Journal of Statistical Physics, Vol. 10, No. 5, 1974

A Comment on Fluctuations Around Nonequilibrium Steady States

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Received November 12, 1973

We study fluctuations around nonequilibrium steady states of some model nonlinear chemical systems. A previous result of Nicolis and Prigogine states that the mean square fluctuation computed from a master equation in the space of internal states of the reacting species is identical to that calculated from Einstein's fluctuation formula. Our analysis of fluctuations based on that master equation leads with the assumption of local equilibrium to a result identical to that obtained from a master equation for the total concentration of the reacting species, which is different from the equilibrium (Einstein relation) result. Nicolis and Prigogine approximated one term in their master equation, and a discussion of this approximation is presented. The master equation without this approximation yields at equilibrium the result expected on the basis of Einstein's formula.

KEY WORDS: Fluctuations; nonequilibrium steady states; nonlinear chemical kinetics.

1. INTRODUCTION

The analysis of fluctuations around steady states of chemically reacting systems is conventionally based on a master equation written in analogy to

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Work supported in part by the National Science Foundation and Project SQUID, Office of Naval Research.

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the macroscopic chemical rate equations.(1–3) In this master equation the chemical rate laws are used as transition probabilities in a birth and death process for the relevant chemical species and one calculates the joint probability distribution in the space of the population of the internal states of the reacting species.

Recently Nicolis(4) (see also Nicolis and Prigogine(5)) has used this method for the study of fluctuations of nonlinear chemical systems around far-from-equilibrium steady states. In the particular example(4,5)

$$\begin{aligned} A + M &\xrightarrow{k_1} X + M \\ 2X &\xrightarrow{k_1} E + D \end{aligned} \tag{1}$$

(reverse reactions neglected) one obtains a master equation of the form[2]

$$\begin{aligned} \partial P(X, t)/\partial t = {} & k_1 AMP(X - 1, t) - k_1 AMP(X, t) \\ & + k_2(X + 2)^2 P(X + 2, t) - k_2 X^2 P(X, t) \end{aligned} \tag{2}$$

which, in the limit of small fluctuations, can be approximated by a Fokker–Planck equation

$$\frac{\partial P(\xi, T)}{\partial t} = 4X_0 \frac{\partial}{\partial \xi} [\xi P(\xi, t)] + \left(\frac{k' AM}{2k_2} + 2X_0{}^2\right) \frac{\partial^2 P(\xi, t)}{\partial \xi^2} \tag{3}$$

where X_0 is the steady-state number density of X molecules obtained from the macroscopic kinetic equations of the scheme (1), and ξ is defined by

$$\xi = X - X_0 \tag{4}$$

The steady-state solution of Eq. (3) then yields the second moment

$$\langle \xi^2 \rangle = \int_{\infty}^{\infty} P(\xi) \xi^2 \, d\xi = \tfrac{3}{4} X_0 \tag{5}$$

This result, which depends on the particular chemical mechanism considered, is contrasted by Nicolis(4) with the result for a linear system. In that case the steady-state distribution is known to be of the Poisson form(2) with

$$\langle \xi^2 \rangle = X_0 \tag{6}$$

According to Nicolis,(4) the result (5) is unacceptable for systems constrained to be in local equilibrium. He argues that under this constraint fluctuations should be given by the Einstein formula for fluctuations around equilibrium

$$P(\xi) \sim \exp[(\delta^2 S)_0 / 2k_B] \tag{7}$$

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[2] Nicolis writes the nonlinear rates in the form $k_2 X(X - 1)$ and $k_2(X + 2)(X + 1)$; for a macroscopic system with a large number of particles the difference is negligible.

or its extension to nonequilibrium steady states, in which the second-order excess entropy is evaluated around the steady state. This formula (7), which Nicolis expects to hold under the local equilibrium assumption, is compatible with the result (6) for linear systems but not with the result (5) for nonlinear systems.

