(t)$ is not suitable for the calculation (a general formula for $\mathrm{Prob}\,\{N_A(t) = j \mid N_A(0) = i\}$ is derived in[5]). For N large and $t \gg 1/\alpha N$, it is possible to approximate $P_{N/2,N/2}(t)$ by the value of maximum of normal density with the mean $N/2$ and the variance $N[1 - \exp(-2\alpha t)]/4$:

$$P_{N/2,N/2}(t) = (2/\pi N)^{1/2}/[1 - \exp(-2\alpha t)]^{1/2}\,. \qquad (4)$$

If the operator of the Laplace transform is applied to both sides of Eq. (2) then, by using the convolution theorem, we find the Laplace transform, $F(p)$, of the density $f_{N,N/2}(t)$ in the form

$$F(p) = (N/2)\, B(p/2\alpha + 1/2\,,\, (N - 1)/2)/B(1/2, (N - 1)/2)\,(p/2\alpha + N/2)\,, \quad (5)$$

where $B(\ldots)$ is the beta function (the Euler integral of the first kind)^7 and p is the complex transform variable. $F(p)$ will be approximated by the leading term of the expansion of the right-hand side of Eq. (5) with respect to N:

$$F(p) = B(p/2\alpha + 1/2, (N - 1)/2)/B(1/2, (N - 1)/2)\,. \qquad (6)$$

An inverse transform^8 gives the result

$$f_{N,N/2}(t) = [2\alpha/B(1/2, (N - 1)/2)]\, \exp(-\alpha t)\,(1 - \exp(-2\alpha t))^{(N-3)/2}\,, \qquad (7)$$

while $B(1/2, (N - 1)/2) \approx (2\pi/N)^{1/2}$ for N large.

In such a way derived density $f_{N,N/2}(t)$ is normalized and has the shape illustrated in Fig. 1. The $f_{N,N/2}(t)$ reaches its maximum value for $t_{\max} \approx (1/2\alpha) \ln N$ and $f_{N,N/2}(t_{\max}) \approx \alpha(2/\pi e)^{1/2}$ does not depend on N. The mean first passage time, $\bar{t}_f$, is

$$\bar{t}_f = \int_0^\infty t f_{N,N/2}(t)\, dt \approx (1/2\alpha)(\ln N + \ln 2 + C)$$
$$\approx (1/2\alpha)(\ln N + 1{\cdot}27)\,, \qquad (8)$$

where C is the Euler constant ($C = 0{\cdot}577\ldots$). (The mean $\bar{t}_f$ can be derived directly from the Laplace transform (5) by using the relation $\bar{t}_f = -dF(p)/dp|_{p=0}$. The result shows that approximating (5) by (6) we neglect only an additive term of the order of N^{-1} in the expression for $\bar{t}_f$). This result is in very good agreement with the previously derived time needed to attain the band of equilibrium fluctuations^{3,4} and $\bar{t}_f$ can be considered as a further possible definition of the time necessary for establishing the chemical equilibrium. For N of the order of 10^{20}, $\bar{t}_f$ is approximately 24 times longer than the relaxation time.

The mean number of elementary reaction events (conversions of the particle A to B and B to A) realized in the system till the first entry to the state $N/2$ is

$$\overline{n_{N,N/2}} = \bar{t}_f kN \approx N(\ln N + 1{\cdot}27)/4\,, \tag{9}$$

where $(kN)^{-1}$ is the mean time interval per one reaction event. This result may be compared with the inequality

$$-5 + N(5/2 - 2\ln 2) < \overline{n_{N,N/2}} < N(2\ln N + 1)/4 \tag{10}$$

derived for the Ehrenfest model of diffusion[9] (this model and the reaction (*1*) are defined by the same matrix of the transition probabilities[10]).

Returns to the State of Exact Equilibrium

Let us consider now the same system at a time $t \gg \bar{t}_f$ when its composition may be described by the limiting stationary distribution[5]

$$\lim_{t\to\infty} P_{N,j}(t) \equiv P_j^e = \binom{N}{j}/2^N\,. \tag{11}$$

The probability that the system will be outside the state $N/2$ at a time t and will pass to the state $N/2$ during an interval $(t, t + \Delta s)$, $\Delta s \to 0$, is $(P^e_{N/2+1} + P^e_{N/2-1})\, kN\, \Delta s/2 \approx k(2N/\pi)^{1/2}\, \Delta s$. The probability that the system in the same time interval will not pass to the state $N/2$ is consequently $1 - k(2N/\pi)^{1/2}\, \Delta s$. The probability that the system

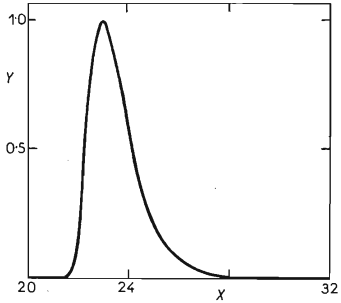

FIG. 1

Probability Density of First Passage Times for the State $N/2$

$N = 10^{20}$, $X = \alpha t$, $Y = f_{N/2,N/2}(t) : f_{N/2,N/2}(t_{max})$.

in the interval $(t, t + s)$ will not pass to the state $N/2$ and it will pass to this state in the interval $(t + s, t + s + \Delta s)$, $\Delta s \to 0$, is

$$\lim_{\Delta s \to 0} \{k(2N/\pi)^{1/2} [1 - k(2N/\pi)^{1/2} \Delta s]^{s/\Delta s}\} \Delta s =$$
$$= k(2N/\pi)^{1/2} \exp[-k(2N/\pi)^{1/2} s] \Delta s . \qquad (12)$$

Since the successive returns to the state $N/2$ represent a process without memory, the density (*12*) is connected with a distribution function, $F_{N/2,N/2}(s)$, of recurrence times for the state $N/2$ (*i.e.* the intervals between leaving the state $N/2$ and subsequent return to this state) by the relation[11,12]

$$k(2N/\pi)^{1/2} \exp[-k(2N/\pi)^{1/2} s] = [1 - F_{N/2,N/2}(s)]/\bar{s}_r , \qquad (13)$$

where $\bar{s}_r$ is the mean recurrence time for the state $N/2$. From here we find that the probability density of recurrence times is

$$f_{N/2,N/2}(s) = k(2N/\pi)^{1/2} \exp[-k(2N/\pi)^{1/2} s] \qquad (14)$$

and the mean recurrence time is

$$\bar{s}_r = (\pi/2N)^{1/2}/k . \qquad (15)$$

This value is identical with the result derived five years ago by another method[10] and, on the discrete time scale, it corresponds to the mean number of elementary reaction events between subsequent returns to the state $N/2$ derived for the Ehrenfest model of diffusion[9]. For N of the order of 10^{20}, the ratio of $\bar{s}_r$ and the relaxation time of reaction is of the order of 10^{-10}.

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Translated by J. Linek.