Journal of Statistical Physics, Vol. 14, No. 4, 1976

Correlations in Stochastic Theories of Chemical Reactions

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Received June 9, 1975

A comprehensive study of correlations in linear and nonlinear chemical reactions is presented using coupled chemical and diffusion master equations. As a consequence of including correlations in linear reactions the approach to the steady-state Poisson distribution from an initial non-Poissonian distribution is given by a power law rather than the exponential predicted by neglecting correlations. In nonlinear reactions we show that a steady-state Poisson distribution is achieved in small volumes, whereas in large volumes a non-Poissonian distribution is built up via the correlation. The spatial correlation function is calculated for two examples, one which exhibits an instability, the other which exhibits a second-order phase transition, and correlation length and correlation time are calculated and shown to become infinite as the critical point is approached. The critical exponents are found to be classical.

KEY WORDS: Diffusion theory; chemical reactions; fluctuations; instabilities; master equations; phase transitions; stochastic processes; nonequilibrium thermodynamics.

1. INTRODUCTION

The fluctuation theory of chemical reactions, and, in particular, those maintained away from equilibrium, is currently of considerable interest.

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This contribution to the subject, based on the use of stochastic master equations to describe both the chemical nature and spatial location of a molecule, aims to give a broad treatment of correlation phenomena in this subject. The results are not all new, but we have aimed here at a treatment which is comprehensive in its treatment of correlations from our point of view. The work of Nitzan *et al.*(1) have treated similar material, though mainly from the point of view of Langevin equations linearized about a steady state, which is not necessarily equivalent to our treatment. A connected subject is the description of local Poissonian and global non-Poissonian fluctuations in nonequilibrium reactions, which has been treated by Nicolis, Prigogine, and co-workers,(2–7) Kuramoto,(8) Nitzan and Ross,(9) and Gardiner *et al.*(10) Nicolis and co-workers simplified the problem by assuming a local factorization of the bivariate probability distribution describing the numbers of molecules, respectively, in a small cell and the remainder of the system. Kuramoto(8) and Nitzan and Ross(9) suggested that it is just the small correlations that were neglected that give rise to the difference in nature between global and local fluctuations. However, Nicolis *et al.*(6,7) derived, neglecting correlations, a nonlinear master equation which possesses solutions exhibiting Poissonian behavior in small volumes and non-Poissonian behavior globally.

We have found that, in fact, linear systems exhibit many features which can shed light on this subject. We therefore start with an investigation of possibly the simplest linear diffusion-reaction system, that of simple isomerization. We show that there are actually many possible equilibrium states, depending on the type of statistical mechanical ensemble chosen to represent the system, but, with the choice of the grand canonical ensemble, one finds that the equilibrium distribution is a factorizable multi-Poisson distribution. We show, as has also been noted by Malek-Mansour and Nicolis,(7) that this is exactly the result expected from equilibrium statistical mechanics, provided our description in space is sufficiently coarse-grained for us to be able to neglect the correlations that arise from the finite range of chemical forces. The system then behaves in this respect like an ideal mixture, though, of course, it is not, since a chemical reaction is proceeding, and chemical fluctuations exist. Furthermore, we show that in this particular case, factorizable multi-Poisson time-dependent solutions also exist, a property which is possessed uniquely by this type of system. The question of the rate of relaxation to a Poisson form of solution then arises, and we show how a study of correlation functions can shed some light on this. We find that provided the system is initially correlated over a short range, the Poissonian form *is* rather rapidly approached. But, more interestingly, an initial non-Poissonian, but factorizable, distribution function becomes nonfactorizable in the process of relaxing finally to the factorizable Poissonian form. The amount of correlation introduced is small (1%) but not infinitesimal. This same relaxation to Poisson problem can also be treated by the nonlinear master equation of Nicolis *et al.*,(6,7) which neglects correlations at all times. In spite of the smallness of the correlations which arise, we find that the result given by the nonlinear master equation is only qualitatively correct. The true power law decay of diffusion terms is replaced by an exponential.

In Section 3 we give a brief discussion of generating function methods and the forms of master equations for nonlinear systems, and show how the multi-Poisson form in equilibrium arises from these master equations. Section 4 treats two examples of nonlinear systems, the first of which is exactly soluble, and the second of which is soluble if we neglect higher than second-order terms in the power series expansion of the logarithm of the generating function. The behavior of all the correlation functions is similar in both cases, but our second model exhibits a phase transition, unlike the first, which merely becomes unstable above its critical point, and ceases to have a steady-state solution. The model with the phase transition involves a bimolecular reaction in the reactants of interest. Such a reaction is, in principle, nonlocal, and in letting the volume of the cells used to describe spatial location in the system go to zero the necessity for a nonlocal theory for an adequate description becomes apparent.

In Section 5 we show how both models do indeed exhibit the Poissonian property when one considers small volumes, and, as a result of correlations, exhibit non-Poissonian behavior when one considers large volumes. An investigation of the correlation between a large volume and the remainder of the system shows that this correlation is proportional to the small volume, and is thus of the same order of magnitude as the variance of the fluctuations. This correlation is thus never negligible, even though the statistical correlation coefficient goes to zero in the limit that the system is infinite.

Notation. We use the notation $\langle A, B\rangle = \langle AB\rangle - \langle A\rangle\langle B\rangle$ for the correlation between A and B. We write $\langle x^n\rangle_f = \langle x(x-1)\cdots(x-n+1)\rangle$ for the nth factorial moment.

2. CORRELATIONS AND FACTORIZATION IN LINEAR SYSTEMS

The stochastic theory of linear chemical diffusion reaction systems is mathematically completely soluble, and provides a useful starting point for our considerations. We shall investigate in this section only one linear system, but it will become clear that this is typical. A linear system is loosely defined as one in which the deterministic equations are linear (a more precise definition is given in terms of generating function equations in Section 3). For chemical systems, this implies that the reactions described are transformations between isomeric terms of the same chemical compound, or systems of the form

$$A + X \rightleftharpoons C + Y$$

in which the concentrations of A and C are considered to be held fixed. Since this can in practice occur only approximately, one should strictly consider such a reaction as a limit of a nonlinear system.

2.1. Diffusion Reaction Master Equation

Let us consider a typical linear system, consisting of an isomerization reaction

$$X \underset{k_1}{\overset{k_2}{\rightleftharpoons}} Y \tag{1}$$

The type of situation which we consider will be in principle inhomogeneous, and characterized by a multivariate probability distribution

$$P(x_1, x_2, \ldots, x_i, \ldots, x_N, y_1, y_2, \ldots, y_j, \ldots, y_N) \equiv P(\mathbf{x}, \mathbf{y}) \tag{2}$$

where the indices i, j, etc., label positions of cells in space, and the quantities x_i, y_i, etc. are the numbers of molecules of the component in the corresponding cell. The cells will be identical, and of an unspecified but small size.

A master equation which contains the possibility of the reaction (1) as well as diffusion, viewed in our case as a jump of a given molecule from one cell to an adjacent cell with probability d, is

$$\begin{aligned}\frac{\partial P(\mathbf{x}, \mathbf{y})}{\partial t} = {} & \sum_{\substack{i,j \\ i \neq j}} \{d_{ij}(x_i + 1)P(x_i + 1, x_j - 1, \hat{\mathbf{x}}, \mathbf{y}) - d_{ij}x_i P(\mathbf{x}, \mathbf{y}) \\ & + d_{ij}(y_i + 1)P(\mathbf{x}, y_i + 1, y_j - 1, \hat{\mathbf{y}}) - d_{ij}y_i P(\mathbf{x}, \mathbf{y})\} \\ & + \sum_i \{k_1(y_i + 1)P(x_i - 1, y_i + 1, \hat{\mathbf{x}}, \hat{\mathbf{y}}) \\ & + k_2(\mathbf{x}_i + 1)P(x_i + 1, y_i - 1, \hat{\mathbf{x}}, \hat{\mathbf{y}}) - (k_1 y_i + k_2 x_i)P(\mathbf{x}, \mathbf{y})\}\end{aligned} \tag{3}$$

Here

$$\begin{aligned} d_{ij} &= 0, \qquad i \text{ not adjacent to } j \\ &= d, \qquad i \text{ adjacent to } j \end{aligned} \tag{4}$$

We use the notation $\hat{\mathbf{x}}$ to indicate that all variables not explicitly written have their usual values.