In order to take the condition of local equilibrium into account explicitly, Nicolis and Prigogine(4,5) suggest that one should work not in the space of the number of molecules [where $P(\xi)$ is calculated], but in the "phase space"(4,5) of X, which includes all the internal states of molecules X—including their momentum and position. Instead of having X as a stochastic variable, they introduce a vector $\mathbf{F}$ of stochastic variables, where F_i denotes the number of molecules X in the state i. The probability distribution $P(X, t)$ is now replaced by another joint probability distribution $P(\mathbf{F}, t)$ which satisfies the master equation[3]

$$\begin{aligned}\partial P(\mathbf{F}, t)/\partial t = {} & \sum_i B_i[P(F_i - 1, \mathbf{F}', t) - P(\mathbf{F}, t)] \\ & + \sum_{i,j} A_{ij}[(F_i + 1)(F_j + 1)P(F_i + 1, F_j + 1, \mathbf{F}', t) \\ & - F_iF_jP(\mathbf{F}, t)]\end{aligned} \tag{8}$$

where in both terms on the rhs $\mathbf{F}'$ represents the set $\mathbf{F}$ from which those populations that are explicitly written are excluded. B_i and A_{ij} are rate constants which are related to the quantities defined by Nicolis by

$$B_i = \sum_{jkl} B_{jkil}F_k{}^AF_j{}^M \tag{9a}$$

$$A_{ij} = \sum_{kl} A_{ijkl} = A_{ji} \tag{9b}$$

(the symbols on the rhs are defined in Refs. 4 and 5).

In the limit of small fluctuations Eq. (8) can again be approximated by a Fokker–Planck differential equation

$$\begin{aligned}\partial P(\mathbf{f}, t)/\partial t = {} & 2\sum_{ij} A_{ij}(\partial/\partial f_i)[(F_j{}^0f_i + F_i{}^0f_j)P(\mathbf{f}, t)] \\ & + \sum_i \left(\tfrac{1}{2}B_i + F_i{}^0 \sum_j A_{ij}F_j{}^0\right)(\partial^2/\partial f_i{}^2)P(\mathbf{f}, t) \\ & + \sum_{ij} A_{ij}F_i{}^0F_j{}^0(\partial^2/\partial f_i\, \partial f_j)P(\mathbf{f}, t)\end{aligned} \tag{10}$$

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[3] Equation (8) is in the form given by Nicolis. In fact the second term, for $i = j$, takes the form $\sum_i A_{ii}(\mathrm{F}_i + 2)^2P(F_i + 2, F, t) - \mathrm{F}_i{}^2P(F, t)$ but the contribution of such terms is negligible. Although we take this correction into account later [Eq. (17a)], this has no bearing on the issues discussed here.

where $\mathbf{F}^0$ is the steady-state solution of the deterministic kinetic equation [or alternatively, the point of maximum steady-state distribution $P_{st}(\mathbf{F})$]

$$\mathbf{f} = \mathbf{F} - \mathbf{F}^0 \tag{11}$$

Nicolis then proceeds by neglecting the last term on the rhs of Eq. (10) and solves the resulting approximate Fokker–Planck equation, getting a solution for

$$P_{st}^1(f_\alpha) = \int \cdots \int \prod_{i \neq \alpha} df_i \, P_{st}(\mathbf{f}) \tag{12}$$

in the form

$$P_{st}^1(f_\alpha) = (2\pi F_\alpha{}^0)^{-1/2} \exp(-f_\alpha{}^2/2F_\alpha{}^0) \tag{13}$$

This leads to

$$\langle (f_\alpha)^2 \rangle = F_\alpha{}^0 \tag{14}$$

which suggests that the result (6) also holds in this case.[4]

Without going into the question of the validity of Einstein's fluctuation formula for far-from-equilibrium steady states of nonlinear systems, we expect that strict adherence to local equilibrium (that is, assuming that the internal state distributions remain practically equilibrium distribution on the chemical time scale) should lead to a result identical to that obtained from Eq. (2) or (3) [that is, the result (5)]. It is exactly the assumption of local equilibrium which allows us to reduce a set of coupled kinetic equations for all the different internal states of the chemical species to a single equation for the total amount of X, with an averaged rate constant [k_1 and k_2 in Eqs. (2) and (3)].

First a note on the meaning of local equilibrium in this system is necessary. Nicolis and Prigogine(4,5) take account of local equilibrium by neglecting the contribution of nonreactive collisions to the rate of change of $P(\mathbf{F}, t)$, Eq. (8). In addition we assume that B_i, the rate of formation of species i, and $\sum_j A_{ij}F_iF_j$, the rate of annihilation of this species, are modified by the fast nonreactive collisions in such a way that they do not change the internal state distribution. This means

$$B_i/F_i, \quad \sum_j A_{ij}F_j \qquad \text{independent of } i \tag{15}$$

This assumption does not influence the procedure which leads to the Prigogine–Nicolis result, Eq. (14). We now proceed to show that under this assumption Eq. (8) [or alternatively Eq. (10)] actually leads to the result (5).

