POISSON REPRESENTATION METHODS FOR STOCHASTIC MODELS OF CHEMICAL REACTIONS

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Abstract

A comprehensive discussion of the stochastic master equation approach to chemical reactions is presented. After a review of the various system size expansion methods that have been developed for an asymptotic solution of stochastic master equations, a new technique, the Poisson representation method is introduced. The technique is based on an expansion of the probability distribution in Poisson distributions and enables chemical master equations to be transformed into exact Fokker-Planck equations.

The Fokker-Planck equations obtained using the Poisson representation are used to investigate some general features of chemical reaction systems whose steady state is thermodynamic equilibrium. The solutions for such systems are discussed from grand canonical and canonical ensemble points of view.

Basic formulae for the two time correlation functions are derived using the Poisson representation method. The formulae for the chemical systems in thermodynamic equilibrium are shown to relate directly to the fluctuation-dissipation theorems which may be derived from equilibrium statistical mechanical considerations. For non-equilibrium systems, the formulae are shown to be generalisations of these fluctuation-dissipation theorems, but containing an extra term which arises entirely from the non equilibrium nature of the system.

In a chemical reaction mechanism, if only bimolecular reactions occur, the Fokker-Planck equations derived using the Poisson representation method involve no higher than second order derivatives. The mathematical equivalence between Fokker-Planck equations and stochastic differential equations is used to derive stochastic differential equations for chemical reaction systems. When trimolecular or higher reactions are present, the Fokker-Planck equations involve third or higher order derivatives. It is shown how the concept of a stochastic differential equation may be generalised in such cases.

The stochastic differential equations lend themselves to a straightforward perturbative expansion in the inverse powers of the system size. These perturbative methods are applied to some interesting examples of non equilibrium reaction systems. Some novel features of the Poisson representation quasi probability which arise in these cases are discussed.

A chemical reaction model which exhibits a second order phase transition behaviour is investigated in detail (including the process of spatial diffusion) and the first two terms in a perturbative expansion for the spatial and two time correlation functions are calculated.

A stochastic model of a chemical reaction which exhibits spatial and temporal oscillations is analysed below the instability thresholds. The same model is used to show how the Poisson representation method may be applied to calculate the spatial and two time correlation functions in finite systems with boundary conditions.

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CHAPTER 1

RATIONALE FOR THE MASTER EQUATION APPROACH

1.1 Introduction

The phenomena of transition of a macroscopic system from a disordered, chaotic state to an ordered state in far from thermodynamic equilibrium situations are currently the subject of much theoretical and experimental interest.[1-3] The formation of Benard cells in a fluid layer heated from below, the laser transition, spatial and temporal oscillations in Belousov-Zhabotinsky reaction, are some of the examples where beyond a certain critical distance from the thermodynamic equilibrium, the initially chaotic state becomes unstable and gives rise to spatially and temporally organised structures - the dissipative structures. Numerous examples of such symmetry breaking instabilities may be found in a wide variety of disciplines such as hydrodynamics, physics, biochemistry, ecology, etc.[4-7] Instabilities which are not symmetry breaking also play an important role in diverse biological phenomena such as membrane transport, nerve excitation, enzymatic reactions where multiple steady states are possible[3-8].

The importance of fluctuations in bringing about the transitions of the type discussed above is now well established[1-7] and consequently any mathematical description of systems which exhibit these transitions must include fluctuations. The master equation approach provides such a description. In this thesis our main concern is with the master equation approach to chemical kinetics,[9-22] specifically with developing mathematical techniques for solving these equations. We first discuss the rationale behind a master equation to macroscopic systems in general. The arguments presented are not original and rely heavily on those put forth by Green, Zwanzig, van Kampen, Penrose and Balescu.[23-28] We then consider the validity of such an approach to chemical kinetics.

1.2 Master Equation Approach: General Considerations

The first step in a physical description of a macroscopic system consists in selecting a few quantities which describe the system as a whole such as volume, charge, magnetisation, temperature, etc. The choice of these quantities is based on past experience or physical intuition. In trying to understand the gross behaviour of the system either on intuitive or empirical grounds it may be necessary to introduce a few more quantities. For mathematical convenience we may have to introduce local concepts such as charge density, concentration etc. This process continues until, of all the macroscopic quantities introduced, we may select a minimal set $\bar{a}_i$ which provides the simplest and the most complete description of the system. By a complete description we mean that given the initial values of $\bar{a}_i$ we should be able to predict their values at a later time and hence the future macroscopic state of the system.

Thus the macroscopic description is complete when we specify the phenomenological equations

$$\frac{d\bar{a}_i}{dt} = F_i(\underline{a}) \qquad (1.1)$$

Familiar examples of such equations are Navier-Stokes equation in hydrodynamics, rate equations in chemical kinetics, Fourier equation in heat conduction etc. These equations may usually be derived from some general principles such as conservation laws together with some specific phenomenological assumptions. For most purposes these equations may be sufficient, i.e. given the initial values of $\bar{a}_i$ one may calculate their values at a later time which agree with the observed values within the experimental precision Δa_i with which these quantities may be measured. However, situations may arise in which we find large scale deviations from the expected behaviour. This may happen for example, if the system under consideration is an open system and the parameters involved in the phenomenological equations may be externally controlled. In such a case we may find that for certain values of the parameters, the solution of the phenomenological equations becomes unstable. If this happens then a slight fluctuation δa_i from $\bar{a}_i$ would begin to grow with time. This fluctuation may either be externally induced or may arise spontaneously. In a macroscopic system with many degrees of freedom, occurrence of a spontaneous fluctuation is certainly possible. In order to gain a better understanding of spontaneous fluctuations and to find an alternative to the phenomenological equations in a regime in which they are untenable it is necessary to examine the system from a microscopic view point.

At the microscopic level, a complete description of the system is provided by f coordinates $q_1 \cdots q_f$ and f conjugate momenta $p_1 \ldots p_f$ where f is the number of molecules in the system. The dynamics of the system is determined by the classical equations

$$\frac{dq_k}{dt} = \frac{\partial H(\underline{p},\underline{q})}{\partial p_k} \; ; \quad \frac{dp_k}{dt} = -\frac{\partial H(\underline{p},\underline{q})}{\partial q_k} \qquad (1.2)$$

Geometrically the state of the system may be represented by a point $x \equiv (\underline{q},\underline{p})$ in the $2f$ dimensional phase space also referred to in the literature as the Γ-space. Given the initial value of x, the solutions of the classical equations trace out a smooth trajectory in the Γ-space. In principle all information is contained in (1.2), but needless to say that for a macroscopic system with 10^{23} molecules, the specification of the initial conditions and an exact solution of the microscopic equations is beyond human means. Ideally even if it were possible to accomplish this it would hardly help in answering the questions asked in the description of a macroscopic phenomena. To bridge the gap between the two levels of description, introduction of statistical concepts, in particular, the concept of a Gibbs ensemble is unavoidable. We may learn a great deal about the status of phenomenological equations and how spontaneous fluctuations may arise by examining what an experiment on a macroscopic system means from the phase space point of view.

In correspondence with the macroscopic quantities $\bar{a}_i$ we now introduce phase space functions $a_i(x)$. The state of the system is specified in complete microscopic detail by the phase space point x in the Γ-space. Once the location of x is known each $a_i(x)$ may in principle be calculated. Each observation on the macroscopic system corresponds to determining the value of the phase space functions $a_i(x)$ with a certain precision Δa_i. We shall denote the set of all values accessible to $a_i(x)$ by a_i.

For each i and a given value of a_i the interval

$$a_i < a_i(x) < a_i + \Delta a_i \tag{1.3}$$

defines a slice in the Γ-space and the totality of such intervals divides the Γ-space into phase-space cell which we shall label by the index J. Each macroscopic observation corresponds to determining in which phase space cell the phase space point x is located. It is therefore clear that a macroscopic observation by no means fixes uniquely the position of the phase space point x; in fact there may be an infinity of phase space points which are all compatible with the macroscopic observation. Given the initial macroscopic state of the system all we know is that the phase space point x_0 is located somewhere in the appropriate phase space cell. As the system evolves the phase space point maps out a trajectory according to the classical equations and the phase space functions change from $\underline{a}(x_0)$

to $\underline{a}(x_t)$. If the experiment is repeated several times with the same macroscopic initial conditions, the overwhelming chances are that each time we would start with a different phase space point in the appropriate cell. One is thus led to an ensemble description in which the macroscopic observations are interpreted as an ensemble average over all possible points in the phase space which are compatible with the macroscopic initial conditions. Mathematically this may be expressed by introducing a phase space distribution function $\rho(x)$ which gives a certain weight to all possible microscopic configurations which are compatible with the initial conditons. Thus at $t=0$ we represent the macroscopic initial value $\bar{a}_i(0)$ as

$$\bar{a}_i(0) = \int dx_0 \, a_i(x_0) \, \rho(x_0) \tag{1.4}$$

and at a later time t the outcome as

$$\begin{aligned} \bar{a}_i(t) &= \int dx_0 \, a_i(x_t) \, \rho(x_0) \\ &= \int dx_0 \left[e^{Lt} a_i(x_0) \right] \rho(x_0) \end{aligned} \tag{1.5}$$

where L is the Liouvillian operator.

In practice, given the initial macroscopic state, the outcome of an experiment is fairly close to the ensemble average, i.e. macroscopic experiments are reproducible within the experimental precision. However, from the above considerations it also follows that we cannot exclude the possibility of fluctuations away from this average. Given the system Hamiltonian and the phase space distribution in principle, we ought to be able to calculate the magnitude of these fluctuations and find an alternative to the phenomenological equations when the fluctuations are large. In practice, however, this may be an arduous task and may involve all kinds of assumptions and approximations which may not be any better than the ones on the basis of which the phenomenological equations are derived. Also specification of the Hamiltonian and the precise form of the phase space distribution may not be always possible. The form of the phase space distribution, in equilibrium situations is now fairly well understood but in non equilibrium situations this still remains an open question. It is therefore clear that what we need is an intermediate level of description which goes beyond the macroscopic description through phenomenological equations in that it includes flutuations but avoids the problem of having to specify the Hamiltonian and the form of the phase space disbribution function. This level of description, to use van Kampen's terminology, will be referred to as the mesoscopic description. This is achieved by introducing the concept of an a - space in the following way.

The a-space consists of all possible realisable values of the phase space functions $a_i(x)$. Each point in a- space corresponds to a cell in Γ- space and thus we have a many to one mapping. Given a point in a- space at time $t = 0$ the phase space point x lies somewhere in, say, the cell J. Each time we repeat the experiment we are most likely to start from a different point in cell J . In each repetition, after a time t much larger than the typical microscopic time scale, the phase space points x_t may be located wide apart from each other owing to their different initial positions and we may get significantly different values for $a_i(x_t)$. It is clear therefore that the sample paths in a- space corresponding to several repetitions of a macroscopic experiment, resemble those of a random process. To characterise this random process in a- space we introduce the concept of an a- space probability $P(\underline{a},t)$. Specifically the probability that the values of the phase space functions $a_i(x)$ lie between a_i and $a_i + \Delta a_i$ at time t

$$a_i < a_i(x) < a_i + \Delta a_i \tag{1.6}$$

is given by

$$P(\underline{a},t)\,\Delta\underline{a} \equiv P(a_1 \cdots\cdots a_n, t)\,\Delta a_1 \cdots\cdots \Delta a_n \tag{1.7}$$

However the mere knowledge of $P(\underline{a},t)$ is not sufficient to characterise a random process. If we know that the phase space functions have a value $\underline{a}^{(1)}$ at time t_1 then this knowledge will influence the probability of finding a value $\underline{a}^{(2)}$ at time t_2. In other words the joint probability $P(a^{(2)}, t_2; a^{(1)}, t_1)$ cannot be inferred from the knowledge of $P(\underline{a}^{(1)}, t_1)$ Hence for a complete characterisation of the random process we must satisfy all the joint probabilities $P(\underline{a}^{(1)}, t_1)$, $P(\underline{a}^{(2)}, t_2; \underline{a}^{(1)}, t_1)$

$P(\underline{a}^{(3)}, t_3;\ \underline{a}^{(2)}, t_2;\ P(\underline{a}^{(1)}, t_1)\ \cdots$ and so on.

These joint probabilities are not all independent, they must be compatible with all the lower order ones.

$$\int d\underline{a}^{(k+1)} \cdots\cdots d\underline{a}^{(n)}\, P(\underline{a}^{(n)}, t_n; \cdots\cdots; \underline{a}^{(1)}, t_1) = P(\underline{a}^{(k)}, t_k; \cdots; \underline{a}^{(1)}, t_1) \tag{1.8}$$

for all $k < n$ whatever the values of the times $t_{k+1} \cdots t_n$. We may now try to classify these random processes according to the number of joint probabilities required for its complete characterisation with a view to finding which one of these offers the best description of the random process in a-space.

The simplest case is the one in which the knowledge of $P(\underline{a}^{(1)}, t_1)$ is sufficient. This process, referred to as the purely random process, satisfies the following

$$P(\underline{a}^{(2)}, t_2 ; \underline{a}^{(1)}, t_1) = P(\underline{a}^{(2)}, t_2)\, P(\underline{a}^{(1)}, t_1) \tag{1.9}$$

i.e. correlations in time are completely nonexistent. This process, however would be very unrealistic for describing a physical process because we know that at a microscopic level we have a completely causal description which must reflect itself in macroscopic dynamics.

The next simplest case and the most important one from statistical physics point of view is the Markov process. The whole information is contained in the joint probabilities $P(\underline{a}^{(1)}, t_1)$ and $P(\underline{a}^{(2)}, t_2 ; \underline{a}^{(1)}, t_1)$. To understand the physical circumstances a Markov process describes it is convenient to introduce the concept of a conditional probability

$$P(\underline{a}^{(2)}, t_2 \mid \underline{a}^{(1)}, t_1) \tag{1.10}$$

which expresses the probability that given the values $\underline{a}^{(1)}$ at t_1 we have values $\underline{a}^{(2)}$ at t_2, and is related to the joint probabilities through the relation

$$P(\underline{a}^{(2)}, t_2 ; \underline{a}^{(1)}, t_1) = P(\underline{a}^{(2)}, t_2 \mid \underline{a}^{(1)}, t_1)\, P(\underline{a}^{(1)}, t_1) \tag{1.11}$$

Higher order conditional probabilities $P(\underline{a}^{(3)}, t_3 | \underline{a}^{(2)}, t_2 | \underline{a}^{(1)}, t_1)$ etc. may analogously be defined.

A Markov process is defined by the following condition

$$P(\underline{a}^{(n)}, t_n | \underline{a}^{(n-1)}, t_{n-1} | \cdots | \underline{a}^{(1)}, t_1) = P(\underline{a}^{(n}, t_n | \underline{a}^{(n-1}, t_{n-1}) \qquad (1.12)$$

for $n \geqslant 2$. This equation implies that, in a Markov process the probability of transition at time t_{n-1} from a value $\underline{a}^{(n-1)}$ to a value $\underline{a}^{(n)}$ at time t_n depends only on the value of $\underline{a}$ at time t_{n-1} of the transition and not at all on the previous history of the system. This assumption is enough to show that a Markov process is completely specified once we know $P(\underline{a}^{(2)}, t_2 | \underline{a}^{(1)}, t_1)$ and $P(\underline{a}^{(1)}, t_1)$; all higher order joint probabilities may be expressed in terms of these.

Let us see if it is reasonable to assume that the random process in a-space may be regarded as a Markov process. Physically, the Markovian assumption (1.12) means that if we produce an arbitrary past history of a system by artificial means, i.e. by acting on the system from outside, the behaviour of the system after the outside influence has been stopped depends only on the state of the system at the time of stopping. Thus if a metal bar is heated at a varying rate and then isolated, its temperature distribution can only depend on the time of isolation. There must of course be a short time after the isolation during which the past history has some influence because of the continuity of physical phenomena at a microscopic level and hence as long as the difference between any two times between macroscopic observations is much longer relative to the microscopic time scale, Markovian assumption is reasonable.

Penrose[27] in his work on the foundations of statistical mechanics has examined the Markovian postulate in great detail together with other approaches to statistical mechanics such as the ergodic approach and the hypothesis of equal apriori probability. He concludes that certain interpretational difficulties which arise in the hypothesis of equal apriori probabilities, and certain problems encountered when the ergodic approach is extended to non equilibrium systems can only be resolved when supplemented with a Markovian Postulate. In fact he goes on to show that the concept of a Gibbs ensemble along with the Markovian assumption is sufficient to build a satisfactory theory of statistical physics rich enough to include both equilibrium and non equilibrium systems.

It must be made clear that the Markovian assumption can be valid only if certain conditions are satisfied. The first condition is that the time scale at which macroscopic observations are made must be much longer relative to that of the microscopic phenomena. The second and the most important requirement is that the set of macroscopic variables chosen to describe the system, and hence the set of phase space functions must be just right. Thus for example the phenomena of Brownian motion cannot be described by a Markov process if only the position of the

Brownian particle is taken as a macroscopic variable. It however becomes a Markov process if the velocity is also introduced as an observable. In general, the question of what variables to select so that the system may be described by a Markov process is a very difficult one and it still remains an open problem in statistical mechanics. Green[23] in his work has made some progress in this direction but the answer to this problem is yet far from being conclusive. All one can say is that the set of macroscopic quantities should not be too large otherwise the phase space cells would be too small with the result that the sample paths in a-space would no longer be those of a random process. On the other hand it should not be too small because then they would not fully describe the macroscopic aspects of the system.

If we assume the validity of the Markovian assumption, then it may be shown that the conditional probability satisfies the Chapman-Kolmogorov equation

$$P(\underline{a}^{(3)}, t_3 \mid \underline{a}^{(1)}, t_1) = \int d\underline{a}^{(2)}\, P(\underline{a}^{(3)}, t_3 \mid \underline{a}^{(2)}, t_2)\, P(\underline{a}^{(2)}, t_2 \mid \underline{a}^{(1)}, t_1) \tag{1.13}$$

A physical interpretation of this equation from phase space point of view may be found in van Kampen's work.[26]

Multiplying (1.13) by $P(\underline{a}^{(1)}, t_1)$ and integrating over $\underline{a}^{(1)}$ we have

$$P(\underline{a}^{(3)}, t_3) = \int d\underline{a}^{(2)}\, P(\underline{a}^{(3)}, t_3 \mid \underline{a}^{(2)}, t_2)\, P(\underline{a}^{(2)}, t_2) \tag{1.14}$$

Eqn. (1.14) may also be written in a differential form as

$$\frac{\partial P(\underline{a},t)}{\partial t} = \int d\underline{a}' [W(\underline{a}|\underline{a}') P(\underline{a}',t) - W(\underline{a}'|\underline{a}) P(\underline{a},t)] \quad (1.15)$$

where $W(\underline{a}|\underline{a}')$ represent the transition probabilities per unit time from $\underline{a}'$ to $\underline{a}$. This equation known as the master equation provides the desired mesoscopic description.

An alternative mesoscopic description is based on the analogy between the sample paths in a-space and that of a Brownian particle. Following the success of Langevin equation in describing Brownian motion, one writes an analogous equation for the sample paths in a space by adding a noise term to the macroscopic equation.

$$\frac{da_i}{dt} = F_i(\underline{a}) + \sum_j B_{ij}(\underline{a}) \xi_j(t) \quad (1.16)$$

The added noise terms are assumed to account for the fluctuations about the macroscopic motion. However, it must be borne in mind that this approach is valid under much stronger conditions than the master equation approach. An equation such as (1.16) or its equivalent Fokker Planck equation may be derived from the Chapman Kolmogorov equation under the assumption that $P(\underline{a}^{(2)}, t_2 | \underline{a}^{(1)}, t_1)$ depends only on $t_2 - t_1$ and that the third and higher transition moments satisfy the following

$$\int (a_i - a_i^{(0)})(a_k - a_k^{(0)})(a_l - a_l^{(0)}) P(\underline{a}, t | \underline{a}^{(0)}, t_0) d\underline{a}^{(0)} \quad (1.17)$$
$$= O[(t-t_0)^2]$$

1.3 Master Equation Description of Chemical Kinetics

To be able to describe a macroscopic system by a master equation we need to know the transition probabilities

$W(a|a')$. In principle we ought to be able to calculate these in terms of the phase space distribution function and the system Hamiltonian. Zwanzig[29] and Penrose[27] have shown how this may be accomplished. While Zwanzig starts with the Liouville equation and under certain assumptions derives the master equation, thus obtaining an expression for $W(a|a')$ in terms of the system Hamiltonian, Penrose chooses the Markovian assumption at the mesoscopic level and Gibbs ensemble description at a more fundamental level as the starting points and shows how one may establish contact between the two. However, the success of the master equation approach lies in the fact that in a large number of physical, chemical and biological systems, guided by the knowledge of the macroscopic equations, one can write down the transition probabilities by means of plausibility arguments.

Consider for example the chemical reaction

$$2X \xrightarrow{k_1} A \tag{1.18}$$

The traditional method of analysis of the reaction kinetics which may be found in any text book on chemical kinetics proceeds via the rate equations

$$\frac{dX}{dt} = -k_1 X^2 \tag{1.19}$$

where k_1 is the rate constant and X is the number of molecules of type X.

The master equation for this reaction may be written as

$$\frac{dP(X,t)}{dt} = W(X|X+2)\,P(X+2,t) - W(X-2|X)\,P(X) \tag{1.20}$$

Here $W(X|X+2)$ has the following interpretation: For a small time interval Δt, $W(X|X+2)\,\Delta t$ is the probability that out of $X+2$ molecules we start with two of them will react in the interval Δt so that the final number is X . This must, clearly, be equal to the probability that two molecules chosen at random will react in the interval Δt multiplied by the number of ways in which this reactable pair may be chosen. Thus

$$W(X|X+2)\,\Delta t = k_1 \Delta t\,(X+2)(X+1) \tag{1.21}$$

Therefore

$$W(X|X+2) = k_1 (X+2)(X+1) \tag{1.22}$$

Substituting this in (1.20) we have the desired master equation

$$\frac{dP(X,t)}{dt} = k_1 \left[(X+2)(X+1)\,P(X+2,t) - X(X-1)\,P(X,t)\right] \tag{1.23}$$

The equation for $\langle X \rangle$ calculated from (1.23) when the fluctuations are neglected, i.e. if we put average of a product equal to product of the average, is the same as the macroscopic equation (1.19). However, the master equation also enables us to calculate the fluctuations about this average.

It should be noted that the macroscopic equation may also be obtained from the master equation if, instead of

$$W(X|X+2) = (X+2)(X+1) \tag{1.24}$$

we had put

$$W(X|X+2) = X^2 \tag{1.25}$$

This is quite justified because the number of molecules is assumed to be large, and hence $(X+1)(X+2)$ is approximately equal to X^2. However, the correct choice of the combinatorial factors has one great advantage namely in the case of a reaction whose steady state is thermodynamic equilibrium, this choice gives Poisson distributions as an exact solutions of the master equation in the steady state. We shall discuss this in detail in Chapter 7.

The descritpion of a chemical system by the master equation (1.23) can be valid only if the system is spatially homogeneous. This is because in calculating $W(X|X+2)$ as in (1.21) we ascribed equal probability of reaction to a pair of molecules irrespective of their spatial locations. Physically this homogeneity may be achieved by an external stirring mechanism, this description would be valid provided that the conditions are such that the natural motions of the molecules keep the system well mixed. This circumstance would be realised if the non reactive (elastic) collisions between the molecules which have the effect of randomizing the positions of the molecules occur much more frequently than the reactive encounters. A detailed discussion of this point may be found in ref.[30]

From spatially homogeneous systems we may go a step further, and try to describe spatially inhomogeneous systems in which spatial diffusion is present. This may be accomplished by dividing the system into cells labelled by index i, with number of molecules $X(i)$ in cell i as the macroscopic variables. The master equation for the diffusion system may be written in analogy with the chemical master equation by regarding the process of diffusion as a chemical reaction

$$X(i) \xrightarrow{d_{ij}} X(j) \tag{1.26}$$

and using the combinatorial arguments as before. This is explained in Chapter 4. This will be an adequate description for an inhomogeneous chemical system in which the velocity distribution in each cell is of the Maxwell Boltzmann form and is not greatly perturbed by the chemical reactions.

A further step in simulating a realistic chemical system by a master equation is to incorporate the effects of changes brought about by molecular collisions. As has been shown by Brenig, Malek Mansour and Horsthemke,[31] the hydrodynamic effect may be taken into account by considering $X(i,r)$ as the macroscopic variables where r is the velocity index, and regarding molecular collisions as a chemical process

$$X(i,r) + X(i,s) \xrightarrow{\sigma(r,s;t,u)} X(i,t) + X(i,u) \tag{1.27}$$

taking place in each cell i. Here $\sigma(r,s;t,u)$ denotes the collision cross section. The macroscopic equation which this master equation purports to describe is one in which the coupling between the chemical reactions and the hydrodynamic effects are taken into account via a Boltzmann equation.

1.4 Langevin Equation Approach[32-34]

As we have seen earlier the Langevin equations or the equivalent Fokker-Planck equations follow from the Markovian postulate along with certain assumptions on the third and higher transition moments. For the latter assumptions one does not have any a priori justification. Even if their validity is taken for granted, one is faced with the problem of specifying the noise coefficients. Unlike the Langevin equation approach to Brownian motion, where the noise term represents a random force arising from the random collisions, the noise term in a chemical system or any other macroscopic system does not have any such interpretation and hence physical intuition cannot guide us in guessing what the noise coefficients should be.

In the context of chemical reactions, Langevin equations were espoused by Nitzan Ortoleva, Deutch and Ross[32] and most clearly enunciated by Keizer.[33] Their work relies on the assumption that the probability distribution in the large volume limit is asymptotically Gaussian. This assumption has been rigorously proved by Kurtz[35] by an asymptotic solution of the master equation. In these Langevin formulations of chemical kinetics, the macroscopic equation

$$\frac{d\bar{a}_i}{dt} = F_i(\underline{\bar{a}}) \tag{1.28}$$

are supplemented by a linear Langevin equation for the fluctuations $\delta\underline{a}$

$$\frac{d\,\delta a_i}{dt} = \sum_j A_{ij}\,\delta a_j + \sum_j g_{ij}(\underline{\bar{a}})\,\xi_j(t) \tag{1.29}$$

where $A_{ij} = \frac{\partial F_i}{\partial \bar{a}_j}$
is the relaxation matrix.

In the case of chemical systems whose steady state is the thermodynamic equilibrium, the noise coefficient $g_{ik}(\bar{\underline{a}})$ can be calculated by making use of the fluctuation dissipation theorem which is known to be valid in the thermodynamic equilibrium as has been shown by Gardiner[36] and Grossman[37]. The knowledge of the macroscopic equations is then enough to fix the noise coefficients. In non equilibrium situations, however, this is not possible and one cannot specify the noise coefficients without recourse to the master equation. In Keizer's work[33] the noise coefficients are determined by using an asymptotic form of the master equation in the Gaussian approximation which can be derived by using van Kampen's system size expansion.

Thus it is clear that the Langevin equation approach simply amounts to a transcription of the master equation in the Gaussian approximation, and this procedure, although convenient for calculational purposes, is not really a new approach for a mesoscopic description of chemical systems.

In recent years, in a specific context, some doubts were raised about the validity of master equation approach to chemical kinetics[19]. These criticisms have now been adequately answered by Görtz and Walls[38] and Oppenheim et al[39].

1.5 Outline of Following Chapters

A critical survey of the various system size expansion methods that have been developed for an asymptotic solution of the master equation is presented in Chapter 2. The Poisson representation method is introduced in Chapter 3 and it is shown how chemical master equations may be transformed into exact Fokker-Planck equations. In Chapter 4 this method is applied to chemical reactions whose steady state is the thermodynamic equilibrium, and the resulting solutions are examined from a statistical mechanics point of view. It is shown that the fluctuations in a small sub-volume in the limit of a large volume are always Poissonian. In Chapter 5 formulae for the two time correlation functions are derived and their relation to fluctuation-dissipation theorems is discussed. Stochastic differential equation methods are introduced in Chapter 6 where perturbative methods of solution in the context of chemical systems are also discussed. The lowest order approximation is shown to correspond to approximating Poisson-representation quasi-probability distribution by a Gaussian. The relation between this Gaussian approximation and the ones introduced in the other system size expansion methods is investigated. In Chapter 6 and 7 stochastic differential equation methods are applied to some representative examples of equilibrium and non-equilibrium reactions and it is shown how the variance and the two time correlation functions can be calculated in the Gaussian approximation together with the next higher corrections. In the cases where the system exhibits an instability, the corrections are shown to be divergent near the critical points. A model which exhibits a second order phase transition behaviour is studied in Chapter 9 taking into account spatial diffusion. The first two terms in a systematic expansion of the correlation functions are calculated. The relation between the divergence of the spatial correlation function near the critical point and the dimensionality of the system is examined. Chapter 10 contains a detailed discussion of a model which exhibits spatial and temporal oscillations beyond the instability point and the same model is used in Chapter 11 to demonstrate how the Poisson-representation methods may be used to calculate correlation functions in the case of finite systems with boundary conditions.

The basic idea on the usefulness of a Poisson expansion in the context of chemical master equations evolved out of discussions with Dr. C.W. Gardiner and Dr. D.F. Walls. A letter based on this work has since been published[44]. Subsequent work on extending this technique to multivariate master equation and into the realm of two time correlation functions was done in close collaboration with Dr. C.W. Gardiner. The calculations presented in Chapters 3,4, and 7-11, are the work of the author.[45,46] Contents of Chapter 10 and 11 developed out of work initiated by I.S. Matheson and Dr. D.F. Walls. This work is to be published in the Journal of Statistical Physics.[47]

CHAPTER 2

A REVIEW OF THE METHODS FOR SOLVING MARKOVIAN MASTER EQUATIONS.

2.1 Introduction

In the previous chapter we discussed the rationale behind a Markovian master equation approach for a stochastic description of physical systems, in particular, we discussed the validity of such an approach for chemical reaction systems. We now turn our attention to the various techniques that have been developed to solve such equations.

A general single variable Markovian master equation may be written in the following form

$$\frac{dP(X,t)}{dt} = \int dX'[W(X|X')P(X',t) - W(X'|X)\,P(X,t)] \tag{2.1}$$

This equation is assumed to provide a stochastic description of a system of size V , and characterised by an extensive variable or a macrovariable X . In (2.1) $P(X,t)$ denotes the probability of finding the macrovariable X at the value X at time t and $W(X|X')$ represents the transition probability per unit time from X' to X and may depend on t , although its time dependence will not be explicitly noted. Writing $W(X|X') = W(X', X-X') \equiv W(X',r)$ so that r is the size of the jump, (2.1) may be cast in the following form

$$\frac{dP(X,t)}{dt} = \int dr\,[W(X',r)\,P(X',t) - W(X,-r)\,P(X,t)] \tag{2.2}$$

The master equation (2.1), includes, as a special case, the birth-death master equations which may be written in the following form,

$$\frac{dP(X,t)}{dt} = \sum_r \left[W^{+(r)}(X-r)\,P(X-r,t) - W^{+(r)}(X)\,P(X,t) \right] + \sum_r \left[W^{-(r)}(X+r)\,P(X+r,t) - W^{-(r)}(X)\,P(X,t) \right] \tag{2.3}$$

in which variable X now takes only integer values.

2.2 Notation

We shall now state the notation used for various quantities which we shall come across in this chapter quite frequently.

The notation used is as follows:

(i) The nth moment of $P(X,t)$ will be denoted by $\langle X^n \rangle$ and the associated moment generating function by

$$Q(\xi) = \langle e^{i\xi X} \rangle \tag{2.4}$$

$$\langle X^n \rangle = \left[\frac{\partial^n Q}{\partial (i\xi)^n} \right]_{\xi = 0} \tag{2.5}$$

(ii) The nth factorial moment of $P(X,t)$ will be represented by $\langle X^n \rangle_f$ The factorial moments are related to the moments by the following equation

$$\langle X^n \rangle_f = \langle X(X-1) \cdots\cdots (X-n+1) \rangle \tag{2.6}$$

The factorial moment generating function will be denoted by

$$G(s) = \langle s^x \rangle \tag{2.7}$$

$$\langle x^n \rangle_f = \left[\frac{\partial^n G}{\partial s^n} \right]_{s=1} \tag{2.8}$$

(iii) The cumulants of $P(x,t)$ will be represented by q_n. The cumulant generating function will be denoted by $q(\xi)$ and is defined to be the logarithm of the moment generating function

$$q(\xi) = \ln Q(\xi) \tag{2.9}$$

and the cumulants q_n are defined to be the coefficients of $\frac{(i\xi)^n}{n!}$ in a power series expansion of $q(\xi)$ in ξ

$$q(\xi) = \sum \frac{(i\xi)^n}{n!} q_n(\xi) \tag{2.10}$$

$$q_n(\xi) = \left[\frac{\partial^n q(\xi)}{\partial (i\xi)^n} \right]_{\xi=0} \tag{2.11}$$

The relation between the cumulants and the moments may be obtained by differentiating both sides (2.9) with respect to $i\xi$ and setting $\xi = 0$

For $n = 1$ and 2 we have

$$q_1 = \langle x \rangle \tag{2.12}$$

$$q_2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{2.13}$$

The second cumulant is thus equal to the variance for which we shall often use the notation σ .

(iv) The factorial cumulants of $P(x,t)$ will be denoted by $[x^n]$. The factorial cumulant generating function will be denoted by $g(s)$ and is defined to be the logarithm of the factorial moment generating function $G(s)$

$$g(s) = \ln G(s) \tag{2.14}$$

The factorial cumulants are defined to be the coefficients of $\frac{(s-1)^n}{n!}$ in a power series expansion of $g(s)$ in $s-1$.

$$g(s) = \sum_{n=1}^{\infty} \frac{(s-1)^n}{n!} [x^n] \tag{2.15}$$

$$[x^n] = \left[\frac{\partial^n g}{\partial s^n}\right]_{s=1} \tag{2.16}$$

The relation between the factorial cumulants and the factorial moments may be obtained by differentiating both sides of (2.14) with respect to s and setting $s = 1$.

For $n = 1$ and 2 we have

$$[x] = \langle x \rangle \tag{2.17}$$

$$[x^2] = \langle x^2 \rangle_f - \langle x \rangle^2 \tag{2.18}$$

(v) The moments of the transition probabilities $W(x,r)$ will be denoted by

$$C_n(x) = \int dr\, r^n W(x,r) \tag{2.19}$$

In the case of birth-death master equations $C_n(X)$ are given by

$$C_n(X) = \sum_r r^n \left[(-1)^n W^{-(r)}(X) + W^{+(r)}(X) \right] \tag{2.20}$$

2.3 Assumptions regarding the transition probabilities

We shall assume that $W(X|X')$ depends on V in the following way

$$W(X|X') \equiv W(X',r) = V\left[\omega_0\left(\frac{X'}{V},r\right) + \frac{1}{V}\,\omega_1\left(\frac{X'}{V},r\right) + \quad \right] \tag{2.21}$$

i.e. the probability that a transition takes place from X' to X in an infinitesimal time interval is at least proportional to the size of the system. In a number of macroscopic systems this assumption is quite plausible. To see this let us consider a specific example of a chemical reaction

$$2X \longrightarrow A \tag{2.22}$$

The macrovariable here is the number of molecules X of the type X, and the system makes a transition from a state where one has $X+2$ molecules to a state where one has X molecules after the reaction has occurred. Let us now calculate the transition probability $W(X|X+2)$ Following an argument given by Kurtz[35], assume that the system is divided up into n boxes. Then the probability that a particular pair of molecules will collide and react in an infinitesimal time interval is proportional to the probability that two molecules placed at random in n boxes end up in the same box. This of course is proportional to $\frac{1}{n}$ and hence to V^{-1}. To obtain $W(X|X+2)$ we have to multiply this by the number of ways in which two molecules may be selected at random from $(X+2)$ molecules, i.e. by $(X+2)(X+1)$. Thus $W(X|X+2)$ is proportional to $V^{-1} \times V^{2} = V$. A number of other examples of macroscopic systems chosen from a wide variety of fields such as semiconductor physics, population dynamics, spin systems etc., may be found in the work of van Kampen[22,41] and Kubo et al,[42] where the volume dependence of $W(X|X')$ as given by (2.21) may be justified on the basis of physical arguments.

2.4 Methods for solving Markovian master equations

In this section we shall first consider the techniques developed by van Kampen[40,41] and Kubo et al,[42] which are aimed at an asymptotic solution of the general Markovian master equation (2.2). Then we shall go to more specialised techniques which are applicable only to birth-death master equations of the form (2.3). These include the method developed by Görtz and Walls,[38,43] the asymptotic techniques developed by Nicolis et al,[15] using the generating function method, and a factorization ansatz introduced by Gardiner etal.[18]

2.5 van Kampen's system size expansion[40,41]

Substituting (2.21) in (2.2) and assuming that w_1 etc are zero (although their presence does not materially alter the argument) one gets

$$\frac{dP(X,t)}{dt} = V\int dr\left[\, w_0\!\left(\frac{X-r}{V}, r\right) P(X-r,t) - w_0\!\left(\frac{X}{V}, -r\right) P(X,t)\right] \qquad (2.23)$$

The next setp in van Kampen's expansion consists in postulating the way in which $P(X,t)$ depends on V . It is assumed that $P(X,t)$ has a sharp peak located at some point $V x_0$ with a width of order $V^{1/2}$. Hence one transforms the variable X to a new variable x_1 as follows

$$X = V x_0 + V^{1/2} x_1 \qquad (2.24)$$

This transforms $P(X,t)$ into $\Pi(x_1,t)$ as follows

$$\Pi(x_1,t) = V^{1/2} P(V x_0 + V^{1/2} x_1, t) \qquad (2.25)$$

Substituting (2.24) and (2.25) in (2.23), (2.23) may be written as

$$\frac{\partial \Pi(x_1,t)}{\partial t} - V^{1/2}\frac{dx_0}{dt}\frac{\partial \Pi}{\partial x_1} = \int dr\left[-V^{1/2} r\frac{\partial}{\partial x_1} + \frac{1}{2} r^2 \frac{\partial^2}{\partial x_1^2} - \cdots\right] \times w_0(x_0 + V^{-1/2} x_1, r)\,\Pi(x_1,t) \qquad (2.26)$$

Expanding $w_0(x_0 + V^{-1/2} x_1, r)$ in a Taylor series and equating terms of order $V^{1/2}$ one obtains the macroscopic equation

$$\frac{dx_0}{dt} = C_1(x_0) \qquad (2.27)$$

and rest gives

$$\begin{aligned}\frac{\partial \Pi}{\partial t} = & -\frac{\partial}{\partial x_1}\left[C_1' x_1 + \frac{1}{2} V^{-1/2} C_1'' x_1^2 + \frac{1}{3!} V^{-1} C_1''' x_1^3 + \cdots\right]\Pi(x_1,t) \\ & + \frac{1}{2}\frac{\partial^2}{\partial x_1^2}\left[C_2 + V^{-1/2} C_2' x_1 + \frac{1}{2} V^{-1} C_2'' x_1^2 + \cdots\right]\Pi(x_1,t) \\ & - \frac{1}{3!}\frac{\partial^3}{\partial x_1^3}\left[V^{-1/2} C_3 + V^{-1} C_3' x_1 + \cdots\cdots\right]\Pi(x_1,t) \qquad (2.28) \\ & + \frac{1}{4!}\frac{\partial^4}{\partial x_1^4}\left[V^{-1} C_4 + \cdots\right]\Pi(x_1,t)\end{aligned}$$

where the primes on $C_n(x_0)$ denote differentiation with respect to x_0. In (2.28) all terms of order V^{-1} have been written. The structure of (2.28) is clear; each order of $V^{-1/2}$ adds one powers of x_1 to the coefficients and at the same time an additional derivative appears.