We have, for simplicity, assumed that d is the same for both X and Y, though this assumption need not be made.

Similar master equations have been written by Kitahara$^{(11)}$ and Kuramoto.$^{(8)}$

2.2. Time-Dependent Multi-Poisson Solutions

Equation (3) can be solved exactly, and a class of solutions of particular simplicity is given by the multi-Poisson form

$$P(\mathbf{x}, \mathbf{y}, t) = \prod_i \left\{ \frac{e^{-\langle x_i(t)\rangle} \langle x_i(t)\rangle^{x_i}}{x_i!} \, \frac{e^{-\langle y_i(t)\rangle} \langle y_i(t)\rangle^{y_i}}{y_i!} \right\} \tag{5}$$

where the mean numbers $\langle x_i(t)\rangle$ and $\langle y_i(t)\rangle$, in the limit that the position may be replaced by a continuous variable **r** and higher than second derivatives may be neglected, satisfy the equations

$$\begin{aligned} \frac{\partial\langle x(\mathbf{r}, t)\rangle}{\partial t} &= D\, \nabla^2\langle x(\mathbf{r}, t)\rangle + k_1\langle y(\mathbf{r}, t)\rangle - k_2\langle x(\mathbf{r}, t)\rangle \\ \frac{\partial\langle y(\mathbf{r}, t)\rangle}{\partial t} &= D\, \nabla^2\langle y(\mathbf{r}, t)\rangle - k_1\langle y(\mathbf{r}, t)\rangle + k_2\langle x(\mathbf{r}, t)\rangle \end{aligned} \tag{6}$$

In the case of a cubic cell system with cell length l we find that

$$D = l^2 d \tag{7}$$

Thus D corresponds exactly to Fick's diffusion coefficient. We see that a multi-Poisson distribution of the form (5), once achieved, persists in form, and all variation is contained in the time rate of change of the mean values, which is given by the macroscopic equations (6). The assumption leading to Eqs. (6) is not really restrictive. It essentially means that we have a description of fluctuations valid only for wavelengths somewhat longer than the cell length, which may be arbitrarily small, subject only to the requirement that the cell be large enough for a stochastic description to be valid.

The Poissonian nature of this probability distribution and the factorizability of the form (5) are central features of the stochastic theory of chemical reactions. It is therefore natural to investigate under what conditions these features are achieved. We should point out that the solution (5) is by no means unique. For example, a solution of a multinomial form also exists, as found by Darvey and Staff.(12) It corresponds to a canonical distribution,[2] whereas ours corresponds to a grand canonical distribution. In addition, of course, there are as many time-dependent solutions as there are initial distributions. The main question that arises is whether these other less desirable distributions are achievable, and if so, whether they represent a sensible definition of a system. To do this, we investigate correlations.

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[2] The fact that one has both possibilities arises from the conservation of the total number of particles implicit in Eq. (3). By specifying that the distribution in total number be Poisson, we obtain our grand canonical solution. Since total number is conserved, the Poisson in total number will be preserved in time. There are, in fact, as many steady-state solutions as there are initial distributions in total number.

2.3. The Time Development of Spatial Correlations

We shall develop our arguments from the point of view of ensemble theory, since the ensemble average is essentially the only one available when we wish to deal with non-steady states. We must introduce the concept of the ensemble corresponding to a certain initial probability distribution and consider how in practice we would create such a thing. Our initial state would most reasonably correspond to an ensemble of systems which were made as nearly *identical as possible* in concentrations, etc. This corresponds to an initial distribution which has a narrow-peaked form. If we are considering homogeneous systems, we will be considering an initial ensemble of systems which are themselves as homogeneous as possible. Such systems would be set up in practice by mixing the appropriate chemicals and stirring the mixture at a rate typically faster than the chemical reactions. Because of the random nature of stirring, averaging over ensembles would generate zero correlations between concentrations at different spatial points. If such a situation is not obtained, one would not consider that the mixtures had been thoroughly stirred—in other words, a mathematical formulation of the assumption of an ensemble of well-stirred systems would be the postulate of zero initial correlations, or, at least, very short-range correlations.

The master equation (3) yields equations of motion for the correlation functions as follows. Taking a homogeneous isotropic ensemble of systems, for which the correlation functions can depend only on $|\mathbf{r}_i - \mathbf{r}_j|$, we define functions f, g, and h by

$$\begin{aligned} \langle x_i, x_j\rangle &= \delta_{ij}\langle x_i\rangle + g(|\mathbf{r}_i - \mathbf{r}_j|) \\ \langle x_i, y_j\rangle &= f(|\mathbf{r}_i - \mathbf{r}_j|) \\ \langle y_i, y_j\rangle &= \delta_{ij}\langle y_i\rangle + h(|\mathbf{r}_i - \mathbf{r}_j|) \end{aligned} \tag{8}$$

Notice particularly the terms linear in the mean values, which arise from the fact that the master equation we use gives rise to equations for *factorial* moments. Thus, again using the diffusion approximation, we derive the equations of motion

$$\begin{aligned} \frac{\partial g(r,t)}{\partial t} &= 2D\,\nabla^2 g(r,t) - 2k_2 g(r,t) + 2k_1 f(r,t) \\ \frac{\partial f(r,t)}{\partial t} &= 2D\,\nabla^2 f(r,t) - (k_1 + k_2) f(r,t) + k_1 h(r,t) + k_2 g(r,t) \\ \frac{\partial h(r,t)}{\partial t} &= 2D\,\nabla^2 h(r,t) - 2k_1 h(r,t) + 2k_2 f(r,t) \end{aligned} \tag{9}$$

The solutions to these equations are quite straightforward to derive. The steady-state solution is

$$g(r) = \xi k_1^2, \qquad f(r) = \xi k_1 k_2, \qquad h(r) = \xi k_2^2 \tag{10}$$

where ξ is an arbitrary parameter. The corresponding steady-state solutions of (6) are

$$\langle x(\mathbf{r}_i)\rangle = \eta k_1, \qquad \langle y(\mathbf{r}_i)\rangle = \eta k_2 \tag{11}$$

where η is another arbitrary parameter. In the case that $\xi = 0$, we recover the Poissonian situation, where

$$\begin{aligned} \langle x(\mathbf{r}_i), x(\mathbf{r}_j)\rangle &= \delta_{ij}\langle x(\mathbf{r}_i)\rangle \\ \langle x(\mathbf{r}_i), y(\mathbf{r}_j)\rangle &= 0 \\ \langle y(\mathbf{r}_i), y(\mathbf{r}_j)\rangle &= \delta_{ij}\langle y(\mathbf{r}_i)\rangle \end{aligned} \tag{12}$$

However, other solutions exist, corresponding to the different possible ensembles that the stochastic equation can represent. Thus, a solution corresponding to a canonical ensemble would correspond to a multinomial distribution instead of a multi-Poisson, and be given by

$$\xi = -\eta/[N(k_1 + k_2)]$$

where N is the number of cells in the system.

Since we are dealing with a grand canonical ensemble, we must make the choice $\xi = 0$, and shall do so from this point onwards.

Time-dependent solutions for any initial condition can easily be developed. In the case that the solutions are initially homogeneous, uncorrelated, and Poissonian, (12) is satisfied as an initial condition, and thus f, g, and h are initially all zero, and clearly remain so. Thus an uncorrelated Poissonian form is preserved in time.