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[4] To prove (6), one needs a result in the form $\langle f_\alpha f_{\alpha'} \rangle = F_\alpha{}^0 \delta_{\alpha\alpha'}$, which yields (6) by summing over α and α' and using $\sum_\alpha f_\alpha = \xi$; $\sum_\alpha F_\alpha{}^0 = X_0$. This is not shown by Nicolis.(4)

In what follows we calculate the fluctuations around the steady state according to Eq. (8) and show that under the assumption of local equilibrium it leads to the same result, Eq. (5), as that obtained from Eq. (2). Thus the problem of the discrepancy between the results (5) and (6) is not resolved by extending the master equation from the form (2) to that of (8), at least when local equilibrium is maintained.

2. METHOD OF MOMENTS(7)

Equation (8) can be rewritten in the form

$$\partial P(\mathbf{F}, t)/\partial t = -\sum_{\mathbf{F}'} T(\mathbf{F}, \mathbf{F}')P(\mathbf{F}', t) \tag{16}$$

where the transition operator is defined by

$$\begin{aligned} T(\mathbf{F}, \mathbf{F}') = {} & \left(\sum_i B_i + \sum_{ij} A_{ij}F_iF_j\right)\delta(\mathbf{F}', \mathbf{F}) \\ & - \sum_i B_i \delta_{F_i', F_i - 1} \prod_{l=1} \delta_{F_l', F_l} \\ & - \sum_{i,j} A_{ij} \delta_{F_i', F_i + 1} \delta_{F_j', F_j + 1} \prod_{l=i,j} \delta_{F_l, F_l} F_i F_j' \\ & - \sum_i A_{ii} \delta_{F_i', F_i + 2} \prod_{l=i} \delta_{F_l, F_l'} (F_i)^2 \end{aligned} \tag{17a}$$

The quantity $\delta(\mathbf{F}, \mathbf{F}')$ is

$$\delta(\mathbf{F}, \mathbf{F}') = \prod_l \delta_{F_l', F_l} \qquad (\text{all } l) \tag{17b}$$

and δ_{ij} is the Kronecker delta.

The first and second moments of the transition operation are sufficient for the calculation of fluctuation amplitudes in the limit of small fluctuations. These moments are defined by

$$\mathbf{M}^1(\mathbf{F}') = -\sum_{\mathbf{F}} T(\mathbf{F}, \mathbf{F}')(\mathbf{F} - \mathbf{F}') = -\sum_{\mathbf{F}} T(\mathbf{F}, \mathbf{F}')\mathbf{F} \tag{18a}$$

$$\mathsf{M}^2(\mathbf{F}') = -\tfrac{1}{2}\sum_{\mathbf{F}} T(\mathbf{F}, \mathbf{F}')(\mathbf{F} - \mathbf{F}')^2 \tag{18b}$$

and their calculation is presented in Appendix A. The results are

$$M_i^1(\mathbf{F}) = B_i - 2F_i \sum_j A_{ij}F_j \tag{19}$$

$$M_{ij}^2(\mathbf{F}) = \left(\tfrac{1}{2}B_i + F_i \sum_l A_{il}F_l\right)\delta_{ij} + A_{ij}F_iF_j \tag{20}$$

At steady state F^0 the first moment vanishes

$$B_i - 2F_i^0 \sum_j A_{ij} F_j^0 = 0 \qquad \text{(every } i\text{)} \tag{21}$$

This is obtained from the deterministic kinetic equation.(4) Equations (19) and (21) can now be used to calculate the steady-state fluctuation amplitudes according to(7,8)

$$2\langle \mathsf{M}^2(\mathbf{F})\rangle + \langle \mathbf{M}^1(\mathbf{F})\mathbf{f}\rangle + \langle \mathbf{f}\mathbf{M}^1(\mathbf{F})\rangle = 0 \tag{22}$$

In the limit of small fluctuations $\mathbf{M}^1$ and M^2 can be replaced by the first nonvanishing terms in their expansion around $\mathbf{F}^0$. This means replacing $\mathbf{M}^1(\mathbf{F})$ according to

$$M_i^1(\mathbf{F}) \rightarrow -(B_i/F_i^0)f_i - 2F_i^0 \sum_j A_{ij} f_j \tag{23}$$

and giving $\mathsf{M}^2(\mathbf{F})$ its steady-state value, that is,

$$M_{ij}^2(\mathbf{F}) \rightarrow M_{ij}^2(F^0) = B_i \delta_{ij} + A_{ij} F_i^0 F_j^0 \tag{24}$$