2.5.1 The Gaussian or the linear noise approximation

Retaining only the terms of order V^0 in (2.28) one obtains a linear Fokker-Planck equation with time dependent coefficients.

$$\frac{\partial \Pi}{\partial t} = \left[-\frac{\partial}{\partial x_1} C_1'(x_0)\, x_1 + \frac{1}{2}\frac{\partial^2}{\partial x_1^2} C_2(x_0)\right]\Pi(x_1,t) \qquad (2.29)$$

The solution of (2.29) is a Gaussian distribution with the mean and variance given by

$$\frac{d\langle x_1\rangle}{dt} = C_1'(x_0)\langle x_1\rangle \qquad (2.30)$$

$$\frac{d}{dt}\langle x_1^2\rangle = 2C_1'(x_0)\langle x_1^2\rangle + C_2(x_0) \qquad (2.31)$$

Equations for higher moments may easily be deduced from (2.29)

It is possible to improve the equation for $\langle X \rangle$ by one order without going beyond the linear noise approximation. This may be achieved by approximating (2.28) by the following equation

$$\frac{\partial \Pi}{\partial t} = -\frac{\partial}{\partial x_1}\left[C_1'(x_0)\, x_1 + \frac{1}{2} V^{-1/2} C_1''(x_0)\, x_1^2 \right] \Pi(x_1,t) + \frac{1}{2} \frac{\partial^2}{\partial x_1^2}\left[C_2(x_0)\right] \Pi(x_1,t) \tag{2.32}$$

which gives

$$\frac{d\langle x_1 \rangle}{dt} = C_1'(x_0)\langle x_1 \rangle + \frac{1}{2} V^{-1/2} C_1''(x_0)\langle x_1^2 \rangle \tag{2.33}$$

Thus to solve for $\langle x_1 \rangle$ and $\langle x_1^2 \rangle$ one has to now solve the coupled equations (2.31) and (2.33). The solution gives $\langle x \rangle$ to order V^0 and $\langle x^2 \rangle - \langle x \rangle^2$ to order V .

2.5.2 Higher order corrections

Beyond the Gaussian approximation the solution of (2.28) is impossible although the moments can be calculated to any given order quite straightforwardly. For example, to calculate next higher order corrections to the Gaussian approximation results for the mean and the variance one has to retain all the terms to order V^{-1} in (2.33). For the mean and variance this gives

$$\frac{d\langle x_1 \rangle}{dt} = C_1'\langle x_1 \rangle + \frac{1}{2} V^{-1/2} C_1''\langle x_1^2 \rangle + \frac{1}{3!} V^{-1} C_1'''\langle x_1^3 \rangle \tag{2.34}$$

$$\frac{d\langle x_1^2\rangle}{dt} = 2c_1'\langle x_1^2\rangle + V^{-1/2}c_1''\langle x_1^3\rangle + \frac{1}{3}V^{-1}c_1'''\langle x_1^3\rangle + c_2 + V^{-1}c_2'\langle x_1\rangle + V^{-1}\langle x_1\rangle \qquad (2.35)$$

From (2.34) and (2.35) it is clear that to calculate next higher correction to $\langle x_1\rangle$ and $\langle x_1^2\rangle$ we need $\langle x_1^3\rangle$ to order $V^{-1/2}$.

$$\frac{d}{dt}\langle x_1^3\rangle = 3c_1'\langle x_1^3\rangle + \frac{3}{2}V^{-1/2}c_1''\langle x_1^4\rangle + 3c_2\langle x_1\rangle + 3V^{-1/2}\langle x_1^2\rangle + V^{-1/2}c_3 \qquad (2.36)$$

which in turn requires $\langle x_1^4\rangle$ to order 1 .

$$\frac{d}{dt}\langle x_1^4\rangle = 4c_1'\langle x_1^3\rangle + 6c_2\langle x_1^2\rangle \qquad (2.37)$$

It is clear from (2.36) that $\langle x_1^3\rangle$ is of the order of $V^{-1/2}$ and hence we may drop the term $\frac{1}{3!}V^{-1}c_1'''\langle x_1^3\rangle$ in (2.34) and $\frac{1}{3}V^{-1}c_1'''\langle x_1^3\rangle$ in (1.21b) as they are of order $V^{-3/2}$ Equations (2.34) to (2.37) then determine $\langle x_1\rangle$ and $\langle x_1^2\rangle$ to the next order.

2.5.3 Two-time correlation functions

In the Gaussian approximation, the calculation of two time correlation function is trivial. First we solve (2.30) as a function of its initial value which gives

$$\langle x_1(t)\rangle_{x_1(0)} = e^{c_1'(x_0)}\,x_1(0) \qquad (2.38)$$

and then multiply (2.38) by $x_1(0)$ and replace the initial average $\langle x_1^2(0)\rangle$ by the steady average. Thus

$$\langle\langle x_1(t)\rangle_{x_1(0)}\ x_1(0)\rangle = e^{C_1'(x_0)}\langle x_1^2\rangle_{ss} \qquad (2.39)$$

To calculate next higher correction to (2.39) one has to solve (2.34) to (2.36) subject to the initial conditions $\langle x_1(0)\rangle = x_1(0)$, $\langle x_1^2(0)\rangle = x_1^2(0)$, $\langle x_1^3(0)\rangle = x_1^3(0)$ and thus calculate $\langle x_1(t)\rangle_{x_1(0)}$ to the desired order. The two time correlation function is then obtained by multiplying the result by $x_1(0)$ and replacing all the initial averages by the steady state averages.

2.5.4 Critical Fluctuations

The expansion outlined above is valid provided the macroscopic equation (2.27) has a stable solution, i.e. provided that

$$C_1'(x_0) < 0 \qquad (2.40)$$

If $C_1'(x_0) > 0$ then it can be seen from (2.31) that the fluctuations begin to grow exponentially and the expansion given above, which relies on the smallness of the fluctuations, breaks down. To obtain a reasonable picture of the behaviour of the fluctuations in such unstable situations, one replaces (2.24) by a more general decomposition

$$X = V x_0 + V^{p} x_1 \qquad 0 < p < 1 \qquad (2.41)$$

where p depends on the nature of the instability.

If the instability is such that the first $(q-1)$ derivatives of $C_1(\chi_0)$ vanish near the instability point while $C_1^{(q)}(\chi_0) \neq 0$, then van Kampen has shown that a consistent expansion of the master equation is possible with

$$p = \frac{q}{q+1} \tag{2.42}$$

and the most dominant terms in the expansion yield a non-linear Fokker Planck equations for $\Pi(\chi_1,t)$

$$\frac{\partial \Pi}{\partial t} = V^{-(q-1)/(q+1)} \left[\frac{1}{q!} C_1^{(q)} \frac{\partial}{\partial \chi_1} \chi_1^{q} + \frac{1}{2} C_2 \frac{\partial^2}{\partial \chi_1^2} + \cdots \right] \Pi \tag{2.43}$$

which gives

$$\frac{d\langle \chi_1 \rangle}{dt} = V^{-(q-1)/(q+1)} \frac{1}{q!} C_1^{(q)} \langle \chi_1^{q} \rangle \tag{2.44}$$

Note that the fluctuations vary on a slower time scale than the macroscopic quantity χ_0 which is still given by (2.27). Also when q is even it follows that positive fluctuations grow and the negative ones decay or vice versa depending on the sign of $C_1^{(q)}$ and according to (2.44) they even become infinite after a time of order $t \sim V^{(q-1)/(q+1)}$ but of course the expansion breaks down as soon as they are of order $\chi_1 \sim V^{1-p} = V^{-(q+1)}$ because then the distinction (2.41) between a macroscopic and a fluctuating part becomes undefined.

2.6 The system size expansion of Kubo et al[42]

In their work, Kubo Matsuo and Kitahara show that $P(X,t)$ obeying (2.2) has the following asymptotic form

$$P(X,t) = \epsilon\, P(x,t) = \exp\left[\frac{1}{\epsilon}\left\{\phi_0(x,t)+\epsilon\,\phi_1(x,t)+\cdots\right\}\right] \quad (2.45)$$

where $x = \frac{X}{V}$, $\epsilon = \frac{1}{V}$

They show that this form, although not unique, has the property that it propagates in time in the sense that if a solution of (2.23) has the form (2.45) then this form will be preserved at later times. This property is referred to by them as the extensive property of the probability distribution of a macrovariable.

We shall first outline their derivation of the evolution equations for the moments of $P(x,t)$ which are subsequently used to prove the extensive property of $P(x,t)$ Following Kubo et al,we then show how the extensive property of $P(x,t)$ may be utilised for its asymptotic construction.

2.6.1 Moment Equations

Equation (2.2) may formally be written as

$$\epsilon \frac{\partial}{\partial t} P(x,t) \doteq \int dr \left[\exp\left(-\epsilon r \frac{\partial}{\partial x}\right) - 1\right] w_0(x,r)\, P(x,t) \quad (2.46)$$

For the moment generating function $Q(\xi,t)$ defined by

$$Q(\xi,t) = \int dx\, e^{i\xi x}\, P(x,t) \quad (2.47)$$

one obtains from (2.46) after some simple algebraic manipulations, the following equation,

$$\frac{\partial}{\partial t} Q(\xi,t) = \frac{1}{2\pi} \int dr \int d\eta \int_0^r ds \; i\xi \, e^{i\epsilon\xi s} \, Q(\xi-\eta,t) \, \tilde{w}(\eta,r) \qquad (2.48)$$

where $\tilde{w}(\eta,r)$ is the Fourier transform of $w(x,r)$. Introducing the cumulant generating function $q(\xi,t)$ thus

$$Q(\xi,t) = \exp q(\xi,t) \qquad (2.49)$$

and assuming that $q(\xi,t)$ is analytic in ξ one obtains on expanding $q(\xi,t)$ in a power series in ξ

$$q(\xi,t) = \sum_{n=1}^{\infty} \frac{(i\xi)^n}{n!} q_n(t) \qquad (2.50)$$

the following equation for the cumulants $q_n(t)$

$$\frac{1}{n} \frac{dq_n(t)}{dt} = \frac{1}{2\pi} \int d\eta \int dr \, e^{q(-\eta,t)} \tilde{w}(\eta,r) \int_0^r ds \, m_{n-1}(\epsilon,s,\eta,t) \qquad (2.51)$$

where m_n are given by

$$\exp\left[i\xi s\epsilon + \sum_{n=1}^{\infty} \frac{(i\xi)^n}{n!} h_n(\eta,t) \right] = \sum_{n=0}^{\infty} \frac{(i\xi)^n}{n!} m_n(\epsilon,s,\eta,t) \qquad (2.52)$$

with

$$h_n(\eta,t) = \sum_{m=1}^{\infty} \frac{1}{m!} (i\eta)^m q_{n+m}(t) \qquad (2.53)$$

Assuming that $q_n(t)$ have the following expansion in powers of ϵ

$$q_n(t) = \sum_{m=0}^{\infty} \epsilon^{n+m-1} q_{n,m}(t) \qquad (2.54)$$

it follows from the definition of h_n and m_n that they have the following expansions

$$h_n(t) = \sum_{m=0}^{\infty} \epsilon^{n+m} h_{n,m} \tag{2.55}$$

and

$$m_n(t) = \sum_{m=0}^{\infty} \epsilon^{n+m} m_{m,n} \tag{2.56}$$

Substituting these expansions in (2.51) one finds that both sides of (2. 51) start from ϵ^{n-1} thus showing the consistency of the ansatz (2.54). On equating terms of like powers of ϵ on both sides one obtains evolution equations for q_{nm} the first few members of which are

$$\frac{dq_{10}}{dt} = c_1(q_{1,0}) \tag{2.57}$$

$$\frac{dq_{20}}{dt} = c_2(q_{1,0}) + 2c_1'(q_{1,0})\, q_{2,0} \tag{2.58}$$

$$\frac{dq_{1,1}}{dt} = c_1'(q_{1,0})\, q_{1,1} + \frac{1}{2} c_1''(q_{1,0})\, q_{2,0} \tag{2.59}$$

Making appropriate identifications these equations are identical to (2.30), (2.31) and (2.33) derived from van Kampen's expansion method. Equations for higher order corrections to q_2 i.e. the variance and higher moments may likewise be derived from (2.51).

2.6.2 Proof of the extensive property of $P(X,t)$

The ansatz (2.54) gives the following form for

$$Q(\xi,t) = \exp\left[\frac{1}{\epsilon}\left\{\psi_0(i\epsilon\xi,t) + \epsilon\psi_1(i\epsilon\xi,t) + \right\}\right] \tag{2.60}$$

with

$$\psi_k(u,t) = \sum_{n=1}^{\infty} \frac{u^n}{n!}\, q_{n,k}(t) \qquad (2.61)$$

This shows that if $Q(\xi,t)$ has the form (2.60) at time t_0 then with $q_{n,k}(t)$ determined by (2.51) this form is preserved at later time. An asymptotic evaluation of the Fourier inverse of $Q(\xi,t)$ then shows that $P(x,t)$ also has this property.

It should be noted that the proof outlined above assumes analyticity of $q(\xi,t)$, an assumption which breaks down near instability points and consequently the form (2.45) for $P(x,t)$ is not valid in critical regions.

2.6.3 Asymptotic construction of $P(x,t)$

Having proved that $P(x,t)$ has the form (2.45) at least in normal situations, one may solve for ϕ_0, ϕ_1 etc., in the following manner.

Substituting (2.45) in (2.46) one gets

$$\frac{\partial \phi_0}{\partial t} = \int dr \left[w(x,r) \left[\exp\left(-r\frac{\partial \phi_0}{\partial x}\right) - 1 \right] \right] \qquad (2.62)$$

$$\frac{\partial \phi_1}{\partial t} = \int dr \left[w(x,r) \left(\frac{1}{2} r^2 \frac{\partial^2 \phi_0}{\partial x^2} - r\frac{\partial \phi_1}{\partial x} \right) - r\frac{\partial w}{\partial x} \right] \exp\left(-r\frac{\partial \phi_0}{\partial x}\right) \qquad (2.63)$$

Putting

$$x = x_0 + y \qquad (2.64)$$

$$\phi_0(x,t) = g_0(y,t)$$

(2.62) becomes

$$\begin{aligned}\frac{\partial g_0}{\partial t} - \frac{d\chi_0}{dt}\frac{\partial g_0}{\partial y} &= \sum_{n=1}^{\infty} \frac{1}{n!}(-1)^n \left(\frac{\partial g_0}{\partial y}\right)^n c_n(\chi_0+y) \\ &= \sum_{n=1}^{\infty} \frac{1}{n!}(-1)^n \left(\frac{\partial g_0}{\partial y}\right)^n \left[c_n(\chi_0) + c_n'(\chi_0)\,y + \cdots\right]\end{aligned} \tag{2.65}$$

Choosing $\chi_0(t)$ such that

$$\frac{d\chi_0}{dt} = c_1(\chi_0) \tag{2.66}$$

we get

$$\begin{aligned}\frac{\partial g_0}{\partial t} &= -\left[c_1' y + \frac{1}{2} c_1'' y^2 + \cdots\right] \frac{\partial g_0}{\partial y} \\ &+ \frac{1}{2}\left[c_2 y + c_2' y + \cdots\right]\left(\frac{\partial g_0}{\partial y}\right)^2 \\ &+ \sum_{n=3}^{\infty} \frac{1}{n!}(-1)^n \left[c_n + c_n' y + \frac{c_n''}{2!} y^2 + \cdots\right]\left(\frac{\partial g_0}{\partial y}\right)^n\end{aligned} \tag{2.67}$$

To solve (2.67) one expands $g_0(y,t)$ in a power series in y.

$$g_0(y,t) = \sum_{n=2}^{\infty} a_n(t)\, y^n \tag{2.68}$$

which when substituted in (2.67) yields, on equating like powers of y, evolution equations for $a_n(t)$ the first few of which are

$$\begin{aligned}\frac{da_2}{dt} &= c_2(\chi_0) - 2c_1'(\chi_0)\, a_2 \\ \frac{da_3}{dt} &= 6c_2(\chi_0)\, a_2 a_3 - \frac{4}{3} c_2(\chi_0)\, a_2^3 - 3c_1(\chi_0)\, a_3 + 2c_2'(\chi_0)\, a_2^2 \\ &\quad - c_1'(\chi_0)\, a_2\end{aligned} \tag{2.69}$$

Equations (2.66) and (2.69) may, in principle, be solved successively thus enabling one to determine g_0 and hence ϕ_0. Having solved for ϕ_0 one may proceed to calculate ϕ_1 etc. and thus construct $P(x,t)$.

If only the quadratic term in y in (2.68) is retained the resulting $P(x,t)$ is a Gaussian with the variance $\sigma(t)$ related to $a_2(t)$ by

$$a_2(t) = -\frac{1}{2\sigma(t)}$$

and obeys

$$\frac{d\sigma(t)}{dt} = 2c_1'(x_0)\,\sigma + c_2(x_0) \tag{2.70}$$

which again is identical to the one obtained from van Kampen's procedure to the same degree of approximation.

2.6.4 Path integral representation of the master equation

Equation (2.46) may be written as

$$\epsilon \frac{\partial P(x,t)}{\partial t} = -H\left(x, \epsilon\frac{\partial}{\partial x}, t\right) P(x,t) \tag{2.71}$$

where

$$H(x,p,t) = \sum_r (1 - e^{-rp})\, w_0(x,r) \tag{2.72}$$

Written in this form, the master equation has a formal resemblance to the Schrodinger equation in quantum mechanics although the "Hamiltonian" is completely different from those encountered in quantum mechanics. Exploiting this formal analogy with the Schrodinger equation, Kubo et al derive the following path integral representation for the Green's function for the master equation (2.71)

$$P(x,t \mid x_0,t_0) = \int \mathcal{D}[x(s,\sigma)]\, \exp\left[\frac{1}{\epsilon}\int_{t_0}^{t} ds\, \mathcal{L}(x(s,\sigma), \dot{x}(s,\sigma))\right] \tag{2.73}$$

where the summation is made over all paths $x(s,\sigma)$, $t_0 \leqslant s \leqslant t$ which are parameterized by σ and satisfy the initial and final conditions $x(t_0) = x_0$, $x(t) = x$. The "Lagrangian" $\mathcal{L}$ is given by

$$\mathcal{L}(x,\dot{x},t) = -H(x,p,t) + \dot{x}p \tag{2.74}$$

and

$$\begin{aligned} \dot{x} &= \frac{\partial H(p,x,t)}{\partial t} \\ &= C_1(x) - C_2(x)p + \frac{1}{2}C_3(x)p^2 - \cdots \end{aligned} \tag{2.75}$$

The power series (2.75) may be inverted to give

$$p = p_0 + \frac{C_3}{2C_2}p_0^2 + \left(\frac{C_3^2}{2C_2^2} - \frac{C_4}{6C_2}\right)p_0^3 + \cdots \tag{2.76}$$

where

$$p_0 = \frac{C_1(x) - \dot{x}}{C_2(x)} \tag{2.77}$$

Substituting (2.76) in (2.74) one obtains

$$\mathcal{L}(x,\dot{x},t) = -C_2(x)\left[\frac{1}{2}p_0^2 + \frac{C_3}{6C_2}p_0^3 + \cdots\right] \tag{2.78}$$

Retaining only the first term in (2.78) one obtains

$$P(x,t\,|\,x_0,t_0) = \int \mathcal{D}[x(s,\sigma)]\, \exp\left[\int_{t_0}^{t} ds\, \mathcal{L}_G(x(s,\sigma),\dot{x}(s,\sigma))\right] \tag{2.79}$$

with

$$\mathcal{L}_G(x,\dot{x},t) = -\left[\frac{\dot{x} - C_1(x)}{C_2(x)}\right]^2 \tag{2.80}$$

Equation (2.79) is the Green's function for the master equation in the Gaussian approximation.

2.6.5 Two time averages

Using the path integral representation (2.79) for $p(x,t\,|\,x_0,t_0)$ in the Gaussian approximation Kitahara[21] has investigated two time averages for non-linear non-stationary systems. Of particular interest is the two time correlation function

$$\langle x(t), x(0)\rangle = \langle x(t)x(0)\rangle - \langle x(t)\rangle\langle x(0)\rangle \tag{2.81}$$

which in the steady state is shown to be given by

$$\langle x(t), x(0)\rangle = \left[\frac{\partial x_0(t\,|\,x_0',t_0)}{\partial x_0'}\right]_{x_0'=x_0(ss)} \left[\langle x^2\rangle - \langle x\rangle^2\right]_{ss} \tag{2.82}$$

where $x_0(t)$ obeys the macroscopic equation.

$$\frac{dx_0}{dt} = c_1(x_0) \quad . \tag{2.83}$$

and $x_0(t\,|\,x_0',t_0)$ denotes the solution of (2.83) subject to the initial conditions

$$x_0(t_0\,|\,x_0,t_0) = x_0' \tag{2.84}$$

2.6.6 Langevin Equations

Kitahara[21] has shown that the most probable path, i.e. the path that maximises the measure of the path integral (2.79) satisfies the following equations

$$\sigma_m : \quad \frac{dx}{dt} = c_1(x) \tag{2.85}$$

which of course is the macroscopic equation. Paths other than σ_m can be described by adding a noise to the macroscopic equation.

$$\dot{x}(t,\sigma) = C_1(x(t,\sigma)) + f(t,\sigma) \tag{2.86}$$

such that $f(t,\sigma_m) = 0$. Substituting (2.86) in (2.79) and expanding the Lagrangian about the most probable path one finds that $f(t,\sigma)$ is a Gaussian stochastic process with

$$\begin{aligned} \langle f(t,\sigma) \rangle &= O(\epsilon) \\ \langle f(s,\sigma) f(s',\sigma) \rangle &= \epsilon C_2(x(s,\sigma_m))\,\delta(s-s') \\ &\quad + O(\epsilon^2) \end{aligned} \tag{2.87}$$

Equation (2.86) together with (2.87) is the Langevin equation equivalent to the master equation in the Gaussian approximation.

2.6.7 Hamilton Jacobi technique

Using the extensive property of $P(x,t)$ i.e.

$$P(x,t) = \exp\left[\frac{1}{\epsilon}\,\phi_0(x,t)\right] \tag{2.88}$$

and the representation (2.71) for the master equation one finds that ϕ_0 obeys

$$\frac{\partial \phi_0(x,t)}{\partial t} + H\left(x, \frac{\partial \phi_0}{\partial x}\right) = 0 \tag{2.89}$$

which is similar to the Hamilton Jacobi equation encountered in classical mechanics. Making use of this analogy Kubo etal investigate the asymptotic stability of the solution of the master equation by studying the flow patterns in the phase space. Details may be found in the work of Kubo, Matsuo, Kitahara,[42] and Kitahara.[21]

2.7 The method of Görtz and Walls[38,43]

This method is applicable only to the birth-death master equations of the form (2.3). The method is based on transforming the master equation (2.3) into an equation for a function $q(X,t)$ defined as

$$q(X,t) = \frac{P(X+1,t)}{P(X,t)} \tag{2.90}$$

which is a slowly varying function of X as compared to $P(X,t)$.

If $q(X,t)$ is known, $P(X,t)$ may be found by the following relation

$$P(X,t) = P(0,t)\prod_{r=0}^{X-1} q(r,t) \tag{2.91}$$

2.7.1 The relation between $q(X,t)$ and the position and width of the peak of $P(X,t)$

Putting $x = \frac{X}{V}$ in (2.90) we get

$$q(x,t) = \frac{P(\frac{X+1}{V},t)}{P(\frac{X}{V},t)} = 1 + \frac{1}{V}\frac{d}{dx}\ln P(x,t) + O(\tfrac{1}{V^2}) \tag{2.92}$$

Thus

$$P(x,t) = P(0,t)\, e^{V\phi(x,t)} \tag{2.93}$$

with

$$\phi(x,t) = \int_0^x dx' \left[q(x',t) - 1\right] \tag{2.94}$$

The peak of $P(x,t)$ lies at

$$\frac{d\phi}{d\chi} = 0$$

i.e.

$$q(\chi_0(t)) = 1 \tag{2.95}$$

Expanding $\phi(\chi,t)$ around χ_0 by substituting

$$\chi = \chi_0(t) + V^{-1/2}\chi_1$$

we get

$$P(\chi,t) \approx C\, e^{\frac{1}{2}\left[\frac{\partial q(\chi,t)}{\partial \chi}\right]_{\chi=\chi_0} \chi_1^2} \tag{2.96}$$

a Gaussian with the variance

$$\sigma(t) = -\left[\frac{\partial q(\chi,t)}{\partial \chi}\right]^{-1}_{\chi=\chi_0} \tag{2.97}$$

2.7.2 Equation obeyed by $q(\chi,t)$

From the definition of $q(\chi,t)$ and (2.3) it follows that

$$\begin{aligned}\frac{\dot{q}(X,t)}{q(X,t)} = \sum_r \Big[& W^{+(r)}(X-r+1)\prod_{j=0}^{r-1} q^{-1}(X-j) - W^{+(r)}(X-r)\prod_{j=1}^{r} q^{-1}(X-j) \\ & + W^{-(r)}(X+r+1)\prod_{j=1}^{r} q(X+j) - W^{-(r)}(X+r)\prod_{j=0}^{r-1} q(X+j) \\ & - \left(W^{+(r)}(X+1) - W^{+(r)}(X)\right) \\ & - \left(W^{-(r)}(X+1) - W^{-(r)}(X)\right)\Big]\end{aligned} \tag{2.98}$$

Putting $\chi = \dfrac{X}{V}$,

$$W(X) = V\, W\left(\frac{X}{V}\right) = V\,\varpi(\chi)$$

one obtains on expanding $W\left(\frac{X+j+1}{V}\right)$ and $q\left(\frac{X+r}{V}\right)$ etc, thus

$$W\left(\frac{X+r}{V}\right) = w(x) + \frac{r}{V}\frac{\partial}{\partial x} w(x) + O\left(\frac{1}{V^2}\right)$$

$$q\left(\frac{X+r}{V}\right) = q(x) + \frac{r}{V}\frac{\partial}{\partial x} q(x) + O\left(\frac{1}{V^2}\right) \tag{2.99}$$

and neglecting terms of $O\left(\frac{1}{V^2}\right)$ the following equation for

$$\frac{\dot{q}(x,t)}{q(x,t)} = \sum_r \frac{\partial}{\partial x}\Big[w^{+(r)}(x)\, q^{-r}(x,t) + w^{-(r)}(x)\, q^{r}(x,t) - w^{+(r)}(x) - w^{-(r)}(x) \Big] \tag{2.100}$$

2.7.3 <u>Steady State solution</u>

The steady state solution of (2.100) invovles solving an algebraic equation for $q(x)$

$$\sum \Big[w^{+(r)}(x)\, q^{-r}(x) + w^{-(r)}(x)\, q^{r}(x) - w^{+(r)}(x) - w^{-(r)}(x) \Big] = 0 \tag{2.101}$$

Only one solution of (2.101) leads to a normalizable $P(x)$

Having found the $q(x)$ which does lead to a normalizable $P(x)$ the position of the peak and the variance may easily be calculated with the help of (2.95) and (2.97) and $P(x)$ itself, may be determined using (2.90). In particular if $r = 1$ this method gives a result identical to the exact result obtained by detailed balance which holds for single step birth-death master equations. Otherwise the solution for $P(x)$, obtained by this method is only approximate.

2.7.4 Moment equations

Implicit differentiation of (2.95) gives

$$\frac{dx_0}{dt} = -\frac{\dfrac{\partial q(x_0,t)}{\partial t}}{\dfrac{\partial q(x_0,t)}{\partial x_0}} \tag{2.102}$$

Using (2.100) it is easy to see that

$$\frac{dx_0}{dt} = C_1(x_0) \quad ; \; C_1(x_0) \equiv \sum_r r\left[w^{+(r)}(x_0) - w^{-(r)}(x_0)\right] \tag{2.103}$$

which is the familiar macroscopic equation.

From (2.100) one obtains the following equation for $\left[\dfrac{\partial q(x,t)}{\partial x}\right]_{x=x_0}$

$$\frac{d}{dt}\left(\frac{\partial q(x_0,t)}{\partial x_0}\right) = \left[\frac{\partial q(x_0,t)}{\partial x_0}\right]^2 C_2(x_0) - 2\,C_1'(x_0)\left[\frac{\partial q(x_0,t)}{\partial x_0}\right] \tag{2.104}$$

$$C_2(x_0) \equiv \sum_r r^2\left[w^{+(r)}(x_0) + w^{-(r)}(x_0)\right]$$

where terms proportional to $\dfrac{\partial^2 q}{\partial x_0^2}$ have been neglected.

Using (2.97) one obtains the familiar equation for σ

$$\frac{d\sigma}{dt} = C_2(x_0) + 2\,C_1'(x_0)\,\sigma(t) \tag{2.105}$$

2.8 Generating function method

A method useful for a further restricted class of master equations viz. birth-death master equations with $W^{\pm(r)}(x)$ polynomials in x is the generating function method introduced by Macquarrie.[9,10]

By introducing

$$G(s,t) = \sum_x s^x P(x,t) \tag{2.106}$$

the master equation may be transformed into a linear partial differential equation for $G(s,t)$. Successive differentiation of the generating function equation (GFE) with respect to s and evaluation of both sides at $s=1$ enables one to obtain equations for $\langle x^n \rangle_f$ in a straightforward manner.

Apart from a few simple cases the moment equations form a hierarchy and some approximation procedure is necessary for their solution.

In the following sections we shall be mainly concerned with the application of this technique to chemical master equations where $W^{\pm(q)}(X)$ have the following form

$$W^{\pm(q)}(X) = \sum_{\ell} a^{\pm}_{q,\ell} \cdot \frac{X!}{(X-\ell)!} \tag{2.107}$$

where $a^{\pm}_{q,\ell}$, which represent reaction rates, have the following volume dependence

$$a^{\pm}_{q,\ell} = V^{-\ell+1} \, \hat{a}^{\pm}_{q,\ell} \tag{2.108}$$

Thus

$$W^{\pm(q)}\left(\frac{X}{V}\right) = V\left[\, w^{\pm(q)}(x) + O\left(\tfrac{1}{V}\right)\right]$$

$$w^{\pm(q)}(x) = \hat{a}_{q,\ell}\, x^{\ell} \tag{2.109}$$

with $W^{\pm(q)}(X)$ given by (2.107) the GFE turns out to be

$$\frac{\partial G}{\partial t} = \sum_{q,\ell} (1-s^q)\, s^{\ell-q} \left(a^{-}_{q,\ell} - s^q a^{+}_{q,\ell} \right) \frac{\partial^{\ell} G}{\partial s^{\ell}} \tag{2.110}$$

which has been derived previously by Gardiner et al. [18]

2.8.1 Boundary conditions for the Generating Function Equation

If $max[l]=1$ in (2.110), the GFE may be solved by standard techniques for solving first order partial differential equations.

If $max[l]=m>1$ then the standard procedure to solve (2.110) is to put

$$G(s,t) = e^{-\lambda t} G_\lambda(s) \tag{2.111}$$

which yields an ordinary differential equation of order m for $G_\lambda(s)$ and in general has m linearly independent solutions. Only one of these m solutions gives a generating function that corresponds to an admissible probability distribution and hence in order to eliminate the extraneous solutions it is essential to impose boundary conditions on the equation for $G_\lambda(s)$. In a specific context, Mazo,[68] Malek-Mansour and Nicolis[19] have suggested the boundary conditions on the generating function equation. In the following, we shall formulate these boundary conditions from fairly general considerations. This, to our knowledge, has not been done before.

It follows from the definition of $G(s,t)$ that if $P(X,t)$ and all its moments exist then $G(s,t)$ is an analytic function of s on and inside the unit circle in the complex s plane. In particular $G_\lambda(s)$ and all its derivatives must exist at $s=-1$. In practice this criterion is sufficient to determine the solution of the GFE which corresponds to an admissible probability distribution.

Finiteness of $G_\lambda(s)$ and its derivatives at is guaranteed provided that $P(X,t)$ and all its moments do exist, something which is not guaranteed by the master equation itself. As a matter of fact it is possible to conceive a master equation where all moments beyond a certain order are divergent. In such cases all that one can require from general considerations is the analyticity of $G_\lambda(s)$ <u>inside</u> the unit circle.

2.8.2 Moment Equations

Apart from a few cases the solution of the GFE even in steady state is difficult. In any case, one is generally interested only in an asymptotic evaluation or better still an asymptotic expansion of the first few moments in powers of V^{-1}. A systematic procedure suggested by Nicolis et al[15] along the same lines as that due to Kubo et al[42] is to put

$$G(s,t) = e^{V\,g(s,t)} \tag{2.112}$$

in the GFE which yields the following equation for $g(s,t)$.

$$\frac{\partial g}{\partial t} = \sum_{q,\ell}(1-s^q)\,s^{\ell-q}\,(\hat{a}^-_{q,\ell} - s^q\hat{a}^+_{q,\ell})\left[\left(\frac{\partial g}{\partial s}\right)^{\ell} + \frac{\ell(\ell-1)}{V}\left(\frac{\partial g}{\partial s}\right)^{\ell-2}\left(\frac{\partial^2 g}{\partial s^2}\right) + O\!\left(\frac{1}{V^2}\right)\right] \tag{2.113}$$

$g(s,t)$ is the factorial cumulant generating function, i.e.

$$g(s,t) = \sum_{n=1}^{\infty}\left[\frac{\partial^n g}{\partial s^n}\right]_{s=1}\frac{(s-1)^n}{n!} \tag{2.114}$$

$$\left[\frac{\partial^n g}{\partial s^n}\right]_{s=1} = \frac{1}{V}[x^n] \tag{2.115}$$

If terms of $O(\frac{1}{V})$ and higher are neglected, the resulting equation yields evolution equations for factorial cumulants which are such that each factorial cumulant is related to itself and to the lower order ones only and hence can be solved successively. The equations for the first two factorial cumulant turn out to be

$$\frac{d\langle x\rangle}{dt} = \sum_{q\ell} q\,(a^{+}_{q,\ell} - a^{-}_{q,\ell})\langle x\rangle^{\ell} \equiv C_1(\langle x\rangle) \tag{2.116}$$

$$\begin{aligned}\frac{d}{dt}[x^2] &= \sum_{q,\ell}[q(q-1)(a^{+}_{q,\ell} - a^{-}_{q,\ell}) + 2q^2 a^{-}_{q,\ell} - 2q\ell(a^{-}_{q,\ell} - a^{+}_{q,\ell})]\langle x\rangle^{\ell} \\ &\quad + \sum_{q,\ell} 2[q(a^{+}_{q,\ell} - a^{-}_{q,\ell})\,\ell\langle x\rangle^{\ell-1}][x^2]\end{aligned} \tag{2.115}$$

From which it follows that the variance obeys

$$\begin{aligned}\frac{d\sigma}{dt} &= \sum_{q,\ell} q^2(a^{+}_{q,\ell} + a^{-}_{q,\ell})\langle x^{\ell}\rangle + 2\sum_{q\ell} q(a^{+}_{q,\ell} - a^{-}_{q,\ell})\,\ell\langle x\rangle^{\ell-1}\sigma \\ &\equiv C_2(\langle x\rangle) + 2C_1'(\langle x\rangle)\sigma\end{aligned} \tag{2.118}$$

Thus to $O(V)$ the mean and variance are given by equations identical to the ones obtained by methods outlined earlier.

2.8.3 Higher order approximations

To calculate $\langle x\rangle$ to order V^0 and to the variance to the leading order, the procedure is to retain the contribution from the term of order $\frac{1}{V}$ in (2.113) and to neglect its contribution to the variance equation. This leads to the following equation for

$$\frac{d\langle x\rangle}{dt} = C_1(\langle x\rangle) + \frac{V^{-1}}{2} C_2''(\langle x\rangle)\,\sigma \tag{2.119}$$

which now becomes coupled to the variance equation. Likewise evaluation of variance to the next order involves retaining terms of $O(V^{-2})$ in (2.113) and requires solution of three coupled equations and so on. Equations thus obtained are of course identical to those derived from van Kampen's or Kubo et al's method.

2.9 The Method of Gardiner et al[18]

To close the hierarchy of moment equations derivable from the master equation a method suggested by Gardiner etal consists in approximating $G(s,t)$ by a Gaussian, i.e. by retaining only the first two terms in (2.114).

$$g(s,t) = \frac{1}{V}\left[\langle x\rangle (s-1) + [x^2](s-1)^2\right] \tag{2.120}$$

This then implies that the third and higher moments factorize in terms of the first two. Thus for example

$$\langle x^3\rangle_f = 3\langle x^2\rangle_f \langle x\rangle - 2\langle x\rangle^3 \tag{2.121}$$

and the desired closure of the hierarchy of moment equations is thus achieved. In Chapter 6 we shall discuss the relation between this method and the Poisson representation method to be introduced later.

2.10 Some Critical Remarks

We have seen that, to the lowest order in a system size expansion, all the methods outlined above lead to the same results. The system size expansion of van Kampen that of Kubo et al and the generating function methods are systematic expansion methods in the sense that in principle it is possible to calculate next higher corrections. Of these three methods, in our opinion van Kampen's method is the most straightforward to use in practice if higher corrections to the moments and to the two time correlation functions are desired. An advantage of the method of Kubo et al over van Kampen's method is that, in principle, it enables one to asymptotically construct the probability distribution function.

The method of Görtz and Walls and that of Gardiner et al are not capable of being extended beyond the lowest order calculations and therefore do not constitute a systematic expansion procedure. An advantage of the method of Görtz and Walls is that in the case of birth-death master equations with polynomial transition probabilities, it enables one to asymptotically calculate the probability distribution function in the steady state.

In multivariate situations, the lowest order calculations may be done, using any of these methods with the exception of the method of Görtz and Walls which is incapable of handling multivariate master equations. The calculations using any of these methods may become rather cumbersome in multivariate situations and in particular when spatial diffusion is present.

CHAPTER 3

THE POISSON-REPRESENTATION METHOD

3.1 Introduction

In this chapter we shall introduce the Poisson representation method, a technique particularly suited for chemical master equations We shall show how this method enables one to transform chemical master equations into generalised Fokker-Planck equations. To illustrate the technique we shall consider, in detail, its application to a specific example.

From a mathematical point of view, this method is inspired by the Glauber-Sudarshan P- representation or the coherent state representation[48,49], a well known technique in quantum optics. We shall discuss the relation between the two methods.

3.2 The Poisson Representation Technique

The Poisson representation method is based on expanding the probability distribution $P(x,t)$ thus

$$P(x,t) = \mathcal{N} \int_C d\alpha \, e^{-\alpha} \frac{\alpha^x}{x!} f(\alpha,t) \tag{3.1}$$

where $\mathcal{N}$ is the normalisation factor and $f(\alpha,t)$ is the "Poisson-transform" of $P(x,t)$ and henceforth would be referred to as the quasi-probability distribution. The α - integration in (3.1) is to be carried out along the contour C which depends on the specific problem under consideration and will be left unspecified at this stage.

We saw in the last chapter that the moment equations derived from chemical master equations are most conveniently written in terms of factorial moments. A major advantage of the Poisson-representation is the following relation between the factorial moments of $P(X,t)$ and the ordinary moments of $f(\alpha,t)$

$$\langle X^r \rangle_f = \mathcal{N}\int d\alpha\, \alpha^r f(\alpha,t) = \langle \alpha^r \rangle \tag{3.2}$$

3.2.1 An Application

To illustrate the technique we shall consider the following example.

$$\begin{aligned} A + X &\xrightarrow{k_2} 2X \\ B + X &\underset{k_3}{\overset{k_1}{\rightleftharpoons}} C \end{aligned} \tag{3.3}$$

described by the master equation

$$\begin{aligned} \frac{dP(X,t)}{dt} = {} & k_1 B (X+1) P(X+1,t) + k_3 C\, P(X-1,t) \\ & + k_2 A (X-1)\, P(X-1,t) \\ & - [\, k_1 B X + k_3 C + k_2 A X\,]\, P(X,t) \end{aligned} \tag{3.4}$$

On substituting (3.1) in (3.4) and integrating by parts we get the following Fokker-Planck equation

$$\frac{\partial f(\alpha,t)}{\partial t} = -\frac{\partial}{\partial\alpha}\left[(K_3 V + (K_2 - K_1)\alpha) f(\alpha,t) - \frac{\partial}{\partial\alpha} K_2 \alpha f(\alpha,t) \right] \tag{3.5}$$

where we have defined

$$K_3 V = k_3 C \;, \quad k_1 B = K_1 \;, \quad k_2 A = K_2 \tag{3.6}$$

In deriving (3.5) it was assumed that the terms evaluated at the end points of the contour, which arise from integration by parts, vanish. This is so provided that $f(\alpha,t)$ and its first derivative vanish at the end points of the contour. Thus the choice of the contour C in (3.1) thus far unspecified, is made by solving (3.5) for $f(\alpha,t)$ and finding a contour such that $f(\alpha,t)$ and its first derivative vanish at its end points. Evidently the choice of C depends on the reaction mechanism in question.