The problem of relaxation to the Poisson is best dealt with by assuming a specific form for the initial correlation function; for example, consider the situation of an initially uncorrelated but non-Poissonian system, represented by

$$g(r, 0) = \alpha\delta(\mathbf{r}), \qquad f(r, 0) = \beta\delta(\mathbf{r}), \qquad h(r, 0) = \gamma\delta(\mathbf{r}) \tag{13}$$

Then the time-dependent solutions are

$$\begin{pmatrix} g(r, t) \\ f(r, t) \\ h(r, t) \end{pmatrix} = \frac{\exp(-r^2/8Dt)}{(8\pi Dt)^{3/2}} \begin{pmatrix} k_1^2\varepsilon_1 - 2k_1\varepsilon_2 e^{-(k_1+k_2)t} + \varepsilon_3 e^{-2(k_1+k_2)t} \\ k_1k_2\varepsilon_1 + (k_1 - k_2)\varepsilon_2 e^{-(k_1+k_2)t} - \varepsilon_3 e^{-2(k_1+k_2)t} \\ k_2^2\varepsilon_1 + 2k_2\varepsilon_2 e^{-(k_1+k_2)t} + \varepsilon_3 e^{-2(k_1+k_2)t} \end{pmatrix} \tag{14}$$

where

$$\begin{aligned} \varepsilon_1 &= (\alpha + 2\beta + \gamma)/(k_1 + k_2)^2 \\ \varepsilon_2 &= [k_1(\beta + \gamma) - k_2(\alpha + \beta)]/(k_1 + k_2)^2 \\ \varepsilon_3 &= [k_2{}^2\alpha + k_1{}^2\gamma - 2k_1k_2\beta]/(k_1 + k_2)^2 \end{aligned} \tag{15}$$

Some noteworthy points of this solution are:

(i) The terms ε_1, ε_2, and ε_3 correspond, respectively, to deviations from uncorrelated Poissonian of the quantities $\langle (x_i + y_i), (x_j + y_j) \rangle$, $\langle (x_i + y_i), (k_1 y_j - k_2 x_j) \rangle$, and $\langle (k_1 y_i - k_2 x_i), (k_1 y_j - k_2 x_j) \rangle$, which are essentially density fluctuations, correlation between density fluctuation and chemical imbalance, and fluctuations in chemical imbalance. We notice a characteristic diffusion form multiplying a chemical time dependence appropriate to the respective terms.

(ii) The time taken for the deviation from Poissonian uncorrelated form given by Eq. (13) to become negligible compared to the Poissonian depends, of course, on the magnitude of the initial deviation. Assuming, however, that α, β, γ, $\langle x_i \rangle$, and $\langle y_i \rangle$ are all of comparable size, one can make a rough estimate as follows. We consider a small spherical volume of radius R much larger, however, than our basic cells. Then in this small volume V we find that

$$\begin{aligned} \sigma_x{}^2[V, 0] &= \langle x[V, 0] \rangle + \alpha V/l^3 \\ \sigma_y{}^2[V, 0] &= \langle y[V, 0] \rangle + \gamma V/l^3 \\ \langle x[V, 0], y[V, 0] \rangle &= \beta V/l^3 \end{aligned} \tag{16}$$

while after a time $t \gg R^2/4D$ these quantities satisfy approximately

$$\begin{aligned} \sigma_x{}^2[V, t] &\approx \langle x[V, t] \rangle \\ &\quad + \frac{V^2}{(8\pi D t)^{3/2}} (k_1{}^2\varepsilon_1 - 2k_1\varepsilon_2 e^{-(k_1+k_2)t} + \varepsilon_3 e^{-2(k_1+k_2)t}) \\ \sigma_y{}^2[V, t] &\approx \langle y[V, t] \rangle \\ &\quad + \frac{V^2}{(8\pi D t)^{3/2}} (k_2{}^2\varepsilon_1 + 2k_2\varepsilon_2 e^{-(k_1+k_2)t} + \varepsilon_3 e^{-2(k_1+k_2)t}) \\ \langle x[V, t], y[V, t] \rangle &\approx \frac{V^2}{(8\pi D t)^{3/2}} \\ &\quad \times [k_1k_2\varepsilon_1 + (k_1 - k_2)\varepsilon_2 e^{-(k_1+k_2)t} - \varepsilon_3 e^{-2(k_1+k_2)t}] \end{aligned} \tag{17}$$

Thus the diffusion has reduced the overall deviation from Poissonian uncorrelated behavior by a factor of the order of magnitude of $R^3/(Dt)^{3/2}$. However, notice that in the case of an initial non-Poissonian, but also uncorrelated situation, corresponding to $\beta = 0$, we find that a correlation has appeared between X and Y, which, if the chemical rate constants are sufficiently large, can be quite substantial.

Furthermore, it is clear that correlations at different spatial points also arise even though the initial distribution was uncorrelated, and the correlation length is essentially the mean square distance traveled by a diffusing particle. If D is large, this can be quite large. The maximum correlation occurring at a distance r is of the order of magnitude of

$$\frac{\langle x\rangle e^{-1/6}}{(6\pi)^{3/2}}\frac{l^3}{r^3} \tag{18}$$

where l is again the length of the cell. Thus, even between adjacent cells, where $r = l$, this is only of the order of 1% of the initial deviation from Poissonian, which is indeed almost negligible.

(iii) As a more general case, one can consider the case when the delta functions in Eq. (13) are replaced by a Gaussian of the form

$$\exp(-r^2/2\mu^2)$$

The solutions are similar to (10), except that the first factor in front of the matrix on the right-hand side is replaced by

$$\frac{8\mu^3 \exp[-r^2/(8Dt + 2\mu^2)]}{[\pi(8Dt + 2\mu^2)]^{3/2}}$$

In this case there will be no significant change in this factor until $t \sim \mu^2/4D$. In an ensemble theory, an initially homogeneous ensemble with long-range correlations (i.e., large μ) could only be achieved by taking systems which are themselves systematically inhomogeneous, but for which the ensemble average is homogeneous. In practice, thorough stirring is expected to make the correlation length small. If we wish to be able to ignore spatial correlations, we would require that they vanish much more rapidly than the speed of the chemical reaction, which occurs if $k_1 + k_2 \ll 4D/\mu^2$.

(iv) We note that one often considers a reaction of the form $X \rightleftharpoons A$ where A is held fixed. This may be mimicked in this formulation by considering a case when $\langle y_i\rangle$ becomes infinite while k_1 becomes zero, in such a way that $k_1\langle y_i\rangle$ is finite. In this case, we would derive equations for g, $k_1 f$, and $k_1{}^2 h$ all of which would be expected to be finite, and specify initial conditions with $k_1 f$ and $k_1{}^2 h$ zero. In this case we find that $k_1 f$ and $k_1{}^2 h$ remain zero, and g is given by

$$g(r, t) = \frac{8\mu^3\alpha}{[\pi(8Dt + 2\mu^2)]^{3/2}} \exp\left[-\frac{r^2}{(8Dt + 2\mu^2)} - 2k_2 t\right] \tag{19}$$

The fluctuations arising purely from diffusion no longer occur.

(v) The above has treated a homogeneous system, for which the deviation from Poissonian would occur globally. In an alternative situation, we may consider a deviation from the Poissonian which occurs locally at the point $\mathbf{r}_0$. In this case the delta functions in Eqs. (13) would be replaced by

$\delta(\mathbf{r} - \mathbf{r}_0)\delta(\mathbf{r}' - \mathbf{r}_0)$ and the solutions can simply be derived to be the same as in Eq. (14), but the factor outside the matrix is replaced by

$$\frac{\exp\{-[(\mathbf{r} - \mathbf{r}_0)^2 + (\mathbf{r}' - \mathbf{r}_0)^2]/4Dt\}}{(4\pi Dt)^3}$$

and consequent changes occur in Eqs. (17). Notice that the relaxation of standard deviation eventually follows a t^{-3} law in this case, rather than $t^{-3/2}$ as in Eq. (16).

2.4. The Relaxation to Poisson Form as Described by a Nonlinear Master Equation

By using the postulate of complete factorization of the probability distribution into a product of distributions, one for each cell, a master equation for the probability distribution inside a cell can easily be derived, as has been done directly by Nicolis *et al.*(6,7) We have shown in Section 2.3 that this can only be rigorously true if the initial state is both uncorrelated and Poissonian, in which case it remains so. However, we have also shown that if the initial state is non-Poissonian and factorized, the maximum possible correlation between adjacent cells is very small indeed. We shall therefore investigate this method also.