In obtaining Eqs. (23) and (24), the steady-state condition (21) has been used. Inserting these values of M^1 and M^2 into Eq. (22), we get

$$\begin{aligned} 2B_i\delta_{ij} + 2A_{ij}F_i^0F_j^0 = {} & [(B_i/F_i^0) + (B_j/F_j^0)]\langle f_i f_j\rangle \\ & + 2\sum_l (F_j^0 A_{jl}\langle f_i f_l\rangle + F_i^0 A_{il}\langle f_l f_j\rangle) \end{aligned} \tag{25}$$

Summing over all i and j and using Eq. (21), we have

$$3\sum_i B_i = 4\sum_{i,j} (B_i/F_i^0)\langle f_i f_j\rangle \tag{26}$$

Utilizing Eq. (15), and using $\sum_i F_i^0 = X_0$ and $\sum_i f_i = \xi$, we finally get

$$\langle \xi^2\rangle = \tfrac{3}{4} X_0 \tag{27}$$

which is, as anticipated, identical to the result (5) obtained directly from Eq. (2).

3. FOKKER–PLANCK EQUATION

The linear approximation (small amplitude of fluctuations) which leads to Eq. (25) is the same one used to turn the master equation (8) into the Fokker–Planck equation (10). The result (27) thus also should be obtainable from (10). To check this, we multiply Eq. (10) by $f_i f_j$ and integrate over all f_i, using the boundary condition

$$[(f_i)^n P(\mathbf{f})]_{f_i = \pm\infty} = 0 \tag{28}$$

This procedure leads again to the same result, Eq. (25).

4. CONCLUSIONS

The results obtained above lead to the conclusion that Nicolis results [Ref. 4, Eqs. (25)–(31)] are inconsistent with strict maintenance of local equilibrium as expressed by Eq. (15). Obviously the approximation which neglects the last term in the reduced Fokker–Planck equation [Ref. 4, Eq. (22)] cannot be applied under these conditions. This approximation amounts essentially to neglecting correlations between f_i and f_j (i.e., $\langle f_i f_j \rangle = 0$ for $i \neq j$). To see why this procedure fails, we return to Eq. (25) and consider the special case where $A_{ij} = A$ and $B_i = B$ are independent of the internal states. Then $f \equiv \langle f_i^2 \rangle$, $f' \equiv \langle f_i f_j \rangle$, and $F \equiv F_i^0$ are also constants. For $i = j$ Eq. (25) yields

$$2B + 2AF^2 = 2(B/F)f + 4AF[f + (N - 1)f'] \tag{29}$$

where N is the number of internal states, while for $i \neq j$ we obtain

$$2AF^2 = 2(B/F)f' + 4AF[f + (N - 1)f'] \tag{30}$$

In addition, the steady-state equation (21) yields for this case

$$B = 2AF^2 N \tag{31}$$

Equations (29)–(31) are easily solved, with the results

$$f = F(4N - 1)/4N \tag{32a}$$

$$f' = -F/4N \tag{32b}$$

For $N \to \infty$, $f' \to 0$, which is consistent with Nicolis' approximation; however,

$$\langle \xi^2 \rangle = \sum_{i,j} \langle f_i f_j \rangle = Nf + N(N - 1)f' = \tfrac{3}{4}FN = \tfrac{3}{4}X_0 \tag{33}$$

as before. The contribution of f' to $\langle \xi^2 \rangle$ is, for any N, of the same order as that of f and is not negligible.

In order to see that the identity between the results (27) and (5) is not accidental, we consider in Appendix B a different example

$$A \xrightarrow{k_1} X, \qquad 3X \xrightarrow{k_2} B \tag{34}$$

In this system we obtain for the noise amplitude

$$\langle \xi^2 \rangle = \tfrac{2}{3}X_0 \tag{35}$$

using either the number (of molecules X) space approach or the "phase space" approach.

The results obtained here must lead to one and may lead to both of the following two conclusions: (a) Einstein's fluctuation formula is not valid for fluctuations around nonequilibrium steady states even when local equilibrium prevails; or (b) a phenomenological master equation of the type (2) [or equivalently (8)] does not describe currectly the concentration fluctuations which arise from chemical reactions.