Let us first consider the steady state solution of (3.5)

$$-\frac{d}{d\alpha}\left[(K_3V+(K_2-K_1)\alpha)f(\alpha) - \frac{d}{d\alpha}(K_2\alpha)f(\alpha)\right] = 0$$

$$\text{i.e.}\quad \frac{d}{d\alpha}K_2\alpha f(\alpha) - (K_3V+(K_2-K_1)\alpha)f(\alpha) = K \qquad (3.7)$$

where K is the constant of integration. This constant must be set equal to zero as is clear from the following argument. Let a and b be the end points of the contour C such that $f(\alpha)$ and its first derivative vanish at these points. Then integrating (3.9) from a to α we get

$$\left[(K_3V+(K_2-K_1)\alpha)f(\alpha) - \frac{d}{d\alpha}K_2\alpha f(\alpha)\right]_a \qquad (3.8)$$

$$-\left[(K_3V+(K_2-K_1)\alpha)f(\alpha) - \frac{d}{d\alpha}K_2\alpha f(\alpha)\right]_\alpha = 0$$

The first term in (3.8) vanishes from the boundary condition and the steady state solution is given by

$$\frac{d}{d\alpha}\left[K_2 \alpha f(\alpha) - (K_3 V + (K_2 - K_1)\alpha) f(\alpha) \right. = 0 \tag{3.9}$$

The above argument of course applies to any single variable Fokker-Planck equation.

The solution of (3. 7) is

$$f(\alpha) = \exp\left[- \frac{(K_1 - K_2)\alpha}{K_2}\right] \quad \alpha^{\left(\frac{K_3 V}{K_2} - 1\right)} \tag{3.10}$$

and obviously for $K_1 > K_2$ the contour C goes from 0 to ∞ .

To obtain the time dependent solution of (3.5) we put

$$f(\alpha, t) = e^{-\lambda t} f(\alpha)\, g_\lambda(\alpha) \tag{3.11}$$

in (3.5). This gives

$$K_2 \alpha \frac{d^2 g_\lambda}{d\alpha^2} + (K_3 V - (K_1 - K_2)\alpha) \frac{d g_\lambda}{d\alpha} + \lambda g_\lambda = 0 \tag{3.12}$$

which may be solved to give

$$g_\lambda(\alpha) = M\left(\frac{-\lambda}{K_1 - K_2}, \frac{K_3 V}{K_2}, \frac{K_1 - K_2}{K_2}\alpha\right) \tag{3.13}$$

where $M(a, b, z)$ is the confluent hypergeometric function.

Thus

$$f(\alpha, t) = e^{-\lambda t} e^{-\left(\frac{K_1 - K_2}{K_2}\right)\alpha} \alpha^{\left(\frac{K_3 V}{K_2} - 1\right)} M\left(\frac{-\lambda}{K_1 - K_2}, \frac{K_3 V}{K_2}, \frac{K_1 - K_2}{K_2}\alpha\right) \tag{3.14}$$

From the behaviour of $M\left(\frac{-\lambda}{K_1 - K_2}, \frac{K_3 V}{K_2}, \frac{K_1 - K_2}{K_2}\alpha\right)$, $\alpha \to \infty$ it follows that $f(\alpha, t)$ and its first derivative vanish as $\alpha \longrightarrow \infty$ provided that

$$\lambda = m(K_1 - K_2) \qquad (3.15)$$

where m is any positive integer. In that case the confluent hypergeometric function reduces to Laguerre polynomials and the desired solution of (3.5) is

$$f(\alpha,t) = e^{-\left(\frac{K_1-K_2}{K_2}\right)\alpha} \, \alpha^{\left(\frac{K_3V}{K_2}-1\right)} \sum_m a_m e^{-m(K_1-K_2)t} \, L_m^{\frac{K_3V}{K_2}-1}\left(\frac{K_1-K_2}{K_2}\alpha\right) \qquad (3.16)$$

where the a_m are determined by the initial conditions. To obtain $P(X,t)$ corresponding to (3.16), the α - integration is to be done along the contour $(0,\infty)$, for $f(\alpha,t)$ and its first derivative vanish at its end points.

The right hand side of (3.16) may be simplified if we choose $a_m = 1$ is which case we get

$$f(\alpha,t) = \left(\frac{\alpha}{\chi(t)}\right)^{\frac{K_3V}{K_2}} \frac{1}{\alpha} \, e^{-\frac{(K_1-K_2)}{K_2}\frac{\alpha}{\chi(t)}} \qquad (3.17)$$

with $\chi(t) = 1 - e^{-(K_1-K_2)t}$

It follows from (3.17) that the choice $a_m = 1$ corresponds to

$$f(\alpha,0) = \delta(\alpha) \qquad (3.18)$$

which in turn corresponds to

$$P(X,0) = \delta_{X,0} \qquad (3.19)$$

From (3.1) and (3.17) $P(x,t)$ and all its moments may be calculated exactly. Thus

$$\begin{aligned} \langle x^r \rangle_f &= [\chi(t)]^r \frac{\int_0^\infty \alpha^{\left(\frac{K_3V}{K_2}+r-1\right)} e^{-\left(\frac{K_1-K_2}{K_2}\right)\alpha} \, d\alpha}{\int_0^\infty \alpha^{\left(\frac{K_3V}{K_2}-1\right)} e^{-\left(\frac{K_1-K_2}{K_2}\right)\alpha} \, d\alpha} \\ &= [\chi(t)]^r \frac{\Gamma\left(\frac{K_3V}{K_2}+r\right)}{\Gamma\left(\frac{K_3V}{K_2}\right)} \end{aligned} \tag{3.20}$$

corresponding to the initial condition (3.19).

Thus, in this case, the Poisson representation technique yields an exact solution of the master equation (3.4). In particular, it illustrates how the contour of integration in (3.1) is to be chosen. Later in Chapter 7 we shall see, in the case of two bi-molecular reaction mechanisms, that, in general, there may be several contours of integration which satisfy the requirement necessary for the Fokker-Planck equation for $f(\alpha,t)$ to be equivalent to the master equation, namely $f(\alpha,t)$ and its first derivative must vanish at the end points of the contour of integration. However as we shall see that only one of these gives an admissible probability distribution and we shall also discuss the criteria which may be used to arrive at the correct choice.

3.2.2 The Fokker Planck Equation for a General Reaction

To avoid having to derive the Fokker-Planck equation in each individual situation we shall write down the Fokker-

Planck equation corresponding to a general reaction mechanism. From the structure of the general Fokker-Planck equation it will become clear how the Fokker-Planck equations for a specific case may be written down.

Consider a general n component reaction mechanism involving s reaction

$$\sum_{r=1}^{n} N_r^p X_r \underset{k_p^B}{\overset{k_p^F}{\rightleftharpoons}} \sum_{r=1}^{n} M_r^p X_r \quad ; p = 1 \cdots s \tag{3.21}$$

where $N_r^p (M_r^p)$ represents the number of molecules of type X_r that appear on the left hand side (right hand side) of the pth reaction and k_p^F, k_p^B are the corresponding forward and backward reaction rates.

The master equation for (3.21) is

$$\begin{aligned}\frac{dP(\underline{X},t)}{dt} = & \sum_{p=1}^{s} k_p^F \Big[\Big(\prod_{r=1}^{n} \frac{(X_r + N_r^p - M_r^p)!}{(X_r - M_r^p)!} \Big) P(\underline{X} + \underline{N}^p - \underline{M}^p, t) \\ & \quad - \Big(\prod_{r=1}^{n} \frac{X_r!}{(X_r - N_r^p)!} \Big) P(\underline{X},t) \Big] \\ & + \sum_{p=1}^{s} k_p^B \Big[\Big(\prod_{r=1}^{n} \frac{(X_r + M_r^p - N_r^p)!}{(X_r - N_r^p)!} P(\underline{X} + \underline{M}^p - \underline{N}^p, t) \\ & \quad - \Big(\prod_{r=1}^{n} \frac{X_r!}{(X_r - M_r^p)!} \Big) P(\underline{X},t) \Big]\end{aligned} \tag{3.22}$$

Generalising the Poisson representation to n variables

$$P(\underline{X},t) = \int_R d\underline{\alpha} \Big(\prod_{r=1}^{n} e^{-\alpha_r} \frac{\alpha_r^{X_r}}{X_r!} \Big) f(\underline{\alpha},t) \tag{3.23}$$

where R denotes the region of integration in $\underline{\alpha}$ space, we obtain on substituting (3.23) in (3.22) the Fokker-Planck equation corresponding to (3.21)

$$\frac{\partial f(\underline{\alpha},t)}{\partial t} = \sum_{p=1}^{S}\left[\prod_{r=1}^{n}\left(\frac{-\partial}{\partial\alpha_r}+1\right)^{M_r^p} - \prod_{r=1}^{n}\left(\frac{-\partial}{\partial\alpha_r}+1\right)^{N_r^p}\right] J_p(\underline{\alpha}) f(\underline{\alpha},t) \qquad (3.24)$$

where

$$J_p(\underline{\alpha}) = \left(\prod_{r=1}^{n} k_p^F \alpha_r^{N_r^p} - \prod_{r=1}^{n} k_p^B \alpha_r^{M_r^p}\right) \qquad (3.25)$$

Note that only a finite number of derivatives occur in (3.26). Again, as a generalisation of the single variable case, the region of integration R in (3.23) is such that $f(\underline{\alpha},t)$ and its appropriate derivatives vanish at its boundary.

If a particular component in (3.21) is held at a fixed concentration then the corresponding α variable in (3.24) should be set equal to a constant and the corresponding derivative dropped. This merely amounts to setting the appropriate M_r^p (N_r^p) equal to zero along with a redefinition of k_p^B (k_p^F).

It is evident from (3.24) that if $\sum_{r=1}^{n} M_r^p$ and $\sum_{r=1}^{n} N_r^p$ are not greater than two, i.e. if (3.21) involves only bimolecular reactions (which is almost always the case in realistic situations), then the Fokker-Planck equation (3.24) involves derivatives of no more than second order. When this is the case, (3.24) may be written as

$$\frac{\partial f(\underline{\alpha},t)}{\partial t} = -\sum_{r=1}^{n}\frac{\partial}{\partial\alpha_r}\left(\sum_{p=1}^{S} A_r^p J_p(\underline{\alpha})\right) f(\underline{\alpha},t) + \frac{1}{2}\sum_{r,s=1}^{n}\frac{\partial^2}{\partial\alpha_r\partial\alpha_s} B_{rs}[\underline{J}(\underline{\alpha})]\, f(\underline{\alpha},t) \qquad (3.26)$$

where

$$A_r^p = M_r^p - N_r^p \qquad (3.27)$$

and

$$\begin{aligned} B_{rs}[\underline{J}(\underline{\alpha})] = {} & \delta_{rs}\sum_{p=1}^{S}[M_r^p(M_r^p-1)-N_r^p(N_r^p-1)]J_p(\underline{\alpha}) \\ & +(1-\delta_{rs})\sum_{p=1}^{S}[M_r^p M_s^p - N_r^p N_s^p]J_p(\underline{\alpha}) \end{aligned} \qquad (3.28)$$

If trimolecular or higher order reactions are involved in (3.21) then (3.24) will contain third and higher order derivatives. However, as we shall see later, if only the dominant contributions to the moments in an asymptotic expansion in the inverse powers of the system size are required, then it will be sufficient to work with (3.26).

3.3 Poisson representation and the Glauber-Sudarshan P-representation

In quantum statistical problems, the analogue of a classical probability distribution function is the density operator which obeys the Liouville equation

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] \qquad (3.29)$$

where H is the Hamiltonian operator for the system. In the context of quantum optical problems where one is dealing with interaction of photons and atoms, the Hamiltonian H consists of three terms, the Hamiltonian for the photons, that for the field and a term which describes the interaction between the atoms and the photons. If one is only interested in the statistics of the photon field, then it is appropriate to trace over the atomic variables. This may be achieved by using projection techniques developed by Zwanzig.[50] Under Born and Markov approximation,[51,52] this yields a master equation for the photon denisty operator. These equations as such are, in general, inaccessible to analytic solutions. The solution of such problems is greatly facilitated by the use of Glauber-Sudarshan P-representation.

$$\rho(a,a^{\dagger},t) = \int \frac{d^2\beta}{\pi} |\beta\rangle\langle\beta| \,\bar{\rho}^{(a)}(\beta,\beta^*,t) \tag{3.30}$$

where a, $a^{\dagger}$ represents photon destruction and creation operators respectively, $|\beta\rangle$ is a coherent state, and $\bar{\rho}^{(a)}(\beta,\beta^*,t)$ is a c-number function of β,β^* obtained by writing $\rho(a,a^{\dagger},t)$ in an antinormal form and replacing a and $a^{\dagger}$ by β and β^* respectively.

Let us now consider the case when the density operator is diagonal in the number representation

$$\rho(a,a^{\dagger},t) = \sum_{n} P(n,t)\, |n\rangle\langle n| \tag{3.31}$$

where $|n\rangle$ is a number state, then from (3.30) we have the following representation for

$$P(n,t) = \int \frac{d^2\beta}{\pi}\, e^{-\beta\beta^*} \frac{(\beta\beta^*)^n}{n!}\, \bar{\rho}^{(a)}(\beta,\beta^*,t) \tag{3.32}$$

Also when (3.31) holds $\bar{\rho}^{(a)}(\beta,\beta^*,t)$ is a function of $\beta\beta^*$ only. Hence on introducing the variables

$$\beta = \sqrt{\alpha}\, e^{i\varphi} \tag{3.33}$$

in (3.32) and carrying out the trivial φ integral we obtain

$$P(n,t) = \int d\alpha \, e^{-\alpha} \frac{\alpha^n}{n!} \, \bar{P}^{(a)}(\alpha,t) \tag{3.34}$$

Now $P(n,t)$ has all the attributes of a classical probability distribution, i.e.

$$P(n,t) \geqslant 0 \quad , \quad \sum_n P(n,t) = 1 \tag{3.35}$$

and therefore (3.34) corresponds exactly to the expansion of a probability distribution in terms of Poisson distribution.

Thus it is clear that the Poisson representation is a special case of the more general Glauber-Sudarshan P- representation. It must be emphasized that the similarity between the two methods is only at a mathematical level, and from a physical point of view the systems under consideration in the two cases and the role the two representations play are quite different. In the quantum optical context, one is considering a quantum statistical ensemble of photons and the Poissonian nature of the photon number distribution arises when one has a single mode of the electromagnetic field, i.e. when one has a quantum mechanical coherent state. On the other hand the Poisson distribution in mean number of molecules in the context of chemical systems arises from the averaging of the grand canonical ensemble distribution in thermodynamic equilibrium over the many modes in which a chemically reacting molecule may exist. We shall see this in the next chapter. A further major difference between the two representations is the role which the quasi-probabilities $\bar{\varrho}^{a}(\beta,\beta^{*})$ in the Glauber-Sudarshan P- representation and $f(\alpha,t)$ in the Poisson - representation play in the description of the corresponding physical systems. $\bar{\varrho}^{(a)}(\beta,\beta^{*})$ is a measure of the deviation of the quantum optical system from the more interesting coherent behaviour, which occurs in a non equilibrium situation, whereas $f(\alpha)$ is a measure of the deviation of the chemical systems from the uninteresting Poissonian behaviour which arises in the thermodynamic equilibrium.

CHAPTER 4

FOKKER PLANCK EQUATIONS FOR EQUILIBRIUM REACTIONS

4.1 Introduction

This chapter is devoted entirely to the application of the Poisson representation method to chemical master equations corresponding to systems whose steady state is thermodynamic equilibrium. The steady state solution of these master equations are arbitrary up to multiplication by any function of the conserved quantities. To illustrate this point, let us consider a two component linear reaction

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y \tag{4.1}$$

described by the master equations

$$\begin{aligned}\frac{dP(X,Y,t)}{dt} = {} & k_1 \left[(X+1)\, P(X+1, Y-1,t) - X\, P(X,Y,t)\right] \\ & + k_2 \left[(Y+1)\, P(X-1, Y+1,t) - Y\, P(X,Y,t)\right]\end{aligned} \tag{4.2}$$

It is a trivial matter to check that the steady state solution of (4.2) is

$$P(X,Y) = \mathcal{N} \frac{(\hat{X})^X}{X!} \frac{(\hat{Y})^Y}{Y!} \phi(X+Y) \tag{4.3}$$

with

$$k_1 \hat{X} = k_2 \hat{Y} \tag{4.4}$$

and $\phi(X+Y)$ is any arbitrary function of $(X+Y)$ which in this case is the only conserved quantity.

From a physical point of view this arbitrariness in the solutions of the master equations for equilibrium systems arises from the arbitrariness in the choice of the ensemble chosen for a statistical description of the system.

If $\phi(X+Y)$ is chosen to be a constant, $P(X,Y)$ is a Poisson distribution

$$P(X,Y) = e^{-\hat{X}} e^{-\hat{Y}} \frac{(\hat{X})^X}{X!} \frac{(\hat{Y})^Y}{Y!} \qquad (4.5)$$

and if $\phi(X+Y)$ is set equal to $\delta_{X+Y,N}$, $P(X,Y)$ is a binomial distribution

$$P(X,Y) = \mathcal{N} \frac{(\hat{X})^X}{X!} \frac{(\hat{Y})^Y}{Y!} \delta_{X+Y,N} \qquad (4.6)$$

We shall show from purely statistical thermodynamic considerations, that under ideal gas or solution theory, a grand canonical ensemble description always gives Poisson distributions, whereas, the solutions of the type (4.6) which explicitly incorporate the conservation laws arise from a canonical ensemble description. We then show how these solutions are obtained from the corresponding Fokker-Planck equations. Next following Gardiner et al[18] and Kitahara,[21] we introduce a model for transport of reacting molecules from one spatial region to another and discuss the solutions of the associated Fokker-Planck equations. Finally we discuss the appropriateness of a grand canonical ensemble description and show that in the limit of a large system, the flucutations in a small subsystem are always Poissonian. In the past there has been a considerable discussion on the nature of fluctuations in a chemical system in thermodynamic equilbirium[19,55] and we hope that our analysis clarifies this question once and for all.

4.2 Statistical Mechanical Systems described by Chemical Master Equations: Grand Canonical and Canonical Ensembles in Thermodynamic Equilibrium

If we consider a reacting system

$$\sum_{r=1}^{n} N_r X_r \rightleftharpoons \sum_{r=1}^{n} M_r X_r$$

consisting of chemical components $X_1 \cdots X_r \cdots$ the thermodynamic equilibrium distribution function in the grand canonical ensemble is

$$P(I) = Z^{-1} \exp\left[\frac{1}{kT} \sum_r \mu_r X_r(I) - E(I)\right] \tag{4.7}$$

where the index I denotes the microscopic state of the system (here by"microscopic state" of the system we mean a particular configuration in the phase space). $X_r(I)$ is the number of molecules of X_r is the state I, $E(I)$ is the energy of the state, μ_r is the chemical potential corresponding to the component X_r and

$$Z = \sum_I \exp\left[\frac{1}{kT} \sum_r \mu_r X_r(I) - E(I)\right] \tag{4.8}$$

is the grand canonical partition function.

The fact that the components can react requires certain relations between the chemical potentials to be satisfied, since a state I can be transformed in a state J only if

$$\sum_r \nu_r^A X_r(I) = \sum_r \nu_r^A X_r(J) \; ; \quad A = 1 \cdots (n-1) \tag{4.9}$$

where ν_r^A are certain integers. The relations (4.9) are the stoiciometric constraints. One has $(n-1)$ such constraints n being the number of chemically reacting components in the system.

The canonical ensemble for a reacting system is defined by requiring

$$\sum_r \nu_r^A X_r(I) = \tau^A \tag{4.10}$$

whereas the grand canonical ensemble is defined by requiring

$$\sum_I P(I) \sum_r \nu_r^A X_r(I) = \sum_r \nu_r^A \langle X_r \rangle = \tau^A \tag{4.11}$$

Maximisation of entropy subject to the constraint (4.11) (and the usual constraints of fixed total probability and mean energy) gives the grand canonical form (4.7) in which the chemical potentials also satisfy the relation

$$\mu_r = \sum_A \kappa_A \nu_r^A \tag{4.12}$$

When one takes the ideal solution or gas limit, in which the interaction energies (but not the kinetic energies) are neglected, there is no difference between the distribution function for an ideal reacting system and an ideal non-reacting system, apart from the requirement that the chemical potentials are expressible in the form (4.12)

The distribution in the total numbers X_r of molecules of the reacting components in the grand canonical ensemble of an ideal reacting system is easily evaluated, namely

$$P(\underline{X}) = Z^{-1}\left(\exp\left[\frac{1}{kT}\sum_r \mu_r X_r\right]\right)\sum_I \delta_{X_r(I),\, X_r} \exp\left[-\frac{E(I)}{kT}\right] \tag{4.13}$$

The sum over states is the same as for the canonical ensemble of an ideal non reacting mixture so that

$$P(\underline{X}) = Z^{-1}\left(\exp\left[\frac{1}{kT}\sum_r \mu_r X_r\right]\right)\prod_r \frac{1}{X_r!}\left(\sum_\ell e^{-\frac{E_\ell(r)}{kT}}\right)^{X_r} \qquad (4.14)$$

where $E_\ell(r)$ are the energy eigenstate ℓ of a single molecule of type X_r. The result is a multivariate Poisson distribution with mean numbers given by

$$\log\langle X_r\rangle = \frac{\mu_r}{kT} + \log\left(\sum_\ell e^{-\frac{E_\ell(r)}{kT}}\right) \qquad (4.15)$$

which when combined with (4.11) and (4.12) gives the law of mass action as may be seen from the following considerations.

Since from (4.11) $\sum \nu_r^A \langle X_r\rangle$ is conserved, ν_r^A must be orthogonal to the changes in $\langle X_r\rangle$ produced by the reaction. Hence we have

$$\sum_r \nu_r^A (N_r - M_r) = 0 \qquad (4.16)$$

This when combined with (4.12) gives

$$\sum_r \mu_r (N_r - M_r) = 0 \qquad (4.17)$$

On substituting for μ_r from (4.15) we have

$$k_F \prod_{r=1}^{n} \langle X_r\rangle^{N_r} = k_B \prod_{r=1}^{n} \langle X_r\rangle^{M_r} \qquad (4.18)$$

where k_F and k_B may be identified as the forward and backward reaction rates.

The number distribution in the canonical ensemble is not so simple because now the entropy is to be maximised subject to the stronger constraint (4.10). However, as (4.10) implies the weaker constraint (4.11) all the manipulations leading to (4.14) are the same except that the constraint (4.10) must appear explicitly as a factor of the form

$$\prod_A \delta_{\sum_r \nu_r^A X_r(I),\, \tau^A} \tag{4.19}$$

The distribution function in total numbers for the canonical ensemble is therefore

$$P(\underline{X}) \propto \left[\prod_r \frac{1}{X_r!}\left(\sum_\ell e^{-\frac{E_\ell(r)}{kT}}\right)^{X_r}\right] \prod_A \delta_{\sum_r \nu_r^A X_r(I),\, \tau^A} \tag{4.20}$$

which is qualitatively different for every kind of reacting system (including a non reacting system as a special case).

4.3 Fokker Planck Equations for Equilibrium Reactions

4.3.1 A Linear Reaction

Let us again consider the two component linear reaction (4.1) described by the master equation (4.2). On substituting

$$P(X,Y,t) = \int_R d\alpha_x \, d\alpha_y \, \frac{\alpha_x^X}{X!} \, \frac{\alpha_y^Y}{Y!} \, e^{-\alpha_x-\alpha_y} f(\alpha_x,\alpha_y,t) \tag{4.21}$$

in (4.2) we get

$$\frac{\partial f(\underline{\alpha},t)}{\partial t} = \left(-\frac{\partial}{\partial \alpha_x} + \frac{\partial}{\partial \alpha_y}\right)(k_1\alpha_x - k_2\alpha_y) f(\alpha_x,\alpha_y,t) \tag{4.22}$$

The diffusion coefficient in the above Fokker Planck equation is zero. This is a characteristic feature of the Fokker Planck equations for linear reactions.

In the steady state a fairly general class of solutions of (4.22) may be written as

$$f(\alpha_x,\alpha_y,t) = \delta(k_1\alpha_x - k_2\alpha_y)\, \phi(\alpha_x,\alpha_y) \tag{4.23}$$

where $\phi(\alpha_X,\alpha_Y)$ is any arbitrary function of α_X and α_Y
If ϕ is chosen to be

$$\phi(\alpha_X,\alpha_Y) = \delta(\alpha_X - \bar{X}) \tag{4.24}$$

then we have

$$f(\alpha_X,\alpha_Y) = \delta(k_1\alpha_X - k_2\alpha_Y)\,\delta(\alpha_X - \bar{X}) \tag{4.25}$$

and the corresponding steady state distribution is

$$P(X,Y) = \int_R d\alpha_X\, d\alpha_Y\, e^{-\alpha_X-\alpha_Y} \frac{\alpha_X^{X}}{X!}\frac{\alpha_Y^{Y}}{Y!}\,\delta(k_1\alpha_X - k_2\alpha_Y)\,\delta(\alpha_X-\bar{X}) \tag{4.26}$$

where the region of integration R should be such that $f(\alpha_X,\alpha_Y)$ vanishes on its boundary. In this case, clearly R is any region in (α_X,α_Y) plane which contains the point where the arguments of the two delta functions in (4.25) vanish.

From (4.26) we get

$$P(X,Y) = e^{-\bar{X}-\bar{Y}} \frac{(\bar{X})^{X}}{X!}\frac{(\bar{Y})^{Y}}{Y!} \tag{4.27}$$

a Poisson distribution in X and Y, $\bar{X}$ and $\bar{Y}$ being related by the deterministic equation

$$k_1\bar{X} - k_2\bar{Y} = 0$$

If instead of (4.24) we choose $\phi(\alpha_X,\alpha_Y)$ to be

$$\phi(\alpha_X,\alpha_Y) = (-1)^N\,\delta^N(\alpha_Y)\,e^{\alpha_X+\alpha_Y} \tag{4.28}$$

where $\delta^N(\alpha_Y)$ is the Nth derivative of $\delta(\alpha_Y)$ with respect to α_Y, we obtain

$$P(X,Y) = \mathcal{N}\frac{(\hat{X})^{X}}{X!}\frac{(\hat{Y})^{Y}}{Y!}\,\delta_{X+Y,N} \tag{4.29}$$

with

$$k_1 \hat{X} = k_2 \hat{Y} = \frac{k_1 k_2}{k_1 + k_2} N \tag{4.30}$$

a binomial distribution corresponding to the canonical ensemble.

4.3.2 A Non-linear Reaction

Let us consider a reaction of the form

$$\ell W + m X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} p Y + q Z \tag{4.31}$$

Specialising (3.22) to the reaction (4.31), the Fokker Planck equation turns out to be

$$\frac{\partial f(\underline{\alpha},t)}{\partial t} = \left[\left(\frac{-\partial}{\partial \alpha_W}+1\right)^{\ell}\left(\frac{-\partial}{\partial \alpha_X}+1\right)^{m} - \left(\frac{-\partial}{\partial \alpha_Y}+1\right)^{p}\left(\frac{-\partial}{\partial \alpha_Z}+1\right)^{q}\right] \times \left[\left(k_2 \alpha_Y^{p} \alpha_Z^{q} - k_1 \alpha_W^{\ell} \alpha_X^{m}\right) f(\underline{\alpha},t)\right] \tag{4.32}$$

the steady state solution of which is of the form

$$\delta\left(k_1 \alpha_W^{\ell} \alpha_X^{m} - k_2 \alpha_Y^{p} \alpha_Z^{q}\right) \phi(\alpha_W, \alpha_X, \alpha_Y, \alpha_Z) \tag{4.33}$$

(we again require that the region of integration in $\underline{\alpha}$ plane be such that $f(\underline{\alpha},t)$ and its appropriate derivatives vanish on the boundary of the region of integration R) Different forms of $\phi(\alpha_W, \alpha_X, \alpha_Y, \alpha_Z)$ give different distributions for $P(W,X,Y,Z)$.

By choosing

$$\phi(\alpha_W, \alpha_X, \alpha_Y, \alpha_Z) = \delta(\alpha_W - \hat{W})\, \delta(\alpha_X - \hat{X})\, \delta(\alpha_Y - \hat{Y})\, \theta(\alpha_Z) \tag{4.34}$$

where $\theta(\alpha_Z)$ is the step function, we obtain the multi-

Poisson solution for $P(W,X,Y,Z)$

The alternative

$$\delta(k_1\alpha_W^{\ell}\alpha_X^{m} - k_2\alpha_Y^{p}\alpha_Z^{q})\,\phi(\alpha_W,\alpha_X,\alpha_Y,\alpha_Z)$$

$$= e^{\alpha_W+\alpha_X+\alpha_Y+\alpha_Z}\,\delta^K(-\alpha_W)\,\delta^M(-\alpha_X)\,\delta\left[\alpha_Z - \left(\frac{k_1\alpha_W^{\ell}\alpha_X^{m}}{k_2\alpha_Y^{p}}\right)^{\frac{1}{q}}\right] \tag{4.35}$$

gives the solution

$$P(W,X,Y,Z) = \frac{K!\,M!\,N!}{W!\,X!\,Y!\,Z!}\,\delta_{K,W+\frac{z\ell}{q}}\,\delta_{M,X+\frac{zm}{q}}\,\delta_{N,Y-\frac{pz}{q}}\left(\frac{k_1}{k_2}\right)^{\frac{z}{q}} \tag{4.36}$$

which is not normalised.

By defining

$$k_1\hat{W}^{\ell}\hat{X}^{m} = k_2\hat{Y}^{p}\hat{Z}^{q} \tag{4.37}$$

we can rewrite (4.36) as

$$P(W,X,Y,Z) = \mathcal{N}\,\frac{\hat{W}^W}{W!}\,\frac{\hat{X}^X}{X!}\,\frac{\hat{Y}^Y}{Y!}\,\frac{\hat{Z}^Z}{Z!}\,\delta_{K,W+\frac{z\ell}{q}}\,\delta_{M,X+\frac{zm}{q}}\,\delta_{N,Y-\frac{pz}{q}} \tag{4.38}$$

This corresponds to a canonical distribution. The conserved quantities for (4.31) are

$$A = mW - \ell X\ ,\quad B = qY - pZ,\quad C = pq(mW+\ell X) + m\ell(qY+pZ) \tag{4.39}$$

and the product of Kronecker deltas in (4.38) can be written as

$$\delta_{A,mK-\ell M}\,\delta_{B,qN}\,\delta_{C,m\ell qN+pq\ell M+pqmK} \tag{4.40}$$

Thus we find that the probability distributions which arise from the choice for ϕ given by (4.35) is a multivariate Poisson multiplied by Kronecker deltas which fix the values of the conserved quantities.

van Kampen[55] has shown that a general chemical Master equation admits solutions of the form (4.20) of which (4.38) is a special case.

It is clear that not all possible distributions of the canonical form are obtained by the choice (4.35) in which α_Z is integrated first, but by selecting α_W, α_X and α_Y in turn we can get every possibility.

4.3.3 General Solutions

The functions ϕ in the last two reactions are arbitrary and the most general solution corresponds to an arbitrary distribution over all values of the conserved quantities. However, these give from the statistical mechanics point of view, distributions which one does not normally consider. In order to keep close contact with statistical mechanics we have considered only the canonical and grand canonical distributions.

4.4 Reactions including Spatial Diffusion

Any realistic description of a chemical reaction must incorporate diffusion of reacting molecules from one spatial region to another. A number of authors have written chemical master equations which include diffusion as a stochastic process. In order to fix our notation we shall follow ref 18 and consider an arbitrary chemical reaction including diffusion of two species X and Y

Let us assume that the reaction-diffusion system is divided into n identical cells of a small but unspecified size, and is characterized by a multivariate probability distribution

$$P(X(1);\cdots X(i);\cdots X(n),\ Y(1)\cdots Y(j)\cdots Y(n)) \equiv P(\underline{X},\underline{Y}) \tag{4.41}$$

where the indices i, j lavel the positions of cells in space, and the quantities $X(i)$, $Y(i)$ are the numbers of molecules of the component X, Y in the cell i . A master equation which contains the possibility of reaction between X and Y as well as diffusion, the latter being viewed as a jump of a given molecule of $X(Y)$ from one cell i into cell j with probability d^X_{ij} (d^Y_{ij}) is

$$\begin{aligned}\frac{dP(\underline{X},Y)}{dt} &= \sum_{ij}\left[d^X_{ij}(X(i)+1)\,P(X(i)+1, X(j)-1, \hat{\underline{X}}, \hat{\underline{Y}}, t) - d^X_{ij}\,X(i)\,P(\underline{X},\underline{Y},t)\right]\\ &+ \sum_{ij}\left[d^Y_{ij}(Y(i)+1)\,P(Y(i)+1, Y(j)-1, \hat{\underline{X}}, \hat{\underline{Y}}, t) - d^Y_{ij}\,Y(i)\,P(\underline{X},Y,t)\right]\\ &+ \sum_i \left(\frac{\partial P}{\partial t}\right)_{i,\,chem}\end{aligned} \tag{4.42}$$

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

The chemical part $\left(\frac{\partial P}{\partial t}\right)_{i,chem}$ for each cell is determined from the appropriate reaction.

A simple choice for d_{ij} is to assume that

$$d_{ij} = \begin{cases} d & \text{adjacent} \\ 0 & \text{otherwise} \end{cases} \tag{4.43}$$

Using the Poisson representation, the master equation (4.42) transforms into the following Fokker Planck equation

$$\begin{aligned}\frac{\partial f(\underline{\alpha}_X,\underline{\alpha}_Y,t)}{\partial t} = &-\sum_i \frac{\partial}{\partial \alpha_X(i)}\left[\sum_j d_{ij}^X\,(\alpha_X(j)-\alpha_X(i))\,f(\underline{\alpha}_X,\underline{\alpha}_Y,t)\right]\\ &-\sum_i \frac{\partial}{\partial \alpha_Y(i)}\left[\sum_j d_{ij}^Y\,(\alpha_Y(j)-\alpha_Y(i))\,f(\underline{\alpha}_X,\underline{\alpha}_Y,t)\right]\\ &+\sum_i \left(\frac{\partial f(\underline{\alpha}_X,\underline{\alpha}_Y,t)}{\partial t}\right)_{i,\,\mathrm{chem}}\end{aligned} \qquad (4.44)$$

An important feature of the above Fokker Planck equation is that the noise arises only from the chemical terms and is entirely independent of the spatial diffusion which is a linear process. This considerably simplifies the treatment of reaction-diffusion systems.

Let us now consider the steady state solution of (4.44) for the reaction

$$\ell X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} mY \qquad (4.45)$$

Again, as before we have a certain arbitrariness in the steady state solution.

The choice

$$f(\alpha_X,\alpha_Y,t) = \prod_{i=1}^{n-1}\delta(\alpha_X(i)-\alpha_X(i+1))\prod_{i=1}^{n}\delta(k_1\alpha_X^{\ell}(i)-k_2\alpha_Y^{m}(i))\;\delta(\alpha_X(n)-\bar{X}) \qquad (4.46)$$

gives a multipoisson solution for $P(\underline{X},\underline{Y})$.

The alternative canonical form arises from

$$f(\underline{\alpha}_X,\underline{\alpha}_Y,t) = \prod_{i=1}^{n-1}\delta(\alpha_X(i)-\alpha_X(i+1))\prod_{i=1}^{n}\delta(k_1\alpha_X^{\ell}(i)-k_2\alpha_Y^{m}(i))\,\delta^{n}(\alpha_X(n)) \times (-1)^n\, e^{\sum_i \alpha_X(i)+\sum_i \alpha_Y(i)} \qquad (4.47)$$

which gives

$$P(\underline{X},\underline{Y}) = \prod_{i=1}^{n}\frac{(\hat{X})^{x_i}}{x_i!}\frac{(\hat{Y})^{y_i}}{y_i!}\,\delta_{\sum_{i=1}^{n}(m x_i+\ell y_i),\,N} \qquad (4.48)$$

4.5 Appropriateness of the Grand Canonical Ensemble and Poisson Distributions

It is usual to state that it is quite unimportant for physical purposes which ensemble is used and this is of course true. However what is unfortunately also true is that many stochastic master equations describe quite unphysical quantities, and in these cases, there may be very large differences between the two ensembles. This is no fault of the master equations - rather it is a fault of the investigator in choosing to study unmeasurable quantities. Consider for example the reaction (4.1) taking place in a macroscopic vessel e.g. a test tube. Then the grand canonical ensemble gives for variance and correlations

$$\sigma_{XX} = \langle X \rangle \quad , \quad \sigma_{YY} = \langle Y \rangle \quad , \quad \sigma_{XY} = 0 \tag{4.49}$$

while the canonical ensemble gives

$$\sigma_{XX} = \sigma_{YY} = \sigma_{XY} = \frac{\langle X \rangle \langle Y \rangle}{\langle X \rangle + \langle Y \rangle} \tag{4.50}$$

From the point of view of flucutations, there is a world of difference between the two ensembles. In practice, as is well known, it is quite impossible to measure these quantities for a macroscopic system and the choice of which ensemble to use is purely a matter of taste, as both results are equally irrelevant to physics.

What are of interest, though, are locally fluctuating quantities. In such a case one divides the system into cells labelled i as suggested in section 3.3 and introduces local numbers $X_r(i)$. Since transport can occur between cells, all stoichiometric relations will include summation over all cells, i.e. (4.10) becomes

$$\sum_r \nu_r^A \sum_i X_r(i) = \tau^A \tag{4.51}$$

and one obtains for the grand canonical distribution

$$P(\underline{X}) = Z^{-1}\left(\exp\left[\frac{1}{RT}\sum_{r,i} \mu_r X_r(i)\right]\right) \prod_{r,i} \frac{1}{X_r(i)!}\left(\sum_\ell e^{-\frac{E_\ell(r)}{RT}}\right)^{X_r(i)} \tag{4.52}$$

and for the canonical distribution

$$P(\underline{X}) \propto \prod_A \delta_{\sum_{r,i}\nu_r^A X_r(i),\, \tau^A} \prod_{r,i} \frac{1}{X_r(i)!}\left(\sum_\ell e^{-\frac{E_\ell(r)}{RT}}\right)^{X_r(i)} \tag{4.53}$$

In the next sub-section we show that as far as the fluctuations in a small sybsystem in the limit of a large system are concerned, the two descriptions are equivalent and at this level the behaviour of the fluctuations is always Poissonian regardless of the choice of canonical or grand canonical ensemble description. Since the grand canonical ensemble description is so much easier to work with we shall take that to be the basis of our study of the chemically reacting systems in thermodynamic equilibrium.