It is instructive, however, to derive a reduced master equation first without a factorization assumption. We define

$$\hat{P}(x_r, y_r) = \sum_{\substack{\{x_i y_i\}\\ i \neq r}} P(\mathbf{x}, \mathbf{y}) \tag{20}$$

and can straightforwardly derive the equation

$$\begin{aligned}
(\partial/\partial t)&\hat{P}(x_r, y_r, t)\\
&= \sum_{i \neq r} \{d_{ri}(x_r + 1)\hat{P}(x_r + 1, y_r, t) - d_{ir}x_r\hat{P}(x_r, y_r, t)\\
&\quad + d_{ri}(y_r + 1)\hat{P}(x_r, y_r + 1, t) - d_{ir}y_r\hat{P}(x_r, y_r, t)\\
&\quad + d_{ir}\bar{x}_i(x_r - 1, y_r, t)\hat{P}(x_r - 1, y_r, t) - d_{ri}\bar{x}_i(x_r, y_r, t)\hat{P}(x_r, y_r, t)\\
&\quad + d_{ir}\bar{y}_i(x_r, y_r - 1, t)\hat{P}(x_r, y_r - 1, t) - d_{ri}\bar{y}_i(x_r, y_r, t)\hat{P}(x_r, y_r, t)\}\\
&\quad + k_1(y_r + 1)\hat{P}(x_r - 1, y_r + 1, t) + k_2(x_r + 1)\hat{P}(x_r + 1, y_r - 1, t)\\
&\quad - (k_1 y_r + k_2 x_r)\hat{P}(x_r, y_r, t)
\end{aligned} \tag{21}$$

In this equation the functions $\bar{x}_i(x_r, y_r t)$ and $\bar{y}_i(x_r, y_r, t)$ are the mean values of x_i and y_i evaluated at definite values of x_r and y_r: precisely,

$$\bar{x}_i(x_r, y_r, t)\hat{P}(x_r, y_r, t) = \sum_{\substack{\{x_j, y_j\}\\ j \neq r}} x_i P(\mathbf{x}, \mathbf{y}, t) \tag{22}$$

with a similar definition for $\bar{y}_i(x_r, y_r, t)$.

In the case of an isotropic system with a cubic cell system, the only terms $\bar{x}_i(x_r, y_r, t)$ and $\bar{y}_i(x_r, y_r, t)$ occurring in Eq. (21) will be those for which i and r represent adjacent cells, which will therefore have values independent of i, which we designate by $\bar{x}(x_r, y_r, t)$ and $\bar{y}(x_r, y_r, t)$. Under these conditions, we find that

$$\begin{aligned}\partial\hat{P}(x,y,t)/\partial t = \mathscr{D}\{&(x+1)\hat{P}(x+1,y,t) - x\hat{P}(x,y,t) + (y+1)\hat{P}(x,y+1,t)\\ &- y\hat{P}(x,y,t) + \bar{x}(x-1,y,t)\hat{P}(x-1,y,t) - \bar{x}(x,y,t)\hat{P}(x,y,t)\\ &+ \bar{y}(x,y-1,t)\hat{P}(x,y-1,t) - \bar{y}(x,y,t)\hat{P}(x,y,t)\}\\ &+ k_1(y+1)\hat{P}(x-1,y+1,t) + k_2(x+1)\hat{P}(x+1,y-1,t)\\ &- (k_1 y + k_2 x)\hat{P}(x,y,t) \end{aligned} \tag{23}$$

where

$$\mathscr{D} = 6d = 6D/l^2 \tag{24}$$

This equation is almost that of Nicolis *et al.*,(6,7) but at this stage no assumption of factorizable probability distributions has been made. This manifests itself in the dependence of the mean values $\bar{x}$ and $\bar{y}$ on the variables x and y. On assuming factorizability, this dependence disappears and we recover the equation of Nicolis *et al.* for this system. With the same assumption, the equation is also valid in inhomogeneous systems provided we interpret the $\bar{x}$ and $\bar{y}$ to be

$$\begin{aligned}\mathscr{D}\bar{x}(x,y,t) &= \tfrac{1}{6}\sum_{\substack{\text{cell}\\ \text{neighbors}}} d\bar{x}_i(x,y,t)\\ \mathscr{D}\bar{y}(x,y,t) &= \tfrac{1}{6}\sum_{\substack{\text{cell}\\ \text{neighbors}}} d\bar{y}_i(x,y,t)\end{aligned} \tag{25}$$

If we consider that factorizability is sufficiently true, we can set

$$\bar{x}(x,y,t) = \langle x(t)\rangle, \qquad \bar{y}(x,y,t) = \langle y(t)\rangle \tag{26}$$

and derive equations for the standard deviation and correlation functions. Defining

$$s_{xx} = \sigma_x{}^2 - \langle x\rangle, \qquad s_{yy} = \sigma_y{}^2 - \langle y\rangle, \qquad s_{xy} = \langle x, y\rangle \tag{27}$$

we find

$$\begin{aligned} ds_{xx}/dt &= -(2\mathscr{D} + 2k_2)s_{xx} + 2k_1 s_{xy}\\ ds_{xy}/dt &= -(2\mathscr{D} + k_1 + k_2)s_{xy} - k_1 s_{yy} - k_2 s_{xx}\\ ds_{yy}/dt &= -(2\mathscr{D} + 2k_1)s_{yy} + 2k_2 s_{xy}\end{aligned} \tag{28}$$

These are very similar to Eqs. (9), and predict similar solutions, in which, however, the characteristic diffusion factor is replaced by $\exp(-12Dt/l^2)$.

Since this master equation describes one given cell in the system, Eqs. (28) will describe the time development of deviations from the Poissonian in one part of the system, for which we have derived exact solutions in Section 2.4(v). Thus, the general features of the behavior of the second moments are correctly given by ignoring correlations between cells, but the actual manner of relaxation to a Poisson is only qualitatively given.

2.5. Two-Time Correlation Functions in the Steady State

We can define the two-time correlation functions as

$$\langle x_i(t), x_j(t')\rangle = \sum_{\substack{\{x,x'\}\\ \{y,y'\}}} x_i x_j' P(\mathbf{x}, \mathbf{y}, t; \mathbf{x}', \mathbf{y}', t') \tag{29}$$

and similarly for the averages $\langle x_i(t), y_j(t')\rangle$ and $\langle y_i(t), y_j(t')\rangle$. The quantity $P(\mathbf{x}, \mathbf{y}, t; \mathbf{x}', \mathbf{y}', t')$ is the joint probability, i.e., the probability that the system is in state $\mathbf{x}$, $\mathbf{y}$ at time t and in state $\mathbf{x}'$, $\mathbf{y}'$ at time t', and is clearly given by

$$P(\mathbf{x}, \mathbf{y}, t; \mathbf{x}', \mathbf{y}', t') = P(\mathbf{x}, \mathbf{y}, t) P(\mathbf{x}, \mathbf{y}, t | \mathbf{x}', \mathbf{y}', t') \tag{30}$$

where $P(\mathbf{x}, \mathbf{y}, t)$ is the probability the system is in state $\mathbf{x}$, $\mathbf{y}$ at time t, and $P(\mathbf{x}, \mathbf{y}, t | \mathbf{x}', \mathbf{y}', t')$ is the conditional probability that the system is in state $\mathbf{x}'$, $\mathbf{y}'$ at time t' given that it was in state $\mathbf{x}$, $\mathbf{y}$ at time t. The conditional probability clearly satisfies the master equation (3) in the primed variables, so that one easily derives equations for the steady-state correlation functions. In the case that we deal with the steady state, which is homogeneous and isotropic, the correlation functions will depend only on $|\mathbf{r}_i - \mathbf{r}_j|$ and $t' - t$. We define precisely

$$\begin{aligned} G(|\mathbf{r}_i - \mathbf{r}_j|, t' - t) &= \langle x_i(t), x_j(t')\rangle_{\mathrm{ss}} \\ F^+(|\mathbf{r}_i - \mathbf{r}_j|, t' - t) &= \langle x_i(t), y_j(t')\rangle_{\mathrm{ss}} \\ F^-(|\mathbf{r}_i - \mathbf{r}_j|, t' - t) &= \langle y_i(t), x_j(t')\rangle_{\mathrm{ss}} \\ H(|\mathbf{r}_i - \mathbf{r}_j|, t' - t) &= \langle y_i(t), y_j(t')\rangle_{\mathrm{ss}} \end{aligned} \tag{31}$$

which obey the equations

$$\begin{aligned} \partial G(r, t)/\partial t &= D\,\nabla^2 G(r, t) - k_2 G(r, t) + k_1 F^+(r, t) \\ \partial F^+(r, t)/\partial t &= D\,\nabla^2 F^+(r, t) - k_1 F^+(r, t) + k_2 G(r, t) \\ \partial F^-(r, t)/\partial t &= D\,\nabla^2 F^-(r, t) - k_2 F^-(r, t) + k_1 H(r, t) \\ \partial H(r, t)/\partial t &= D\,\nabla^2 H(r, t) - k_1 H(r, t) + k_2 F^-(r, t) \end{aligned} \tag{32}$$

We find the solutions

$$\begin{pmatrix} G(r,t) \\ F^{+}(r,t) \\ F^{-}(r,t) \\ H(r,t) \end{pmatrix} = \frac{\langle x+y\rangle}{(k_1+k_2)^2}\,\frac{\exp(-r^2/4Dt)}{(4\pi Dt)^{3/2}} \begin{pmatrix} k_1{}^2 + k_1k_2e^{-(k_1+k_2)t} \\ k_1k_2[1-e^{-(k_1+k_2)t}] \\ k_1k_2[1-e^{-(k_1+k_2)t}] \\ k_2{}^2 + k_1k_2e^{-(k_1+k_2)t} \end{pmatrix} \tag{33}$$

which satisfy the appropriate boundary conditions at $t = 0$.