Since no proofs exist for either the validity of Einstein's formula for nonequilibrium steady states or for the applicability of the phenomenological master equation, it is impossible to decide whether conclusion (a) or (b) is correct (or both are correct). It is useful in this context to verify that the master equation approach gives the correct fluctuation behavior (as calculated from the Einstein relation(6)) at equilibrium. We show this for a general one-variable system in Appendix C. This result, while being no definite proof for the validity of the master equation approach, tells us that this method does give the proper result at equilibrium.

While we were preparing this paper for publication an article by Kuramoto(9) was published in which he addresses himself to the issues discussed here. Kuramoto's analysis is based on the generating function method and he obtains the result (5) for the special case of constant rates $A_{ij} = A$ and $B_i = B$. Here we obtained this result by invoking the far less restrictive local equilibrium assumption (15). We gratefully acknowledge the additional insight obtained from Kuramoto's work as detailed in Eqs. (32)–(33).

APPENDIX A. CALCULATION OF THE MOMENTS

First Moment

Inserting Eq. (17a) into Eq. (18a), we get

$$\begin{aligned}\mathbf{M}^1(\mathbf{F}') &= -\Big(\sum_i B_i + \sum_{ij} A_{ij}F_i'F_j'\Big)\mathbf{F}' \\ &\quad + \sum_i B_i(\mathbf{F}' + \mathbf{1}_i) + \sum_{ij} A_{ij}F_i'F_j'(\mathbf{F}' - \mathbf{1}_i - \mathbf{1}_j) \\ &= \sum_i B_i\mathbf{1}_i - \sum_{ij} A_{ij}F_i'F_j'(\mathbf{1}_i + \mathbf{1}_j) \\ &= \sum_i B_i\mathbf{1}_i - 2\sum_{ij} A_{ij}F_i'F_j'\mathbf{1}_i \qquad \text{(A.1)}\end{aligned}$$

where $\mathbf{1}_i$ is a vector with ith element equal to one and all the other elements equal to zero. The last equality in (A.1) results from the symmetry condition (9b). Taking the kth term of the vector equation (A.1) and noting that $(\mathbf{1}_i)_k = \delta_{ij}$, we have

$$M_k{}^1(\mathbf{F}') = B_k - 2F_k \sum_j A_{kj}F_j \qquad \text{(A.2)}$$

Second Moment

Inserting Eq. (17a) into Eq. (18b), we obtain [note that the term with $(F')^2$ does not contribute]

$$
\begin{aligned}
2\mathbf{M}^2(\mathbf{F}') = {} & \Bigl(\sum_i B_i + \sum_{ij} A_{ij}F_iF_j\Bigr)\mathbf{F}'\mathbf{F}' \\
& + \sum_i B_i[(\mathbf{F}' + \mathbf{1}_i)^2 - (\mathbf{F}' + \mathbf{1}_i)\mathbf{F} - \mathbf{F}(\mathbf{F}' + \mathbf{1}_i)] \\
& + \sum_{ij} A_{ij}F_i'F_j'[(\mathbf{F}' + \mathbf{1}_i + \mathbf{1}_j)^2 - (\mathbf{F}' + \mathbf{1}_i + \mathbf{1}_j)\mathbf{F}' - \mathbf{F}'(\mathbf{F}' + \mathbf{1}_i + \mathbf{1}_j)] \\
= {} & \sum_i B_i\mathbf{1}_i\mathbf{1}_i + 2\sum_{ij} A_{ij}F_i'F_j'(\mathbf{1}_i\mathbf{1}_j + \mathbf{1}_i\mathbf{1}_i) \qquad \text{(A.3)}
\end{aligned}
$$

Taking the (kl) matrix element, we have

$$2M_{kl}^2(\mathbf{F}') = B_k\delta_{kl} + 2A_{kl}F_k'F_l' + 2\Bigl(\sum_j A_{kj}F_k'F_j'\Bigr)\delta_{kl}$$

APPENDIX B. CALCULATION OF FLUCTUATIONS IN THE SYSTEM (34)