4.5.1 Local Fluctuations in the Grand Canonical and Canonical Ensembles: Poisson Distributions

Let us consider the canonical distribution (4.48) for the reaction (4.45). Then on introducing the following representation for the Kronecker delta

$$\delta_{\sum_i m X(i) + \ell Y(i),\, N} = \frac{1}{2\pi i} \oint dz\, z^{-N-1+\sum_i m X(i) + \sum_i \ell Y(i)} \qquad (4.54)$$

where the contour encircles the origin, we have

$$P(\underline{X},\underline{Y}) = \frac{\mathcal{N}}{2\pi i} \oint dz\, z^{-N-1} \prod_{j=1}^{n} \frac{(\hat{X} z^{m})^{X(j)}}{X(j)!} \frac{(\hat{Y} z^{\ell})^{Y(j)}}{Y(j)!} \qquad (4.55)$$

We now wish to project this probability distribution corresponding to a volume V consisting of n cells into a small volume ΔV consisting of say r cells. This is most conveniently accomplished by defining the generating function

$$G_n(\underline{s},\underline{t}) = \sum_{\underline{X},\underline{Y}} \left(\prod_{i=1}^{n} s_i^{X(i)} t_i^{Y(i)} \right) P(\underline{X},\underline{Y}) \qquad (4.56)$$

$$= \frac{N}{2\pi i} \oint \frac{dz}{z} z^{-N} \exp\left[\sum_{i=1}^{n} \hat{X} z^{m} s_i + \hat{Y} z^{\ell} t_i \right] \qquad (4.57)$$

The desired projection is then achieved by setting $s_i = t_i = 1$ for all i not contained in ΔV. The projected generating function then is

$$G_r(\underline{s},t) = \frac{\mathcal{N}}{2\pi i} \oint \frac{dz}{z} z^{-N} \exp\left[n(\hat{X} z^{m} + \hat{Y} z^{\ell}) + \sum_{i \in \Delta V} [\hat{X}(s_i - 1) z^{m} + \hat{Y}(t_i - 1) z^{\ell}] \right] \qquad (4.58)$$

Note that since $\hat{X}$ and $\hat{Y}$ are not equal (although proportional) to $\langle X(i) \rangle$ and $\langle Y(i) \rangle$ one does not necessarily have

$$n[m\hat{X} + \ell\hat{Y}] = N \qquad (4.59)$$

However, because of the delta function on the RHS of (4.57) we may always scale $\hat{X}$ and $\hat{Y}$ by the transformation $\hat{X} \to \lambda^{m}\hat{X}$, $\hat{Y} \to \lambda^{m}\hat{Y}$ altering only the normalisation in such a way that (4.59) is satisfied. Assuming that $\hat{X}$ and $\hat{Y}$ have been chosen thus, on substituting

$$\begin{aligned} n\hat{x} &= \frac{N}{m}\beta \\ n\hat{y} &= \frac{N}{\ell}(1-\beta) \end{aligned} \tag{4.60}$$

in (4.58) we get

$$G_r(\underline{s},\underline{t}) = \frac{N}{2\pi i}\oint \frac{dz}{z}\exp\Big[N\Big(\frac{z^m}{m}\beta+\frac{z^\ell}{\ell}(1-\beta)-\log z\Big) + \sum_{i\in\Delta V}[\hat{x}z^m(s_i-1)+\hat{y}z^\ell(t_i-1)]\Big] \tag{4.61}$$

In the limit $N\to\infty$ the integral may be evaluated asymptotically by the saddle point method. The saddle points are given by

$$\frac{d}{dz}\Big[\frac{z^m}{m}\beta + \frac{z^\ell}{\ell}(1-\beta) - \log z\Big] = 0 \tag{4.62}$$

which gives

$$z^m\beta + z^\ell(1-\beta) - 1 = 0 \tag{4.63}$$

which has a root at $z = 1$. For small values of the integers ℓ and m it may be checked that $z = 1$ is the root that gives the most dominant contribution to the integral and we conjecture that it is always the dominant root. Hence

$$G_r(\underline{s},\underline{t}) \xrightarrow[\frac{n}{N}\text{ finite}]{N\to\infty} \exp\Big[\sum_{i\in\Delta V}\hat{x}(s_i-1)+\hat{y}(t_i-1)\Big] \tag{4.64}$$

which is the generating function corresponding to a multivariate Poisson distribution. Similar considerations apply to more general reactions.

From a physical point of view this result is obvious. All it says is that the correlations which may arise from global conservation laws have little effect on local fluctuations; the correlations which the global conservation laws give rise to are continuously broken up by the process of diffusion.

These considerations provide a physical rationale for choosing Poisson distributions as a basis in which to expand a probability distribution. In non equilibrium system such an expansion has the effect of factoring out equilibrium fluctuations leaving only the effects that arise from the non equilibrium nature of the system.

CHAPTER 5

THE TWO TIME CORRELATION FUNCTIONS

5.1 Introduction

In the second chapter we saw that the single time averages of $P(\underline{X},t)$ bear a simple relationship to those of $f(\underline{\alpha},t)$ the single time factorial moments of $P(\underline{X},t)$ being equal to the ordinary moments of $f(\underline{\alpha},t)$. In this chapter we shall investigate how the two time averages of $P(\underline{X},t)$ translate into Poisson notation. The formulae, although not as simple as those for single time averages, have, from a physical point of view a very appealing stucture. For equilibrium systems, they relate the two time correlation function in $\underline{X}$ - space to certain response functions in α - space and are analogous to the results obtained by Bernard and Callen.[56,57] The results of Bernard and Callen constitute a new kind of fluctuation-dissipation theorem and we shall show how these may be obtained from purely statistical mechanical considerations. In the case of non equilibrium systems one has in addition to the response functions, an extra term which arises entirely from the non-equilibrium nature of the system. Finally we shall show how our formulae may be mathematically deduced from those derived in quantum optical context, using Glauber-Sudarshan P- representation.

5.2 Basic Formulae for Two Time Correlation Functions

The two time correlation function is directly related to the mean product function

$$\langle x_r(t)\, x_s(t')\rangle = \sum_{\underline{x},\underline{x}'} x_r\, x_s\, P(\underline{x},t\,|\,\underline{x}',t')\, P(\underline{x}',t') \qquad (5.1)$$

where $P(\underline{x}',t)$ is the unconditional probability that the system is in a state $\underline{x}'$ at time t' and $P(\underline{x},t\,|\,\underline{x}',t')$ is the conditional probability that the system is in state $\underline{x}$ at time t given that it was in state $\underline{x}'$ at time t'. Both $P(\underline{x}',t')$ and $P(\underline{x},t\,|\,\underline{x}',t')$ will obey a master equation over respectively the variables $\underline{x}', t'$ and $\underline{x}, t$. In transforming to the Poisson representation, we must transform both of these, and this is not straightforward. We will wish to express our results in terms of appropriate Poisson-quasiprobability.

We note that

$$P(\underline{x}',t') = \int d\underline{\alpha}' \left[\prod_k e^{-\alpha_k'} \frac{\alpha_k'^{\,x_k'}}{x_k'!}\right] f(\underline{\alpha}',t) \qquad (5.2)$$

which defines $f(\underline{\alpha}',t')$

We now define $f(\underline{\alpha},t\,|\,\underline{x}',t')$ by

$$P(\underline{x},t\,|\,\underline{x}',t') = \int d\underline{\alpha} \left[\prod_i e^{-\alpha_i} \frac{\alpha_i^{x_i}}{x_i!}\right] f(\underline{\alpha},t\,|\,\underline{x}',t') \qquad (5.3)$$

So that $f(\underline{\alpha},t\,|\,\underline{x}',t')$ is the quasiprobability in $\underline{\alpha}$-space arising from an initially sharp $\underline{x}$-space state. Noting that

$$P(\underline{x},t'\,|\,\underline{x}',t') = \delta_{\underline{x},\underline{x}'} \qquad (5.4)$$

we see that

$$f(\underline{\alpha},t'\,|\,\underline{x}',t') = \prod_j \left[e^{\alpha_j} (-1)^{x_j'}\, \delta^{x_j'}(\alpha_j)\right] \qquad (5.5)$$

We now define the $\underline{\alpha}$-space conditional probability $f(\underline{\alpha},t\,|\,\underline{\alpha}',t')$ to be conditional $\underline{\alpha}$-space probability of the system being in the state $\underline{\alpha}$ at time t, given that it was in state $\underline{\alpha}'$ at time t', so that it will be the solution to the $\underline{\alpha}$ space Fokker-Planck equation with the initial condition

$$f(\underline{\alpha},t'\,|\,\underline{\alpha}',t') = \delta(\underline{\alpha}-\underline{\alpha}') \tag{5.6}$$

Since the Fokker-Planck equation is a linear equation we find that

$$f(\underline{\alpha},t\,|\,\underline{X}',t) = \int d\underline{\alpha}'' \prod_j \left[e^{\alpha_j''}(-1)^{X_j'}\delta^{X_j'}(\alpha_j'')\right] f(\underline{\alpha},t\,|\,\underline{\alpha}'',t) \tag{5.7}$$

We now substitute (5.7), (5.3) and (5.2) into (5.1) and get

$$\begin{aligned}\langle X_r(t)\,X_s(t')\rangle = \sum_{\underline{X},\underline{X}'} X_r X_s' \int d\underline{\alpha}\, d\underline{\alpha}'\, d\underline{\alpha}'' \prod_i \left[e^{-\alpha_i}\frac{\alpha_i^{X_i}}{X_i!}\right] \prod_j e^{\alpha_j''}(-1)^{X_j'}\delta^{X_j'}(\alpha_j'') \\ \prod_k \left[e^{-\alpha_k'}\frac{\alpha_k'^{X_k'}}{X_k'!}\right] \\ f(\underline{\alpha},t\,|\,\underline{\alpha}'',t')\, f(\underline{\alpha}',t')\end{aligned} \tag{5.8}$$

In (5.8) sum over $\underline{X}$ is trivial. It merely replaces X_r by α_r. Sum over $\underline{X}'$ involves two types of terms.

$$\sum_{X_s'} e^{\alpha_s''-\alpha_s'}(-1)^{X_s'}\,\delta^{X_s'}(\alpha_s'')\,\frac{\alpha_s'^{X_s'}}{X_s'!} \tag{5.9}$$

and

$$\sum_{X_s'} X_s'\, e^{\alpha_s''-\alpha_s'}(-1)^{X_s'}\,\delta^{X_s'}(\alpha_s'')\,\frac{\alpha_s'^{X_s'}}{X_s'!} \tag{5.10}$$

Noting that

$$\sum_{X_s'} (-1)^{X_s'}\,\delta^{X_s'}(\alpha_s'')\,\frac{(\alpha_s')^{X_s'}}{X_s'!} = \delta(\alpha_s''-\alpha_s') \tag{5.11}$$

the LHS of (5.11) being the Taylor expansion of $\delta(\alpha_s'' - \alpha_s')$, we have

$$\sum_{x_s'} e^{\alpha_s'' - \alpha_s'} (-1)^{x_s'} \delta^{x_s'}(\alpha_s'') \frac{\alpha_s'^{\,x_s'}}{x_s'!} = \delta(\alpha_s'' - \alpha_s') \qquad (5.12)$$

and

$$\sum_{x_s'} x_s' e^{\alpha_s'' - \alpha_s'} (-1)^{x_s'} \delta^{x_s'}(\alpha_s'') \frac{\alpha_s'^{\,x_s'}}{x_s'!} = e^{\alpha_s'' - \alpha_s'} \frac{\partial}{\partial \alpha_{s'}} \delta(\alpha_s'' - \alpha_s')$$

Using (5.12) and (5.13), (5.8) becomes

$$\langle x_r(t)\, x_s(t')\rangle = \int d\underline{\alpha}\, d\underline{\alpha}'\, d\underline{\alpha}''\, e^{\sum_i (\alpha_i'' - \alpha_i')} \alpha_s' \alpha_r \left[\frac{\partial}{\partial \alpha_s'} \delta(\underline{\alpha}'' - \underline{\alpha}')\right] f(\underline{\alpha}, t | \underline{\alpha}', t')\, f(\underline{\alpha}', t') \qquad (5.14)$$

and integrating by parts

$$\langle x_r(t)\, x_s(t') = \int d\underline{\alpha}\, d\underline{\alpha}'\, \alpha_r \alpha_s'\, f(\underline{\alpha}, t | \underline{\alpha}', t')\, f(\underline{\alpha}'; t) + \int d\underline{\alpha}' \left[\alpha_s' \frac{\partial}{\partial \alpha_s'} \int d\underline{\alpha}\, \alpha_r f(\underline{\alpha}, t | \underline{\alpha}'; t')\right] f(\underline{\alpha}', t') \qquad (5.15)$$

we can now identify two types of terms.

The first term is the two time mean product function in the Poisson representation, $\langle \alpha_r(t)\, \alpha_s'(t')\rangle$. The second term is the average over the initial distribution $f(\underline{\alpha}', t')$ of the response function to a variation of the initial condition. Thus, writing

$$\int d\underline{\alpha}\, \alpha_r f(\underline{\alpha}, t | \underline{\alpha}', t') \equiv \langle \alpha_r(t) | [\underline{\alpha}', t']\rangle \qquad (5.16)$$

i.e. the mean of α_r given the initial condition $\underline{\alpha}'$, the second term may be written as

$$\int d\underline{\alpha}'\, \alpha_s' \frac{\partial}{\partial \alpha_s'} \langle \alpha_r(t) | [\underline{\alpha}', t]\rangle f(\underline{\alpha}', t') = \left\langle \alpha_s' \frac{\partial}{\partial \alpha_s'} \langle \alpha_r(t) | [\underline{\alpha}', t']\rangle \right\rangle \qquad (5.17)$$

Thus the second term is the average over the initial quasi-probability of a response function. Remembering that the

$\underline{\alpha}$ - space mean $\langle \alpha_r(t)\rangle$ is equal to $\langle X_r(t)\rangle$ for all t we derive

$$\langle X_r(t), X_s(t')\rangle = \langle \alpha_r(t), \alpha_s(t')\rangle + \left\langle \alpha_s' \frac{\partial \langle \alpha_r(t) | [\underline{\alpha}', t']\rangle}{\partial \alpha_s'} \right\rangle \qquad (5.18)$$

This is the basic formula that expresses the two time correlation function in $\underline{X}$-space in terms of Poisson notation.

5.3 Application to Equilibrium systems

We showed in chapter 4 that in equilibrium situations (in a grand canonical ensemble) the $\underline{\alpha}$ - space distribution is Poissonian so that the corresponding quasi-probability is a delta function.

$$f_{eq}(\underline{\alpha}) = \delta(\underline{\alpha} - \underline{\alpha}(eq)), \quad \underline{\alpha}(eq) = \langle x\rangle_{eq} \qquad (5.19)$$

There are two results of this

(i) The variables $\alpha(t)$ and $\alpha(t')$ are non fluctuating quantities with values $\underline{\alpha}$ (eq.) Thus

$$\langle \alpha_r(t), \alpha_s(t')\rangle_{eq} = 0$$

(ii) The equilibrium mean in the second term is trivial. Thus

$$\langle X_r(t), X_s(t')\rangle = \left[\alpha_s' \frac{\partial \langle \alpha_r(t) | [\underline{\alpha}', t']\rangle}{\partial \alpha_s'}\right]_{\underline{\alpha}' = \underline{\alpha}(eq)} \qquad (5.20)$$

This may also be derived by substituting (5.19) in (5.15). It must be emphasised that a simple relation such as (5.20) for the two time correlation function holds only in a grand canonical description for the equilibrium system.

In a canonical ensemble description the form of $f_{eq}(\alpha)$ is not a simple as that given by (5.19) and consequently (5.20) is not valid. In fact, we have seen in the previous chapter, that for each reaction mechanism $f_{eq}(\underset{\sim}{\alpha})$ has a different form with the result that the expression for two time correlation function obtained by substituting the canonical form for $\langle X_r(t), X_s(t')\rangle$ in (5.15) is not only complicated but is also different for each reaction mechanism. From this discussion it is clear that the Poisson representation method is not suitable for a canonical description of chemically reacting systems in thermodynamic equilibrium.

5.4.1 Two Time Correlation Functions for Equilibrium Systems from Statistical Considerations: Fluctuation-Dissipation Theorems.

The result (5.20) obtained by using the Poisson representation is in fact exactly that of Bernard and Callen which relate the two time correlation function to a derivative of a mean quantity with respect to a thermodynamically conjugate variable. The proof of this result is quite simple, and we shall explain it in a form suitable for our work.

Using the notation of section (4.2) the thermodynamic equilibrium distribution for a reacting system in the grand canonical ensemble is given by

$$P(I) = Z^{-1}(\underset{\sim}{\mu})\, \exp\left[\sum_r \mu_r X_r(I) - E(I)\right] \tag{5.21}$$

In equilibrium, the chemical potentials satisfy the stoichiometric constraints (4.12).
Now we define the quantities

$$\langle X_r, t \,|\, [I, t'] \rangle \quad , \quad t > t' \tag{5.22}$$

to be the mean values of the quantities X_r under the condition that the system was in a state I at time t
Then a quantity of interest is the mean value of (5.22) over the distribution (5.21) of initial conditions, namely

$$\langle X_r, t \,|\, [\underline{\mu}, t'] \rangle = \sum_{I} \langle X_r, t \,|\, [I, t'] \rangle \, Z^{-1}(\underline{\mu}) \exp\left[\frac{1}{kT}\left(\sum_{s} \mu_s X_s(I) - E(I)\right)\right] \tag{5.23}$$

when the chemical potentials satisfy the equilibrium constraints (4.12), this quantity will be time independent and equal to the mean of X_r in equilibrium, but otherwise it will have a time dependence. Then, with a little manipulation one finds that

$$\left[kT \frac{\partial}{\partial \mu_s} \langle X_r, t \,|\, [\underline{\mu}, t'] \rangle \right]_{\underline{\mu} = \mu(eq)} = \langle X_r(t), X_s(t') \rangle_{eq} \tag{5.24}$$

The left hand side is a response function, of the mean value to the change in the chemical potentials, around equilibrium, and is thus a measure of dissipation, while the right hand side, the two time correaltion function in equilibrium is a measure of fluctuations.

This is a different form of fluctuation-dissipation theorem from that most often considered. In the derivation of such fluctuation dissipation theorems one usually adopts a canonical ensemble description and, by introducing an external field in the Hamiltonian one obtains a relation between the generalised susceptibility and the imaginary part of the Fourier-transform of the two time correlation function. An excellent discussion on this, both in classical and quantum mechanical context may be found in ref [28]. In a grand canonical ensemble description, however, the introduction of an external field is not necessary; the term $\sum_r \mu_r X_r$ now plays the role of an external Hamiltonian with μ_r as the external fields. This may be understood from the following. Suppose that at time $t<0$ the system is in equilibrium so that the chemical potentials μ_r satisfy the stoichiometric constraints (4.12). Now if at $t=0$, μ_r are changed by a small amount, the system would no longer be in its equilibrium state and thus changing μ_r achieves the same end as an external field in so far as both have the effect of driving the system away from the equilibrium state. From this discussion it is also clear that the result (5.24) may also be derived following the usual treatment of fluctuation-dissipation theorems assuming a step function time dependence for the external field. To make connection with the Poisson representation result (5.20) we make use of the relation (4.15).

$$\mu_s = kT \log \langle X_s \rangle + \text{const.} \qquad (5.25)$$

derived in section 4.2 (Note that $\langle X_r \rangle$ are the equilibrium mean values only if μ_r satisfy the equilibrium constraints. Using (5.25), (5.24) becomes

$$\langle X_r(t), X_s(t')\rangle = \left[\langle X_s\rangle \frac{\partial}{\partial\langle X_s\rangle}\langle X_r, t \,|\, [\langle \underline{X}\rangle, t']\rangle\right]_{\langle\underline{X}\rangle = \langle\underline{X}\rangle_{eq}} \qquad (5.26)$$

Since ideal solution theory gives rise to a distribution in X_r which is Poissonian, it follows that in that limit

$$\langle X_r, t \,|\, [\langle \underline{X}\rangle, t']\rangle = \langle \alpha_r, t \,|\, [\underline{\alpha}', t']\rangle \qquad (5.27)$$

where $\alpha_s' = \langle X_s\rangle$ and (5.26) becomes

$$\langle X_r(t), X_s(t')\rangle = \left[\alpha_s' \frac{\partial}{\partial\alpha_s'}\langle \underline{\alpha}_r, t \,|\, [\underline{\alpha}', t']\rangle\right]_{\underline{\alpha}' = \alpha(eq)} \qquad (5.28)$$

which is identical to (5.20).

5.5. <u>Non Equilibrium Steady States</u>

The general formula (5.18) is considerably different from the equilibrium result and the two terms are directly interpretable. The second term is the equilibrium contribution, a response function, but since the system is not in a well defined equilibrium state, we take the average of the equilibrium result over the various contributing $\underline{\alpha}$-space state. The first term is the contribution from the $\underline{\alpha}$-space fluctuations themselves and is not directly related to a response function.

By integrating the second term in (5.15) by parts we may also derive a slightly different formula

$$\begin{aligned}\langle X_r(t), X_s(t')\rangle = {} & \langle \alpha_r(t), \alpha_s(t')\rangle - \langle \alpha_r(t)\rangle \\ & - \left\langle \alpha_r(t)\,\alpha_s(t') \frac{\partial}{\partial\alpha_s(t')}\log f(\underline{\alpha}', t')\right\rangle\end{aligned} \qquad (5.29)$$

which is useful when $f(\underline{\alpha}, t)$ is explicitly known.

5.6 Two Time Correlation Functions from Glauber-Sudarshan P-representation

We have seen in section 3.3 how the Poisson representation arises as a special case of the Glauber-Sudarshan P - representation. We shall now investigate the relationship between the expressions for the two time averages.

For a quantum Markoffian system, it may be shown[58,59] that two time operator averages may be expressed in the P- representation as

$$\begin{aligned} &\langle M(a,a^{+},t)\, N(a,a^{+},t')\rangle \\ &\quad = \int \frac{d^2\beta}{\pi}\, \frac{d^2\beta'}{\pi}\, \bar{\rho}^{(a)}(\beta,\beta^{*},t \mid \beta',\beta'^{*},t')\, \bar{M}^{(n)}(\beta,\beta^{*}) \\ &\qquad \times \left[\, \bar{N}^{(n)}\left(\beta'^{*} - \frac{\partial}{\partial\beta'},\, \beta'\right) \bar{\rho}^{(a)}(\beta',\beta'^{*},t')\, \right] \end{aligned} \tag{5.30}$$

where

$$\langle M(a,a^{+},t)\, N(a,a^{+},t')\rangle = \mathrm{Tr}\left[M(a,a^{+},t)\, N(a,a^{+},t')\, \rho(a,a^{+},t')\right]$$

and $\bar{\rho}^{(a)}(\beta,\beta^{*},t \mid \beta',\beta'^{*},t')$ is the conditional probability in the P- representation.

For the photon number correlation function (5.30) gives

$$\begin{aligned} \langle a^{+}(t)\, a(t)\, a^{+}(0)\, a(0)\rangle = \int \frac{d^2\beta}{\pi}\, \frac{d^2\beta'}{\pi}\, \beta^{*}\beta \cdot \bar{\rho}^{(a)}(\beta,\beta^{*},t \mid \beta',\beta'^{*},t') \\ \times \left(\beta'^{*} - \frac{\partial}{\partial\beta'}\right) \beta'\, \bar{\rho}^{(a)}(\beta,\beta'^{*},t') \end{aligned} \tag{5.31}$$

we now assume that at time $t = t'$ the density operator is diagonal in the number representation and further that the dynamics of the system is such that it stays diagonal at a later time. This implies that $\bar{\rho}^{(a)}(\beta',\beta'^{*},t')$ and $\bar{\rho}^{(a)}(\beta,\beta^{*}t \mid \beta',\beta'^{*},t')$ are functions of $\beta'\beta'^{*}$ and $\beta\beta^{*}$ only. Under these assumptions on introducing the variables

$$\beta = \sqrt{\alpha}\, e^{i\varphi}, \quad \beta' = \sqrt{\alpha'}\, e^{i\varphi'}$$

(5.31) becomes

$$\begin{aligned}\langle n(t)\, n(0)\rangle &= \int d\alpha\, d\alpha'\, \alpha\alpha'\, \bar{e}^{(a)}(\alpha,t\,|\,\alpha',t')\, \bar{e}^{(a)}(\alpha',t') \\ &\quad + \int d\alpha' \frac{\partial}{\partial\alpha'}\left[\int d\alpha\, \alpha\, \bar{e}^{(a)}(\alpha,t\,|\,\alpha',t')\right] \bar{e}^{(a)}(\alpha',t') \qquad (5.32)\end{aligned}$$

which is identical to the result (5.15) for a single variable case.

CHAPTER 6

STOCHASTIC DIFFERENTIAL EQUATION METHODS

6.1 Introduction

In the previous chapters we have seen how chemical master equations may be transformed into generalised Fokker-Planck equations. The Fokker-Planck equations thus obtained are not solved directly, except in the steady state, and even in this case no easy method of solution exists in multivariate situations, in particular, when spatial diffusion is taken into account.

A Fokker-Planck equation which involves no higher than second order derivatives, under certain conditions may be shown to be equivalent to a stochastic differential equation or Langevin equation.[60] This may be accomplished by the use of two formalisms, that of Itô and that of Stratonovich. The two formalisms yield different stochastic differentials equations corresponding to the same Fokker-Planck equation and have different integration rules, so that the solutions of the different stochastic differential equation forms are the same[†]. A discussion

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[†] In a number of physical problems, one way to introduce fluctuations in a deterministic equation is to add a stochastic noise source. If the coefficient of the noise source, on some physical grounds, turns out not to be a constant, then one has to decide how the stochastic differential equation is to be interpreted, i.e. which of the two formalisms correspond to physical reality. This has been discussed in ref [60] and [62]. This difficulty does not arise here, since we start with a Fokker-Planck equation and may make our own choice of correspondence with complete physical and mathematical equivalence.

of the mathematical differences between the two formalisms is given in the appendix A . Our aim here is to briefly discuss the Itô formalism so as to obtain certain rules which would be used later for iterative calculations. We shall exclusively work with the Itô formalism, because of its greater simplicity and elegance, as well as the fact that in iterative solutions it guarantees vanishing of a large number of terms.

As we have seen in chapter 3, if a chemical reaction mechanism involves a trimolecular or higher reactions, then the corresponding Fokker-Planck equations involve third and higher order derivatives. It is therefore essential to develop stochastic differential equations for such Fokker-Planck equations. We show how this may be done for a Fokker- Planck equation involving third order derivatives with obvious generalisations to higher orders.

In the later chapters we shall almost exclusively work with stochastic differential equations and hence we shall write them down for the general reaction (3.21) with and without spatial diffusion. This helps to fix our notation used later on.

6.2 Stochastic Differential Equations Equivalent to Fokker-Planck Equations

The rule for associating a stochastic differential equation with a Fokker-Planck equation is as follows - for a multivariate Fokker-Planck equation

$$\frac{dP(\underline{Y},t)}{dt} = -\sum_i \frac{\partial}{\partial Y_i} a_i(\underline{Y})\, P(\underline{Y},t) + \frac{1}{2}\sum_{i,j}\frac{\partial^2}{\partial Y_i \partial Y_j} b_{ij}(\underline{Y})\, P(\underline{Y},t) \quad (6.1)$$

the equivalent stochastic differential equation is

$$dY_i(t) = a_i(\underline{Y}(t)) + \sum_j g_{ij}(\underline{Y}(t))\, dW_j(t) \quad (6.2)$$

where

$$g_{ij} = (\sqrt{b})_{ij} \quad (6.3)$$

The $dW_j(t)$ are the increments of the Wiener process which is a Gaussian stochastic process and satisfy the following

(i) $$dW_j(t) = W_j(t+dt) - W_j(t) \quad (6.4)$$

(ii) The distribution of $dW_j(t)$ is Gaussian with mean zero

$$\langle dW_j(t) \rangle = 0 \quad (6.5)$$

and variance dt

$$\langle dW_i(t)\, dW_j(t') \rangle = \delta_{ij}\, dt \quad (6.6)$$

(iii) $dW_j(t)$ are statistically independent of $W_i(t) - W_i(t_0)$ so that in particular

$$\langle dW_j(t)[W_i(t) - W_i(t_0)] \rangle = 0 \ , \ t \geqslant t_0 \quad (6.7)$$

where

$$W_i(t) - W_i(t_0) = \int_{t_0}^{t} dW_i(t') \quad (6.8)$$

The last property of statistical independence is stronger that (5.7) and means that the joint probability distribution of the $W_i(t)$ for a set of increasing times t_i satisfies

$$P(\underline{w}(t_1); \underline{w}(t_2); \cdots \underline{w}(t_n))$$
$$= P(\underline{w}(t_1))\, P(\underline{w}(t_2) - \underline{w}(t_1)) \cdots P(\underline{w}(t_n) - \underline{w}(t_{n-1})) \qquad (6.9)$$

It is this aspect of independent increments - the increment at time t' being independent of $\underline{w}(t')$ for $t \geqslant t'$ which characterises the Itô method, and yields simple formulae. The connection with the physicists' way of writing a stochastic differential equation is obtained by setting

$$\xi_i(t)\,dt = dw_i(t) \qquad (6.10)$$

so that (6.2) becomes

$$\frac{dy_i}{dt} = a_i(\underline{y}(t)) + \sum_j g_{ij}(\underline{y}(t))\, \xi_j(t) \qquad (6.11)$$

From (6.5), (6.6) and (6.9) it follows that

$$\langle \xi_i(t) \rangle = 0 \qquad (6.12)$$

$$\langle \xi_i(t)\, \xi_j(t') \rangle = \delta_{ij}\, \delta(t-t') \qquad (6.13)$$

Now using (6.10) and (6.13) we find that

$$\langle dw_i(t)\,[\,w_i(t) - w(t_0)\,] \rangle = \int_{t_0}^{t} dt'\, \delta(t-t_0) \qquad (6.14)$$

It follows from (6.7) that the RHS of (6.14) must be zero. Thus the Itô prescription requires us to give zero weight to a delta function singularity which occurs at the upper limit of a time integral, i.e.

$$\int_{t_0}^{t} dt'\, \delta(t-t') = 0 \qquad (6.15)$$

$$\int_{t_0}^{t} dt'\, \delta(t'-t_0) = 1 \qquad (6.16)$$

As we shall see in Appendix A, Stratronovich's definition of the increment is

$$dw_j(t) = \frac{1}{2}\left[w_j(t+dt) - w_j(t-dt)\right] \qquad (6.17)$$

in which case both the integrals (6.15) and (6.16) become equal to $\frac{1}{2}$.

We make this point here because in the calculation of quantities of interest from the stochastic differential equations using an iterative procedure, integrals with delta function singularities at the upper limit frequently occur. It will be apparent that the Itô choice, which makes them all vanish, yields a much simpler procedure.

6.3 Stochastic Differential Equation Methods for Higher Order Fokker Planck Equations

The relationship between Fokker Planck equations and the stochastic differential equations discussed in the previous section is valid only for the case when the Fokker Planck equation is no more than second order. Our techniques can yield Fokker Planck equations which are of higher but always finite order, and it is appropriate to devise stochastic differential equation methods for Fokker Planck equations of higher order. This subject does not seem to have been discussed until very recently[†] We now show how this can be done for a third order Fokker Planck equations from which it will be clear how the procedure may be generalised to include Fokker-Planck equations with derivatives of arbitrary order.

Introduce the stochastic variable $\vartheta(t)$ whose probability distribution $P(\vartheta,t)$ obeys the third order partial differential equation

$$\frac{\partial P(\vartheta,t)}{\partial t} = -\frac{1}{6}\frac{\partial^3 P(\vartheta,t)}{\partial \vartheta^3} \tag{6.18}$$

We then know the solution of (6.18), subject to the boundary condition

$$P(\vartheta,t_0) = \delta(\vartheta-\vartheta_0) \tag{6.19}$$

is given, by Fourier transform methods, as the conditional probability,

$$P(\vartheta,t\,|\,\vartheta_0,t_0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dq\, e^{i\left[q(\vartheta-\vartheta_0)+\frac{1}{6}q^3(t-t_0)\right]} \tag{6.20}$$

[†] In a recent preprint Hochberg[63] has shown how the Wiener process may be generalised to higher order Fokker Planck equations involving even order derivatives only,

$$\partial P/\partial t = (-1)^{n+1}\, \partial^{2n} P/\partial x^{2n}$$

The reason why odd order derivatives are not considered is perhaps that in that case the positivity of the probability distributions is not guaranteed. Since we deal with Fokker Planck equations obeyed by a quasi-probability distribution (which may be negative or indeed complex) this problem does not arise and hence we are able to extend stochastic differential equation methods to Fokker Planck equations with derivatives of arbitrary order. Admittedly our derivations cannot be considered as mathematically rigorous, but, in practice, the results do not seem to cause any problems.

The moments of $P(\vartheta,t)$ can be calculated, after a partial integration are found to be $\langle [\vartheta(t)-\vartheta_0]^n \rangle = 0$ n not a multiple of 3.

$$\langle [\vartheta(t)-\vartheta_0]^{3m} \rangle = \left(\frac{1}{6}\right)^m \frac{3m!}{m!} (t-t_0)^m \qquad (6.21)$$

Further, since the process (6.18) is a generalised Markov process, the joint probability distribution that has the value ϑ_1 at time t_1 and ϑ_2 at the later time t_2 is given by

$$P(\vartheta_2,t_2;\vartheta_1,t_1) = P(\vartheta_2,t_2|\vartheta_1 t_1)\, P(\vartheta_1,t_1) \qquad (6.22)$$

and from (6.3) we see the first factor is a function of only $\vartheta_2-\vartheta_1$ and t_2-t_1 so that the variable $\vartheta(t_2)-\vartheta(t_1)$ is statistically independent of $\vartheta(t_1)$ so that this process is a process with independent increments: thus $d\vartheta(t)$ will be independent of $\vartheta(t)$.

The rigorous definition of stochastic integration with respect to $\vartheta(t)$ is a task which we shall not attempt at this stage. We can show, however, that a stochastic differential equation of the form

$$dY(t) = a(Y(t))\,dt + b(Y(t))\,dw(t) + c(y)\,d\vartheta(t) \qquad (6.23)$$

(with $w(t)$ and $\vartheta(t)$ independent processes) is equivalent to a third order Fokker Planck equation. It is clear that because $w(t)$ and $\vartheta(t)$ are Markov Processes, that $Y(t)$ is a Markov process. We then calculate

$$\lim_{t\to t_0} \frac{\langle [Y(t)-Y(t_0)]^n \rangle}{(t-t_0)} = \lim_{dt_0\to 0} \frac{\langle [dY(t_0)]^n \rangle}{dt_0} \qquad (6.24)$$

where $Y(t_0)$ is a numerical initial value, not a stochastic variable. From (6.23), it is clear that $Y(t)$ depends on $\varpi(t')$ and $\vartheta(t')$ for only $t' \leq t$ and since $d\varpi(t)$ and $d\vartheta(t)$ are independent of $Y(t)$. Thus

$$\begin{aligned}\langle dY(t_0)\rangle &= \langle a\ Y(t_0))\rangle dt_0 + \langle b(Y(t_0))\rangle \langle d\varpi(t_0)\rangle \\ &\quad + \langle c(Y(t_0))\rangle \langle d\vartheta(t_0)\rangle \\ &= \langle a(Y(t_0)\rangle\ dt_0 \\ &= a(Y(t_0))\end{aligned} \tag{6.25}$$

since $Y(t_0)$ is a numerical initial value. Similarly,

$$\begin{aligned}\langle dY^2(t_0)\rangle &= [a(Y(t_0))]^2 (dt_0)^2 + [b(Y(t_0)]^2 \langle (d\varpi(t_0)^2\rangle \\ &= [a(Y(t_0))]^2 (dt_0)^2 + [b(Y(t_0))]^2 dt_0\end{aligned} \tag{6.26}$$

$$\begin{aligned}\langle dY^3(t_0)\rangle &= [a(Y(t_0))]^3 (dt_0)^3 + [c(Y(t_0))]^3 \langle (d\vartheta(t_0))^3\rangle \\ &= [a(Y(t_0))]^3 (dt_0)^3 + [c(Y(t_0)]^3 dt_0\end{aligned} \tag{6.27}$$

Thus we find

$$\begin{aligned}\lim_{t\to t_0} \left\langle \frac{Y(t)-Y(t_0)}{t-t_0}\right\rangle &= a(Y(t_0)) \\ \lim_{t\to t_0} \frac{\langle [Y(t)-Y(t_0)]^2\rangle}{t-t_0} &= b^2(Y(t_0)) \\ \lim_{t\to t_0} \frac{\langle [Y(t)-Y(t_0)]^3\rangle}{t-t_0} &= c^3(Y(t_0))\end{aligned} \tag{6.28}$$

and all higher powers give a zero result. This is sufficient[4, 6, 60] to show that $Y(t)$ is a generalised diffusion process, whose generalised Fokker Planck equation is

$$\begin{aligned}\frac{\partial P(Y,t)}{\partial t} &= -\frac{\partial}{\partial Y}[a(Y)\ P(Y,t)] + \frac{1}{2}\frac{\partial^2}{\partial Y^2}[b^2(Y)\,P(Y,t)] \\ &\quad + \frac{1}{3!}\frac{\partial^3}{\partial Y^3}[c^3(Y)\ P(Y,t)]\end{aligned} \tag{6.29}$$

We define a noise source $\xi(t)$ by

$$d\vartheta(t) = \xi(t)\,dt \tag{6.30}$$

where

$$\langle \xi(t) \rangle = \langle \xi(t)\,\xi(t') \rangle = 0 \tag{6.31}$$

$$\langle \xi(t)\,\xi(t')\,\xi(t'') \rangle = \delta(t-t')\,\delta(t'-t'') \tag{6.32}$$

and higher moments can be readily calculated from the moments of $d\vartheta(t)$. The independence of increments means that, as in the previous case, integrals which have a delta function singularity at their upper limit are to be taken as zero.

6.4 Stochastic Differential Equations Equivalent to Chemical Master Equations

If the general reaction (3.21) involves only bimolecular reactions, we have shown that (3.26) is exactly equivalent to the corresponding master equation. Following the rules given in the previous section, the stochastic differential equation equivalent to (3.26) may be written as

$$\frac{d\alpha_r}{dt} = \sum_p A_r^p J_p(\underline{\alpha}) + \sum_s C_{rs}[\underline{J}(\underline{\alpha})]\,\xi_s(t) \tag{6.33}$$

where $\xi_s(t)$ are Gaussian stochastic noise sources with

$$\langle \xi_r(t) \rangle = 0 \;, \quad \langle \xi_r(t)\,\xi_s(t') \rangle = \delta_{rs}\,\delta(t-t') \tag{6.34}$$

The matrix C is the square root of the matrix B,

$$C_{rs}[\underline{J}(\underline{\alpha})] = [\sqrt{B(\underline{J}(\underline{\alpha}))}]_{rs} \tag{6.35}$$

the matrix B being given by (3.28). The matrix C being the square root of a matrix is not unique. However, when various averages are calculated from (6.33) only the square of the matrix C appears. This arises from the fact that averages of an odd number of $\underline{\xi}$ vanish. The various averages obtained from (6.33) are therefore uniquely defined.

Equation (6.33) is then the stochastic differential equation exactly equivalent to the chemical master equations for a general bi-molecular reaction mechanism.