By a little rearranging, we find the following:

$$\begin{aligned} \langle x_i(t)+y_i(t), x_j(t')+y_j(t')\rangle_{\text{ss}} &= \frac{\langle x+y\rangle \exp(-r^2/4D|t-t'|)}{(4\pi D|t-t'|)^{3/2}} \\ \langle x_i(t)+y_i(t), k_2x_j(t')-k_1y_j(t')\rangle &= 0 \qquad \text{for all } t \text{ and } t' \\ \langle k_2x_i(t)-k_1y_i(t), k_2x_j(t')-k_1y_j(t')\rangle & \\ = \frac{k_1k_2\langle x+y\rangle}{(4\pi D|t-t'|)^{3/2}} &\exp\left[\frac{-r^2}{4D|t-t'|} - (k_1+k_2)|t-t'|\right] \end{aligned} \tag{34}$$

where $r = |\mathbf{r}_i - \mathbf{r}_j|$. Thus the two-time correlations are nonzero only between fluctuations of the same kind (i.e., the first line corresponds to density fluctuations, the last to fluctuations in chemical imbalance, the middle line is the cross-correlation between the two), and the nonzero correlations have decay rates appropriate to their nature.

3. THE STOCHASTIC THEORY OF GENERAL CHEMICAL SYSTEMS: GENERATING FUNCTION METHODS AND NONLINEAR SYSTEMS

In the remainder of the paper we shall deal with systems in which all but one chemical species are considered to be held at fixed concentrations, mainly to simplify the equations.

Our most general master equation will then consist of a diffusion term, which is exactly the same as that in Eq. (3), and a chemical term

$$\begin{aligned} \left.\frac{\partial P(\mathbf{x},t)}{\partial t}\right|_{\text{Chem}} = \sum_{i,q} \{ & t_-{}^q(x_i+q)P(x_i+q, \hat{\mathbf{x}}, t) - t_-{}^q(x_i)P(\mathbf{x},t) \\ & + t_+{}^q(x_i-q)P(x_i-q, \hat{\mathbf{x}}, t) - t_+{}^q(x_i)P(\mathbf{x},t)\} \end{aligned} \tag{35}$$

Here q will correspond to a reaction step involving q molecules of X simultaneously.

We define a generating function

$$G(\mathbf{s},t) = \sum_{\{\mathbf{x}\}} \prod_{i=1}^{N} s_i{}^{x_i} P(\mathbf{x},t) \tag{36}$$

N is, as before, the number of cells in our system. The equation of motion for the generating function can easily be derived. In the case that the transition probabilities per unit time have the form

$$t_{\pm}{}^{q}(x_i) = \sum_{l} a_{q,l}^{\pm} \frac{(x_i)!}{(x_i - l)!} \tag{37}$$

the generating function equation becomes

$$\left.\frac{\partial G(\mathrm{s}, t)}{\partial t}\right|_{\mathrm{Chem}} = \sum_{i,q,l} (1 - s_i{}^{q}) s^{l-q} (a_{q,l}^{-} - s_i{}^{q} a_{q,l}^{+}) \frac{\partial^l G(\mathrm{s}, t)}{\partial s_i{}^{l}} \tag{38}$$

From this equation we derive equations for the means

$$\langle x_i \rangle = \left.\frac{\partial G}{\partial s_i}\right|_{\{\mathrm{s}\} = \{1\}} \tag{39}$$

and second moments

$$\langle x_i x_j \rangle - \delta_{ij} \langle x_i \rangle = \left.\frac{\partial^2 G}{\partial s_i \partial s_j}\right|_{\{\mathrm{s}\} = \{1\}} \tag{40}$$

These equations of motion are, when the diffusion term is also included,

$$\frac{\partial \langle x_i \rangle}{\partial t} = D\, \nabla_{\mathbf{r}_i}^2 \langle x_i \rangle - \sum_{q,l} q(a_{q,l}^{-} - a_{q,l}^{+}) \langle x_r(x_r - 1) \cdots (x_r - l + 1) \rangle \tag{41}$$

and

$$\begin{aligned} \frac{\partial}{\partial t} & \{\langle x_i x_j \rangle - \delta_{ij} \langle x_i \rangle\} \\ &= D(\nabla_{\mathbf{r}_i}^2 + \nabla_{\mathbf{r}_j}^2) \{\langle x_i x_j \rangle - \delta_{ij} \langle x_i \rangle\} \\ &\quad - \sum_{q,l} q(a_{q,l}^{-} - a_{q,l}^{+}) \{\langle x_i x_j (x_j - 1) \cdots (x_j - l + 1) \rangle \\ &\quad + \langle x_j x_i (x_i - 1) \cdots (x_i - l + 1) \rangle\} \\ &\quad + \delta_{ij} \sum_{q,l} \{q[(q - l)(a_{q,l}^{-} - a_{q,l}^{+}) + 2q a_{q,l}^{+}] \langle x_i (x_i - 1) \cdots (x_i - l + 1) \rangle\} \end{aligned} \tag{42}$$

We have again made a continuum approximation for the diffusion terms. For systems involving reactions of the form

$$n\mathrm{X} + \mathrm{A} \rightleftharpoons m\mathrm{X} + \mathrm{B} \qquad (m > n) \tag{43}$$

and no other reactions, if we have the requirement

$$\begin{aligned} t_{+}^{m-n}(x_i) &= k_1 A x_i (x_i - 1) \cdots (x_i - n + 1) \\ t_{-}^{m-n}(x_i) &= k_2 B x_i (x_i - 1) \cdots (x_i - m + 1) \end{aligned} \tag{44}$$

we can simply demonstrate that the exact steady-state solution is Poissonian, and Eq. (42) also gives a solution which has no correlations. However, in general, if one has a different form for the transition probabilities, it appears that correlations will exist. Equations (42) cannot be solved, but by making various plausible approximations, we find that the coefficient of δ_{ij} does not vanish, and this term gives an inhomogeneity in the differential equation which causes a correlation to arise. How this happens can be shown in specific examples.

The terms involving δ_{ij} in the correlation functions arise from powers of the s_i higher than the first, i.e., from nonlinear terms in the s_i. For, if no correlations do arise, we must have no nonlinear terms in the s_i, and this arises only if

$$\begin{aligned} a_{q,l}^{-} &= 0 \qquad \text{unless} \quad l = q = 1 \\ a_{q,l}^{+} &= 0 \qquad \text{unless} \quad l = 0, \quad q = 1 \end{aligned} \tag{45}$$

Thus the most natural definition of a nonlinear system comes from the generating function equation: A system is nonlinear if its generating function equation is nonlinear in the generating function variables $\{s_i\}$. A sufficient condition for this definition to be satisfied is for the deterministic equations to be nonlinear, but this is not a necessary condition, a counterexample being the reaction to be studied in Section 4.1.