The "number space" master equation is

$$\frac{\partial P(X, t)}{\partial t} = k_1A\left[\exp\left(-\frac{\partial}{\partial x}\right) - 1\right]P(x, t) + k_2\left[\exp\left(3\frac{\partial}{\partial x}\right) - 1\right]x^3P(x, t) \qquad \text{(B.1)}$$

where $\exp(n\,\partial/\partial x)$ is a displacement operator

$$\exp(n\,\partial/\partial x)f(x) = f(x + n) \qquad \text{(B.2)}$$

From Eq. (B.1) we obtain by the standard methods (that is, linearized moments or linearized Fokker–Planck equation) the mean square fluctuation

$$\langle\xi^2\rangle = \langle(x - x_0)^2\rangle = \tfrac{2}{3}x_0 \qquad \text{(B.3)}$$

In the "phase space" approach x is replaced by the vector $\mathbf{F}$ as described for the previous example. The master equation for $P(\mathbf{F}, t)$ now takes the form

$$
\begin{aligned}
\frac{\partial P(\mathbf{F}, t)}{\partial t} = {} & \sum_i B_i\left[\exp\left(-\frac{\partial}{\partial F_i}\right) - 1\right]P(\mathbf{F}, t) \\
& + \sum_{ijk} A_{ijk}\left[\left(\exp\frac{\partial}{\partial F_i}\exp\frac{\partial}{\partial F_j}\exp\frac{\partial}{\partial F_k}\right) - 1\right]F_iF_jF_kP(\mathbf{F}, t) \qquad \text{(B.4)}
\end{aligned}
$$

A_{ijk} must be symmetric to permutations of any two of its indices.

The moments are now calculated as described in Appendix A [or alternatively by expanding the exponentials in Eq. (B.4)$^{(8)}$]. The results are

$$M_i^1(\mathbf{F}) = B_i - 3F_i \sum_{jk} A_{ijk}F_jF_k \tag{B.5}$$

$$M_{ij}^2(\mathbf{F}) = \left(\tfrac{1}{2}B_i + \tfrac{3}{2}F_i \sum_{lk} A_{ilk}F_lF_k\right)\delta_{ij} + 3\sum_k A_{ijk}F_iF_jF_k \tag{B.6}$$

At steady state the first moment vanishes,

$$B_i - 3F_i^0 \sum_{ij} A_{ijk}F_j^0F_k^0 = 0, \qquad i = 1, 2,... \tag{B.7}$$

Equations (B.5) and (B.6) are next inserted into Eq. (22) and the linearization procedure which is described after Eq. (22) is performed. This results in the equation

$$2M_{ij}^2(\mathbf{F}^0) = \sum_k \Lambda_{ik}\langle f_kf_j\rangle + \sum_k \langle f_if_k\rangle\Lambda_{jk} \tag{B.8}$$

where

$$M_{ij}^2(\mathbf{F}^0) = B_i\delta_{ij} + 3\sum_k A_{ijk}F_i^0F_j^0F_k^0 \tag{B.9}$$

and

$$\Lambda_{ij} = -\left(\frac{\partial M_i^1(\mathbf{F})}{\partial F_j}\right)_{\mathbf{F}^\circ} = 6F_i^0 \sum_k A_{ijk}F_k^0 + 3\left(\sum_{lk} A_{ilk}F^0F_k^0\right)\delta_{ij} \tag{B.10}$$

Inserting Eqs. (B.9) and (B.10) into Eq. (B.8) and summing over all i and j results in

$$4\sum_i B_i = 6\sum_{ij} (B_i/F_i^0)\langle f_if_j\rangle \tag{B.11}$$

where Eq. (B.7) has been used. As before, local equilibrium implies

$$B_i/F_i^0 \qquad \text{independent of } i$$

This yields

$$\langle\xi^2\rangle = \tfrac{2}{3}x_0 \tag{B.12}$$

which is identical to the result (B.3).

APPENDIX C. EQUILIBRIUM FLUCTUATIONS

Here we show that in a general chemical system with one variable x which participates in any number of chemical reactions the master equation approach yields under equilibrium conditions

$$\langle\xi^2\rangle = x_0 \tag{C.1}$$

identical to the result obtained from the Einstein fluctuation formula.⁽⁶⁾ As in the cases of the nonequilibrium steady states described above, the concentrations of all the chemical components besides x are assumed to be fixed. More precisely, the concentrations of all other species fluctuate on a different time scale.⁽²⁾ The conditions under which this may be achieved have been described by Nicolis and Babloyantz.⁽²⁾ However, in the present case we take these fixed concentrations to be the equilibrium concentrations of these components. For these conditions the master equation can be written in the general form