To introduce an expansion parameter we define

$$\underline{\alpha} = \underline{\eta} V \tag{6.36}$$

and
$$K_p^F = k_p^F (V)^{-\sum_r N_r^p+1}, \quad K_p^B = k_p^B (V)^{-\sum_r M_r^p+1} \tag{6.37}$$

and thereby explicitly exhibit the volume dependence of various quantities involved. Equation (6.33) then becomes

$$\frac{d\eta_r}{dt} = \sum_p A_r^p J_p(\underline{\eta}(t)) + \varepsilon \sum_s C_{rs}[\underline{J}(\underline{\eta}(t))]\, \xi_s(t) \tag{6.38}$$

where

$$\varepsilon = \frac{1}{\sqrt{V}} \tag{6.39}$$

and
$$J_p(\underline{\eta}) = \prod_{r=1}^{n} K_p^F \eta_r^{N_r^p} - \prod_{r=1}^{n} K_p^B \eta_r^{M_r^p} \tag{6.40}$$

Perturbative calculations from (6.38) may then be done by expanding

$$\underline{\eta}(t) = \underline{\eta}_0(t) + \varepsilon\, \underline{\eta}_1(t) + \varepsilon^2 \underline{\eta}_2(t) \tag{6.41}$$

The equations for $\underline{\eta}_0(t)$ correspond exactly to the macroscopic equations while those for $\underline{\eta}_i(t)$, $i \geqslant 1$ describe the fluctuations. Note that van Kampen's system size expansion of the master equation is based on the assumption that the fluctuations are down by a factor of $\frac{1}{\sqrt{V}}$ relative to the macroscopic motion, an assumption which is inspired by the central limit theorem, valid for systems in thermodynamic equilibrium and has been proved only recently by Kurtz[35] for chemical master equations. In our work, at least in the chemical reaction context, no such ansatz be made; the fluctuations naturally appear with the correct scale relative to the macroscopic motion. When spatial diffusion is included, as in Chapter 4, the stochastic differential equation then becomes

$$\frac{d\eta_r(i,t)}{dt} = \sum_j D_{ij}^{r}\, \eta_r(j,t) + \sum_p A_r^p\, J_p(\underline{\eta}(i,t)) + \frac{1}{\sqrt{\Delta V}} \cdot \sum_s C_{rs}[\underline{J}(\underline{\eta}(i,t)]\, \xi_s(i,t) \tag{6.42}$$

where ΔV is the cell volume, i, j are the cell labels,

$$D_{ij}^{r} = d_{ij}^{r} - (\sum_k d_{ik}^{r})\, \delta_{ij} \tag{6.43}$$

$$\eta_r(j,t) = \frac{\alpha_r(j,t)}{\Delta V} \tag{6.44}$$

and $\langle \xi_r(i,t) \rangle = 0$, $\langle \xi_r(i,t)\, \xi_s(j,t) \rangle = \delta_{rs}\delta_{ij}\delta(t-t')$ (6.45)

Here $\eta_r(j,t)$ corresponds to the chemical component r in cell j.

$J_p(\underline{\eta}(i,t))$ has the same form as in (6.40) but K_p^F and K_p^B

are now given by

$$K_p^F = k_p^F (\Delta V)^{-\sum_r N_r^p + 1} \, , \, K_p^B = k_p^B (\Delta V)^{-\sum_r M_r^p + 1} \qquad (6.46)$$

A note worthy aspect of (6.42) is that unlike conventional Langevin equations [22,36,64,65], despite the addition of spatial diffusion,noise coefficient remains spatially local.

When trimolecular or higher reactions are present equation (6.33) or (6.42) are only approximate ; they are equivalent to the Fokker Planck equations in which third and higher derivatives are omitted.

The expansion parameter in (6.42) is $1/\sqrt{\Delta V}$. For the perturbation expansion to make sense ΔV should not be too small. This question will be discussed at length in Chapter 9.

The higher order derivative terms in the Fokker Planck equations may be taken into account by adding additional noise sources to (6.33) or (6.42) along the lines explained in the previous section. In most applications, where only the dominant contributions in the system size expansion are required it is sufficient to work with (6.33) or (6.42). In Chapter 7 we will give an example where we include the noise terms arising from the third order derivative terms in the Fokker Planck equations and show how the perturbative calculations may be performed.

6.5 The Gaussian Approximation

Retaining only the first two terms in the expansion (6.41) and substituting it in (6.33) one obtains, on neglecting terms of order ε^2 or higher, a deterministic equation for

$$\frac{d\eta_{r,0}}{dt} = \sum_p A_r^p \, J_p(\underline{\eta}_0(t)) \tag{6.47}$$

and a linear stochastic differential equation for

$$\frac{d\eta_{r,1}}{dt} = -\sum F_{rs}\, \eta_{s,1}(t) + \sum_s K_{rs}\, \xi_s(t) \tag{6.48}$$

where the matrices F and K are given by

$$F_{rs} = -\sum_p A_r^p \frac{\partial J_p(\underline{\eta}_0(t))}{\partial \eta_{s,0}} \tag{6.49}$$

and

$$K_{rs} = C_{rs}[\underline{J}(\underline{\eta}_0(t))] \tag{6.50}$$

This linear approximation of the stochastic differential equation (6.38) will be referred to as the Gaussian approximation, for, it corresponds exactly to approximating $f(\underline{\alpha})$ by a Gaussian

$$f(\underline{\alpha}) = \exp[-\tfrac{1}{2} V (\eta_r - \eta_{r,0})(G^{-1})_{rs} (\eta_s - \eta_{s,0})] \tag{6.51}$$

This is so because the solution of the Fokker Planck equation equivalent to (6.48) may be shown to be a Gaussian. The matrix G in (6.51) is given by

$$G_{rs} = \langle \eta_{r,1}\, \eta_{s,1} \rangle \tag{6.52}$$

6.5.1 Relation to van Kampen's Gaussian Approximation

In contrast to our Gaussian approximation, where we approximate $f(\underline{\alpha})$ by a Gaussian, van Kampen's Gaussian approximation corresponds to approximating $P(\underline{X})$ by a Gaussian. We shall now show that these two Gaussian approximations are asymptotically equivalent.

Substituting (6.51) in

$$P(\underline{X}) = \int d\underline{\alpha} \prod_{r=1}^{n} \left(e^{-\alpha_r} \frac{\alpha_r^{X_r}}{X_r!} \right) f(\underline{\alpha}) \tag{6.53}$$

and using the Stirling's approximation for $\log X!$ we have

$$P(\underline{X}) = \int d\eta \, e^{-V\phi(\underline{\eta}, x)} \tag{6.54}$$

where
$$\begin{aligned} \phi(\underline{\eta}, \underline{x}) = {} & \sum_r [\eta_r - x_r \log \eta_r + x_r \log x_r - x_r] \\ & + \frac{1}{2} \sum_{r,s} (\eta_r - \eta_{r,0})(G^{-1})_{rs}(\eta_s - \eta_{s,0}) \end{aligned} \tag{6.55}$$

and, as before we have put $x = \frac{X}{V}$, $\eta = \frac{\alpha}{V}$.

Using the method of steepest descent to asymptotically evaluate the LHS of (6.53) we have

$$P(\underline{X}) = e^{-V\psi(\underline{x})} \tag{6.56}$$

where
$$\begin{aligned} \psi(\underline{x}) = {} & \sum_r [\bar{\eta}_r - x_r \log \bar{\eta}_r + x_r \log x_r - x_r] \\ & + \frac{1}{2} \sum_{r,s} (\bar{\eta}_r - \eta_{r,0})(G^{-1})_{rs}(\bar{\eta}_s - \eta_{s,0}) \end{aligned} \tag{6.57}$$

and $\bar{\eta}_r$ are given by

$$1 - \frac{x_k}{\bar{\eta}_k} + \sum_s (\bar{\eta}_r - \eta_{r,0})(G^{-1})_{rs} \tag{6.58}$$

which may be used to express $\bar{\eta}_r$ in terms of $\underline{x}$.

Now if $P(\underline{X})$ is approximated by a Gaussian by expanding $\psi(\underline{x})$ in a Taylor series about its maximum, then after a little algebra which is given in appendix B , one gets

$$P(\underline{X}) \sim e^{-V\sum_{rs}(x_r - x_{r,0})(G+M)^{-1}_{rs}(x_s - x_{s,0})}, \qquad M_{rs} \equiv x_{s,0}\,\delta_{rs} \tag{6.59}$$

Noting the relation between the factorial moments in $\underline{\alpha}$ - variables and the moments in x- variables it is easily seen that the matrix $(G+M)_{rs}$ is in fact the variance matrix σ_{rs} in x - variables and van Kampen's Gaussian approximation is thus recovered.

6.4.2 Relation to the Gaussian Approximation of Gardiner et al

With $f(\underline{\alpha})$ given by (6.51) the factorial moment generating function

$$G(\underline{s}) = \sum_{\underline{X}} \left(\prod_r s_r^{x_r}\right) P(\underline{x},t)$$

is

$$G(\underline{s}) = \int d\eta\, e^{V[\sum_r (s_r-1)\eta_r - \frac{1}{2}\sum_{rs}(\eta_r-\eta_{r,0})(G^{-1})_{rs}(\eta_s-\eta_{s,0})} \tag{6.60}$$

An asymptotic evaluation of the LHS of (6.60) gives

$$G(\underline{s}) \sim e^{V[\sum_r (s_r-1)\bar{\eta}_r + \frac{1}{2}\sum_{rs}(\bar{\eta}_r-\eta_{r,0})(G^{-1})_{rs}(\bar{\eta}_s-\eta_{s,0})} \tag{6.61}$$

with $\bar{\eta}_r$ given by

$$\sum_s (G^{-1})_{rs}(\bar{\eta}_s-\eta_{s,0}) = (s_r-1) \tag{6.62}$$

Substituting for $\bar{\eta}_r$ from (6.62) in (6.60) we recover the Gaussian approximation of Gardiner et al.

$$G(s) = e^{V[\sum_r (s_r-1)\eta_{r,0} + \frac{1}{2}\sum_{rs}(s_r-1)(G^{-1})_{rs}(s_s-1)} \tag{6.63}$$

CHAPTER 7

APPLICATIONS TO EQUILIBRIUM SYSTEMS

7.1 Introduction

In this chapter we shall investigate chemical systems in thermodynamic equilibrium using stochastic differential equation method. We shall study a few simple reactions with a view to bringing out some special features of the corresponding stochastic differential equations. This, to some extent, would be a restatement of the Poissonian nature of equilibrium fluctuations mentioned earlier, but now formulated in terms of stochastic differential equations. We then discuss the conditions under which a Poissonian steady state is achieved. Next we investigate the two time correlation functions for chemical systems in thermodynamic equilibrium and obtain in the lowest order in the system size expansion, the well known fluctuation-dissipation result which has also been obtained previously by Kaizer,[33] van Kampen[41] and Kubo et al.[42] Our formulation of the two time correlation functions as a response function in the $\underline{\alpha}$-space coupled with the stochastic differential equation in $\underline{\alpha}$ variables enable us to calculate next higher order corrections in a straightforward manner. We do this for two representative cases and thereby explain the rules that have to be taken into account because of our choice of Ito form of stochastic differential equations while carrying out a perturbation expansion.

7.2 Application of Stochastic Differential Equations to Simple Equilibrium Reactions

Consider a two variable linear reaction

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y \tag{7.1}$$

for which the stochastic differential equations are

$$\frac{d\alpha_X}{dt} = -k_1\alpha_X + k_2\alpha_Y \tag{7.2}$$

$$\frac{d\alpha_Y}{dt} = k_1\alpha_X - k_2\alpha_Y \tag{7.3}$$

Here we find that there are no noise terms and the equations for α_X and α_Y are in fact non stochastic differential equations. Thus if the initial conditions are fixed numerical values, the solutions to (7.2) and (7.3)are deterministic numerical values which are the mean value parameters of a bivariate Poisson distribution. Thus a linear system possesses time dependent Poisson distribution solutions.

Consider a two variable non linear reaction

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Y \tag{7.4}$$

for which the stochastic differential equations are

$$\frac{d\alpha_X}{dt} = -k_1\alpha_X + k_2\alpha_Y^2 \tag{7.5}$$

$$\frac{d\alpha_Y}{dt} = 2(k_1\alpha_X - k_2\alpha_Y^2) + \sqrt{2(k_1\alpha_X - k_2\alpha_Y^2)}\,\xi(t)$$

In contrast to (7.2) and (7.3), (7.5) does have a noise term and the solutions are in general stochastic variables, indicating that the probability distribution is non Poissonian.

However at the steady state, when

$$k_1\alpha_X = k_2\alpha_Y^2 \tag{7.6}$$

the noise terms vanish and the probability distribution becomes Poissonian.

The existence of the noise term shows that, for this system a time dependent Poisson is not a solution, even if the initial values of α_X and α_Y are fixed initially (i.e. a Poissonian initial condition), the time evolution will cause a spreading of the probability distribution, which eventually, in the steady state becomes Poissonian. Notice also that the coefficient of $\xi(t)$ is not real if $k_2\alpha_Y^2 > k_1\alpha_X$ and the noise is thus purely imaginary. This may at first seem an alarming effect, for one never encounters an imaginary noise coefficient in conventional Langevin equations, as that would correspond to a negative variance. However, it should be remembered that in the stochastic differential equations derived using Poisson representation, the coefficient of the noise source is a measure of fluctuations relative to Poisson fluctuations, and an imaginary noise coefficient simply has the effect of reducing the variance in $\underline{X}$-space to less than the Poissonian value. In actual calculations the variance in $\underline{X}$-space always turns out to be positive as it must.

A point worth noting here is that, in the steady state for this system, we have two values of α_y namely

$$\alpha_y^{\pm} = \pm\sqrt{\frac{k_1\alpha_x}{k_2}} \tag{7.7}$$

Now since $\langle Y\rangle_{eq} = \alpha_y$, the root obtained by choosing the negative sign seems to be unphysical. However this root does have a meaning and is related to the fact that since in (7.4) the Y molecules are always created or destroyed in pairs, the probability of having an odd number of Y molecules, is entirely independent from that of even Y molecules. The general probability distribution in the steady state, is there-fore a superposition of the Poisson distribution corresponding to the two values of α_y in (7.7). Thus

$$P(X,Y) = e^{-\alpha_x}\frac{\alpha_x^{X}}{X!}\left[\lambda e^{-\alpha_y^{+}}\frac{(\alpha_y^{+})^{Y}}{Y!} + (1-\lambda)e^{-\alpha_y^{-}}\frac{(\alpha_y^{-})^{Y}}{Y!}\right] \tag{7.8}$$

which is positive provided that

$$[1+e^{-2\alpha_y^{+}}]^{-1} \leqslant \lambda \leqslant [1+e^{-2\alpha_y^{-}}]^{-1} \tag{7.9}$$

The lower and upper extreme values give probability distributions allowing respectively an odd and even values of Y.

7.3 Conditions under which a Poissonian Steady State is Achieved

In a simple reversible reaction such as (7.1) or (7.4) we always find that the noise term and the drift term vanish simultaneously - thus a Poissonian steady state results. Further in any linear system there is no noise term so the Poissonian steady state again results. If we have a set of reactions such as

$$\sum_{r=1}^{n} N_r^p X_r \underset{k_p^B}{\overset{k_p^F}{\rightleftharpoons}} \sum M_r^p X_r \qquad (7.10)$$

then in thermodynamic equilibrium, each reaction in this chemical reaction system occurs as often as its reverse i.e. one has a detailed balance. In the master equation, the detailed balance condition implies the following

$$k_p^F \prod_{r=1}^{n} \frac{X_r!}{(X_r-N_r^p)!} P(\underline{X}) = k_p^B \prod_{r=1}^{n} \frac{(X_r+M_r^p-N_r^p)!}{(X_r-M_r^p)!} P(\underline{X}+\underline{M}^p-\underline{N}^p) \qquad (7.11)$$

for each p. This recursion formula is in fact enough to show that Poisson distribution is a steady state solution of the master equation.

The detailed balance condition (7.11) when translated into Poisson notation becomes

$$J_p(\underline{\eta}) = 0 \qquad \text{for each } p \qquad (7.12)$$

and it is immediately obvious from the Fokker-Planck equation or the equivalent stochastic differential equation (6.38) that when (7.12) holds, the noise terms also vanish and thus one has a Poissonian steady state.

It should be noted that the combinatorial form for the transition probabilities is crucial for the above statement to be exact. Our conclusion is that any reaction system, that obeys combinatorial kinetics and is such that its steady state is reached by detailed balancing of each reaction, has a Poissonian steady state. However, there are situations which do not have a detailed balance in the steady state, and yet the steady state is Poissonian. For example, the steady state distribution of

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} nX \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B \tag{7.13}$$

is always Poissonian, though a net flow form A to B may exist. In this case, one has a Poissonian steady state away from the thermodynamic equilibrium.

7.4 Two Time Correlation Functions in Thermodynamic Equilibrium: Results to the Lowest Order in the System Size Expansion

Consider the stochastic differential equation (6.38)

$$\frac{d\eta_r}{dt} = \sum_p A_r^p J_p(\underline{\eta}(t)) + \varepsilon \sum_s C_{rs}[\underline{J}(\underline{\eta}(t))]\, \xi_s(t) \tag{7.14}$$

Substituting

$$\underline{\eta}(t) = \underline{\eta}(eq) + \varepsilon\, \underline{\eta}_1(t) \tag{7.15}$$

in (7.14) and using the fact that

$$J_p(\underline{\eta}(eq)) = 0 \tag{7.16}$$

we obtain to the lowest order in ε the following linear equation for $\eta_{r,1}$

$$\frac{d\eta_{r,1}}{dt} = -\sum_s F_{rs}\, \eta_{s,1} \tag{7.17}$$

where

$$F_{rs} = -\sum_p A_r^p \left[\frac{\partial J_p(\underline{\eta})}{\partial \eta_s}\right]_{\underline{\eta} = \underline{\eta}(eq)} \tag{7.18}$$

Eqn. (7.14) has no noise term, because when (7.16) is satisfied the noise coefficient to the lowest order vanishes as well.

Now

$$\frac{\partial}{\partial \alpha'_s}\langle \alpha_r, t \,|\, [\underline{\alpha}', t]\rangle = \frac{\partial}{\partial \eta'_{s,1}}\langle \eta_{r,1}, t \,|\, [\underline{\eta}_{,1}, t']\rangle = \left(\exp[-F(t-t')]\right)_{rs} \tag{7.19}$$

where we have used (7.17).

Substituting (7.19) in (5.20) we have, to the lowest order, in ε

$$\begin{aligned}\langle x_r(t), x_s(t')\rangle &= V\left(\exp[-F(t-t')]\right)_{rs} \langle \eta_s(eq)\rangle \\ &= V\left(\exp[-F(t-t')]\right)_{rs} \langle x_s\rangle_{eq}\end{aligned} \tag{7.20}$$

which is the well known result valid in thermodynamic equilibrium. Thus at this level the time dependence of the two time correlation function is entirely determined by the macroscopic equations of motion which define F .

When the reaction mechanism admits certain conserved quantities some of the eigenvalues of F vanish and we have non decaying terms present in the two time correlation functions as we shall see in section 7.5.2.

7.5 Next Higher Order Corrections

In this section we shall calculate next higher order corrections to the lowest order result (7.20). Higher order corrections, in a specific case, have also been calculated by van Kampen using his system size expansion.[41] We shall consider two examples. Our first example is a simple non linear reaction with a Poissonian steady state and serves to illustrate the technique. The second one is a two variable equilibrium reaction with a conservation law.

7.5.1 A Non Linear Reaction with a Poissonian Steady State

Consider the reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X \tag{7.21}$$

the stochastic differential equation for which is

$$\frac{d\eta}{dt} = (K_1 - K_2\eta^2) + \varepsilon\sqrt{2(K_1 - K_2\eta^2)}\,\xi(t) \tag{7.22}$$

Because we hold the total quantity of A fixed (7.21) is not a genuine equilibrium reaction. However it has a Poissonian steady state as a consequence of which we have

$$K_1 - K_2\,\eta^2(s.s) = 0$$

exactly.

To solve (7.22) perturbatively we expand $\eta(t)$thus

$$\eta(t) = \eta_0(t) + \varepsilon\eta_1(t) + \varepsilon^2\eta_2(t) \tag{7.23}$$

Substituting (7.23) in (7.22) and equating like powers of ε we get

$$\frac{d\eta_0}{dt} = K_1 - K_2\eta_0^2 \tag{7.24a}$$

$$\frac{d\eta_1}{dt} = -2K_2\eta_0\eta_1 + \sqrt{2(K_1 - K_2\eta_0^2)}\,\xi(t) \tag{7.24b}$$

$$\frac{d\eta_2}{dt} = -2K_2\eta_0\eta_2 - K_2\eta_0^2 - \frac{2K_2\,\eta_0\eta_1}{\sqrt{2(K_1 - K_2\eta_0^2)}}\,\xi(t) \tag{7.24c}$$

Note that if we put $\eta_0(t) = \eta(s.s)$, the above equations become singular. This arises because of the square root nature of the noise coefficient and the fact that the expansion is being done about a point at which the flucuations vanish.

Defining

$$G(t,t') = \exp\left[-2K_2 \int_{t'}^{t} dt'' \, \eta_0(t'')\right] \qquad (7.25)$$

and solving (7.24a) to (7.24c) subject to the initial condition

$$\eta_i(0) = 0 \ , \ i \geqslant 1 \qquad (7.26)$$

(henceforth we shall choose the initial time to be zero) we obtain

$$\eta_1(t) = \int_0^t dt' \, G(t,t') \sqrt{2(K_1 - K_2\eta_0^2(t'))} \, \xi(t') \qquad (7.27a)$$

$$\begin{aligned} \eta_2(t) = &- K_2 \int_0^t dt' \, G(t,t') \, \eta_1^2(t') \\ &- 2K_2 \int_0^t dt' \, G(t,t') \, \frac{\eta_0(t')\eta_1(t')\xi(t')}{\sqrt{2(K_1 - K_2\eta_0^2(t'))}} \end{aligned} \qquad (7.27b)$$

where $\eta_0(t)$ is the solution of (7.24a) as a function of its initial condition.

It follows from (7.27) that

$$\langle \eta_1^2(t) \rangle = \int_0^t dt' \, G^2(t,t') \, [2(K_1 - K_2\eta_0^2(t'))] \qquad (7.28)$$

Taking averages on both sides of (7.27) we have

$$\begin{aligned} \langle \eta_2(t) \rangle = &- K_2 \int_0^t dt' \, G(t,t') \, \langle \eta_1^2(t') \\ &- 2K_2 \int_0^t dt' \, G(t,t') \, \eta_0(t') \, \frac{\langle \eta_1(t')\xi(t') \rangle}{\sqrt{2(K_1 - K_2\eta_0^2(t'))}} \end{aligned} \qquad (7.29)$$

Now let us calculate $\langle \eta_1(t)\xi(t) \rangle$

$$\langle \eta_1(t)\xi(t) \rangle = \int_0^t dt' \, G(t,t') \sqrt{2(K_1 - K_2\eta_0^2(t'))} \, \delta(t-t') \qquad (7.30)$$

The integral on the LHS of (7.30) has a delta function singularity at the upper limit of the time integral and hence in accordance with Itô rules must be set equal to zero.

Thus

$$\langle \eta_2(t)\rangle = -k_2 \int_0^t dt'\, G(t,t')\, \langle \eta_1^2(t')\rangle \tag{7.31}$$

Now we wish to calculate the desired response function which has the following expansion.

$$\left.\frac{\partial\langle\eta(t)\rangle}{\partial\eta(0)}\right|_{\eta(0)=\eta(s.s)} = \left.\frac{\partial\eta_0(t)}{\partial\eta_0(0)}\right|_{\eta_0(0)=\eta(s.s)} + \epsilon^2 \left.\frac{\partial\langle\eta_2(t)\rangle}{\partial\eta_0(0)}\right|_{\eta_0(0)=\eta(s.s)} \tag{7.32}$$

where we have used the abbreviated notation

$$\frac{\partial\langle\eta(t)\rangle}{\partial\eta(0)} = \frac{\partial\langle\eta(t)\,|\,[\eta(0),0]\rangle}{\partial\eta(0)} \tag{7.33}$$

for the response function, we have simply to carry out the appropriate differentiation in (7.32) and evaluate these at the steady state. It is clear that

$$\left.\frac{\partial\eta_0(t)}{\partial\eta_0(0)}\right|_{\eta_0(0)=\eta(s.s)} = \left.G(t,0)\right|_{\eta_0(0)=\eta(s.s)} = \exp[-2k_2\eta(s.s)t] \tag{7.34}$$

The next term involves the derivative of (7.29) with respect to $\eta_0(0)$ but since the final factor is zero when $\eta_0(0)=\eta(s.s)$ only the term in which it is differentiated is non zero at this point. Thus proceeding it is straightforward to derive the second term. Substituting all these in the formula for the two time correlation function we have

$$\langle X(t), X(0)\rangle = V\eta(s.s)\, e^{-2k_2\eta(s.s)t} \times \left[1 + \frac{1}{V}\left\{\frac{k_2}{2}\left(t - \frac{1}{2k_2\eta(s.s)}\right) + \frac{1}{2k_2\eta(s.s)}\, e^{-2k_2\eta(s.s)t}\right\}\right] \tag{7.35}$$

7.5.2 An Equilibrium Reaction with a Conserved Quantity

We now consider a genuine equilibrium reaction with a conservation law

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Y \tag{7.36}$$

The stochastic differential equations for which are

$$\frac{d\eta_1}{dt} = -[K_1\eta_1 - K_2\eta_2^2] \qquad (7.37a)$$

$$\frac{d\eta_2}{dt} = 2[K_1\eta_1 - K_2\eta_2^2] + \varepsilon\sqrt{2(K_1\eta_1 - K_2\eta_2^2)}\ \xi(t) \qquad (7.37b)$$

To display the conserved quantity we define

$$\chi_1(t) = \eta_1(t) \qquad (7.38a)$$

$$\chi_3(t) = 2\eta_1(t) + \eta_2(t) \qquad (7.38b)$$

which gives

$$\frac{d\chi_1}{dt} = -[K_1 - K_2\chi_3^2 + 4K_2\chi_3\chi_1 - 4K_2\chi_1^2] \qquad (7.39a)$$

$$\frac{d\chi_3}{dt} = \varepsilon\sqrt{2[K_1 - K_2\chi_3^2 + 4K_2\chi_3\chi_1 - 4K_2\chi_1^2]}\ \xi(t) \qquad (7.39b)$$

It follows from (7.39b) that

$$\frac{d}{dt}\langle\chi_3(t)\rangle = 0 \qquad (7.40)$$

i.e.

$$\chi_3(eq) = \langle\chi_3(0)\rangle = \langle 2X + Y\rangle \qquad (7.41)$$

The equilibrium value of $\eta_1(eq) = \chi_1(eq)$ is given in terms of $\chi_3(eq)$ by

$$K_1 - K_2\chi_3^2(eq) + 4\chi_3(eq)\chi_1(eq) - 4K_2\chi_1^2(eq) = 0 \qquad (7.42)$$

exactly. $\eta_2(eq)$ may be deduced by using the conservation law. In terms of χ_1 and χ_3 the two time correlations may be written as

$$\langle 2X(t) + Y(t),\ X(0)\rangle = \chi_1(eq) \qquad (7.43a)$$

$$\langle 2X(t) + Y(t),\ Y(0)\rangle = \chi_3(eq) - 2\chi_1(eq) \qquad (7.43b)$$

$$\langle X(t),X(0)\rangle = x_1(eq)\left[\frac{\partial\langle x_1(t)\rangle}{\partial x_1(0)} + 2\frac{\partial\langle x_1(t)\rangle}{\partial x_3(0)}\right]_{\underline{x} = x(eq)} \tag{7.43c}$$

$$\langle X(t), Y(0)\rangle = [x_3(eq) - 2x_1(eq)]\left[\frac{\partial\langle x_1(t)\rangle}{\partial x_3(0)}\right]_{\underline{x} = \underline{x}(eq)} \tag{7.43d}$$

Thus to evaluate the various two time correlations, one only needs to calculate the response functions $\left.\frac{\partial\langle x_1(t)\rangle}{\partial x_1(0)}\right|_{eq}$ and $\left.\frac{\partial\langle x_1(t)\rangle}{\partial x_3(0)}\right|_{eq}$. Following the procedure outlined above the results are found to be

$$\langle X(t),X(0)\rangle = Vx_1(eq)\left[1-\frac{K_1}{a}(1-e^{-at}) + \frac{1}{V}\left(2-\frac{K_1}{a}\right)H(t)\right] \tag{7.44}$$

$$\langle X(t), Y(0)\rangle = V[x_3(eq)-x_1(eq)]\left(\frac{a-K_1}{2}\right)\left[1-e^{-at}+\frac{1}{V}H(t)\right] \tag{7.45}$$

where

$$\begin{aligned} a &= K_1 + 4K_2 x_3(eq) - 8K_2 x_1(eq) \\ &= K_1\sqrt{1+\frac{8K_2x_3(eq)}{K_1}} \end{aligned} \tag{7.46}$$

and

$$\begin{aligned} H(t) = {} & \frac{2K_2}{a}\left[1-e^{-at}(1+at)\right] \\ & - \frac{4K_2(a-K_1)}{a^2}\left[1-e^{-at}\left(1+at+\frac{a^2t^2}{2}\right)\right] \\ & + 4\frac{K_2(a-K_1)^2}{a^3}\left[1+e^{-at}\left(1-2at-\frac{a^2t^2}{2}\right)-e^{-2at}(2+at)\right] \end{aligned} \tag{7.47}$$

The other two correlation functions, namely $\langle Y(t), Y(0)\rangle$ and $\langle Y(t), X(0)\rangle$ may be calculated using (7.44), (7.45) and (7.43a), (7.43b).

7.5.3 Comparison with the Two Time Correlation Functions in the Canonical Ensemble

The non decaying terms in the two time correlation functions (7.44) and (7.45) arise as a consequence of using the grand canonical ensemble, in which the conserved quantities do not have a sharply defined value. Thus the decay constant of the two time correlation function of such conserved quantities is infinite. In contrast, in a canonical ensemble the conserved quantities do have a sharply defined value and may be used as constraints, to eliminate an equal number of variables. When this is done the non decaying terms do not appear in the two time correlation functions. Thus, for example, we consider the reaction (7.36) using the canonical ensemble description, then after eliminating the variable Y in the master equation using the constraint $2X+Y=N$ we obtain

$$\begin{aligned}\frac{dP(X,t)}{dt} = {} & k_1\left[(X+1)P(X+1,t) - X\,P(X,t)\right] \\ & + k_2\left[(N-2X+2)(N-2X+1)\,P(X-1,t) - (N-2X)(N-2X-1)\,P(X,t)\right]\end{aligned} \qquad (7.48)$$

which is equivalent to the following Fokker-Planck equation

$$\begin{aligned}\frac{\partial f(\alpha,t)}{\partial t} = {} & -\frac{\partial}{\partial\alpha}\left[-k_1\alpha + k_2N(N-1) - 4k_2N(N-1)\alpha + 4k_2\alpha^2\right] f(\alpha,t) \\ & + \frac{\partial^2}{\partial\alpha^2}\left[-4k_2(N-1) + 8K_2\alpha^2\right] f(\alpha,t) - \frac{\partial^3}{\partial\alpha^3}\left[4K_2\alpha^2\right] f(\alpha,t)\end{aligned} \qquad (7.49)$$

In the Gaussian approximation (7.49) gives the following stochastic differential equations

$$\frac{d\eta_0}{dt} = -K_1\eta_0 + K_2 n^2 - 4K_2 n\eta_0 + 4K_2\eta_0^2 \qquad (7.50a)$$

$$\frac{d\eta_1}{dt} = -\left[K_1 + 4K_2 n - 8K_2\eta_0\right]\eta_1 + \sqrt{16K_2\eta_0^2 - 8K_2 n\eta_0}\,\xi(t) \qquad (7.50b)$$

where $n = \frac{N}{V}$. (7.50a) and (7.50b) in the thermodynamic equilibrium give

$$\langle X(t), X(0)\rangle = \frac{K_1}{a}\eta_0(eq)\, e^{-at} \qquad (7.51)$$

In contrast to the grand canonical ensemble result in the Gaussian approximation obtained in section 7.5.a, namely

$$\langle X(t), X(0) \rangle = \frac{\kappa_1 \eta_0(eq)}{a} \left[e^{-at} + \frac{a}{\kappa_1} - 1 \right] \qquad (7.52)$$

the result (7.51) does not have any non decaying terms.

Hence, when spatial dependence is omitted the canonical and grand canonical ensembles give very different results. When spatial diffusion is included, the conservation law in the canonical ensemble then becomes $\sum_i [2X(i) + Y(i)] = N$ where the sum is over the n cells in which the system is assumed to be divided. This constraint then permits us to eliminate one variable out of the $2n$ variables that appear in the master equation. The resulting master equation is not at all easy to handle, and it is entirely unnecessary to do so. As we have seen in Chapter 3, both the canonical and grand canonical ensemble descriptions are equivalentat a local level and consequently, at that level there can be little difference between the two time correlation functions obtained by using the two descriptions. The differences between the two description manifest themselves when we talk in terms of total numbers of molecules in the system, but then it is meaningless to discuss such two time correlation functions as they do not correspond to what one measures experimentally.

CHAPTER 8

APPLICATIONS TO NON EQUILIBRIUM SYSTEMS

8.1 Introduction

The subject matter of this chapter is the application of the techniques developed previously to some interesting examples of non-equilibrium reaction systems. Our first example is a single variable reaction system involving at most bimolecular steps which exhibits a second order phase transition behaviour. The second example is a reaction which gives an imaginary noise coefficient in the α space and thus to a negative variance in the α space. The aim here is to show that such situations may arise in the Poisson representation. In the third example we consider a single variable reaction system involving a trimolecular reaction which exhibits a first order phase transition behaviour. Our purpose here is to show how the "third order" noise terms which arise owing to the presence of a trimolecular reaction may be handled in a perturbative expansion.

The far from equilibrium phase transition aspects of our first and the third example have been investigated quite thoroughly by various authors whose works are appropriately noted. In most of these works the calculations of the mean and variance have been done to the lowest order in the system size expansion. We shall calculate the next order corrections as well and show that these diverge near the critical points.

Finally in section 8.2 we derive expressions for the two time correlation functions in the lowest order in the system size expansion. The calculation of the next higher corrections will be deferred until the next chapter.

8.2 Applications to Non-equilibrium Systems

8.2.1 The Second Order Phase Transition Model

Consider the reaction system

$$\begin{aligned} A + X &\underset{k_4}{\overset{k_2}{\rightleftharpoons}} 2X \\ B + X &\underset{k_3}{\overset{k_1}{\rightleftharpoons}} C \end{aligned} \qquad (8.1)$$

[67]

This model was suggested by Schlögl who used a deterministic analysis to show that this system in a far from equilibrium situation exhibits a transition very similar to an equilibrium second order phase transition behaviour with the mean number as an order parameter and $k_1 B = k_2 A$ being the transition point. In the limit $V \to \infty, k_3 \to 0$ the slope of the mean number versus $\frac{k_2 A}{k_1 B}$ changes discontinuously and the system exhibits a critical slowing down. A number of authors have analysed the phase-transition aspects of this model and whose works have furthered the analogy with an equilibrium second order phase transition behaviour. The details may be found in refs [16, 18]. Our purpose here is simply to illustrate how the Poisson representation methods applies to this well understood system. The stochastic differential equation for (8.1) is

$$\frac{d\eta}{dt} = [\kappa_3 + (\kappa_2 - \kappa_1)\eta - \kappa_4 \eta^2] + \varepsilon \sqrt{2(\kappa_2 \eta - \kappa_4 \eta^2)}\, \xi(t) \qquad (8.2)$$

where

$$K_3 V = k_3 C\,, \quad K_2 = k_2 A\,, \; K_1 = k_1 B\,, \; K_4 V^{-1} = k_4 \tag{8.3}$$

The steady state solution of the macroscopic equation

$$\frac{d\eta}{dt} = K_3 + (K_2 - K_1)\eta - K_4 \eta^2 \tag{8.4}$$

for $K_3 = 0$ and $K_2 > K_1$ is

$$\eta(s.s) = (K_2 - K_1) \tag{8.5}$$

where we have put $K_4 = 1$.

Expanding $\eta(t)$ thus

$$\eta(t) = \eta(s.s) + \varepsilon \eta_1(t) + \varepsilon^2 \eta_2(t) + \varepsilon^3 \eta_3(t) + \cdots \tag{8.6}$$

and equating like powers of ε on both sides of (8.2) we get

$$\frac{d\eta_1}{dt} = -\eta(s.s)\eta_1(t) + \sqrt{2K_1\eta(s.s)}\;\xi(t) \tag{8.7a}$$

$$\frac{d\eta_2}{dt} = -\eta(s.s)\eta_2(t) - \eta_1^2(t) + \frac{(2K_1 - K_2)\,\eta_2(t)\,\xi(t)}{\sqrt{2K_1\eta(s.s)}} \tag{8.7b}$$

$$\frac{d\eta_3}{dt} = -\eta(s.s)\,\eta_3(t) - 2\eta_1(t)\eta_2(t) + \frac{(2K_1 - K_2)\,\eta_2(t)\,\xi(t)}{\sqrt{2K_1\eta(s.s)}} - \frac{K_2^2\,\eta_1^2(t)\,\xi(t)}{2\,[2K_1\eta(s.s)]^{3/2}} \tag{8.7c}$$

which may readily be solved for η_1 etc.

Now the mean and variance in X to $O(1)$ are related to averages in η variables by the following equations.

$$\langle X \rangle = V\eta(s.s) + \langle \eta_2 \rangle \tag{8.8a}$$

$$\langle X^2 \rangle - \langle X \rangle^2 = V\,[\eta(s.s) + \langle \eta_1^2 \rangle] + [2\langle \eta_1\eta_3 \rangle + \langle \eta_2^2 \rangle - \langle \eta_2 \rangle^2 + \langle \eta_2 \rangle] \tag{8.8b}$$

where we have used the fact that $\langle \eta_1 \rangle = \langle \eta_1 \eta_2 \rangle = \langle \eta_3 \rangle = 0$

as they involve odd factors of $\xi(t)$. The various averages appearing on the LHS of (8.8a) and (8.8b) may be calculated straightforwardly using (8.7a) to (8.7c). In the steady state the results are given by

$$\langle X\rangle_{ss} = V(K_2-K_1) - \frac{K_1}{(K_2-K_1)} \tag{8.9a}$$

$$\langle X^2\rangle_{ss} - \langle X\rangle^2_{ss} = VK_2 + \frac{K_1K_2}{(K_2-K_1)^2} \tag{8.9b}$$

As a check on the above results we have also calculated the mean and the variance directly from the steady state solutions of the corresponding Fokker Planck equation.

$$\begin{aligned}\frac{\partial f(\alpha,t)}{\partial t} = &-\frac{\partial}{\partial\alpha}\left[K_3V+(K_2-K_1)\alpha-K_4V^{-1}\alpha^2\right]f(\alpha,t)\\ &+\frac{1}{2}\frac{\partial^2}{\partial\alpha^2}\left[2(K_2\alpha-K_4V^{-1}\alpha^2)\right]f(\alpha,t)\end{aligned} \tag{8.10}$$

The steady state solution of (8.10) is

$$f(\alpha) = e^{\alpha}(K_2V-\alpha)^{V(K_1-\frac{K_3}{K_2})-1}\,\alpha^{(\frac{K_3V}{K_2}-1)} \tag{8.11}$$

To obtain corresponding $P(X)$ or its moments, the α-integration contour should be taken to be from 0 to K_2. Here we wish to point out that there are other possible choices of the integration contour which satisfy the necessary requirements but these do not lead to an admissible probability distribution. This together with related matters will be discussed in appendix C .

Using (8.11) and remembering that the factorial moments of $P(X)$ are related to the moments of $f(\alpha)$ we have

$$\langle X^r\rangle_f = \frac{V^r\int_0^{K_2}d\eta\, e^{V[\eta+(K_1-\frac{K_3}{K_2})\log(K_2-\eta)+\frac{K_3}{K_2}\log\eta]}(K_2-\eta)^{-1}\eta^{r-1}}{\int_0^{K_2}d\eta\, e^{V[\eta+(K_1-\frac{K_3}{K_2})\log(K_2-\eta)+\frac{K_3}{K_2}\log\eta]}(K_2-\eta)^{-1}\eta^{-1}} \tag{8.12}$$

By noting that the integrals in (8.12) are the integral representations of the confluent hyper-geometric functions, we can derive the exact result of McNeil and Walls.[16]

From (8.12) one may obtain a complete asymptotic expansion for the moments in the inverse powers of V using methods outlined in ref 87 . In the limit $\kappa_3 \rightarrow 0$ the first two terms in the expansions for the mean and variance are found to be identical to those given by (8.9a) and (8.9b).

As noted in Chapter 6, the lowest order terms in the system size expansion may simply be obtained by approximating $f(\alpha)$ by a Gaussian.