4. TWO EXAMPLES OF NONLINEAR SYSTEMS

4.1. An Exactly Soluble Model

We consider the reaction system

$$\mathrm{B} + \mathrm{X} \underset{k_3}{\overset{k_1}{\rightleftharpoons}} \mathrm{C}, \qquad \mathrm{A} + \mathrm{X} \xrightarrow[k_2]{} 2\mathrm{X} \tag{46}$$

where A, B, and C have fixed concentrations. We work now in densities defined by

$$\rho(\mathbf{r}_i, t) = x(\mathbf{r}_i, t)/l^3 \equiv x_i(t)/l^3 \tag{47}$$

and by the methods of Section 3 derive equations for the mean and the correlation function. We define

$$g(\mathbf{r}, \mathbf{r}', t) = \langle \rho(\mathbf{r}, t), \rho(\mathbf{r}', t) \rangle - \delta(\mathbf{r} - \mathbf{r}')\langle \rho(\mathbf{r}, t) \rangle \tag{48}$$

so that

$$\partial\langle \rho(\mathbf{r}, t)\rangle/\partial t = D\, \nabla^2 \langle \rho(\mathbf{r}, t)\rangle - (K_1 - K_2)\langle \rho(\mathbf{r}, t)\rangle + K_2\beta \tag{49}$$

and

$$\partial g/\partial t = D(\nabla_{\mathbf{r}}^2 + \nabla_{\mathbf{r}'}^2)g + 2(K_2 - K_1)g + 2K_2\langle \rho(\mathbf{r}, t)\rangle \delta(\mathbf{r} - \mathbf{r}') \tag{50}$$

where

$$\begin{aligned} K_2 &= k_2A/l^3 \equiv k_2[\mathrm{A}] \\ K_1 &= k_1B/l^3 \equiv k_1[\mathrm{B}] \\ \beta &= k_3C/K_2l^3 \equiv k_3[\mathrm{C}]/k_2[\mathrm{A}] \end{aligned} \tag{51}$$

where [ ] indicates concentration of the chemical species. The steady-state solution for the correlation function is

$$\langle\rho(\mathbf{r}), \rho(\mathbf{r}')\rangle_{\mathrm{ss}} = \delta(\mathbf{r}-\mathbf{r}')\langle\rho\rangle + \frac{K_2\langle\rho\rangle}{4\pi D|\mathbf{r}-\mathbf{r}'|}\exp\left[-|\mathbf{r}-\mathbf{r}'|\left(\frac{K_1-K_2}{D}\right)^{1/2}\right] \tag{52}$$

where $\langle\rho\rangle$ is the steady-state solution for the density,

$$\langle\rho\rangle_{\mathrm{ss}} = \beta K_2/(K_1 - K_2) \tag{53}$$

Thus this exactly soluble model does give rise to a nonzero steady-state correlation. The correlation, however, goes to zero as $K_2 \to 0$, which is expected, since in this case the second reaction no longer contributes, and the first reaction is one which can come to equilibrium.

The correlation length l_c is given by

$$l_c = [D/(K_1 - K_2)]^{1/2} \equiv \alpha^{-1} \tag{54}$$

and is the same order of magnitude as the mean distance between reactive collisions as long as K_1 is not close to K_2. [Notice that as $K_2 \to 0$, although the reaction becomes linear, the correlation length does not go to zero. However, Eq. (52) shows that the correlations themselves go to zero.] The length l_c is a rather long distance in general. Substituting the values (51), we find

$$l_c = [D/(k_1[\mathrm{A}] - k_2[\mathrm{B}])]^{1/2} \tag{55}$$

The correlation length is thus inversely proportional to the concentrations of A and B (if the ratio of these is kept fixed), and can be made as large as desired by diluting the systems.

Equation (50) yields a relatively simple solution in the case in which the system is initially homogeneous and the mean concentration has reached its steady-state value; we find that

$$\begin{aligned} \langle\rho(\mathbf{r}, t), \rho(\mathbf{r}', t)\rangle = {} & \delta(\mathbf{r}-\mathbf{r}')\langle\rho\rangle \\ & + \frac{K_2\langle\rho\rangle}{4\pi D|\mathbf{r}-\mathbf{r}'|}\Bigg([\exp(-\alpha|\mathbf{r}-\mathbf{r}'|)] \\ & \times\left\{1 - \frac{1}{2}\operatorname{erfc}\left[\alpha(2Dt)^{1/2} - \frac{|\mathbf{r}-\mathbf{r}'|}{(8Dt)^{1/2}}\right]\right\} \\ & - \frac{1}{2}\exp(\alpha|\mathbf{r}-\mathbf{r}'|)\operatorname{erfc}\left[\alpha(2Dt)^{1/2} + \frac{|\mathbf{r}-\mathbf{r}'|}{(8Dt)^{1/2}}\right]\Bigg) \end{aligned} \tag{56}$$

This behavior would represent the return to correlated behavior after, for example, vigorously stirring the steady state. The relaxation time (found by use of mathematical methods similar to those used for the two-time correlation function later in this section) is

$$\tau_R = \tfrac{1}{2}(K_2 - K_1)^{-1} \tag{57}$$

The two-time correlation function can be calculated by methods similar to those used in Section 2 for the linear system. The equation of motion is found to be, for the steady-state two-time correlation function,

$$g(|\mathbf{r}_i - \mathbf{r}_j|, t' - t) \equiv \langle x(\mathbf{r}_i, t), x(\mathbf{r}_j, t')\rangle \tag{58}$$

$$\partial g(r, \tau)/\partial \tau = D\, \nabla^2 g(r, t) - (K_1 - K_2)g \tag{59}$$

The boundary condition is

$$g(r, 0) = \langle \rho(0), \rho(\mathbf{r})\rangle_{\mathrm{ss}} \tag{60}$$

and the solution satisfying this is

$$\begin{aligned} g(r, \tau) = {} & \frac{\langle\rho\rangle \exp(-r^2/4D\tau - \alpha^2 D\tau)}{(4\pi D\tau)^{3/2}} \\ & + \frac{K_2\langle\rho\rangle}{8\pi Dr}\left\{[\exp(-\alpha r)] \operatorname{erfc}\left[\alpha(D\tau)^{1/2} - \frac{r}{2(D\tau)^{1/2}}\right]\right. \\ & \left. + [\exp(\alpha r)] \operatorname{erfc}\left[\alpha(D\tau)^{1/2} + \frac{r}{2(D\tau)^{1/2}}\right]\right\} \end{aligned} \tag{61}$$

For small τ we find

$$g(r, \tau) \to \langle\rho\rangle\left(\exp\frac{-r^2}{4D\tau}\right)\left\{(4\pi D\tau)^{-3/2} - \frac{4K_2(D\tau)^{3/2}}{r^3\sqrt{\pi}}\right\} + \frac{K_2\langle\rho\rangle e^{-\alpha r}}{4\pi Dr} \tag{62}$$

while for large τ

$$g(r, \tau) \sim \left\{\frac{\exp(-r^2/4D\tau)}{(4\pi D\tau)^{3/2}} + \frac{K_2}{4\pi\alpha r(\pi D^2\tau)^{1/2}}\right\}\langle\rho\rangle \exp(-\alpha^2 D\tau) \tag{63}$$

If the long-time behavior is considered to give the measure of the correlation time, then it is clear that this time τ_c is given by

$$\tau_c = l_c^2/D = (K_2 - K_1)^{-1} \tag{64}$$

a result similar to that found by Graham$^{(13)}$ in his work on the Benard instability.

In the case where we are looking at the number of molecules in a volume much larger than the correlation length, we may integrate over the volume in Eq. (59), and thus eliminate the Laplacian, giving the much simpler solution

$$\langle x[V, \tau], x[V, 0]\rangle = \sigma^2[V, 0]e^{-\tau/\tau_c} \tag{65}$$

4.2. An Approximate Solution for a System Exhibiting a Second-Order Phase Transition

As a further example of a nonlinear system we consider the reaction scheme

$$\mathrm{B} + \mathrm{X} \underset{k_3}{\overset{k_1}{\rightleftharpoons}} \mathrm{C}, \qquad \mathrm{A} + \mathrm{X} \underset{k_4}{\overset{k_2}{\rightleftharpoons}} 2\mathrm{X} \tag{66}$$

where we have retained the reverse reaction in the autocatalytic reaction. Schlögl[14] has given a deterministic analysis of this system and has shown that in the limit $\beta \to 0$ the system undergoes behavior very similar to an equilibrium second-order phase transition, with the density $\langle\rho\rangle$ behaving as an order parameter. The transition point is $K_1 = K_2$, at which the slope of $\langle\rho\rangle$ versus K_2/K_1 changes discontinuously and the system exhibits critical slowing down. A stochastic analysis of this system for the non-space-dependent case has been given by McNeil and Walls[15] and Nitzan *et al.*[1] Using the techniques expounded in the previous sections, we may examine the behavior of the spatial correlations in this system.

The equations for the mean number and correlation function may be derived from the generating function in a similar fashion to the derivation in Section 4.1. The inclusion of the reverse autocatalytic reaction introduces higher order moments to these equations and some approximation is necessary to give closed equations.