$$\begin{aligned}\partial P(x,t)/\partial t = \sum_r \{&[\exp(-n\,\partial/\partial x) - 1]Q_r(x)P(x)\\ &+ [\exp(n\,\partial/\partial x) - 1]R_r(x)P(x)\}\end{aligned} \tag{C.2}$$

where $n = n(r) > 0$ is the change in the number of molecules x due to the reaction r. $Q_r(x)$ is the rate of the reaction r in the direction in which x increases, while $R_r(x)$ is the rate in the reverse direction. At steady state (which is here the equilibrium state) detailed balance holds

$$Q_r(x_0) = R_r(x_0), \qquad \text{all} \quad r \tag{C.3}$$

The moments are found by expanding the exponential operators in Eq. (C.2)⁽⁸⁾; for the first two moments we have

$$M^1(x) = \sum_r n(r)[Q_r(x) - R_r(x)] \tag{C.4}$$

$$M^2(x) = \tfrac{1}{2}\sum_r [n(r)]^2[Q_r(x) + R_r(x)] \tag{C.5}$$

The fluctuation amplitude is obtained from⁽⁷⁾

$$\langle \xi^2 \rangle = M^2(x_0)/\Lambda(x_0) \tag{C.6}$$

where

$$\begin{aligned}\Lambda(X_0) &= -\{(\partial/\partial x)[M^1(x)]\}_{x_0}\\ &= \sum_r n(r)\{(\partial/\partial x)[R_r(x) - Q_r(x)]\}_{x_0}\end{aligned} \tag{C.7}$$

Now, the rates Q_r and R_r can be written quite generally in the form

$$Q_r(x) = A_r X^{\alpha_r}, \qquad \alpha \geqslant 0 \tag{C.8}$$

$$R_r(x) = B_r X^{\beta_r}, \qquad \beta > 0 \tag{C.9}$$

Also, it is seen that

$$\beta_r - \alpha_r = n(r) \tag{C.10}$$

Utilizing Eqs. (C.3) and (C.8)–(C.10), we recast (C.7) in the form

$$\Lambda(x_0) = (1/x_0) \sum_r [n(r)]^2 Q_r(x_0) \tag{C.11}$$

But from Eqs. (C.3) and (C.5) we have

$$M^2(x_0) = \sum_r [n(r)]^2 Q_r(x_0) \tag{C.12}$$

and Eqs. (C.6), (C.11), and (C.12) then lead to

$$\langle \xi^2 \rangle = X_0 \tag{C.13}$$

NOTE ADDED IN PROOF

After submitting this paper for publication we obtained a preprint by Nicolis, Allen and Van Nypelseer, in which they reanalyze the problem discussed in Refs. 4, 5, 9, and in this paper, and argue that the conclusion arrived at by Kuramoto(9) as well as in the present paper are valid only for "macroscopic" fluctuations which characterize a system which is strictly at local equilibrium. We completely agree with this observation. It is important to stress, however, that such fluctuations are not macroscopic in the sense that all the systems fluctuate in a coherent fashion. Local fluctuations (which decay on the time scale of the macroscopic chemical rates and the macroscopic diffusion rates) may be described within this local equilibrium theory (see, e.g., Nitzan, Ortoleva, Deutch, and Ross, *J. Chem. Phys.*, submitted). It is our feeling that experiments on chemical fluctuations of the type performed by Magde, Elson, and Webb [*Phys. Rev. Letters* **29**, 705 (1972)] and by Feher and Weissman [*Proc. Nat. Acad. Sci.* **70**, 870 (1973)] if extended to nonequilibrium steady states would be amenable to interpretation based on a completely local equilibrium theory.

REFERENCES

1. D. M. McQuarrie, *Adv. Chem. Phys.* **XV**:149 (1969).
2. G. Nicolis and A. Babloyantz, *J. Chem. Phys.* **51**:2632 (1969).
3. R. Hawkins and S. A. Rice, *J. Theor. Biol.* **30**:579 (1971).
4. G. Nicolis, *J. Stat. Phys.* **6**:195 (1972).
5. G. Nicolis and I. Prigogine, *Proc. Nat. Acad. Sci. U.S.* **68**:2102 (1971).
6. P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley, London (1971).
7. M. Lax, *Rev. Mod. Phys.* **32**:25 (1960).
8. M. Lax, *Rev. Mod. Phys.* **38**:359 (1966).
9. Y. Kuramoto, *Prog. Theor. Phys.* **49**:1782 (1973).