8.2.2 A Reaction which gives $f(\alpha)$ with a Negative Variance [11,68]

Another interesting example of a non equilibrium reaction system is

$$\begin{gathered} B \xrightarrow{k_1} X \\ 2X \xrightarrow[k_2]{} A \end{gathered} \tag{8.13}$$

the stochastic differential equation for which is

$$\frac{d\eta}{dt} = \kappa_1 - 2\kappa_2 \eta^2 + i\varepsilon\sqrt{2\kappa_2}\,\eta\,\xi(t) \tag{8.14}$$

Using the perturbative techniques of the previous section we have, in the steady state

$$\langle X \rangle_{ss} = V\sqrt{\frac{a}{2}} + \frac{1}{8} + O\left(\frac{1}{V}\right) \tag{8.15a}$$

$$\langle X^2 \rangle_{ss} - \langle X \rangle_{ss}^2 = \frac{3}{4} V\sqrt{\frac{a}{2}} - \frac{1}{16} + O\left(\frac{1}{V}\right) \tag{8.15b}$$

where

$$a = \sqrt{\frac{\kappa_1}{\kappa_2}} \tag{8.16}$$

Note that in (8.14) the coefficient of the noise source is purely imaginary and hence gives a negative value for $\langle \eta^2 \rangle - \langle \eta \rangle^2$ which results in

$$\langle x^2 \rangle - \langle x \rangle^2 < \langle x \rangle \tag{8.17}$$

and thus giving rise to a $P(x)$ which is sharper than a Poisson distribution.

For this reaction system in the steady state we may again solve the corresponding Fokker-Planck equation.

$$\frac{\partial f(\alpha,t)}{\partial t} = -\frac{\partial}{\partial \alpha}\left[K_1 V - 2K_2 V^{-1}\alpha^2\right] f(\alpha,t) - \frac{\partial^2}{\partial \alpha^2}\left[K_2 V^{-1}\alpha^2\right] f(\alpha,t) \tag{8.18}$$

The steady state solution of (8.18) is

$$f(\alpha) = \alpha^{-2} \exp\left[2\alpha + \frac{aV^2}{\alpha}\right] \tag{8.19}$$

and the associated α contour is a closed contour encircling the origin.[†] Here again there is another possible choice of α - contour but it does not lead to an admissible probability distribution as we shall show in appendix C .

From (8.19) we get

$$\langle x^r \rangle_f = V^r \frac{\oint e^{V\left[2\eta + \frac{a}{\eta}\right]} \eta^{r-2}}{\oint e^{V\left[2\eta + \frac{a}{\eta}\right]} \eta^{-2}} \tag{8.20}$$

[†] In this case the argument presented in Chapter 3 to justify the neglect of the first constant of integration in the steady state solution of (8.18) does not apply since the contour of integration here is closed. However the most general solution

$$f(\alpha) = C_1 \alpha^{-2} e^{\left(2\alpha + \frac{aV^2}{\alpha}\right)} + C_2 \alpha^{-2} e^{\left(2\alpha + \frac{aV^2}{\alpha}\right)} \int_0^{\alpha'} e^{-\left(2\alpha' + \frac{aV^2}{\alpha'}\right)} d\alpha'$$

is not a single valued function of α - (8.19) is the only solution which leads to a unique steady state solution for the corresponding .

Unlike the previous example, the coefficient of V in the exponent of the integrand in (8.20) namely $(2\eta + \frac{a}{\eta})$ does not have a maximum at the deterministic steady state $\eta = \sqrt{\frac{a}{2}}$ However in the complex η plane this point is a saddle point and provides the dominant contributions to the integral.

Thus the negative diffusion coefficient in (8.18) (or equivalently the imaginary noise coefficient in (8.14) reflects itself by giving rise to a saddle point in η-plane at the deterministic steady state, which results in the variance of $P(X)$ being less than the mean. From (8.20) all the moments can be calculated exactly.

$$\langle x^r \rangle_f = \left(V\sqrt{\frac{a}{2}}\right)^r \frac{I_r(2\sqrt{2a}\,V)}{I_1(2\sqrt{2a}\,V)} \tag{8.21}$$

Using the large argument expansion for $I_r(2\sqrt{2a}V)$ we have verified (8.15a) and (8.15b) which also agree with the results of ref **11** , and **68** .

8.2.3 The First Order Phase Transition Model

Consider the chemical process

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \;,\; A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} X \tag{8.22}$$

That this model exhibits a first order phase transition behaviour has been shown by Schlögl[67] using a deterministic approach and by Matheson et al[20] using a stochastic approach. In the steady state the deterministic equation is a cubic equation and depending on the values of the parameters

$B = \frac{k_1 A}{k_2}$, $R = \frac{k_4}{k_2}$ and $P = \frac{k_3}{k_1}$ one has either one or three steady states, in the latter case one of the steady states is metastable. Various aspects of this model namely hysterisis, life time of the metastable state nucleation etc. have been investigated by a number of authors and the details may be found in refs[20, 69-71]. In considering this model our aim is to show how a system size expansion of the corresponding stochastic differential equation is to be performed when the "third order noise" terms are to be taken into account owing to the presence of a trimolecular reaction.

The Fokker Planck equation and the stochastic differential equations for (8.22) are

$$\begin{aligned} \frac{\partial f(\alpha,t)}{\partial t} = & -\frac{\partial}{\partial \alpha}\left[K_1 V^{-1}\alpha^2 - K_2 V^{-2}\alpha^3 + K_3 V - K_4 \alpha\right] f(\alpha,t) \\ & + \frac{1}{2}\frac{\partial^2}{\partial \alpha^2}\left[4\left(K_1 V^{-1}\alpha^2 - K_2 V^{-2}\alpha^3\right)\right] f(\alpha,t) \\ & - \frac{1}{3!}\frac{\partial^3}{\partial \alpha^3}\left[6\left(K_1 V^{-1}\alpha^2 - K_2 V^{-2}\alpha^3\right] f(\alpha,t) \right. , \end{aligned} \tag{8.23}$$

$$\begin{aligned} \frac{d\eta(t)}{dt} = & K_1\eta^2 - K_2\eta^3 + K_3 - K_4\eta + \mu^3\left[4\left(K_1\eta^2 - K_2\eta^3\right)\right]^{\frac{1}{2}} \\ & + \mu^4\left[6\left(K_1\eta^2 - K_2\eta^3\right)\right]^{\frac{1}{3}} \xi(t) \end{aligned} \tag{8.24}$$

where $K_1 V^{-1} = k_1 A$, $K_2 V^{-2} = k_2$, $K_3 V = k_3 A$, $K_4 = k_4$ (8.25)

$\eta = \alpha / V$, $\mu = V^{-\frac{1}{6}}$. The "third order noise" source $\xi(t)$ has been defined in Chapter 6.

In the steady state (8.23) reduces to a linear second order differential equation which may be solved in terms of hypergeometric functions and an asymptotic expansion for the various moments may be obtained using methods outlined previously. This procedure, although possible in principle is not very practicable. It is in such cases that the method of stochastic differential equations proves to be very useful in its ease of application.

Equation (8.24) may be solved iteratively by expanding thus

$$\eta(t) = \eta_0(t) + \mu^3\eta_3(t) + \mu^4\eta_4(t) + \mu^6\eta_6(t) + \mu^8\eta_8(t) + \cdots \tag{8.26}$$

which when substituted in (8.24) yields the determinstic equation in the lowest order and linear stochastic differential equations in the higher orders which may be solved as before.

In the steady state the results are

$$\begin{aligned}\langle X\rangle_{ss} &= V\eta_0(ss) + \langle\eta_6\rangle_{ss} + O(\tfrac{1}{V}) \\ &= V\eta_0(ss) + \frac{2ab}{c^2} + O(\tfrac{1}{V})\end{aligned} \tag{8.27a}$$

$$\begin{aligned}\langle X^2\rangle_{ss} - \langle X\rangle^2_{ss} &= V\langle\eta_3^2\rangle_{ss} + \left[2\langle\eta_9\eta_3\rangle + 2\langle\eta_8\eta_4\rangle + \langle\eta_6^2\rangle - \langle\eta_6\rangle^2 + \langle\eta_6\rangle\right]_{ss} + O(\tfrac{1}{V}) \\ &= V\left(\frac{2a}{c}\right) + \left[\frac{28}{3}\frac{a^2b^2}{c^4} + \frac{8ab^2\eta_0(ss)}{c^3} - \frac{36K_2a^3}{c^3} + \frac{8ab}{c^2}\right] \\ &\quad + O(\tfrac{1}{V})\end{aligned} \tag{8.27b}$$

$$\begin{aligned}\langle(X - \langle X\rangle)^3\rangle_{ss} &= V\left[\langle\eta_4^3\rangle - 3\langle\eta_3^2\rangle\langle\eta_6\rangle + 3\langle\eta_3^2\rangle + \eta_0(ss)\right]_{ss} + O(1) \\ &= V\left[\frac{8a}{c} - \frac{12a^2b}{c^3} + \eta_0(ss)\right]\end{aligned} \tag{8.27c}$$

where $a = K_1\eta_0^2(ss) - K_2\eta_0^3(ss)$, $b = 2K_1 - 3K_2\eta_0(ss)$, $c = K_4 - 2K_1\eta_0(ss) + 3K_2\eta_0^2(ss)$ and $\eta_0(ss)$ is the solution of the steady state deterministic equation.

$$K_1\eta_0^2(ss) - K_2\eta_0^3(ss) + K_3 - K_4\eta_0(ss) = 0 \tag{8.28}$$

Here a few remarks are in order. The "third order noise source" $\xi(t)$ contributes to $O(\frac{1}{V})$ to the mean, to $O(1)$ to the variance but contributes to $O(V)$ to the skewness coefficient. To $O(V)$ the results for the mean and variance are identical to those given by the cumulant method and in fact if one is only interested in calculating the mean and the variance to $O(V)$ the third order noise may be dropped from (8.29) and the expansion carried out in the powers of ε. Also note that as $c \to 0$ the variance and the higher order corrections become divergent. This, of course, is due to the fact that in this limit, the reaction system exhibits a first order phase transition type behaviour as has been discussed in references (20, 67).

A further point to note is that our simple iterative method expands about a Poisson whose mean is the deterministic mean. In the case, as arises here, that multiple steady states are possible, it gives an asymptotic expansion for the moments of one or other of the possible stable solutions, but tells nothing about relative stability. The unstable solution, however, gives an iterative solution, which as expected, diverges.

8.3 Two Time Correlations for Non-Equilibrium Systems: The Lowest Order Results

As we have seen in Section 6.5 if (6.38) is linearised by putting

$$\underline{\eta}(t) = \underline{\eta}_0(SS) + \varepsilon \underline{\eta}_1(t) \tag{8.29}$$

where $\underline{\eta}_0(SS)$ are the macroscopic steady state values given by

$$\sum_p A_r^p J_p(\underline{\eta}_0(SS)) = 0 \tag{8.30}$$

then in the lowest order in ε this gives a linear stochastic differential equation for

$$\frac{d\eta_{r,1}}{dt} = -\sum F_{rs}\eta_{s,1} + \sum_{s} K_{rs}\xi_s(t) \qquad (8.31)$$

where F_{rs} and K_{rs} are given by (6.49) and (6.50) and are evaluated at $\underline{\eta}(t)=\eta_0(SS)$. From (8.31) it follows that

$$\langle \alpha_r(t), \alpha_s(t)\rangle = V\sum_{r'} \left(\exp[-F(t-t')]\right)_{rr'} \langle \eta_{r',1}(t')\,\eta_{s,1}(t')\rangle \qquad (8.32)$$

and $$\frac{\partial}{\partial \alpha'_s}\langle \alpha_r, t \mid [\underline{\alpha}', t']\rangle = \frac{\partial}{\partial \eta'_{s,1}}\langle \eta_{r,1}, t \mid [\underline{\eta}'_{,1}, t']\rangle$$
$$= \left(\exp[-F(t-t')]\right)_{rs} \qquad (8.33)$$

So that substituting in (4.18)

$$\langle X_r(t), X_s(t')\rangle = V\sum_{r'} \left(\exp[-F(t-t')]\right)_{rr'} [\langle \eta_{r',1}(t')\,\eta'_{s,1}(t') + \delta_{r's}\eta_s(SS)]$$
$$= \sum_{r'} \left(\exp[-F(t-t')]\right)_{rr'} \langle X_{r'}(t'), X_s(t')\rangle \qquad (8.34)$$

This is the expression for the two time correlation functions for non equilibrium system to the lowest order in the system size expansion. For equilibirum systems, because of the Poissonian nature of the variance matrix (8.34) reduces to (7.20).

To the lowest order, the two time correlation functions for the three models discussed above are

(a) $$\langle X(t), X(0)\rangle = VK_2 \exp[-(K_2-K_1)t] \qquad (8.35a)$$

(b) $$\langle X(t), X(0)\rangle = \frac{3}{4}V\sqrt{\frac{a}{2}}\;\exp\left[-4K_2\sqrt{\frac{a}{2}}\,t\right] \qquad (8.35b)$$

(c) $$\langle X(t), X(0)\rangle = \frac{2aV}{c}\;\exp[-ct] \qquad (8.35c)$$

CHAPTER 9

THE SECOND ORDER PHASE TRANSITION MODEL

9.1 Introduction

This chapter is devoted to the study of a non-equilibrium chemical reactions including the process of spatial diffusion. We shall consider the second order phase transition model[18,67] for which we shall perturbatively calculate the first two terms for the spatial and the two time correlation functions. The leading term for the spatial correlation function is found to be in agreement with the results of Gardiner et al[18], who, in order to close the hierarchy of moment equations used a factorization ansatz (which as we have explained in Chapter 6 is equivalent to a Gaussian approximation). We find, with Gardiner et al, that near the phase transition point, this model exhibits a long range correlated behaviour and to the approximation considered is characterised by a classical critical exponent.

Mori and McNeil,[64] using their scaling theory for non equilibrium non uniform systems, have investigated the validity of the Gaussian approximation, near critical points, as a function of the dimensionality of the system. They find that, for this model, if the dimensionality of the system is greater than four then the corrections to the Gaussian approximation results are negligible as the critical point is approached. Otherwise they are divergent. Our calculations of the next higher corrections to the Gaussian approximation results for the spatial correlation functions explicitly corroborate their results.

The results for the two time correlation function to the lowest order are found to be in agreement with Gardiner et al.[18] The next higher corrections for the two time correlation function as we shall see, also have an interesting analytic structure and suggest the possibility of non classical dynamical exponents for this model.

With the spatial diffusion model as introduced in Chapter 3 and the adoption of a continuum notation to make the stochastic differential mathematically tractable certain problems arise in the higher order corrections. We shall discuss these problems and suggest possible ways for rectifying them.

9.2 The Second Order Phase Transition Model with Diffusion

Following the discussion given in Chapter 6, section 6.4, the stochastic differential equation for a multicell system with spatial diffusion and the chemical reaction

$$\begin{aligned} A + X &\overset{k_2}{\rightleftharpoons} 2X \\ B + X &\underset{k_4}{\overset{k_1}{\rightleftharpoons}} C \end{aligned} \qquad (9.1)$$

may be written as

$$\frac{d\eta(i,t)}{dt} = \sum_j D_{ij}\,\eta(j,t) + K_3 + (K_2-K_1)\,\eta(i,t) - K_4\,\eta^2(i,t) + \frac{1}{\sqrt{\Delta V}}\sqrt{2(K_2\eta(i,t) - K_4\eta^2(i,t))}\;\xi(i,t) \tag{9.2}$$

where $K_3\,\Delta V = k_3 C$, $K_2 = k_2 A$, $K_1 = k_1 B$, $K_4\,\Delta V^{-1} = k_4$. Henceforth we shall put $K_4 = 1$

The mean, the spatial correlation function, and the two time correlation function in X variables are related to those in α variables through the following equations.

$$\langle X(i,t)\rangle = \Delta V\,\langle \eta(i,t)\rangle \tag{9.3a}$$

$$\langle X(i,t), X(j,t)\rangle = (\Delta V)^2\left[\langle \eta(i,t),\eta(j,t)\rangle + \frac{\delta_{ij}}{\Delta V}\langle \eta(i,t)\rangle\right] \tag{9.3b}$$

$$\langle X(i,t), X(j,0)\rangle = (\Delta V)^2\Big[\langle \eta(i,t), \eta(j,0)\rangle + \frac{1}{\Delta V}\Big\langle \eta(j,0)\,\frac{\partial\langle \eta(i,t)|[\underline{\eta}(0),0]\rangle}{\partial\eta(j,0)}\Big\rangle \tag{9.3c}$$

In the continuum limit, i.e. $\Delta V \to 0$, (9.2) and (9.3a) to (9.3c) become

$$\frac{d\eta(\underline{r},t)}{dt} = (\mathcal{D}\eta)(\underline{r},t) + K_3 + (K_2-K_1)\,\eta(\underline{r},t) - \eta^2(\underline{r},t) + \sqrt{2(K_2\eta(\underline{r},t) - \eta^2(\underline{r},t))}\;\xi(\underline{r},t) \tag{9.4}$$

and

$$M(\underline{r},t) = \langle \eta(\underline{r},t)\rangle \tag{9.5a}$$

$$S(\underline{r},\underline{r}',t) = \langle \eta(\underline{r},t), \eta(\underline{r}',t)\rangle + \delta(\underline{r}-\underline{r}')\,\langle \eta(\underline{r},t)\rangle \tag{9.5b}$$

$$T(\underline{r},\underline{r}',t) = \langle \eta(\underline{r},t), \eta(\underline{r}',0)\rangle + \Big\langle \eta(\underline{r}',0)\,\frac{\delta\langle \eta(\underline{r},t)\rangle}{\delta\,\eta(\underline{r}',0)}\Big\rangle \tag{9.5c}$$

where we have introduced the following notation

(i) $$M(\underline{r},t) = \langle \rho(\underline{r},t)\rangle \; ; \; \rho(\underline{r},t) = \frac{X(i,t)}{\Delta V} \qquad (9.6)$$

$\rho(\underline{r},t)$ therefore corresponds to the chemical concentration at point $\underline{r}$.

(ii) The noise source $\xi(\underline{r},t)$ is given by

$$\xi(\underline{r},t) = \frac{\xi_i(t)}{\sqrt{\Delta V}} \qquad (9.7)$$

and satisfies the following

$$\langle \xi(\underline{r},t)\rangle = 0$$
$$\langle \xi(\underline{r},t)\, \xi(\underline{r}',t')\rangle = \delta(\underline{r}-\underline{r}')\, \delta(t-t') \qquad (9.8)$$

(The factor $\frac{1}{\sqrt{\Delta V}}$ in (7.7) arises because of

$$\langle \xi(i,t)\, \xi(j,t')\rangle = \delta_{ij}\, \delta(t-t')$$

and the fact that

$$\lim_{\Delta V \to 0} \frac{\delta_{ij}}{\Delta V} = \delta(r-r')$$

in the continuum notation)

(iii) $S(\underline{r},\underline{r}',t)$ and $T(\underline{r},\underline{r}',t)$ are the spatial and the two time correlation functions respectively

$$S(\underline{r},\underline{r}',t) = \langle \rho(\underline{r},t), \rho(\underline{r}',t)\rangle \qquad (9.9)$$

$$T(\underline{r},r',t) = \langle \rho(\underline{r},t), \rho(\underline{r}',t')\rangle . \qquad (9.10)$$

(iv) $\frac{\delta\langle \eta(\underline{r},t)\rangle}{\delta\, \eta(\underline{r},0)}$ is the function derivative of $\langle \eta(\underline{r},t)\rangle$ with respect to the initial values.

(v) $(\mathfrak{D}\eta)(\underline{r},t)$ is the continuum limit of the spatial diffusion term $\sum_j \mathcal{D}_{ij}\, \eta(j,t)$. With a general form for the transition probabilities, d_{ij}, for the diffusion of one molecule from cell i to cell j

which define D_{ij} through (6.43), we may write $\mathcal{D}$ as a convolution operator

$$(\mathcal{D}\eta)(\underline{r},t) = -\int \mathcal{D}(|\underline{r}-\underline{r}'|)\,\eta(\underline{r}',t)\,dr' \tag{9.11}$$

If we chose the d_{ij} to be

$$d_{ij} = \begin{cases} d \ , \ i,j & \text{adjacent} \\ 0 \ . & \text{otherwise} \end{cases} \tag{9.12}$$

then we have

$$(\mathcal{D}\eta)(\underline{r},t) = D\nabla^2\eta(\underline{r},t) \tag{9.13}$$

where $D = d\ell^2$, ℓ being the cell length.

In most of our work we shall use the form (9.13) for the spatial diffusion terms, although our technique applies equally well to any other choice.

In the following we shall be mainly concerned with calculating $S(\underline{r},\underline{r}',t)$ and $T(\underline{r},r',t)$ in the steady state. With $K_3 = 0$ and $K_2 - K_1 > 0$ the homogeneous steady state solution of the non fluctuating part (or the deterministic part) of (9.4) is

$$\eta(S.S) = K_2 - K_1 \tag{9.14}$$

Substituting

$$\eta(\underline{r},t) = \eta(S.S) + \hat{\eta}(\underline{r},t) \tag{9.15}$$

in (9.4), (9.5a) to (9.5c) we have

$$\frac{d\hat{\eta}(\underline{r},t)}{dt} = [D\nabla^2 - \eta(s.s)]\,\hat{\eta}(\underline{r},t) - \hat{\eta}^2(\underline{r},t) + \sqrt{2(K_1\eta(s.s) + (2K_1-K_2)\hat{\eta}(\underline{r},t) - \hat{\eta}^2(\underline{r},t))}\,\xi(\underline{r},t) \tag{9.16}$$

$$M(\underline{r},t) = \eta(s.s) + \langle\hat{\eta}(\underline{r},t)\rangle \tag{9.17a}$$

$$S(\underline{r},\underline{r}',t) = \langle\hat{\eta}(\underline{r},t),\hat{\eta}(\underline{r}',t)\rangle + [\eta(ss) + \langle\hat{\eta}(\underline{r},t)\rangle]\,\delta(\underline{r}-\underline{r}') \tag{9.17b}$$

$$T(\underline{r},\underline{r}',t) = \langle\hat{\eta}(\underline{r},t),\hat{\eta}(\underline{r}',0)\rangle + \langle[\eta(ss) + \hat{\eta}(\underline{r}',0)]\langle\hat{R}(\underline{r},t;\underline{r}',0)\rangle\rangle \tag{9.17c}$$

where we have introduced the following abbreviation

$$\hat{R}(\underline{r},t;\underline{r}',0) = \frac{\delta\hat{\eta}(\underline{r},t)}{\delta\hat{\eta}(\underline{r}',0)} \tag{9.18}$$

It must be emphasized that the adoption of a continuum form is a mathematical device which enables us to solve (9.4) using standard Fourier transform techniques and it will therefore be necessary to put an upper cut-off on the Fourier transform variables. It is also clear from (9.2) that before the continuum limit is taken, the only natural expansion parameter that appears is $(\Delta V)^{-\frac{1}{2}}$ and hence for the perturbation technique to work ΔV, the cell volume must be sufficiently large. In the continuum notation, this factor of $(\Delta V)^{-\frac{1}{2}}$ gets absorbed in the noise source and we are left without any obvious expansion parameter. So we formally introduce a parameter λ in (9.5) thus

$$\frac{d\hat{\eta}(\underline{r},t)}{dt} = [D\nabla^2 - \eta(s.s)]\,\hat{\eta}(\underline{r},t) - \hat{\eta}^2(\underline{r},t) + \lambda\sqrt{2(K_1\eta(sS) + (2K_1-K_2)\hat{\eta}(\underline{r},t) - \hat{\eta}^2(\underline{r},t))}\,\xi(\underline{r},t) \tag{9.19}$$

and set λ equal to one at the end of the calculation. However, if it is understood that all Fourier integrals have a cutoff $(\Delta V)^{-\frac{1}{3}}$ this will still be in fact a $(\Delta V)^{-1}$

expansion. It also follows from (9.19) that $\hat{R}(\underline{r},t;\underline{r}',0)$ obeys the following stochastic differential equation.

$$\frac{d\hat{R}(\underline{r},t;r',0)}{dt} = [D\nabla^2-\eta(s.s)]\,\hat{R}(\underline{r},t;\underline{r}',0)-2\hat{\eta}(\underline{r},t)\,\hat{R}(\underline{r},t;\underline{r}',0) + \frac{\lambda\,[(2K_1-K_2)-2\hat{\eta}(\underline{r},t)]\,\hat{R}(\underline{r},t;\underline{r}',0)\,\xi(\underline{r},t)}{\sqrt{2(K_1\,\eta(s.s)+(2K_1-K_2)\,\hat{\eta}(\underline{r},t)-\hat{\eta}^2(\underline{r},t))}} \tag{9.20}$$

We now expand $\hat{\eta}(\underline{r},t)$ and $\hat{R}(\underline{r},t;\underline{r}',0)$ thus

$$\begin{aligned}\hat{\eta} &= \lambda\eta_1+\lambda^2\eta_2+\cdots\\ \hat{R} &= R_0+\lambda R_1+\lambda^2R_2+\cdots\end{aligned} \tag{9.21}$$

Substituting (9.21) in (9.19) and (9.20) and equating like powers of λ on both sides we obtain

$$\frac{d\eta_1(\underline{r},t)}{dt} = [D\nabla^2-\eta(ss)]\,\eta_1(\underline{r},t)+\sqrt{2K_1\eta(ss)}\;\xi(\underline{r},t) \tag{9.22a}$$

$$\frac{d\eta_2(\underline{r},t)}{dt} = [D\nabla^2-\eta(s.s)]\,\eta_2(\underline{r},t)-\eta_1^2(\underline{r},t) + \frac{(2K_1-K_2)\eta_2(\underline{r},t)\,\xi(\underline{r},t)}{\sqrt{2K_1\eta(s.s)}}. \tag{9.22b}$$

$$\frac{d\eta_3(\underline{r},t)}{dt} = [D\nabla^2-\eta(ss)]\,\eta_3(\underline{r},t)-2\,\eta_1(\underline{r},t)\,\eta_2(\underline{r},t) + \frac{(2K_1-K_2)}{\sqrt{2K_1\eta(ss)}}\,\eta_2(\underline{r},t)\,\xi(\underline{r},t) - \frac{K_2^2\,\eta_1^2(\underline{r},t)\,\xi(\underline{r},t)}{2[2K_1\eta(s.s)]^{3/2}} \tag{9.22c}$$

$$\frac{dR_0(\underline{r},t;\underline{r}',0)}{dt} = [D\nabla^2-\eta(s.s)]\,R_0(\underline{r},t;\underline{r}',0) \tag{9.23a}$$

$$\frac{dR_1(\underline{r},t;\underline{r}',0)}{dt} = [D\nabla^2-\eta(s.s)].R_1(\underline{r},t;\underline{r}',0)-2\eta_1(\underline{r},t)\,R_0(\underline{r},t;\underline{r}',0) + \frac{(2K_1-K_2)}{\sqrt{2K_1\eta(s.s)}}\,R_0(\underline{r},t;\underline{r}',0)\,\xi(\underline{r},t) \tag{9.23b}$$

The expansions for the various terms on the L.H.S. of (9.17b) and (9.17c) are

$$\langle\hat{\eta}(\underline{r},t),\hat{\eta}(\underline{r},t)\rangle = \lambda^2\langle\eta_1(\underline{r},t)\,\eta_1(r',t)\rangle + \lambda^4\big[\langle\eta_2(\underline{r},t),\eta_2(r',t) + \langle\eta_1(\underline{r},t)\,\eta_3(\underline{r}',t)\rangle+\langle\eta_1(r',t)\,\eta_3(\underline{r},t)\rangle\big] + \cdots \tag{9.24a}$$

$$\eta(s.s) + \langle \hat{\eta}(\underline{r},t) \rangle = \eta(s.s) + \lambda^2 \langle \eta_2(\underline{r},t) \rangle \tag{9.24b}$$

and

$$\begin{aligned} \langle \hat{\eta}(\underline{r},t), \hat{\eta}(\underline{r}',0) \rangle = {} & \lambda^2 \langle \eta_1(\underline{r},t), \eta_1(\underline{r}',0) \rangle \\ & + \lambda^4 \big[\langle \eta_2(\underline{r},t), \eta_2(\underline{r}',0) \rangle \\ & \quad + \langle \eta_1(\underline{r},t), \eta_3(r',0) \rangle + \langle \eta_3(\underline{r},t)\, \eta_1(\underline{r}',0) \rangle \big] \\ & + \cdots \end{aligned} \tag{9.25a}$$

$$\begin{aligned} \langle [\eta(s.s) + \hat{\eta}(\underline{r}',0)] \langle \hat{R}(\underline{r},t;\underline{r}',0) \rangle \rangle = {} & \eta(ss) \langle R_0(\underline{r},t;\underline{r}',0) \rangle \\ & + \lambda^2 [\langle \eta_2(\underline{r}',0) \langle R_0(\underline{r},t;\underline{r}',0) \rangle \rangle \\ & + \langle \eta_1(r',0) \langle R_1(\underline{r},t;\underline{r}',0) \rangle \rangle] \end{aligned} \tag{9.25b}$$

The terms with odd powers of λ vanish identically because they involve averages of odd numbers of factors of $\xi(\underline{r},t)$. Also note that the terms in the expansion (9.24a), (9.25a) differ from the corresponding terms in (9.24b), (9.25b) by a factor of λ^2, they are actually of the same order in terms of the real expansion parameter. Keeping this in mind while grouping the terms order by order on the left hand sides of (9.17b) and (9.17c) we find that the lowest order contributions to $M(\underline{r},t)$ $S(\underline{r},\underline{r}',t)$ and $T(\underline{r},\underline{r}',t)$ are given by

$$M_0(\underline{r},t) = \eta(s.s) \tag{9.26}$$

$$S_0(\underline{r},\underline{r}',t) = \langle \eta_1(\underline{r},t)\, \eta_1(\underline{r}',t) \rangle + \eta_0(ss)\, \delta(\underline{r}-\underline{r}') \tag{9.27}$$

$$\begin{aligned} T_0(\underline{r},\underline{r}',t) = {} & \langle \eta_1(\underline{r},t)\, \eta_1(\underline{r}',0) \rangle \\ & + \eta(s.s) \langle R_0(\underline{r},t;\underline{r}',0) \rangle \end{aligned} \tag{9.28}$$

and the next higher corrections are

$$M_1(\underline{r},t) = \langle \eta_2(\underline{r},t) \rangle \tag{9.29}$$

$$\begin{aligned} S_1(\underline{r},\underline{r}',t) = [&\langle \eta_2(\underline{r},t), \eta_2(\underline{r}',t) \rangle + \langle \eta_2(\underline{r},t) \rangle \delta(\underline{r}-\underline{r}') \\ &+ \langle \eta_1(\underline{r},t) \eta_3(\underline{r}',t) \rangle + \langle \eta_3(\underline{r},t)\, \eta_1(\underline{r}',t) \rangle] \end{aligned} \tag{9.30}$$

$$\begin{aligned} T_1(\underline{r},\underline{r}',t) = [&\langle \eta_2(\underline{r},t), \eta_2(\underline{r}',0) \rangle + \langle \eta_1(\underline{r},t) \eta_3(\underline{r}',0) \rangle \\ &+ \langle \eta_3(\underline{r},t)\, \eta_1(\underline{r}',0) \rangle + \langle \eta_2(r',0) \langle R_0(\underline{r},t;\underline{r}',0) \rangle \rangle \\ &+ \langle \eta_1(\underline{r}',0) \langle R_1(\underline{r},t;\underline{r}',0) \rangle \rangle \end{aligned} \tag{9.31}$$

We shall now show how the left hand sides of (9.26)-(9.31) may be calculated from (9.23a) - (9.24b).

9.2.1 Steady State Spatial Correlation Function to the Lowest Order

Taking the Fourier transform of (9.22a) and (9.27) with respect to the spatial index we have

$$\frac{d\tilde{\eta}_1(\underline{q},t)}{dt} = -[Dq^2 + \eta(ss)]\, \tilde{\eta}_1(\underline{q},t) + \sqrt{2K_1 \eta(ss)}\; \tilde{\xi}(\underline{q},t) \tag{9.32}$$

and

$$\tilde{S}_0(\underline{q},\underline{q}',t) = \langle \tilde{\eta}_1(\underline{q},t) \tilde{\eta}_1(\underline{q}',t) \rangle + \eta(ss)\, \delta(\underline{q}+\underline{q}') \tag{9.33}$$

From (9.32) we have

$$\tilde{\eta}_1(\underline{q},t) = \sqrt{2K_1 \eta(ss)} \int_0^t dt'\, e^{-(Dq^2+\eta(ss))(t-t')}\, \tilde{\xi}(\underline{q},t) \tag{9.33}$$

which gives in the steady state

$$\langle \tilde{\eta}_1(\underline{q},t)\, \tilde{\eta}_1(\underline{q}',t) \rangle_{ss} = \frac{K_1 \eta(ss)\; \delta(\underline{q}+\underline{q}')}{[Dq^2 + \eta(ss)]} \tag{9.34}$$

Thus to the lowest order, the steady state spatial correlation function is given by

$$\tilde{S}_0(\underline{q},\underline{q}') = \eta(ss)\,\delta(\underline{q}+\underline{q}') + \frac{K_1\eta(ss)}{[Dq^2+\eta(ss)]}\,\delta(\underline{q}+\underline{q}') \quad (9.36)$$

Fourier inversions of (9.36) gives

$$S_0(\underline{r},\underline{r}') = \eta(ss)\,\delta(\underline{r}-\underline{r}') + \frac{K_1\eta(ss)}{4\pi D|r-r'|}\,e^{-\frac{|r-r'|}{\ell_c}} \quad (9.37)$$

where ℓ_c is the correlation length

$$\ell_c = \left[\frac{D}{|K_1-K_2|}\right]^{\frac{1}{2}} \quad (9.38)$$

which becomes infinite at the phase transition point, a behaviour closely analogous to the behaviour of the correlation length in a second order phase transition. To the approximation considered the critical exponent has the classical value $\frac{1}{2}$. These results are identical to those of Gardiner et al.[18]

9.2.2 The next Higher Corrections to the Mean

From (9.22b) we have

$$\langle\tilde{\eta}_2(\underline{q},t)\rangle = \int d\underline{q}'\int_0^t dt'\, e^{-[Dq^2+\eta(ss)](t-t')}\langle\tilde{\eta}_1(\underline{q}',t)\tilde{\eta}_1(\underline{q}-\underline{q}',t)\rangle \quad (9.39)$$

Using (9.34) we find that the next higher corrections to the mean concentration are given by

$$\tilde{M}_1(\underline{q},t) = \langle\tilde{\eta}_2(\underline{q},t)\rangle_{ss} = -K_1\int^{\ell^{-1}}\frac{dq_1}{[Dq_1^2+\eta(ss)]} \quad (9.40)$$

All the q - integrations in (9.40) have a cut-off equal to the inverse cell length ℓ^{-1}. If $\ell \to 0$ limit is taken the integral becomes divergent. Thus, with the model for spatial diffusion that we have chosen to work with, the corrections to the mean concentration depend on the cell size in an essential way. We shall discuss this point later in this chapter.

9.2.3 The next higher corrections to the spatial correlation function

By Fourier transforming (9.22a) to (9.22c) with respect to the spatial index, the quantities appearing on the L.H.S. of (9.30) may straightforwardly be calculated. The full expression for $\tilde{S}_1(\underline{q},q')$ in the steady state thus obtained is given in the appendix D . Here we shall only discuss the behaviour of the variance because of its relevance to the results obtained by Mori and McNeil[64] using their scaling theory for non equilibrium systems.

The expression for the variance including both the lowest order and the next order contributions to the steady state spatial correlation function turn out to be

$$[\langle X^2[V]\rangle - \langle X[V]\rangle^2]_{ss} = \int d\underline{r}\, d\underline{r}'\, [S_0(\underline{r},\underline{r}') + S_1(\underline{r},\underline{r}')]$$

$$= K_2 V + \frac{V(K_1^2 + 3K_1\eta(ss))}{2D^2} I_1 + 2VK_1^2\frac{\eta(ss)}{2D^3} I_2 \quad (9.41)$$

where $X[V] = \int_V d\underline{r}\, \rho(\underline{r})$

V being the volume of the system,

and

$$I_1 = \int^{\ell^{-1}} \frac{d^dq}{(q^2+\ell_c^{-2})(q^2+\frac{3}{2}\ell_c^{-2})} \quad (9.42a)$$

$$I_2 = \int^{\ell^{-1}} \frac{d^dq}{(q^2+\ell_c^{-2})^2(q^2+\frac{3}{2}\ell_c^{-2})} \quad (9.42b)$$

where for generality we have put the number of space dimensions equal to d.

In (9.42a) and (9.42b) ℓ_c is the correlation length defined in (9.38) and ℓ^{-1}, inverse of the cell length, is the cutoff on each q integral. The first term in (9.39) is the lowest order term and the next two terms arise from higher order corrections.

We shall now examine the behaviour of I_1 and I_2 as a function of d as the phase transition point $K_2 - K_1 \rightarrow 0$ is approached.

Defining $x = \ell_c |q|$ we have

$$I_1 = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} (\ell_c)^{4-d} \int_0^{\ell_c \ell^{-1}} \frac{x^{d-1}\,dx}{(x^2+1)(x^2+\frac{3}{2})} \tag{9.43a}$$

$$I_2 = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} (\ell_c)^{6-d} \int_0^{\ell_c \ell^{-1}} \frac{x^{d-1}\,dx}{(x^2+1)^2(x^2+\frac{3}{2})} \tag{9.43b}$$

Thus as $K_2 \rightarrow K_1$ i.e. $\ell_c \rightarrow \infty$

$$I_1 = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} (\ell_c)^{4-d} \int_0^{\infty} \frac{x^{d-1}\,dx}{(x^2+1)(x^2+\frac{3}{2})} \tag{9.44a}$$

$$= \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} (\ell_c)^{6-d} \int_0^{\infty} \frac{x^{d-1}\,dx}{(x^2+1)^2(x^2+\frac{3}{2})} \tag{9.44b}$$

Both the x integrals are finite for $d<4$. From (9.44a) (9.44b) and (9.41) it follows that the corrections to the variance diverge like $(\ell_c)^{4-d}$ for $d<4$ and logarithmically for $d=4$. For $d>4$ the corrections are finite but depend on the cell length ℓ and go to zero as $\ell \rightarrow \infty$

Thus we conclude that

(i) For $d>4$ the Gaussian approximation is valid, even near the critical points, in the limit of a large cell size.

(ii) For $d<4$ the Gaussian approximation breaks down in the critical region and the perturbation theory based on the decomposition of η into a "Macroscopic part" and a "Fluctuating part" is no longer valid no matter how large the cell.

This result is clearly related to that of Mori and McNeil[64] who find that the critical dimension for this model is $d=4$.

9.2.4 Steady State Two Time Correlation Function to the Lowest Order

To evaluate $T_0(\underline{r},\underline{r}',t)$ given by (9.28) we have to solve (9.22a) as a function of its initial condition and (9.23a) subject to the initial condition

$$R_0(\underline{r},0;\underline{r}',0) = \delta(\underline{r}-\underline{r}')$$

This gives

$$\tilde{\eta}_1(\underline{q},t) = \tilde{\eta}_1(\underline{q},0)\, e^{-[Dq^2+\eta(ss)]t} + \int_0^t dt'\, e^{-[Dq^2+\eta(ss)]t-t')} \sqrt{2K_1\eta(ss)}\, \tilde{\xi}(\underline{q},t) \tag{9.45}$$

and

$$\tilde{R}_0(\underline{q},t;\underline{q}',0) = e^{-[Dq^2+\eta(ss)]t}\, \delta(\underline{q}+\underline{q}') \tag{9.46}$$

From (9.22a), (9.45) and (9.46) we have, for $\tilde{T}_0(\underline{q},\underline{q}',t)$

$$\tilde{T}_0(\underline{q},\underline{q}',t) = e^{-[Dq^2+\eta(ss)]t}\left[\langle\tilde{\eta}_1(q,0)\tilde{\eta}_1(q',0)\rangle+\eta(ss)\,\delta(q+q')\right] \tag{9.47}$$

The second term in (9.45) gives rise to a term in $\tilde{T}_0(\underline{q},\underline{q}',t)$ which involves the average of a single $\tilde{\xi}(q,t)$ which is therefore zero.