We shall use an approximation which bears a resemblance to the Gaussian approximation, namely

$$\begin{aligned}\langle x_i x_j x_k\rangle_f = {} & [\langle x_i x_j\rangle_f - \langle x_i\rangle\langle x_j\rangle]\langle x_k\rangle + [\langle x_j x_k\rangle_f - \langle x_j\rangle\langle x_k\rangle]\langle x_i\rangle \\ & + [\langle x_i x_k\rangle_f - \langle x_i\rangle\langle x_k\rangle]\langle x_j\rangle + \langle x_i\rangle\langle x_j\rangle\langle x_k\rangle \end{aligned} \tag{67}$$

where $\langle\ \rangle_f$ indicates a factorial moment. This approximation arises from a quadratic approximation to the logarithm of the generating function of the form (37), in the same way as the Gaussian approximation arises from a quadratic approximation to the cumulant generating function. In the limit of large numbers, the approximations become equivalent to each other. The advantage of approximation (67) is that, unlike the Gaussian approximation, it is exactly true for the Poisson distributions found in thermodynamic equilibrium, and further, no extraneous terms which vanish in the limit of large volumes appear when it is employed, since the equations of motion already are naturally formulated in terms of factorial moments. Using this approximation, we derive steady-state equations satisfied by the density of particles and for the correlation function g. These are

$$(K_2 - K_1)\langle\rho\rangle + \beta K_2 - \delta[g(0) + \langle\rho\rangle^2] = 0 \tag{68}$$

where $\delta = k_k l^3$ and because of the spatial homogeneity of the steady state,

$$D\,\nabla^2 g(r) - (K_1 - K_2)g(r) + K_2\langle\rho\rangle\delta(\mathbf{r}) \\ - \delta\{[g(0) + \langle\rho\rangle^2]\,\delta(\mathbf{r}) + 2\langle\rho\rangle g(r)\} = 0 \quad (69)$$

The quantity $g(0)$ occurs explicitly in both these equations, which also imply that, in the approximation that $\mathbf{r}$ is a continuous variable,

$$g(r) = \frac{1}{4\pi D}\frac{e^{-\alpha r}}{r}\,[K_1\langle\rho\rangle - \beta K_2] \quad (70)$$

which clearly implies that $g(0)$ is infinite. If we solve the exact difference equation corresponding to (69), we find that

$$g(0) \sim (\varepsilon/Dl)[K_1\langle\rho\rangle - \beta K_2] \quad (71)$$

where ε is some constant of order of magnitude of one. We can now solve the coupled equations, and find that

$$\delta\langle\rho\rangle^2 - \left[K_2 - K_1\left(1 + \frac{\varepsilon\delta}{lD}\right)\right]\langle\rho\rangle - \beta K_2\left(1 + \frac{\varepsilon\delta}{lD}\right) = 0 \quad (72)$$

We would wish to take the limit $l \to 0$, but doing this, we find

$$\begin{aligned} \langle\rho\rangle &= \beta K_2/K_1 \\ g(r) &= 0 \qquad (r \neq 0) \\ g(0) &\quad \text{finite} \end{aligned} \quad (73)$$

This result, while undoubtedly a rigorous derivation from the theory [subject only to the approximation (67)], need not necessarily have any relevance to the process under study.

The quantity δ/D is of dimensions length, and its order of magnitude can be assessed on the assumption of either a gaseous or a liquid system. In the case of a gas, if A and X are molecules of the same radius a forming the gas, simple collision theory gives[3]

$$\delta = 2\left(\frac{kT}{m}\right)^{1/2} a^2 q \quad (74)$$

where q is the probability of 2X → A + X given that a collision has occurred.

Using the kinetic theory value of the diffusion coefficient,

$$D \approx \tfrac{1}{3}(2/\pi)^{3/2}(mkT)^{1/2}/a^2 m\langle\rho\rangle \quad (75)$$

so that

$$\delta/D = (\tfrac{4}{3}\pi a^3\langle\rho\rangle)(9\sqrt{\pi}aq)/(4\sqrt{2}) \quad (76)$$

The factor $\frac{4}{3}\pi a^3\langle\rho\rangle$ is the fraction of space occupied by the molecules, which

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[3] Derivations and references for this and the following formulas can be found in Ref. 16.

is negligible in a gas. The factor q is at most of the order of one, so that δ/D is an infinitesimal fraction of a, the radius of the molecule.

We can also carry out the calculation under the assumption that the reacting molecules are of large size and move as Brownian particles in an inert gas, using the formula

$$D = kT/6\pi\eta a \tag{77}$$

where η is the gas viscosity, and using the kinetic theory value for the viscosity, we can derive

$$\delta/D = (8/\sqrt{\pi})(a/a_g)^3(2m_g/m)^{1/2}qa_g \tag{78}$$

where m_g and a_g are, respectively, the mass and radius of the inert gas molecules. The assumptions under which (77) are valid are that the mass of the reacting molecule and its diameter are much larger than those of the gas molecules. Assuming that the reacting and gas molecules have similar densities, we find

$$\delta/D \sim (a/a_g)^{1/2}qa \tag{79}$$

A similar result can be derived for a liquid solution of the reactant, but in this case the cage effect will make it possible for the effective q to be much larger in diffusion-controlled reactions.

The limit of $l \to a$ must be regarded as unphysical, however, since the stochastic equations always assume that an infinite number of particles can be put into the volume l^3, which is impossible, and that the mechanism $A + X \leftrightarrows 2X$ takes place inside one cell, which also cannot happen. In order to treat cases where $\delta/D \sim a$, a nonlocal theory of the bimolecular theory would be needed.

We thus leave these cases for a later paper, and consider here only the case where $\delta/Dl \ll 1$, in which case Eq. (72) becomes the same as that which would arise by neglecting $g(0)$, so that we may now set

$$\langle\rho^2\rangle = \langle\rho\rangle^2 + l^{-3}\langle\rho\rangle \tag{80}$$

which corresponds to a Poissonian distribution for local fluctuations.

The steady-state solution for g is

$$g(\mathbf{r}) = \frac{K_1\langle\rho\rangle - \beta K_2}{4\pi Dr}\, e^{-\alpha r} \tag{81}$$

where $\alpha = [(K_1 - K_2)^2 + 4\beta\delta K_2]^{1/4}/D^{1/2}$. In the limit where we neglect the back reaction, i.e., set $\beta = 0$, the transition becomes sharp and the expressions for the steady-state density and correlation function reduce to

$$\begin{aligned} \langle \rho \rangle &= 0 && \text{for} \quad K_2 \leqslant K_1 \\ \langle \rho \rangle &= (K_2 - K_1)/\delta && \text{for} \quad K_2 \geqslant K_1 \end{aligned} \tag{82}$$

and

$$\langle \rho(\mathbf{r}), \rho(\mathbf{r}') \rangle_{\text{ss}} = \delta(\mathbf{r} - \mathbf{r}')\langle \rho \rangle + \frac{K_1 \langle \rho \rangle}{4\pi D |\mathbf{r} - \mathbf{r}'|} \exp -\frac{|\mathbf{r} - \mathbf{r}'|}{l_c} \tag{83}$$

where l_c is the correlation length,

$$l_c = \alpha^{-1} = (D/|K_1 - K_2|)^{1/2} \tag{84}$$

which is symmetric about the transition point $K_1 = K_2$ and becomes infinite at the transition point. This behavior is closely analogous to the behavior of the correlation length in a second-order phase transition. We note that the critical exponent has the classical value of $\frac{1}{2}$.

Similar behavior has been noted by Nitzan *et al.*,(1) who calculate the correlation length in chemical reactions in a linear approximation. The above result is also in agreement with those of Zaitsev and Schliomis,(17) Graham,(13) and Boon,(18) who treat spatial correlations in the Benard instability in liquids.

In a similar manner to the example of Section 4.1, we may calculate the two-time correlation function for this system. In the limit $\beta = 0$ this correlation function has the same form as given in Eqs. (51)–(53) with the substitution $K_2 \to K_1$ and with $\alpha = l_c^{-1}$. The correlation time τ_c is given by

$$\tau_c = l_c^2/D = |K_2 - K_1|^{-1} \tag{85}$$

exhibiting a dynamical critical exponent of one.

