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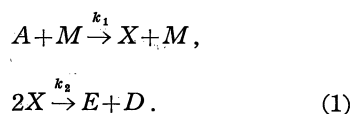
Effects of Diffusion on the Fluctuations in Open Chemical Systems

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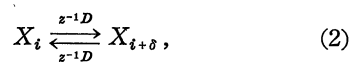
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In the present short communication, we shall study several effects of diffusion on the concentration fluctuations in a system under chemical reactions. Far from equilibrium situation is concerned throughout. In particular, we shall give a clear answer to the current controversial problem on the limit of applicability of the Einstein formula to the concentration fluctuations.^{1),2)} A slightly extended form of the usual stochastic model is needed for our purposes. Let us take an example:^{1),2)}



Suppose that the whole space is filled up with the imaginary cubic cells each with side L . Hereafter, such a cell will be sometimes abbreviated as "the region L ". Let us now express the above reactions taking place inside the i -th cell by assigning the suffix i to each component. One may view, then, that the quantities, e.g., X_i and X_j for $i \neq j$ are as if different chemical species. The number of the molecules of X_i will simply be denoted as X_i . We choose a set of variables $\{X_i\}$ as the state variables. The concentration of the other components are assumed to be constant in time and uniform in space; they form a fixed boundary condition. Then, the number of the molecules of A_i will be denoted as A and so on. Let us introduce the diffusion process which we regard as a kind of chemical reactions and express it as



where $i+\delta$ indicates one of the cells adjacent to the i -th cell; the number of these

adjacent cells has been denoted as z which we have put into the definition of the kinetic constant. The repeated applications of (2) yields the diffusion to remote cells. We are considering nearly perfect chemical gases. Then, for sufficiently short time interval, the nonvanishing transition probabilities per unit time are k_1AM , $k_2X_i^2$ and $z^{-1}DX_i$ for the processes $(X_i \rightarrow X_i+1)$, $(X_i \rightarrow X_i-2)$ and $(X_i \rightarrow X_i-1, X_{i+d} \rightarrow X_{i+d}+1)$, respectively. From these, one may readily derive the master equation for the probability distribution $P(\{X_i\}, t)$. The method of finding the lower order moments from this type of the master equation is given in Ref. 2). Assuming that $X_i \gg 1$ and that the cumulants higher than the second are negligible, one finds at the steady state

$$X_0 \equiv \langle X_i \rangle_{st} = (k_1AM/2k_2)^{1/2} \quad (3)$$

and

$$\langle X_q X_{-q} \rangle_{st} = \frac{3X_0 + k_2^{-1}D(Lq)^2}{4 + k_2^{-1}X_0^{-1}D(Lq)^2}, \quad (Lq \ll 1) \quad (4)$$

where X_q is a spatial Fourier component of X_i . The expression (4) shows several remarkable features of the fluctuations common to a wide class of open chemical systems, which we shall discuss below. For sufficiently large D , one has $\langle X_q X_{-q} \rangle_{st} \simeq X_0$ if q is not too small; the wavenumber-dependence of the mean square fluctuation appears only for very small q , and in this sense we have a very long-range coherence. Under the same condition, one finds $\langle (X_i - X_0)^2 \rangle_{st} \simeq X_0$ and $\langle (X_i - X_0)(X_j - X_0) \rangle_{st} \simeq 0$ ($i \neq j$). This implies that, if the molecules diffuse sufficiently rapidly, the local concentration fluctuation in the region L obeys the Einstein formula as in the thermal equilibrium:³⁾

$$P(X_i) \propto \exp\left(\frac{\delta^2 S}{2k_B}\right)$$

$$= \exp\left\{-\frac{(X_i - X_0)^2}{2X_0}\right\}, \quad (5)$$

which is nothing but the asymptotic form ($X_i \rightarrow \infty$) of the Poisson distribution for randomly distributed particles. We have now to examine this point in more detail. The condition under which (5) holds is roughly given by

$$D/k_2X_0 \gg 1. \quad (6)$$

The left-hand side can be interpreted as the ratio τ_r/τ_L of the two time scales characterizing the reaction and the diffusion processes, respectively. Namely, τ_r is the mean free time with respect to the reactive collisions, and τ_L is the mean time during which a molecule remain within the same cell. Thus, one arrives at the following picture: If the diffusion is rapid enough for a molecule to experience a large number of cells over its lifetime τ_r , then the concentration fluctuation in each cell obeys the Einstein formula. Furthermore, the fluctuations in the different cells are *nearly* independent of each other; the small correlations between them are attributed to the anomalous behavior of the very long-wavelength fluctuations. Thus, the coherence length is very large, still the local fluctuations behave almost in the same way as for a perfect gas at thermal equilibrium. With the aid of our picture, the inequality (6) may also be expressed as $L \ll L'$, where L' represents the net distance covered by a molecule over the lifetime τ_r . On the other hand, one has a relation $L' \simeq l_f \sqrt{\tau_r/\tau_e}$, where l_f and τ_e are the mean free path and the mean free time, respectively, both with respect to the nonreactive (or elastic) collisions, and use is made of the generally accepted fact that $\tau_r \gg \tau_e$.¹⁾ Taking into account that each cell must contain a large number of molecules, the condition that the Einstein formula holds for the concentration fluctuation in the region L is finally given by

$$l_0 \ll L \ll l_f \sqrt{\frac{\tau_r}{\tau_e}}, \quad (7)$$

where l_0 is the mean intermolecular distance. This result does not contain any parameter depending on the specific type of the chemical reactions, and hence is expected to have a wide applicability. It should be remarked, however, that (7) is the sufficient condition and not the necessary one. In fact, it can be proved that the Einstein formula is always valid in the case of unimolecular reactions. When the condition (7) is fulfilled, the dynamical behavior of the fluctuation in the region L is also dominated by the diffusion processes. The normal mode analysis³⁾ around the steady state for any chemical reaction will prove

this directly. Thus, the breakdown of the detailed balance⁴⁾ in some auto-catalytic and cross-catalytic reactions will occur only in those macroscopic regions for which (7) is not fulfilled.

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