To obtain the steady state $\tilde{T}_0(\underline{q},\underline{q}',t)$ we have to replace the initial average that appears on the L.H.S. of (9.47) by the steady state average, i.e.

$$\tilde{T}_0(\underline{q},\underline{q}',t) = e^{-[Dq^2+\eta(ss)]t}\left[\langle\tilde{\eta}_1(q)\,\tilde{\eta}_1(q')\rangle_{ss}+\eta(ss)\,\delta(\underline{q}+\underline{q}')\right] \tag{9.48}$$

The bracketed term on the L.H.S. of (9.48) is, of course the lowest order term for the steady state spatial correlation function.

Hence

$$\begin{aligned}\tilde{T}_0(\underline{q},\underline{q}',t) &= e^{-[Dq^2+\eta(ss)]t}\,\tilde{S}_0(\underline{q},\underline{q}')\\ &= e^{-[Dq^2+\eta(ss)]t}\left[\eta(ss)+\frac{\kappa_1\eta(ss)}{[Dq^2+\eta(ss)]}\right]\end{aligned} \tag{9.49}$$

If (9.49) is Fourier inverted, we find, on examining the behaviour of $T_0(\underline{r},r',t)$ for large t that, to the approximation discussed, the system is characterized by a correlation time

$$t_c = |\kappa_2-\kappa_1|^{-1} = \frac{\ell_c^2}{D} \tag{9.50}$$

and thus by a dynamical critical exponent equal to one. The result (9.49) is in complete agreement with that given by Gardiner et al.[18]

9.2.5 Two Time Correlation Function in the Steady State: Next Higher Corrections

To calculate the next higher correction one proceeds exactly as in 9.2.4 except that the calculations are somewhat more tedious. We shall briefly outline the procedure omitting the calculational details. The first step consists in solving (9.23a) to (9.23c) as a function of the initial values and (9.24a) and (9.24b) subject to the initial conditions

$$
\begin{aligned}
R_0(\underline{r},0;\underline{r}',0) &= \delta(\underline{r}-\underline{r}') \\
R_i(\underline{r},0;\underline{r}',0) &= 0 \qquad i \geqslant 1
\end{aligned}
\tag{9.51}
$$

This then enables one to express the L.H.S. of (9.31) in terms of the initial averages. The next step is to calculate the steady state averages and substitute them for the initial averages that appear in the previous step. These two steps may be carried out rather straightforwardly by Fourier transforming (9.23a) - (9.23c) and (9.24a) - (9.24b) with respect to the spatial variable. Here we shall merely quote the results. The Fourier-Laplace transform of the next higher correction is found to have the following analytic structure

$$
\begin{aligned}
\tilde{T}_1(\underline{q},\underline{q}'s) = \delta(\underline{q}+\underline{q}')\Bigg[& \frac{a(q)}{[s+Dq^2+\eta(ss)]} + \frac{b(q)}{[s+Dq^2+\eta(ss)]^2} \\
& + \int_{Dq^2/2+2\eta(ss)}^{\infty} ds' \, \frac{c(q,s')}{s'+s} + \int_{Dq^2+2\eta(ss)}^{\infty} \frac{d(q,s')}{s+s'} \Bigg]
\end{aligned}
\tag{9.52}
$$

(The full expression for $\tilde{T}_1(\underline{q},\underline{q}'s)$ is rather involved and is presented in the appendix D.

It follows from (9.49) and (9.51) that $\tilde{T}_0(\underline{q},\underline{q}',s)$ has a simple pole at $s = -Dq^2 - \eta(ss)$. When the next higher correction is included, the two time correlation acquires a double pole at $s = -Dq^2 - \eta(ss)$ and branch cuts at $-2\eta(ss) - \frac{Dq^2}{2}$ and $-Dq^2 - \eta(ss)$ As $\eta(ss) \rightarrow 0$ i.e. as the critical point is approached, and as $q \rightarrow 0$ all the singularities of $\tilde{T}(\underline{q},\underline{q}',s)$ collapse to zero. This gives rise to a very singular behaviour near the critical point for long wavelengths, and is probably an indication of non-classical dynamic critical exponents

9.3 A Critique of the Cell Model

The modelling of diffusion as a stochastic process in which molecules jump from one cell to the next seems at first to be very natural. However, the corrections to the mean, given by (9.40) are divergent as $\ell \rightarrow 0$, while this does not happen in the corrections to the variance, which approach a well defined value as long as ℓ is less than the correlation length ℓ_c.

This is a disturbing feature of this method of attacking reaction diffusion equations whose solution is not clear. It is clear that the divergence has its origin in the $\eta^2(\underline{r})$ term, which is local, and implies that only pairs of molecules within a cell react with each other. The very size of the molecules indicates that the interaction must be in some sense non local, and that some term of the form

$$\int dr' dr'' \, g(\underline{r}, \underline{r}', \underline{r}'') \, \eta(\underline{r}') \, \eta(\underline{r}'')$$

should be used, and the fourier transform of $g(\underline{r}, \underline{r}', \underline{r}'')$ would provide a natural cutoff. In fact the cell model before the continuum form is taken, is of this form. The evaluation of the function is however a more tricky task, and requires some more microscopic theory of the reaction diffusion system.

CHAPTER 10

A MODEL WITH SPATIAL AND TEMPORAL OSCILLATIONS

10.1 Introduction

In this chapter we shall consider in detail a two component reaction-diffusion mechanism, the Brusselator. This model has been analysed from various points of view by a number of authors. Glansdorff and Prigogine have carried out the stability analysis of the deterministic equation in ref 1 and found that with the combination of diffusion and non linear chemical kinetics, as a certain chemical parameter is varied, the steady state, which is initially homogeneous may give rise to a dissipative structure which is spatially organized (the soft mode instability) or to temporal oscillations (the hard mode instability). A detailed analysis of the solutions of the deterministic equations for a finite one dimensional system subject to various boundary conditions was given by Auchmuty and Nicolis[74] using Hopf bifurcation theory. Post instability solutions of the deterministic equations for a one dimensional system with periodic boundary conditions have also been investigated by Kuramoto and Tsuzuki[75] using their reductive perturbation approach. A stochastic treatment of this model without diffusion has been given by Tomita et al[76] using a Fokker-Planck equation derived on the basis of van Kampen's System size expansion method[41]. They also used numerical methods to investigate the behaviour of the variances beyond the hard mode instability. Portnow and Kitahara[77] calculated the variances for this model without diffusion using a Langevin equation derived from a path integral method. Effects of diffusion on the fluctuations has been analysed by Nicolis et al[15] using a non linear master equation[19] LeMarchand and Nicolis[78] calculated the correlation functions for a finite one dimensional system subject to two boundary conditions using cumulant expansion methods. Combining van Kampen's system size expansion method with the reductive perturbation method Mashiyama et al[84] and Kuramoto and Tsuzuki[79] have calculated the correlation and the correlation functions in the neighbourhood of the critical points. Similar results have been obtained by Wunderlin and Haken[80] in their work on scaling theory for non-equilibrium systems. Some interesting features of the fluctuation spectrum for this model have been investigated by Mazo[81] and Deutch et al[82].

In none of the above has one a complete stochastic analysis of the spatial correaltion function and the flucutation spectra. Here we shall calculate both of these quantities in the Gaussian approximation for a three dimensional infinite system using our perturbative techniques leaving similar calculations for a finite discreet or continuous system subject to different boundary conditions until the next chapter.

A brief outline of this chapter is as follows. In section 10.2 we derive the stochastic differential dequations for the Brusselator. Section 10.3 contains a discussion of the stability of the homogeneous steady state. In section 10.4 we consider the spatial correlation functions below the instability threshold for a three dimensional infinite system and discuss their behaviour as the instability point is approached. In section 10.5 we calculate the two time correlation functions and the fluctuation spectra in the Gaussian approximation and discuss some of their salient features. Section 10.6 contains a summary of the results.

10.2 Formulation of Stochastic Differential Equation for the Brusselator

The reaction mechanism for the Brusselator is

$$\begin{aligned} A &\xrightarrow{k_1} X \\ B + X &\xrightarrow{K_2} Y + D \\ 2X + Y &\xrightarrow{K_3} 3X \\ X &\xrightarrow{K_4} E \end{aligned} \qquad (10.1)$$

the Fokker Planck equation for which, including spatial diffusion is

$$\frac{\partial f(\underline{\alpha}x, \underline{\alpha}y, t)}{\partial t}$$
$$= \sum_i \frac{\partial}{\partial \alpha_x(i)} \Big[\sum_j D^x_{ij} \alpha_x(j) + K_1 \Delta V - K_2 \alpha_x(i) + K_3 (\Delta V)^{-2} \alpha_x^2(i) \alpha_y(i) - K_4 \alpha_x(i) \Big] f$$
$$- \sum_i \frac{\partial}{\partial \alpha_y(i)} \Big[\sum_j D^y_{ij} \alpha_y(j) + K_2 \alpha_x(i) - K_3 (\Delta V)^{-2} \alpha_x^2(i) \alpha_y(i) \Big] f \; +$$

$$+\sum_i \left(\frac{\partial^2}{\partial \alpha_X^2(i)} - \frac{\partial^2}{\partial \alpha_X(i)\, \partial \alpha_Y(i)} \right) \left(2K_3 (\Delta V)^{-2} \alpha_X^2(i)\, \alpha_Y(i) \right) f$$

$$+\sum_i \left(\frac{\partial^3}{\partial \alpha_X^3(i)} - \frac{\partial^3}{\partial \alpha_X^2 \alpha_Y(i)} \right) \left(2K_3 (\Delta V)^{-2} \alpha_X^2(i)\, \alpha_Y(i) \right) f$$

(10.2)

where $K_1 \Delta V = k_1$, $K_2 = k_2 B$, $K_3 (\Delta V)^{-2} = k_3$, $K_4 = k_4$

Here we are only interested in calculating the mean and the correlation functions in the Gaussian approximation to which, as noted in chapter 8, section 8.2.3 the third order derivative terms do not contribute and would therefore be dropped. The stochastic differential equation equivalent to this approximate Fokker Planck equation is

$$\frac{d}{dt} \begin{pmatrix} \eta_X(i,t) \\ \eta_Y(i,t) \end{pmatrix} = \begin{pmatrix} \sum_j D_{ij}^X \eta_X(j,t) + K_1 - K_2 \eta_X(j,t) + K_3 \eta_X^2(i,t)\, \eta_Y(i,t) - K_4 \eta_X(i,t) \\ \sum_j D_{ij}^Y \eta_Y(j,t) + K_2 \eta_X(i,t) - K_3 \eta_X^2(i,t)\, \eta_Y(i,t) \end{pmatrix}$$
$$+ \frac{1}{\sqrt{\Delta V}} \sqrt{4 K_3 \eta_X^2(i,t)\, \eta_Y(i,t)} \begin{pmatrix} 1 & -1/2 \\ -1/2 & 0 \end{pmatrix}^{1/2} \begin{pmatrix} \xi_X(i,t) \\ \xi_Y(i,t) \end{pmatrix}$$

with (10.3)

$$\langle \xi_\mu(i,t) \rangle = 0 \qquad (10.4)$$

$$\langle \xi_\mu(i,t)\, \xi_\nu(j,t') \rangle = \delta_{\mu\nu}\, \delta_{ij}\, \delta(t-t')$$
$$\mu, \nu = X, Y$$

At this stage we may go over to the continuum notation and proceed as in the previous chapter. However, since some of the equations and the notation introduced would be useful in the next chapter, to avoid repetition, we shall continue to work with the discrete notation for a while.

To derive the stochastic differential equation in the Gaussian approximation we put

$$\eta_\mu(i,t) = \eta_{\mu,0}(i,t) + \frac{1}{\sqrt{\Delta V}}\,\eta_{\mu,1}(i,t) \;;\; \mu = x, y \qquad (10.5)$$

in (10.3) and on neglecting terms of $0\left(\frac{1}{\Delta V^2}\right)$ we have

$$\frac{d}{dt}\begin{pmatrix}\eta_{x,0}(i,t)\\ \eta_{y,0}(i,t)\end{pmatrix}$$

$$= \begin{pmatrix}\sum_j D^x_{ij}\,\eta_{x,0}(j,t) + K_1 - K_2\,\eta_{x,0}(i,t)\,\eta_{y,0}(i,t) + \eta^2_{x,0}(i,t)\,\eta_{y,0}(i,t) - \eta_{x,0}(i,t)\\ \sum_j D^y_{ij}\,\eta_{y,0}(j,t) + K_2\,\eta_{x,0}(i,t)\,\eta_{y,0}(i,t) - \eta^2_{x,0}(i,t)\,\eta_{y,0}(i,t)\end{pmatrix} \qquad (10.6)$$

and

$$\frac{d}{dt}\begin{pmatrix}\eta_{x,1}(i,t)\\ \eta_{y,1}(i,t)\end{pmatrix} = \begin{pmatrix}\sum_j D^x_{ij}\,\eta_{x,1}(j,t)\\ \sum_j D^y_{ij}\,\eta_{y,1}(j,t)\end{pmatrix} + \begin{pmatrix}2\eta_{x,0}(i,t)\eta_{y,0}(i,t) - K_2 - 1 & \eta^2_{x,0}(i,t)\\ -2\eta_{x,0}(i,t)\eta_{y,0}(i,t) + K_2 & -\eta^2_{x,0}(i,t)\end{pmatrix}\begin{pmatrix}\eta_{x,1}(i,t)\\ \eta_{y,1}(i,t)\end{pmatrix}$$

$$+ 2\sqrt{\eta^2_{x,0}(i,t)\,\eta_{y,0}(i,t)}\begin{pmatrix}1 & -1/2\\ -1/2 & 1\end{pmatrix}^{1/2}\begin{pmatrix}\xi_x(i,t)\\ \xi_y(i,t)\end{pmatrix} \qquad (10.7)$$

where for simplicity we have put $K_3 = K_4 = 1$

The homogeneous steady state solution of the deterministic equation (10.6) is

$$\begin{aligned}\eta_{x,0}(i,t) &= K_1\\ \eta_{y,0}(i,t) &= \frac{K_2}{K_1}\end{aligned} \qquad (10.8)$$

Substituting (10.8) in (10.7) we get

$$\frac{d}{dt}\begin{pmatrix}\eta_{x,1}(i,t)\\ \eta_{y,1}(i,t)\end{pmatrix} = \begin{pmatrix}\sum_j D^x_{ij}\,\eta_{x,1}(j,t)\\ \sum_j D^y_{ij}\,\eta_{y,1}(j,t)\end{pmatrix} + \begin{pmatrix}K_2-1 & K_1^2\\ -K_2 & -K_1^2\end{pmatrix}\begin{pmatrix}\eta_{x,1}(i,t)\\ \eta_{y,1}(i,t)\end{pmatrix} \qquad (10.9)$$

$$+ 2\sqrt{K_2 K_1}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_x(i,t)\\ \xi_y(i,t)\end{pmatrix}$$

In the Gaussian approximation, the spatial correlation function is given by

$$\langle \rho_\mu(i,t)\,\rho_\nu(j,t)\rangle = \eta_\mu(i,t)\,\delta_{\mu\nu}\,\frac{\delta_{ij}}{\Delta V} + \langle \eta_{\mu,1}(i,t)\,\eta_{\nu,1}(j,t)\rangle \tag{10.10}$$

For the sake of brevity we shall introduce the following matrix notation

$$S_0(i,j,t) = M(i,t)\,\frac{\delta_{ij}}{\Delta V} + G(i,j,t) \tag{10.11}$$

where

$$S_0(i,j,t) = \langle \rho(i,t),\, \rho^T(j,t)\rangle \tag{10.12}$$

$$M_{\mu\nu}(i,t) = \langle \eta_\mu(i,t)\rangle\,\delta_{\mu\nu} \tag{10.13}$$

$$G(i,j,t) = \langle \underline{\eta}_1(i,t)\,\underline{\eta}_1^T(j,t)\rangle \tag{10.14}$$

In the continuum notation (10.9) and (.10.10) become

$$\frac{d}{dt}\,\underline{\eta}_1(\underline{r},t) = -A\,\underline{\eta}_1(\underline{r},t) + B\,\underline{\xi}(\underline{r},t) \tag{10.14a}$$

and

$$S_0(\underline{r},\underline{r}',t) = M(\underline{r},t)\,\delta(\underline{r}-\underline{r}') + G(\underline{r},\underline{r}',t) \tag{10.15}$$

where

$$A = \begin{pmatrix} -\mathcal{D}_x\nabla^2 - K_2 + 1 & K_1^2 \\ K_2 & -\mathcal{D}_y\nabla^2 + K_1^2 \end{pmatrix}. \tag{10.16}$$

$$B = 2\sqrt{K_2K_1}\begin{pmatrix} 1 & -1/2 \\ -1/2 & 0 \end{pmatrix}^{1/2} \qquad (.10.17)$$

and $\mathcal{D}_x, \mathcal{D}_y$ are the diffusion coefficients for X and Y

10.3 Stability of the Homogeneous Steady State

The Fourier transform of equation (10.14a) is

$$\frac{d}{dt}\,\tilde{\eta}_1(\underline{q},t) = -\tilde{A}(q^2)\,\tilde{\eta}_1(\underline{q},t) + B\,\tilde{\xi}(\underline{q},t) \qquad (10.18)$$

It is clear from (10.18) that the homogeneous state will be stable provided that the eigenvalues of $\tilde{A}(q^2)$ have positive real parts. These eigenvalues are given by

$$\lambda_1, \lambda_2 = \frac{1}{2}\Big[(D_x+D_y)q^2 + 1 + K_1^2 - K_2 \pm \{((D_x+D_y)q^2+K_1^2+1-K_2)^2 - 4((D_xq^2-K_2+1)(D_yq^2+K_1^2)+K_1^2K_2\}^{1/2}\Big] \qquad (10.19)$$

$$= \frac{1}{2}\Big[(D_x+D_y)q^2 + 1 + K_1^2 - K_2 \pm \sqrt{(\delta-K_2+K_1^2)^2 - 4\delta K_1^2}\,\Big] \qquad (10.20)$$

where $\delta = 1+(D_x-D_y)q^2$. The homogeneous steady state becomes unstable when the real parts of λ_1 and λ_2 become negative. The marginal situation corresponds to the case when the real parts of λ_1, λ_2 or both go to zero and occurs if

(a) λ_1, λ_2 real and positive and $\lambda_2 \longrightarrow 0^+$ (the soft mode instability).

(b) λ_1, λ_2 complex and $\mathrm{Re}(\lambda_1,\lambda_2) \rightarrow 0^+$ (the hard mode instability).

It follows from (10.20) that

(i) λ_1 and λ_2 are real if

$$(\delta - K_2 + K_1^2)^2 - 4\delta K_1^2 > 0 \qquad (10.21)$$

For $\delta < 0$, λ_1 and λ_2 are always real.

For $\delta > 0$, λ_1 and λ_2 are real if

$$\begin{aligned} &\text{either} && K_2 > (\sqrt{\delta} + K_1)^2 \\ &\text{or} && K_2 < (\sqrt{\delta} - K_1)^2 \end{aligned} \qquad (10.22)$$

λ_1 and λ_2 are real and positive, if in addition to (10.22) we have

$$(D_x + D_y)q^2 - K_2 + 1 + K_1^2 > 0$$

i.e. $$K_2 < 1 + K_1^2 + (D_x + D_y)q^2 \qquad (10.23)$$

and $$(D_x q^2 - K_2 + 1)(D_y q^2 + K_1^2) + K_1^2 K_2 > 0$$

i.e. $$K_2 < 1 + D_x q^2 + \frac{K_1^2}{D_y q^2} + \frac{D_x K_1^2}{D_y} \qquad (.10.24)$$

$\lambda_2 \rightarrow 0^+$ along the real axis with λ_1 real and positive if (10.22) and (.10.23) are satisfied and

$$K_2 \longrightarrow K_{2s}(q^2) \equiv \left[1 + D_x q^2 + \frac{K_1^2}{D_y q^2} + \frac{D_x K_1^2}{D_y} \right] \qquad (10.25)$$

from below. With K_1, D_x, D_y, fixed, the minimum of $K_{2s}(q^2)$ occurs at

$$|q|^2 = \frac{K_1}{\sqrt{D_x D_y}} \qquad (10.26)$$

and its minimum value is

$$K_{2s} = \left(1 + K_1 \sqrt{\frac{D_x}{D_y}} \right)^2 \qquad (10.27)$$

Equation (10.27) gives the threshold for the soft mode instability. As K_2 is increased beyond K_{2s} the system exhibits spatial oscillations characterized by a wave vector given by (10.26).

(ii) λ_1 and λ_2 are complex if $(\delta - K_2 + K_1^2)^2 - 4\delta K_1^2 < 0$

i.e. $$(\sqrt{\delta} - K_1)^2 < K_2 (\sqrt{\delta} + K_1)^2 \; ; \; \delta > 0 \qquad (10.28)$$

and have positive real parts if

$$(D_x + D_y) q^2 + 1 + K_1^2 - K_2 > 0$$

i.e.
$$K_2 < 1 + K_1^2 + (D_x + D_y) q^2 \tag{10.29}$$

λ_1 and λ_2 become purely imaginary as

$$K_2 \longrightarrow K_{2H}(q^2) \equiv 1 + K_1^2 + (D_x + D_y) q^2 \tag{10.30}$$

from below. The minimum of $K_{2H}(q^2)$ occurs at

$$q = 0 \tag{10.31}$$

and hence the threshold for the hard mode instability is

$$K_{2H} = 1 + K_1^2 \tag{10.32}$$

As K_2 is increased beyond K_{2H} the system exhibits temporal oscillations.

Which of the two instabilities occurs first depends on the relative magnitude of D_x and D_y. Thus the soft mode instability occurs first if

$$\begin{aligned} K_{2S} &< K_{2H} \\ \sqrt{\frac{D_x}{D_y}} &< \sqrt{1 + \frac{1}{K_1^2}} - \frac{1}{K_1} \end{aligned} \tag{10.33}$$

and vice versa.

10.4 Spatial Correlation Fucntions below the Instability Thresholds

10.4.1 $S(\underline{r}, \underline{r}')$ below the instability threshold

From a two dimensional Langevin equation of the type (10.18), in the steady state, one can derive the following expression for $\tilde{G}(\underline{q}, \underline{q}')$ in terms of $\tilde{A}$ and B

$$\tilde{G}(\underline{q},\underline{q}') \equiv \delta(\underline{q}+\underline{q}')\,\tilde{G}(\underline{q})$$

$$\tilde{G}(\underline{q}) = \frac{(\mathrm{Det}\,\tilde{A})\,B^2 + (\tilde{A}-(\mathrm{Tr}\,\tilde{A})I)\,B^2\,(\tilde{A}-(\mathrm{Tr}\,\tilde{A})I)^T}{2\,(\mathrm{Det}\,\tilde{A})\,(\mathrm{Tr}\,\tilde{A})} \qquad (10.34)$$

This relation is derived in Appendix E.

Substituting for $\tilde{A}(q^2)$ and B^2 in (10.34) and using (10.15) we obtain the following expression for the Fourier transform of the spatial correlation function

$$\tilde{S}_0(\underline{q},\underline{q}') \equiv \delta(\underline{q}+\underline{q}')\,\tilde{S}_0(\underline{q})$$

$$\begin{aligned}\tilde{S}_0(\underline{q}) &= M + \tilde{G}(\underline{q}) \\ &= M + \frac{H(q^2)}{[(q^2+\beta_1^2)(q^2+\beta_2^2)(q^2+\beta_3^2)]} \qquad (10.35)\end{aligned}$$

where

$$M = \begin{pmatrix} K_1 & 0 \\ 0 & \frac{K_2}{K_1} \end{pmatrix}. \qquad (10.36)$$

$$H(q^2) = \frac{2K_1K_2}{D_xD_y(D_x+D_y)} \begin{pmatrix} (D_xq^2+K_1^2)[(D_x+D_y)q^2-K_2+1]+K_1^2K_2 & -(D_yq^2+K_1^2)(D_xq^2+1) \\ -(D_yq^2+K_1^2)(D_xq^2+1) & (D_xq^2+1) \end{pmatrix}$$

(10.37)

$$\beta_1^2 = (1-K_2+K_1^2)/(D_x+D_y)$$

$$\beta_2^2, \beta_3^2 = \frac{1}{2}\left[\frac{D_xK_1^2+D_y(1-K_2)}{D_xD_y} \pm i\sqrt{\frac{4K_1^2K_2}{D_xD_y} - \left[\frac{D_xK_1^2+D_y(1-K_2)}{D_xD_y}\right]^2}\,\right] \qquad (10.38)$$

Splitting the second term on the R.H.S. of (10.35) into partial fractions and performing the Fourier inversion, we get the following expression for the spatial correlation function in three space dimensions.

$$\begin{aligned}S_0(|\underline{r}-\underline{r}'|) = M\,\delta(\underline{r}-\underline{r}') &+ a_1\frac{e^{-\beta_1|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|} + a_2\frac{e^{-\gamma_1|\underline{r}-\underline{r}'|}}{|r-r'|}\cos(\gamma_1|\underline{r}-\underline{r}'|) \\ &+ a_3\frac{e^{-\gamma_2|\underline{r}-r'|}}{|\underline{r}-\underline{r}'|}\sin(\gamma_2|\underline{r}-\underline{r}'|) \qquad (10.39)\end{aligned}$$

where

$$\beta_1 = \left[\frac{1-K_2+K_1^2}{D_x+D_y} \right]^{1/2} \tag{10.40}$$

$$\beta_2, \beta_3 = \frac{1}{2\sqrt{D_x}} \left[\left\{ \left(1+K_1\sqrt{\frac{D_x}{D_y}}\right)^2 - K_2 \right\}^{1/2} \pm i \left\{ K_2 - \left(1-\sqrt{\frac{D_x}{D_y}}\,K_1\right)^2 \right\}^{1/2} \right]$$
$$\equiv \gamma_1 + i\gamma_2 \tag{10.41}$$

$$a_1 = \frac{H(-\beta_1^2)}{|(\beta_2^2-\beta_1^2)|^2} \tag{10.42a}$$

$$a_2 = \frac{1}{\mathrm{Im}(\beta_2^2)} \left[\mathrm{Im}\left(\frac{H(-\beta_2^2)}{\beta_2^2-\beta_1^2} \right) \right] \tag{10.42b}$$

$$a_3 = \frac{1}{\mathrm{Im}(\beta_2^2)} \left[\mathrm{Im}\left(\frac{H(-\beta_2^2)}{\beta_3^2-\beta_1^2} \right) \right] \tag{10.42c}$$

The expression for the spatial correlation function is characterized by two correlation lengths

$$\ell_{c,1} = \frac{1}{\beta_1} = \left[\frac{D_x+D_y}{1-K_2+K_1^2} \right]^{1/2} \tag{10.43}$$

$$\ell_{c,2} = \frac{1}{\gamma_1} = \left[\left(1+K_1\sqrt{\frac{D_x}{D_y}}\right)^2 - K_2 \right]^{-1/2} \tag{10.44}$$

and a wave vector

$$\gamma_2 = \left[K_2 - \left(1-K_1\sqrt{\frac{D_x}{D_y}}\right)^2 \right]^{1/2} \tag{10.45}$$

10.4.2 <u>Behaviour of $S_0(r-r')$ near the instability thresholds</u>

(i) As $K_2 \longrightarrow K_{2s}$

$$\ell_{2,c} \longrightarrow \infty \tag{10.46}$$

and γ_2 approaches the critical wave vector

$$q_c = \left[\frac{K_1}{\sqrt{D_x D_y}} \right]^{1/2} \tag{10.47}$$

and the spatial correlation function contains, apart from an exponentially decreasing term, has a purely oscillatory term

modulated by a $\frac{1}{|\underline{r}-\underline{r}'|}$ term.
Actually in this limit, the coefficients of the oscillatory terms become infinite which perhaps reflects the invalidity of the Gaussian approximation near the critical point.

(ii) As $K_2 \longrightarrow K_{2H}$

$$l_{c,1} \longrightarrow \infty \tag{10.48}$$

and (10.39) gives

$$S_0(|\underline{r}-\underline{r}'|) = a_1' \frac{1}{|\underline{r}-\underline{r}'|} + \frac{a_2' e^{-\gamma_1'|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|}\cos(\gamma_2'|\underline{r}-\underline{r}'|) + a_3' \frac{e^{-\gamma_1'|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|}\sin(\gamma_2'|\underline{r}-\underline{r}'|) \tag{10.49}$$

where a_1', γ_1' etc. are the values of a_1, γ_1 etc. as $K_2 \rightarrow K_{2H}$
Thus $S_0(\underline{r}-\underline{r}')$ is characterized by a long large $\frac{1}{|\underline{r}-\underline{r}'|}$ term.

10.5 Two Time Correlation Functions and the Fluctuation Spectra in the Gaussian Approximation

Using (8.34), the steady state two time correlation functions in the Gaussian approximation is given by

$$\tilde{T}_0(\underline{q},\underline{q}',t) = \exp[-\tilde{A}(q^2)|t|]\ \tilde{S}_0(\underline{q},\underline{q}') \tag{10.50}$$

Substituting the spatial correlation matrix $\tilde{S}_0(\underline{q},\underline{q}')$ derived previously we get the two time correlation function in the steady state.

From an experimental point of view, a quantity of interest is the fluctuation spectrum defined by

$$F(\underline{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\,\tilde{T}_0(\underline{q},t) \tag{10.51}$$

A qualitative discussion of the fluctuation spectrum for the Brusselator has been given previously by Deutch et al[82] who also explore the possible use of light scattering for its measurement. A general but comprehensive discussion of the use of light scattering experiments for a study of concentration fluctuation in chemically reacting systems may also be found in ref 83 . In such experiments one typically measures the intensity of the scattered light which is directly related to a linear combination of the matrix elements of $F(\underline{q},\omega)$. In the following we give a complete calculation of the fluctuation spectra.

Using (10.51) and the stochastic differential equation (10.18) one can derive the following expression for the fluctuation spectrum in terms of the matrices $\tilde{A}$, B^2 and M

$$F(\underline{q},\omega) = \frac{1}{2\pi}\,(i\omega+\tilde{A})^{-1}\,[B^2+M\tilde{A}^T+\tilde{A}M]\,(-i\omega+\tilde{A})^{-1} \qquad (10.52)$$

This result is derived in appendix E .

Substituting for $\tilde{A}$, B^2 and M in (10.52) we get

$$F(\underline{q},\omega) = \frac{P(\omega,\underline{q})}{[(\omega^2-\{(D_xq^2+K_2+1)(D_yq^2+K_1^2)+K_1^2K_2\})^2+\omega^2\{(D_x+D_y)q^2+1+K_1^2-K_2\}^2]} \qquad (10.53)$$

where the matrix elements of $P(\omega,\underline{q})$ are

$$P_{xx}(\omega,\underline{q}) = \frac{K_1}{\pi}\left[(D_xq^2+K_2+1)\omega^2+(D_yq^2+K_1^2)\{(D_yq^2+K_1^2)(D_xq^2+K_2+1)-K_1^2K_2\}\right] \qquad (10.54a)$$

$$P_{xy}(\omega,q) = P_{yx}^{*}(\omega,q) = -\frac{K_1K_2}{\pi}\left[\omega^2+\{(D_xq^2+K_2+1)(D_yq^2+K_1^2)-K_1^2K_2\}+2i\omega(D_xq^2+1)\right] \qquad (10.54b)$$

$$P_{yy}(\omega,\underline{q}) = \frac{K_2}{\pi K_1}\left[(D_yq^2+K_1^2)\omega^2+(D_yq^2+K_1^2)(D_xq^2-K_2+1)^2+2K_1^2K_2(D_xq^2+1)\right] \qquad (10.54c)$$

The fluctuation spectrum has poles in the ω plane at

$$\omega = \pm i\Gamma \pm \omega_0 \tag{10.55}$$

where
$$\Gamma = \frac{1}{2}\left[(D_x + D_y)q^2 + 1 + K_1^2 - K_2\right] \tag{10.56}$$

$$\begin{aligned}\omega_0 &= \frac{1}{2}\left[4\left\{(D_x q^2 - K_2 + 1)(D_y q^2 + K_1^2) + K_1^2 K_2\right\} - \left\{(D_x + D_y)q^2 + 1 + K_1^2 - K_2\right\}^2\right]^{1/2}\\ &= \frac{1}{2}\sqrt{4\delta K_1^2 - (\delta - K_2 + K_1^2)^2}\end{aligned} \tag{10.57}$$

(i) It follows from the discussion in section 10.3, equation (10.21) that below the soft mode instability threshold ω_0 is imaginary in which case the fluctuation spectrum is of the following form

$$F(\omega,\underline{q}) = \frac{1}{\pi K_1}\,\frac{P(\omega,\underline{q})}{\left[\omega^2 + (\Gamma - |\omega_0|)^2\right]\left[\omega^2 + (\Gamma + |\omega_0|)^2\right]}. \tag{10.58}$$

and therefore has a peak at $\omega = 0$.

As the soft mode instability threshold is approached, $|\omega_0| \to \Gamma$ and (10.58) becomes

$$F(\omega,\underline{q}) = \frac{1}{\pi K_1}\,\frac{P(\omega,\underline{q})}{\omega^2(\omega^2 + 4\Gamma^2)} \tag{10.59}$$

which exhibits an infinitely sharp peak at $\omega = 0$

(ii) Below the hard mode instability, it follows from (10.28) that ω_0 is real and in this case the fluctuations spectrum has the following form.

$$F(\omega,\underline{q}) = \frac{P(\omega,\underline{q})}{\left[(\omega - \omega_0)^2 + \Gamma^2\right]\left[(\omega + \omega_0)^2 + \Gamma^2\right]} \tag{10.60}$$

Leaving aside the ω dependence of $P(\omega,q)$ the fluctuation spectrum in this case consists of two peaks situated at $\omega = \pm\omega_0$

with a half width equal to Γ.

As the hard mode threshold is approached Γ decreases monotonically, i.e. the peaks become sharper. If K_2 is initially less than $\delta+K_1^2$, ω_0 increases and as K_2 becomes greater than $\delta+K_1^2$, ω_0 begins to decrease and at the threshold it becomes equal to K_1. Thus at the threshold the peak separation becomes

$$2\omega_{oc} = 2K_1 \tag{10.61}$$

and the width of the peaks becomes

$$\Gamma_c = \frac{1}{2}(D_x+D_y)q^2 \tag{10.62}$$

and arises purely due to diffusive effects.

The ω dependence of $P(\omega,\underline{q})$ gives rise to a slight skewness of the two peaks but the qualitative features of the fluctuation spectrum remains basically the same.

10.6 Summary

We have calculated in the Gaussian approximation, the spatial correlation functions and the fluctuation spectra for the Brusselator for a three dimensional infinite system below the instability thresholds. We have shown that as the soft mode instability threshold as approached from below the spatial correlation functions exhibit an oscillatory behaviour modulated by a $\frac{1}{|\underline{r}-\underline{r}'|}$ term. At the critical point however the spatial correlations become infinite. The fluctuation spectrum in this limit exhibits an infinitely sharp peak at $\omega=0$. In the case of the hard mode instability the spatial correlation functions at the instability point exhibit a long range $\frac{1}{|\underline{r}-\underline{r}'|}$ behaviour. The fluctuation spectrum in this case exhibits two peaks below the instability thresholds and as the instability threshold is approached the peaks move towards each other at the same time becoming sharper until at the critical point the separation becomes twice the critical frequency and the widths of the peaks determined solely by the diffusive effects.

If it be desired,the corrections to the Gaussian approximation can be calculated systematically from our Langevin equations although this would require incorporation of the noise sources corresponding to the third order derivatives in the Fokker-Planck equation, as explained in Chapter 6. At the critical point this perturbation method with the inverse of the cell size as the expansion parameter breaks down. It should be noted that most of the work done to date on calculation of the correlation functions near the critical points uses the distance from the critical point as an expansion parameter but relies on a Fokker Planck equation which already assumes the Gaussian approximation. Given the invalidity of the Gaussian approximation near the critical points the whole procedure seems a bit questionable. Our stochastic differential equations however provide an exact starting point for doing calculations near the critical points without having to rely on the Gaussian approximation.

CHAPTER 11

APPLICATIONS TO SYSTEMS WITH BOUNDARY CONDITIONS

11.1 Introduction

In this chapter we consider the application of the stochastic differential equations derived from Poisson representation method to finite discrete and continuous one dimensional systems and show how to calculate the spatial correlation functions and fluctuation spectrum when various boundary conditions are imposed on the system. For illustrative purposes we will consider the model introduced in the previous chapter. The only previous work on this problem is that do to Lemarchand and Nicolis[78] who use the cumulant expansion method to calculate spatial correlation functions in a finite one dimensional system subject to two types of boundary conditions viz (a) fixed concentration boundary conditions and (b) zero flux boundary conditions. We shall confine ourselves to these two types of boundary conditions and rederive the results of Lemarchand and Nicolis[78] rather simply. From the following discussion it will also become clear how one may carry out similar calculations for other types of boundary conditions, for example, periodic boundary conditions. The generalisation to three dimensional finite systems is also straightforward.

11.2 Fixed mean concentration boundary conditions

Here we consider a finite one dimensional system consisting of $(n+2)$ cells labelled $0, 1, ---- n, (n+1)$ We assume that the probability distributions in the boundary cells 0 and $n+1$ is a Poisson distribution with the mean equal to the mean steady state concentration. This boundary condition in terms of $\eta_\mu(i,t)$ variables implies that $\eta_\mu(0,t)$ and $\eta_\mu(n+1,t)$ are nonfluctuating variables and are equal to the steady state concentration. (It should be noted that if the probability distribution in the boundary cells is assumed to factorize from that for the system cells then as a consequence of the linear coupling between the two through diffusion only the mean number in the boundary cells appears as a parameter in the reduced master equation for the system cells and consequently the results are insensitive to the precise nature of the probability distribution in the boundary cells. Thus in this case we get the same results as those of Lemarchand and Nicolis[78] who consider fixed concentration boundary conditions, i.e. a delta function distribution in the boundary cells.)

The linearised stochastic differential equation from the Brusselator as derived in the previous Chapter is

$$\frac{d}{dt}\begin{pmatrix} \eta_{X,1}(i,t) \\ \eta_{Y,1}(i,t) \end{pmatrix} = \begin{pmatrix} \sum_j D^X_{ij}\,\eta_{X,1}(j,t) \\ \sum_j D^Y_{ij}\,\eta_{Y,1}(j,t) \end{pmatrix} + \begin{pmatrix} K_2-K_1 & K_1^2 \\ -K_2 & -K_1^2 \end{pmatrix}\begin{pmatrix} \eta_{X,1}(i,t) \\ \eta_{Y,1}(i,t) \end{pmatrix}$$

$$+ \quad 2\sqrt{K_1K_2}\begin{pmatrix} 1 & -1/2 \\ -1/2 & 0 \end{pmatrix}^{1/2}\begin{pmatrix} \xi_X(i,t) \\ \xi_Y(i,t) \end{pmatrix} \quad i=1\cdots n \tag{11.1}$$

It follows that the appropriate boundary conditions, in this case are

$$\eta_{\mu,1}(0,t) = \eta_{\mu,1}(n+1,t) \tag{11.2}$$

In the continuum limit (11.1) and (11.2) become

$$\frac{d}{dt}\begin{pmatrix}\eta_{x,1}(r,t)\\ \eta_{y,1}(r,t\end{pmatrix} = \begin{pmatrix} d^{x}\ell^{2}\nabla^{2}+K_{2}-1 & K_{1}^{2}\\ -K_{2} & d^{y}\ell^{2}\nabla^{2}-K_{1}^{2}\end{pmatrix}\begin{pmatrix}\eta_{x,1}(r,t)\\ \eta_{y,1}(r,t)\end{pmatrix} + 2\sqrt{K_{2}K_{1}}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_{x}(r,t)\\ \xi_{y}(r,t)\end{pmatrix} \tag{11.3}$$

and

$$\eta_{\mu,1}(0,t) = \eta_{\mu,1}(L,t) \tag{11.4}$$

where ℓ is the cell length and L is the length of the system.