We can also investigate the magnitude of the fluctuations as the critical point is approached. Let ΔV be some subvolume of the system, and consider the number variable within this volume

$$x[\Delta V] = \int_{\Delta V} d^3\mathbf{r}\, \rho(\mathbf{r}) \tag{86}$$

We can calculate the variance of the steady-state distribution by direct integration of the correlation function (83), to give

$$\sigma^2[\Delta V] = \langle x[\Delta V] \rangle \left\{ 1 + \frac{3K_1 l_c^5}{2DR^3} \left[\left(1 - \frac{R^2}{l_c^2} + \frac{2}{3}\frac{R^3}{l_c^3} \right) - e^{-2R/lc} \left(1 + \frac{R}{l_c} \right)^2 \right] \right\} \tag{87}$$

(we assume here that ΔV is a spherical volume of radius R). As we approach the critical point, $l_c \to \infty$, and we obtain

$$\sigma^2[\Delta V] \to \langle x[\Delta V]\rangle\left[1 + \frac{2K_1R^2}{5D}\right] \tag{88}$$

Thus the magnitude of the fluctuation is finite, but can become arbitrarily large as R increases. By keeping l_c finite and letting R become infinite, we obtain

$$\sigma^2[\Delta V] \to \langle x[\Delta V]\rangle K_1 l_c^2/D \tag{89}$$

Thus, for an infinite system, the variance diverges like l_c^2. This behavior will be closely followed by a finite system as long as $l_c \ll R$ but the value at the critical point will be given by (88), and will not be infinite.

5. FLUCTUATIONS IN FINITE VOLUMES

5.1. The Transition from Local Poissonian Form to Global Non-Poissonian Form

It is of interest to investigate the nature of the probability distribution within an arbitrary volume. The result (87) may be used to show for a spherical volume ΔV of radius R, that if $R \ll l_c$,

$$\sigma^2[\Delta V] \sim \langle x[\Delta V]\rangle[1 + (2K_iR^2/5D)] \tag{90}$$

where $i = 1$ for the reaction of Section 4.1 and $i = 2$ for the phase transition reaction of Section 4.2; it is understood that if $i = 1$, all subsequent formulas hold only for $K_1 > K_2$.

In the limit $R \to 0$ the fluctuations become Poissonian in agreement with the postulate of the local equilibrium in small volumes.

For large R, the variance becomes

$$\sigma^2[\Delta V] \approx \langle x[\Delta V]\rangle\left(\frac{K_i}{|K_1 - K_2|} - \frac{3K_il_c}{2|K_1 - K_2|R}\right) \tag{91}$$

As $R \to \infty$ this approaches the variance from a non-space-dependent master equation for the appropriate reaction. However, in the case of the reaction of Section 4.2, it is necessary to make the approximation (87) for the factorial moments in the non-space-dependent master equation and to take the limit that the size of the system is infinite. Neither of these is necessary for the reaction of Section 4.1.

It is of interest to compare these results with those obtained by neglecting correlations, i.e., assuming a factorizable probability distribution. In the case of the reaction of Section 4.1 the calculation is straightforward, and leads to

$$\sigma^2[\Delta V] = \langle x[\Delta V]\rangle\{1 + [K_2/(K_1 - K_2 + \mathscr{D})]\} \tag{92}$$

where $\mathscr{D} \propto D/\lambda^2 \propto D/R^2$ and λ is some typical length of the volume ΔV. In the limits of very small and very large R this result agrees with the exact result, but comparison with Eq. (92) shows that the large-R limit here is approached quadratically in R^{-1} rather than linearly.[4] This is a consequence of the factorization, which would imply vanishing correlations.

5.2. Correlations Between a Small and Large Volume

The factorization ansatz as originally applied by Nicolis was concerned with the fluctuations within a small volume in comparison with the fluctuations in a large surrounding volume. Assuming a factorization of the joint probability distribution essentially neglects correlations between the small volume ΔV and the large volume $V - \Delta V$. In order to examine the validity of this assumption, we shall calculate the correlation function between the two volumes for the reaction of Section 4.1. We define the normalized correlation coefficient

$$C[\Delta V, V - \Delta V] = \langle x[\Delta V], x[V - \Delta V]\rangle / \sigma[\Delta V]\sigma[V - \Delta V] \tag{93}$$

where

$$\langle x[\Delta V], x[V - \Delta V]\rangle = \int_{\Delta V} d^3\mathbf{r} \int_{V-\Delta V} d^3\mathbf{r}' \, \langle \rho(\mathbf{r}), \rho(\mathbf{r}')\rangle \tag{94}$$

and

$$\langle \rho(\mathbf{r}), \rho(\mathbf{r}')\rangle = \langle \rho(\mathbf{r})\rho(\mathbf{r}')\rangle - \langle \rho(\mathbf{r})\rangle\langle \rho(\mathbf{r}')\rangle \tag{95}$$

The integral in Eq. (95) may be expanded as

$$\int_{\Delta V} d^3\mathbf{r} \int_{V-\Delta V} d^3\mathbf{r}' \, \langle \rho(\mathbf{r}), \rho(\mathbf{r}')\rangle$$
$$= \int_{\Delta V} d^3\mathbf{r} \int_{V} d^3\mathbf{r}' \, \langle \rho(\mathbf{r}), \rho(\mathbf{r}')\rangle - \int_{\Delta V} d^3\mathbf{r} \int_{\Delta V} d^3\mathbf{r}' \, \langle \rho(\mathbf{r}), \rho(\mathbf{r}')\rangle \tag{96}$$

The first integral is most easily evaluated by integrating Eq. (52) for the correlation function in the steady state. By assuming that the volume V has dimensions much larger than the correlation length l_c we can ignore the surface contributions of the ∇^2 term. The integration over r merely yields ΔV. The second integral is $\sigma^2[\Delta V]$ and is given by Eq. (87), which we write in the form

$$\sigma^2[\Delta V] = \langle x[\Delta V]\rangle[1 + f(\Delta V)] \tag{97}$$

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[4] In a recent work Malek-Mansour and Nicolis[7] advance arguments that $\mathscr{D}$ is proportional to D/R.

The normalized correlation coefficient for $\Delta V \ll V$ is then

$$C[\Delta V, V - \Delta V] = \frac{(K_2/K_1)^{1/2} - f(\Delta V)}{(K_1 - K_2)^{1/2}} \left(\frac{\Delta V}{V}\right)^{1/2} \tag{98}$$

Thus the normalized correlation between the two volumes has a finite value which only tends to zero in the limit $\Delta V/V \to 0$. Similar results can be derived for the reaction of Section 4.2.

6. SUMMARY AND CONCLUSIONS

Our main thrust in this work has been the comparative formulation of formulas for correlations in different chemical situations. Our whole work depends on the use of stochastic master equations, which, we believe, have a better conceptual and intuitive basis than the fluctuating force formalism of Langevin equations.

It is important to note that our results show that the correlation lengths can in principle be arbitrarily large in these diffusion-reaction systems. The scale of correlation lengths is not microscopic, but is given by the mean distance between reactive collisions, or, more precisely, since our theory is not explicitly based on the collision theory of chemical reactions, by the mean distance traveled by a molecule between individual reactive steps. The measurement of this distance should not present insuperable technical difficulties, e.g., light scattering(19) and fluorescence correlation spectroscopy(20) should be sufficiently powerful techniques. Light scattering itself does measure quite directly the two-time correlation function at one spatial point, and, as can be seen from the results of the preceding sections, the chemical reaction can have a profound effect on this correlation function. Indeed, careful calculations by Berne and Gininger(21) have already shown how the light scattering spectrum would be altered.

We hope the debate on microscopic and macroscopic fluctuation formulas has been clarified by our treatment, which, in fact, presents much of what previous workers have already stated.

The major task in the theory of chemical correlations and phase transitions appears to us to be in the realm of better approximations than those presently used to truncate systems of equations involving arbitrarily high moments. We believe our simple soluble model is valuable in this respect, since approximation schemes can be tested on it. But it is clear that, at the critical point, the approximation we made is unlikely to be true, since it is very similar to a Gaussian approximation, which is known to fail at such points, simply because the standard deviation becomes infinite there. At present, methods for tackling this problem do not appear to be available, though an approach based on the renormalization group could well be fruitful.

A further task is the extension of the methods to those reactions that display first-order critical phenomena and to oscillatory two- or many-variable systems.(22) Haken,(23) Mashiyama *et al.*,(24) and Lemarchand and Nicolis(25) have made significant progress on the latter topic, but a full understanding of the former is a problem yet to be solved.

ACKNOWLEDGMENTS

We wish to thank Prof. G. Nicolis for stimulating conversations and correspondence, and Mr. S. Chaturvedi for useful discussions.

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