11.3 Zero Flux Boundary Conditions

Here we consider the situation in which there is no diffusion between the system cells and the boundary cells. This can be taken into account by modifying the diffusion matrix D_{ij} to

$$D_{ij} - d\,\delta_{i,1}(\delta_{j,0}-\delta_{j,1}) - d\,\delta_{i,n}(\delta_{j,n+1}-\delta_{j,n})$$

where the extra terms cancel the terms present in which allow for diffusion between the cell $1(n)$ and $0(n+1)$ The corresponding stochastic differential equation then becomes

$$\frac{d}{dt}\begin{pmatrix}\eta_{x,1}(i,t)\\ \eta_{y,1}(i,t)\end{pmatrix} = \begin{pmatrix}\sum_{j} D^{x}_{ij}\,\eta_{x,1}(j,t) - d^{x}\delta_{i,1}(\eta_{x,1}(0,t)-\eta_{x,1}(1,t)) - d^{x}\delta_{i,n}(\eta_{x,1}(n+1,t)-\eta_{x,1}(n,t))\\ \sum_{j} D^{y}_{ij}\,\eta_{y,1}(j,t) - d^{y}\delta_{i,1}(\eta_{y,1}(0,t)-\eta_{y,1}(1,t)) - d^{y}\delta_{i,n}(\eta_{y,1}(n+1,t)-\eta_{y,1}(n,t))\end{pmatrix} + \begin{pmatrix}K_{2}-1 & K_{1}^{2}\\ -K_{2} & -K_{1}^{2}\end{pmatrix}\begin{pmatrix}\eta_{x,1}(i,t)\\ \eta_{y,1}(i,t)\end{pmatrix} + 2\sqrt{K_{1}K_{2}}\begin{pmatrix}1 & -1/2\\ -1/2 & 1\end{pmatrix}^{1/2}\begin{pmatrix}\xi_{x}(i,t)\\ \xi_{y}(i,t)\end{pmatrix} \tag{11.5}$$

which may equivalently be written as equation (11.1) subject to the boundary conditions

$$\begin{aligned} \eta_{\mu,1}(0,t) - \eta_{\mu,1}(1,t) &= 0 \\ \eta_{\mu,1}(n,t) - \eta_{\mu,1}(n+1,t) &= 0 \qquad \mu = x,y \end{aligned} \tag{11.6}$$

In the continuum limit the appropriate stochastic differential equation is (11.3) subject to the boundary conditions

$$\left[\frac{\partial \eta_{\mu,1}(r,t)}{\partial r}\right]_{r=0} = \left[\frac{\partial \eta_{\mu,1}(r,t)}{\partial r}\right]_{r=L} = 0 \tag{11.7}$$

11.4 Spatial Correlation Functions and the Fluctuation Spectra

In both the cases the equations for $\eta_{\mu,1}(i,t)$ are identical but because of the boundary conditions different Fourier expansions are required to diagonalize the diffusion terms. The appropriate Fourier expansions are given below.

(a) Fixed Mean concentration boundary conditions.

$$\eta_{\mu,1}(i,t) = \sum_{q=1}^{n} \tilde{\eta}_{\mu,1}(q,t) \sin\left(\frac{iq\pi}{n+1}\right) \tag{11.8}$$

In the continuum limit

$$\eta_{\mu,1}(r,t) = \sum_{q=1}^{\infty} \tilde{\eta}_{\mu,1}(q,t) \sin\left(\frac{qr\pi}{L}\right) \tag{11.9}$$

(b) Zero Flux boundary conditions

$$\eta_{\mu,1}(i,t) = \sum_{q=1}^{n} \tilde{\eta}_{\mu,1}(q,t) \cos\left[(q-1)(2i-1)\frac{\pi}{2n}\right] \tag{11.10}$$

In the continuum limit

$$\eta_{\mu,1}(r,t) = \sum_{q=0}^{\infty} \tilde{\eta}_{\mu,1}(q,t) \cos\left(\frac{q\pi r}{L}\right) \tag{11.11}$$

Substituting these and similar expansions for ξ_μ in the corresponding stochastic differential equations we get

$$\frac{d}{dt}\tilde{\eta}_1(q,t) = -\tilde{A}'(q^2)\,\underline{\tilde{\eta}}_1(q,t) + B\,\underline{\tilde{\xi}}(q,t) \tag{11.12}$$

with

$$\langle \tilde{\xi}_\mu(q,t)\rangle = 0$$

$$\langle \tilde{\xi}_\mu(q,t)\,\tilde{\xi}_\nu(q',t')\rangle = h(q,q')\,\delta(t-t') \tag{11.13}$$

where

$$\tilde{A}' = \begin{pmatrix} d_x g(q)+1-K_2 & -K_1^2 \\ K_2 & d_y g(q)+K_1^2 \end{pmatrix} \tag{11.14}$$

and for

(a) Fixed mean concentration boundary conditions we have

$$g(q) = 2\left(1-\cos\frac{q\pi}{n+1}\right), \quad h(q,q') = \frac{2}{n+1}\,\delta_{q,q'} \tag{11.15}$$

In the continuum limit

$$g(q) = \frac{\ell^2 q^2 \pi^2}{L^2}, \quad h(q,q') = \frac{2}{L}\,\delta_{q,q'} \tag{11.16}$$

(b) For Zero flux boundary conditions, we have

$$g(q) = 2\left(1-\cos\frac{(q-1)\pi}{n}\right), h(q,q') = \frac{2}{n}\,\delta_{qq'}\left(1-\frac{\delta_{q,1}}{2}\right) \tag{11.17}$$

In the continuum limit

$$g(q) = \frac{\ell^2 q^2 \pi^2}{L^2}, \quad h(q,q') = \frac{2}{L}\,\delta_{q,q'}\left(1-\frac{\delta_{q,0}}{2}\right) \tag{11.18}$$

The Fourier transform of the steady state spatial correlation functions and the fluctuation spectrum can be calculated using (10.12), (10.34) and (10.52).

Although the above discussion applies to a one dimensional system, its generalization to more than one dimension is straightforward.

Having thus calculated $\tilde{G}(q,q')$ one may derive expressions for $G(i,j)$ be appropriate Fourier inversions and for the one dimensional case one obtains results identical to those given by Lemarchand and Nicolis[78]. The Fourier inversions are possible analytically only for a one dimensional continuous system and we find with Lemarchand and Nicolis[78] that near the soft mode instability threshold, $G(r,r')$ can be decomposed into a short range part consisting of decaying exponentials and a long range linearly damped oscillatory part of the following form.

$$\begin{aligned} G(r,r') = \; & b_1 \gamma_2 (L-r) \cos \gamma_2 (L-r) \sin \gamma_2 r' \\ & + b_2 \gamma_2 r' \sin \gamma_2 (L-r) \cos \gamma_2 r' + b_3 \end{aligned} \tag{11.19}$$

where γ_2 has been defined previously.

In the limit of $L \rightarrow \infty$ (11.19) is divergent. Direct calculation of $G(r,r')$ for an infinite one dimensional system shows that as the soft mode instability threshold is approached, $G(r,r')$ actually becomes infinite. However it should be remembered that these results are derived in the Gaussian approximation whose validity at the critical point is questionable.

CONCLUDING REMARKS

We have shown how chemical master equations may be transformed into exact Fokker-Planck equations or to equivalent stochastic differential equations by the use of the Poisson representation method. This is to be contrasted with the other systematic expansions of the master equations which yield Fokker-Planck equations of infinite order. The usefulness of the Poisson representation technique is exemplified by our ability to calculate higher order corrections to the correlation functions in a systematic manner in multivariate situations. Similar calculations using other systematic expansion methods turn out to be prohibitively difficult. Apart from these calculational advantages the Poisson notation yields aesthetically satisfying expressions for the two time correlation functions which are of central importance in the study of non equilibrium statistical mechanics.

In a recent work Gardiner[85] has shown that the master equation approach to reaction-diffusion systems may be regarded as a complete theory in itself, in that the near equilibrium theory of Onsager and macroscopic stability criteria far from equilibrium steady states may all be derived from the master equation. In view of this work, Poisson representation method is an important technical development.

The perturbative expansion method used in this work have been in the inverse powers of the system size or the cell size. Owing to the divergence of higher order corrections near the critical point, this perturbative expansion breaks down in that regime. Further work in developing alternative perturbation techniques valid in the critical region is therefore necessary. One possibility in this direction is to consider coupled stochastic differential equations for $\eta(\underline{r},t)$ and $\eta^2(\underline{r},t)$, linearise them about the solutions of the deterministic parts, and then evaluate corrections to the linearised result. If the corrections turn out not to be small near the critical points then one should include the stochastic differential equation for $\eta^3(\underline{r},t)$ etc. and so on. The expansion will then be a sort of self consistent expansion. Another possibility is to use the renormalization group methods, similar to those used by De Dominicis, Brezin and Zinn-Justin[86] in connection with a Langevin equation description of Ginzburg-Landau models. In their work the Langevin equation description is replaced by an equivalent path integral representation which is then used to investigate the critical dynamics of the system. However, in contrast to their Langevin equations in which the noise coefficient is a constant, the Langevin equations derived using our techniques do not have constant noise coefficients. The path integral representation for such Langevin equations is riddled with mathematical and computational difficulties. A problem worthy of future investigation is therefore to apply the renormalization group techniques to the Langevin equations themselves so as to obtain a better understanding of the critical dynamics of the chemical instabilities.

APPENDIX A: Itô and Stratonovich Formalisms

In this appendix our aim is

(a) to bring out the mathematical differences between Itô and Stratonovich formalisms,

(b) to show how one may go from an Itô stochastic differential equation to that of Stratonovich and vice versa,

(c) to derive rules for change of variables in an Itô stochastic differential equation.

The derivation of the formula for change of variables in the Itô Stochastic differential equation and the derivation of Ito stochastic differential equation from that of Stratonovich to be found in most mathematical texts on this subject are extremely complex. Our aim is to derive these formulae in a physicist's way. Rigorous proofs may be found in books by Arnold[60] and Gihman and Skorohod[61].

A stochastic differential equation

$$dX = a(X)\,dt + G(X)\,dW(t) \tag{A.1}$$

should be understood as an abbreviation for the integral equation

$$X(t) = X(t_0) + \int_{t_0}^{t} ds\, a(X(s))\,ds + \int_{t_0}^{t} G(X(s))\,dW(s) \tag{A.2}$$

until a precise definition of the stochastic integral

$$\mathcal{J} = \int_{t_0}^{t} G(X(s))\,dW(s) \tag{A.3}$$

is given. To specify the meaning of $\mathcal{J}$ we divide the interval (t_0, t) into intervals of length Δt

$$t_0 \leqslant t_1 \leqslant t_2 - - - - \leqslant t_n = t \; ; \; t_i - t_{i-1} = \Delta t \qquad \text{(A.4)}$$

and consider the approximation of $\mathcal{J}$ by Riemann-Stieltjes sums of the form

$$S_n = \sum_{i=1}^{n} G(X(\tau_i)) \left[W(t_i) - W(t_n) \right] \qquad \text{(A.5)}$$

where

$$t_{i-1} \leqslant \tau_i \leqslant t_i \qquad \text{(A.6)}$$

It may be shown[60]that the convergence of the sum S_n in the quadratic mean depends on the choice of the intermediate points τ_i . In particular, when

$$G(X) = W \qquad \text{(A.7)}$$

one finds that[60] with $\tau_i = (1-a)t_{i-1} + a t_i$

$$\int_{t_0}^{t} W(s)\, dW(s) = \underset{\Delta t \to 0}{\text{qm-lim}} \; S_n$$

$$= \frac{1}{2} \left[W^2(t) - W^2(t_0) \right] + \left(a - \frac{1}{2}\right)(t - t_0) \cdot \qquad \text{(A.8)}$$

Itô's choice of the intermediate points τ_i corresponds to $a = 0$ i.e. $\tau_i = t_{i-1}$ so that

$$\text{(I)} \qquad \int_{t_0}^{t} W(s)\, dW(s) = \frac{1}{2} \left[W^2(t) - W^2(t_0) \right] - \frac{1}{2}(t - t_0) \qquad \text{(A.9)}$$

and the definition of the stochastic integral $\mathcal{J}$ is taken to be

$$\text{(I)} \qquad \mathcal{J} = \underset{\Delta t \to 0}{\text{qm-lim}} \sum_{i=1}^{n} G(X(t_{i-1})) \; \Delta_I W(t_{i-1}) \qquad \text{(A.10)}$$

where the parenthesized I on the left indicates that (A.6) and (A.7) are defined in the sense of Itô. $\Delta_I W(t_{i-1})$ in (A.10) stands for

$$\Delta_I W(t_{i-1}) = W(t_i) - W(t_{i-1}) \qquad \text{(A.11)}$$

and defines the increment of a wiener process at time t_{i-1} in the sense of Itô.

Stratonovich's choice corresponds to $a = \frac{1}{2}$ i.e. $\tau_i = \frac{t_{i-1}+t_i}{2}$ so that

$$\int_{t_0}^{t} w(s)\, d w(s) = \frac{1}{2}\left[w^2(t) - w^2(t_0)\right] \tag{A.12}$$

and the definition of $\mathcal{J}$ is now taken to be

$$(S) \quad \mathcal{J} = \underset{\Delta t \to 0}{\text{qm-lim}} \sum_{i=1}^{n} G\left(X\left(\frac{t_i + t_{i-1}}{2}\right)\right)\left[w(t_i) - w(t_{i-1})\right] \tag{A.13}$$

In order to bring out the difference between Stratonovich's definition of an increment and that of Itô we write the summand in (A.13) in terms of the midpoints

$$\tau_{i-1} = \frac{t_{i-1}+t_i}{2} \tag{A.14}$$

of the interval (t_{i-1}, t_i) so that (A.13) becomes

$$(S) \quad \mathcal{J} = \underset{\Delta t \to 0}{\text{qm-lim}} \sum_{i=1}^{n} G(X(\tau_{i-1}))\, \Delta_S w(\tau_{i-1}) \tag{A.15}$$

where

$$\Delta_S w(\tau_{i-1}) = w\left(\frac{\tau_i + \tau_{i-1}}{2}\right) - w\left(\frac{\tau_{i-1}+\tau_{i-2}}{2}\right) \tag{A.16}$$

Thus it is clear that while Itô increment at time t

$$\Delta_I w(t) = w(t+\Delta t) - w(t) \tag{A.17}$$

"points into future", that of Stratonovich

$$\Delta_S w(t) = w\left(t+\frac{\Delta t}{2}\right) - w\left(t-\frac{\Delta t}{2}\right) \tag{A.18}$$

"Points half into future and half into past".

An important property of the Itô increment which distinguishes Itô formalism from that of Stratonovich is that $\Delta_I w(t)$ is stochastically independent of $w(t')$ for $t' \leqslant t$ i.e.

$$\langle \Delta_I w(t)\, w(t') \rangle = 0 \quad , \quad t' \leqslant t \tag{A.19}$$

which may be proved using the properties of a Wiener process namely

$$\langle w(t) \rangle = 0 \tag{A.20}$$

$$\langle w(t)\, w(t') \rangle = \min(t, t') \tag{A.21}$$

Stratonovich's increment $\Delta_S w(t)$ does not have the property of being uncorrelated with $w(t')$ for $t' \leqslant t$

Differences in the definitions of increments in the two formalisms lead to different integration rules. Thus, while the LHS in (A.12) is precisely what we get using integration rules of ordinary calculus, the LHS of (A.9) differs from it by an extra term $-\frac{1}{2}(t-t_0)$. Thus, whereas integration rules and hence the differentiation rules of ordinary calculus are valid in the Stratonovich formalism, they are both different in the Itô formalism. In the following we shall formulate the rules of differentiation in the Itô calculus.

Equation (A.9) may be written in a differential form as

$$d w^2(t) = 2 w(t)\, d w(t) + dt \tag{A.22}$$

If we construct the differential of $w^2(t)$ formally, using Taylor's theorem, i.e.

$$\begin{aligned} \Delta w^2(t) &= [w(t+\Delta t)]^2 - w^2(t) \\ &= 2 w(t)\, \Delta w(t) + [\Delta w(t)]^2 \end{aligned} \tag{A.23}$$

we obtain

$$d w^2(t) = 2 w(t)\, d w(t) + [d w(t)]^2 \tag{A.24}$$

comparing (A.22) and (A.24) we have

$$[d w(t)]^2 = dt \tag{A.25}$$

In the multidimensional case (A.25) generalises to

$$d w_i(t)\, d w_j(t) = \delta_{ij}\, dt \tag{A.26}$$

Remembering (A.26), let us consider changes of variables in a multi-dimensional Itô differential equation

$$dX_i = a_i(\underline{X})\,dt + \sum_j G_{ij}(\underline{X})\,dW_j\,, \quad i = 1 \dots n \qquad \text{(A.27)}$$

Let us introduce p new variables

$$Y_r = \phi_r(\underline{X}) \qquad r = 1 \dots p \qquad \text{(A.28)}$$

Then

$$\begin{aligned}\Delta Y_r &= \phi_r(\underline{X} + \Delta\underline{X}) - \phi(\underline{X}) \\ &= \sum_i \frac{\partial \phi_r}{\partial X_i}\Delta X_i + \frac{1}{2}\sum_{ij}\frac{\partial^2 \phi_r}{\partial X_i \partial X_j}\Delta X_i \Delta X_j + \cdots\end{aligned} \qquad \text{(A.29)}$$

It is necessary to include the second order differentials in (A.29) because $\Delta X_i \Delta X_j$ involves $\Delta W_i \Delta W_j$ which is of first order in Δt. Substituting from (A.27)

$$\Delta X_i = a_i(\underline{X})\,\Delta t + \sum_{ij} G_{ij}(\underline{X})\,\Delta W_j(t) \qquad \text{(A.30)}$$

and using (A.26) we obtain

$$\begin{aligned}dY_r = {} & \sum_i \frac{\partial \phi_r}{\partial X_i} a_i(\underline{X})\,dt + \sum_{ij}\frac{\partial^2 \phi_r}{\partial X_i \partial X_j}(GG^T)_{ij}\,dt \\ & + \sum_i \frac{\partial \phi_r}{\partial X_i}\,dW_j(t)\,G_{ij}\end{aligned} \qquad \text{(A.31)}$$

The difference between the LHS of (A.31) and that obtained by rules of ordinary calculus is the occurrence of the second term which essentially arises because of (A.26).

Given a Stratonovich differential equation

$$d_S X_i = a_i(\underline{X})\,dt + \sum_j G_{ij}(\underline{X})\,d_S W_j(t) \qquad \text{(A.32)}$$

let us see how we may write down the equivalent Itô differential equation and vice versa. For finite time interval Δt (A.32) may be written as

$$\begin{aligned}\Delta_S X_i(t) &\equiv X_i(t + \tfrac{\Delta t}{2}) - X_i(t - \tfrac{\Delta t}{2}) \\ &= a_i(\underline{X})\,\Delta t + \sum_j G_{ij}(\underline{X}(t))\left[W_j(t + \tfrac{\Delta t}{2}) - W_j(t - \tfrac{\Delta t}{2})\right]\end{aligned} \qquad \text{(A.33)}$$

Making the replacement $t \to t + \frac{\Delta t}{2}$ and remembering the definition of an Itô increment (A.33) becomes

$$\begin{aligned}\Delta_I X_i(t) &\equiv X_i(t+\Delta t) - X_i(t)\\ &= a_i(\underline{X})\,\Delta t + \sum_j G_{ij}\left(\underline{X}\left(t+\tfrac{\Delta t}{2}\right)\right)\Delta_I W_j(t)\end{aligned}$$

Taylor expansion of $G_{ij}\left(\underline{X}\left(t+\frac{\Delta t}{2}\right)\right) = G_{ij}\left(\underline{X}(t)+\frac{\Delta \underline{X}}{2}\right)$ yields

$$\Delta_I X_i(t) = a_i(\underline{X})\,\Delta t + \sum_j \left[G_{ij}(\underline{X}(t)) + \frac{1}{2}\sum_k \frac{\partial G_{ij}}{\partial X_k}\,\Delta_I X_k(t)\right]\Delta_I W_j(t) \quad (A.34)$$

Since $\Delta X_k(t)\,\Delta W_j(t)$ involves a term proportional to $\Delta_I W_l\,\Delta W_j(t)$ which is equal to $\delta_{jl}\,\Delta t$, in order to write all the terms of order Δt we have to iterate (A.34) once. This gives,

$$\begin{aligned}\Delta_I X_i(t) &= a_i(\underline{X})\,\Delta t + \frac{1}{2}\sum_{jk} \frac{\partial G_{ij}}{\partial X_k}\,G_{kj}\,\Delta t\\ &\quad + \sum_j G_{ij}(\underline{X}(t))\,\Delta_I W_j(t)\end{aligned} \quad (A.35)$$

In the differential notation (A.35) may be written as

$$d_I X_i(t) = a_i(\underline{X})\,dt + \frac{1}{2}\sum_{jk} \frac{\partial G_{ij}}{\partial X_k}\,G_{kj}\,dt + \sum_j G_{ij}(\underline{X})\,d_I W_j(t) \quad (A.36)$$

This is the Itô stochastic differential equation equivalent to the Stratonovich differential equation (A.32). Conversely, the Itô stochastic differential equation

$$d_I X_i(t) = a_i(\underline{X})\,dt + \sum_j G_{ij}(\underline{X})\,d_I W_j(t) \quad (A.37)$$

is equivalent to the Stratonovich differential equation

$$d_S X_i(t) = a_i(\underline{X})\,dt - \frac{1}{2}\sum_{jk} \frac{\partial G_{ij}}{\partial X_k}\,G_{kj}\,dt + \sum_j G_{ij}(\underline{X})\,d_S W_j(t) \quad (A.38)$$

Equations (A.37) and (A.38), although quite different in appearance are equivalent and yield the same results for the averages. Thus for $\langle X_i(t)\rangle$ we have form (A.37)

$$d\langle X_i(t)\rangle = \langle a_i(\underline{X})\rangle\,dt \quad (A.39)$$

the second term in (A.47) does not contribute because of the stochastic independence of $d_I W_j(t)$ i.e.

$$\langle G_{ij}(\underline{X}(t))\, d_I W_j(t) \rangle = 0 \tag{A.40}$$

In the Stratonovich formalism, the $d_S W_j(t)$ are correlated with $W(t)$ at previous times and hence one does not have (A.40) but instead one has

$$\langle G_{ij}(\underline{X}(t))\, d_S W_j(t) \rangle = \frac{1}{2} \sum_{jk} \langle \frac{\partial G_{ij}}{\partial X_k} G_{kj} \rangle \, dt \tag{A.41}$$

which cancels the extra term in (A.38) yielding the same equation (A.39) for $\langle X_i(t) \rangle$.

APPENDIX B: On the Gaussian approximation in X and α variables.

In section 6.5.1, Chapter 6, we showed that if $f(\alpha)$ is assumed to be Gaussian distribution in α , then the corresponding $P(X)$ is asymptotically given by

$$P(\underline{X}) = e^{-V\psi(\underline{x})} \tag{B.1}$$

where

$$\psi(\underline{x}) = \sum_i [\bar{\eta}_i - x_i \ln \bar{\eta}_i + x_i \ln x_i - x_i] + \sum_{ij} \frac{1}{2} (\bar{\eta}_i - \eta_{i,0}) G^{-1}_{ij} (\bar{\eta}_j - \eta_{j,0}) \tag{B.2}$$

and $\bar{\eta}_i$ may be expressed in terms of $\underline{X}$ using

$$1 - \frac{x_k}{\eta_k} + \sum_i (\bar{\eta}_i - \eta_{i,0})(G^{-1})_{ji} \tag{B.3}$$

The aim here is to derive (6.5.9) from (B.1) by expanding $\psi(\underline{x})$ about its maximum. Now

$$\frac{\partial \psi}{\partial x_k} = 0 \tag{B.4}$$

when

$$\sum_i \left[\frac{\partial \bar{\eta}_i}{\partial x_k} - \delta_{ik} \ln \bar{\eta}_i - \frac{x_i}{\eta_i} \frac{\partial \bar{\eta}_i}{\partial x_k} + \delta_{ik} \ln x_i \right] + \sum_{ij} (\bar{\eta}_i - \eta_{i,0})(G^{-1})_{ij} \frac{\partial \bar{\eta}_j}{\partial x_k} = 0 \tag{B.5}$$

It follows from (B.3) that $x_k = \eta_{k,0}$ implies $\bar{\eta}_k = \eta_{k,0}$ and in that case the LHS of (B.5) vanishes. Thus the peak of $\psi(\underline{x})$ lies at

$$x_{k,0} = \eta_{k,0} \tag{B.6}$$

The variance around the peak is determined by

$$\left(\frac{\partial^2 \psi}{\partial x_k \partial x_l} \right)_{\underline{x} = \underline{\eta}_{,0}} = \left[\frac{\delta_{kl}}{\eta_{k,0}} - \sum_i \left\{ \frac{\delta_{ik}}{\eta_{i,0}} \left(\frac{\partial \bar{\eta}_i}{\partial x_l} \right)_0 + \frac{\delta_{il}}{\eta_{i,0}} \left(\frac{\partial \bar{\eta}_i}{\partial x_k} \right)_0 \right\} + \sum_{ij} \left(\frac{\partial \bar{\eta}_i}{\partial x_k} \right)_0 \left(G^{-1}_{ij} + \frac{\delta_{ij}}{\eta_{i,0}} \right) \left(\frac{\partial \bar{\eta}_j}{\partial x_l} \right)_0 \right] \tag{B.7}$$

where

$$\left(\frac{\partial \bar{\eta}_i}{\partial x_k} \right)_0 \equiv \left(\frac{\partial \bar{\eta}_i}{\partial x_k} \right)_{\underline{x} = \underline{\eta}_{,0}} \tag{B.8}$$

Implicit differentiation of (B.3) gives

$$\sum_i (G^{-1}+M^{-1})_{ki}\left(\frac{\partial \bar{\eta}_i}{\partial x_l}\right)_0 = (M^{-1})_{kl} \quad , \quad M_{kl} \equiv \frac{\delta_{kl}}{\eta_{k,0}} \tag{B.9}$$

and hence

$$\left(\frac{\partial \bar{\eta}_i}{\partial x_l}\right)_0 = \left[(G^{-1}+M^{-1})^{-1} M^{-1}\right]_{il} \tag{B.10}$$

Substituting this in (B.7) we have

$$\begin{aligned}\left(\frac{\partial^2 \psi}{\partial x_k \partial x_l}\right)_{\underline{x}=\underline{\eta}_{,0}} &= \left[M^{-1} - M^{-1}(G^{-1}+M^{-1})^{-1} M^{-1}\right]_{kl} \\ &= \left[M^{-1}\left[(G^{-1}+M^{-1})^{-1}(G^{-1}+M^{-1}) - (G^{-1}+M^{-1})M^{-1}\right]\right]_{kl} \\ &= \left[M^{-1}(G^{-1}+M^{-1})^{-1} G^{-1}\right]_{kl} \\ &= (G+M)^{-1}_{kl}\end{aligned} \tag{B.11}$$

Hence $P(\underline{x})$ is asymptotically given by

$$P(\underline{x}) = e^{-V\sum_{ij}(x_i - x_{i,0})(G+M)^{-1}_{ij}(x_j - x_{j,0})} \tag{B.12}$$

APPENDIX C: On the Choice of α contours

The possible choices of the contour of integration for $f(\alpha)$ given by (8.11) are

(i) contour C_1 extending from 0 to K_2

(ii) contour C_2 extending from K_2 to $-\infty$

(iii) contour C_3 extending from 0 to $-\infty$

The contour C_3 gives a solution which is a linear combination of those given by C_1 and C_2 and hence there are only two independent choices of the contour of integration.

In Chapter 2, section 2.8.1, we argued that if the probability distribution and all its moments exist, then the corresponding factorial moment generating function $G(S)$ and all its derivatives must be finite at $S = -1$. This serves as a convenient criterion for choosing the correct contour. For the contour C_2 the generating function corresponding to the probability distribution is

$$G(S) = \int_{K_2}^{-\infty} e^{\alpha(S-1)} e^{\alpha} (K_2V-\alpha)^{V\left(K_1-\frac{K_3}{K_2}\right)-1} \alpha^{\left(\frac{K_3V}{K_2}-1\right)} \tag{C.1}$$

which is infinite at $S = -1$ and therefore does not lead to an admissible probability distribution.

Also note that (8.11) leads to a non trivial $P(X)$ only if the limit $K_3 \to 0$ is taken after the limit $V \to \infty$ If $K_3 = 0$ is set equal to zero in (8.11) in the beginning, then the only permissible contour of integration is a closed contour encircling the origin, in which case all the moments of $P(X)$ vanish, and

$$P(X) = \delta_{X,0} \tag{C.2}$$

That this is the exact solution in the case that $K_3 = 0$ is obvious from the reaction mechanism (8.1). Once all the molecules of X are lost, there is no mechanism for producing molecules of X. However, the $K_3 \longrightarrow 0$ limit of the larger volume limit is well defined, and does not give the trivial solution (C.2).

For $f(\alpha)$ given by (8.19) the two choices of the contour of integration are

(i) closed contour encircling the origin,

(ii) a contour extending from 0^- to $-\infty$

The generating function for the latter choice is

$$G(s) = \int_{0^-}^{-\infty} e^{(s-1)\alpha} \, e^{2\alpha + \frac{aV^2}{\alpha}} \, \frac{d\alpha}{\alpha^2} \qquad (C.3)$$

which, although finite at $s = -1$ has divergent second and higher order derivatives and therefore does not correspond to an admissible probability distribution.

APPENDIX D: Next higher corrections to the correlations for the second order Phase transition model.

D.1 The complete expression for next higher correction to the Fourier transform of the spatial correlation function is as follows

$$\tilde{S}_1(\underline{q},\underline{q}') \equiv \delta(\underline{q}+\underline{q}')\,\tilde{S}_1(\underline{q})$$

$$\begin{aligned}\tilde{S}_1(\underline{q}) = {} & \frac{2K_1\eta^2(ss)}{g(q)}\int\frac{d\underline{q}_1}{[g(q_1)+g(q-q_1)+g(q)]\,g(q_1)\,g(q-q_1)} \\ & + \frac{4K_1\eta(ss)[K_1\eta(ss)-(2K_1-K_2)\,g(q)]}{g^2(q)}\int\frac{d\underline{q}_1}{g(q_1)[g(q_1)+g(q)+g(q-q_1)]} \\ & - \frac{2K_1\eta(ss)\,(2K_1-K_2)}{g^2(q)}\int\frac{d\underline{q}_1}{[g(q_1)+g(q-q_1)+g(q)]} \qquad (D.1) \\ & + \frac{2K_1^2\eta(ss)-K_1^2 g(q)-K_1 g^2(q)}{g^2(q)}\int\frac{dq_1}{g(q_1)}\end{aligned}$$

$$g(q) \equiv Dq^2+\eta(ss) \tag{D.2}$$

D.2 The full expression for the next higher correction to the Fourier Laplace transform o fthe two time correlation function $\tilde{T}_1(\underline{q},\underline{q}',s)$ is as follows

$$\tilde{T}_1(\underline{q},\underline{q}',s) \equiv \delta(\underline{q}+\underline{q}'))\,\tilde{T}_1(\underline{q},s)$$

$$\begin{aligned}\tilde{T}_1(\underline{q},s) = {} & \frac{1}{[s+g(q)]}\Bigg[\frac{2K_1\eta^2(ss)}{g(q)}\int\frac{d\underline{q}_1}{[g(q_1)+g(q-q_1)+g(q)]\,g(q_1)\,g(q-q_1)} \\ & + \frac{4K_1\eta(ss)[K_1\eta(ss)-(2K_1-K_2)\,g(q)]}{g^2(q)}\int\frac{d\underline{q}_1}{g(q_1)[g(q_1)+g(q)+g(q-q_1)]} \\ & - \frac{2K_1\eta(ss)\,(2K_1-K_2)}{g^2(q)}\int\frac{d\underline{q}_1}{[g(q_1)+g(q-q_1)+g(q)]} \\ & + \frac{[2K_1^2\eta(ss)-K_1^2 g(q)-K_1 g^2(q)]}{g^2(q)}\int\frac{dq_1}{g(q_1)}\Bigg] \quad +\end{aligned}$$

$$+ \quad \frac{2K_1^2\eta(ss)}{[S+g(q)]^2}\left[\int \frac{d\underline{q}_1}{g(q_1)}\right]$$

$$- \quad \frac{2K_1\eta(ss)(2K_1-K_2)}{[S+g(q)][S-g(q)]\,g(q)}\left[\int \frac{d\underline{q}_1\,[2g(q)+g(q_1)]}{[g(q)+g(q_1)+g(q-q_1)]} - \int \frac{d\underline{q}_1\,[2g(q)+g(q_1)]}{[S+g(q-q_1)+g(q_1)}\right]$$

$$- \frac{2K_1\eta(SS)}{[S+g(q)]}\left[\int \frac{d\underline{q}_1}{[S+g(q_1)+g(q-q_1)]\,g(q_1)}\right]$$

$$+ \frac{2K_1\eta(ss)}{[S+g(q)]^2 g(q)}\int \frac{d\underline{q}_1\,[2K_1\eta(ss)-(2K_1-K_2)\,g(q)]}{[S+g(\underline{q}_1)+g(q-q_1)]\,g(q_1)} \qquad (D.3)$$

where $g(q)$ is given by (D.2)

It is clear from the above that in the complex S plane $\tilde{T}_1(\underline{q},S)$ has a pole and a double pole at $S=-g(q)$ The pole at $S=g(q)$ which arises from the third term in (D.3) is spurious, for its residue is zero. The last three terms in (D.3) also give rise to cuts. All of these three terms contain an integral of the form

$$I = \int \frac{d\underline{q}_1\, f(q_1)}{[S+g(q-q_1)+g(q_1)} \qquad (D.4)$$

Doing the angular integrals I becomes

$$I = \int \frac{\pi}{D}\,\frac{|q_1|\,d|q_1|}{|q|}\,\ln\left[\frac{S+2\eta(ss)+D|q_1|^2+D(|q|+|q_1|)^2}{S+2\eta(ss)+D|q_1|^2+D(|q|-|q_1|)^2}\right] \qquad (D.5)$$

which gives rise to the cuts at $S=-(D|q|^2+2\eta(ss))$ and $S=-\left(\frac{D|q|^2}{2}+2\eta(ss)\right)$

Having thus determined the analytic structure of $\tilde{T}_1(\underline{q},\underline{q}'_,S)$ in the complex S plane, we may write a dispersion relation for $\tilde{T}_1(\underline{q},\underline{q}'S)$as in (9.52). The residues $a(q)$, $b(q)$ and the discontinuities across the cuts $c(q,S')$and $d(q,S')$ in (9.52) may be calculated from (D.2) if desired.

APPENDIX E: Derivation of the results used in Chapter 10

E.1 The solution of the linear stochastic differential eauation (10.18) is

$$\tilde{\underline{\eta}}_1(\underline{q},t) = \int_0^t e^{-\tilde{A}(t-t')} B\, \tilde{\underline{\xi}}(\underline{q},t')\, dt' \tag{E.1}$$

which gives

$$\tilde{G}(\underline{q},\underline{q}',t) = \langle \tilde{\eta}_1(\underline{q},t)\tilde{\underline{\eta}}_1^T(\underline{q}',t)\rangle = \delta(\underline{q}+\underline{q}')\int_0^t dt' e^{-\tilde{A}t'} B^2 e^{-\tilde{A}^T t'} \tag{E.2}$$

and hence

$$\tilde{G}(\underline{q},t) = \int_0^t e^{-\tilde{A}t'} B^2 e^{-\tilde{A}^T t'} dt' \tag{E.3}$$

In the steady state, taking the limit $t \to \infty$ in (E.3) we get

$$\tilde{G}(\underline{q}) = \int_0^\infty dt' e^{-\tilde{A}t'} B^2 e^{-\tilde{A}^T t'} \tag{E.4}$$

It follows from (E.4) that

$$\tilde{A}\tilde{G} + \tilde{G}\tilde{A}^T = -\int_0^\infty \frac{d}{dt'}\left[e^{-\tilde{A}t'} B^2 e^{-\tilde{A}^T t'}\right] dt' = B^2 \tag{E.5}$$

Now since every matrix obeys its characteristic equation which in the two dimensional case is

$$\tilde{A}^2 - (Tr\tilde{A})\tilde{A} + Det\tilde{A} = 0 \tag{E.6}$$

it follows that $e^{-\tilde{A}t}$ is a polynomial in $\tilde{A}$ of degree 1. Thus taking into account the symmetry of $\tilde{G}$, $\tilde{G}$ must have the following form

$$\tilde{G} = \alpha B^2 + \beta(\tilde{A}B^2 + B^2\tilde{A}^T) + \gamma \tilde{A} B^2 \tilde{A}^T \tag{E.7}$$

Substituting (E.7) in (E.5) and using (E.6) we find that (E.5) is satisfied provided that

$$\begin{aligned} &\alpha + (Tr\tilde{A})\beta - (Det\tilde{A})\gamma = 0 \\ &2(Det\tilde{A})\beta + 1 = 0 \\ &\beta + (Tr\tilde{A})\gamma = 0 \end{aligned} \tag{E.8}$$

Solving (E.8) for α, β, γ and substituting in (E.7) we get

$$\tilde{G} = \frac{(\mathrm{Det}\,\tilde{A})\,B^2 + (\tilde{A}-(\mathrm{Tr}\,\tilde{A})I)\,B^2\,(\tilde{A}-(\mathrm{Tr}\,\tilde{A})I)^T}{2\,(\mathrm{Tr}\,\tilde{A})\,(\mathrm{Det}\,\tilde{A})} \tag{E.9}$$

E.2 From the definition of the eqn. (10.51) fluctuation spectrum it follows that

$$F(\underline{q},\omega) = \frac{1}{2\pi}\int_0^\infty e^{-i\omega t}\,T(\underline{q},t)\,dt + \frac{1}{2\pi}\int_{-\infty}^0 e^{-i\omega t}\,T(\underline{q},t)\,dt \tag{E.10}$$

Changing $t \to -t$ in the second term on the RHS of (E.10) and using the following property of the steady state two time correlation function

$$T(\underline{q},-t) = T^T(\underline{q},t) \tag{E.11}$$

we get

$$F(\underline{q},\omega) = \frac{1}{2\pi}\left[\int_0^\infty e^{-i\omega t}\,T(\underline{q},t) + \int_0^\infty e^{i\omega t}\,T^T(\underline{q},t)\right] \tag{E.12}$$

Substituting for $T(\underline{q},t)$ from (10.50) we get

$$F(\underline{q},\omega) = \frac{1}{2\pi}\left[(i\omega I+\tilde{A})^{-1}\tilde{S}(\underline{q}) + \tilde{S}(\underline{q})(-i\omega I+\tilde{A}^T)^{-1}\right] \tag{E.13}$$

which gives

$$(i\omega I+\tilde{A})\,F(\underline{q},\omega)\,(-i\omega I+\tilde{A}^T) = \frac{1}{2\pi}\left[A\tilde{S}+\tilde{S}\tilde{A}^T\right] \tag{E.14}$$

Using the relation

$$\tilde{S} = M+\tilde{G} \tag{E.15}$$

and (E.5) we get

$$F(q,\omega) = \frac{1}{2\pi}\,(i\omega I+A)^{-1}\left[M\tilde{A}^T+\tilde{A}M+\tilde{B}^2\right](-i\omega I+\tilde{A}^T)^{-1} \tag{E.16}$$

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