The Poisson Representation. II. Two-Time Correlation Functions

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Basic formulas for the two-time correlation functions are derived using the Poisson representation method. The formulas for the chemical system in thermodynamic equilibrium are shown to relate directly to the fluctuation-dissipation theorems, which may be derived from equilibrium statistical mechanical considerations. For nonequilibrium systems, the formulas are shown to be generalizations of these fluctuation-dissipation theorems, but containing an extra term which arises entirely from the nonequilibrium nature of the system. These formulas are applied to two representative examples of equilibrium reactions (without spatial diffusion) and to a nonequilibrium chemical reaction model (including the process of spatial diffusion) for which the first two terms in a systematic expansion for the two-time correlation functions are calculated. The relation between the Poisson representation method and Glauber–Sudarshan *P*-representation used in quantum optics is discussed.

1. INTRODUCTION

In this paper we extend our earlier work[1] (hereafter referred to as I) on the Poisson representation into the realm of two-time correlations, which are of central importance in the study of nonequilibrium statistical mechanics. Our aims in this paper are (i) to provide formulas from which we may calculate two-time correlation functions from Poisson representation techniques, (ii) to show how to carry out such calculations in particular representative cases, and (iii) to relate these formulas to more general statistical mechanics results, in particular to fluctuation-dissipation theorems.

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In I we have shown how chemical master equations can be transformed into exact Fokker–Planck equations by the use of the Poisson representation method and have investigated quite thoroughly all aspects of single-time correlations. In order to make this paper reasonably self-contained, we briefly review the Poisson representation method in Section 2. We derive in Section 3 formulas for two-time correlations in equilibrium and in nonequilibrium steady-state situations.

The equilibrium formulas are directly related to the fluctuation-dissipation theorems of Bernard and Callen,[2,3] but the nonequilibrium formulas contain extra terms, which represent the fluctuations in excess of equilibrium.

In Section 4 we give a brief treatment of the two-time correlations for both equilibrium and nonequilibrium systems in the lowest order of the system size expansion. Section 5 is devoted to an explicit calculation of the next higher correction in three typical cases.

Section 6 is not directly related to the previous parts. In it we relate our formulas to similar formulas which arise in the Glauber–Sudarshan P-representation[5,6] used in quantum optics. This section may be omitted without loss of continuity. Section 7 summarizes our conclusions.

2. A REVIEW OF THE POISSON REPRESENTATION METHOD

The Poisson representation method is based on an expansion of the probability distribution in Poisson distributions. For a multivariate probability distribution $P(\mathbf{X}, t)$ we have

$$P(\mathbf{X}, t) = \int d\boldsymbol{\alpha} \left[\prod_i e^{-\alpha_i}(\alpha_i^{X_i}/X_i!) \right] f(\boldsymbol{\alpha}, t) \tag{1}$$

where $f(\boldsymbol{\alpha}, t)$ is the Poisson representation quasiprobability. Here $\mathbf{X}$ is a vector $(X_1, X_2,..., X_i,..., X_N)$, whose elements X_i are nonnegative integers. In this paper, X_i will be the number of molecules of a certain chemical component X_i.

The moments of $P(\mathbf{X}, t)$ satisfy

$$\langle X_1(X_1 - 1) \cdots (X_1 - r + 1)X_2(X_2 - 1) \cdots (X_2 - s + 1) \cdots \rangle$$
$$= \int d\boldsymbol{\alpha}\, \alpha_1{}^r \alpha_2{}^s \cdots f(\boldsymbol{\alpha}, t) \equiv \langle \alpha_1{}^r \alpha_2{}^r \cdots \rangle \tag{2}$$

so that the factorial moments of $P(\mathbf{X}, t)$ are equal to the moments of $f(\boldsymbol{\alpha}, t)$.

Consider an n-component reacting system involving p different reactions

$$\sum_{i=1}^{n} N_i{}^p X_i \underset{k_p{}^B}{\overset{k_p{}^F}{\rightleftharpoons}} \sum_{i=1}^{n} M_i{}^p X_i, \qquad p = 1,...,s \tag{3}$$

where $N_i{}^p$ $(M_i{}^p)$ represents the number of molecules of X_i that appear on the lhs (rhs) of the pth reaction, and $k_p{}^F$ and $k_p{}^B$ are the corresponding forward and backward reaction rate constants.

The master equation for the reaction (3), based entirely on combinatorial kinetics, may be written as

$$
\frac{dP(\mathbf{X}, t)}{dt} = \sum_{p=1}^{s} k_p{}^F \left[\left(\prod_{i=1}^{n} \frac{(X_i + N_i{}^p - M_i{}^p)!}{(X_i - M_i{}^p)!} \right) P(\mathbf{X} + \mathbf{N}^p - \mathbf{M}^p, t) \right.
$$

$$
\left. - \left(\prod_{i=1}^{n} \frac{X_i!}{(X_i - N_i{}^p)!} \right) P(\mathbf{X}, t) \right]
$$

$$
+ \sum_{p=1}^{s} k_p{}^B \left[\left(\prod_{i=1}^{n} \frac{(X_i + M_i{}^p - N_i{}^p)!}{(X_i - N_i{}^p)!} \right) P(\mathbf{X} + \mathbf{M}^p - \mathbf{N}^p, t) \right.
$$

$$
\left. - \left(\prod_{i=1}^{n} \frac{X_i!}{(X_i - M_i{}^p)!} \right) P(\mathbf{X}, t) \right] \tag{4}
$$

Substituting (1) into (4), we can transform (4) into a generalized Fokker–Planck equation for $f(\boldsymbol{\alpha}, t)$:

$$
\frac{\partial f(\boldsymbol{\alpha}, t)}{\partial t} = \sum_{p=1}^{s} \left[\prod_{i=1}^{n} \left(-\frac{\partial}{\partial \alpha_i} + 1 \right)^{M_i{}^p} - \prod_{i=1}^{n} \left(-\frac{\partial}{\partial \alpha_i} + 1 \right)^{N_i{}^p} \right] J_p(\boldsymbol{\alpha}) f(\boldsymbol{\alpha}, t)
$$

$$
\tag{5}
$$

where

$$
J_p(\boldsymbol{\alpha}) = \left(\prod_{i=1}^{n} k_p{}^F \alpha_i^{N_i{}^p} - \prod_{i=1}^{n} k_p{}^B \alpha_i^{M_i{}^p} \right) \tag{6}
$$

If a particular component in (3) is held at a fixed concentration, then the corresponding α variable in (5) should be set equal to a constant and the corresponding derivative dropped. This merely amounts to setting the appropriate $M_i{}^p$ $(N_i{}^p)$ equal to zero along with a redefinition of $k_p{}^B$ $(k_p{}^F)$.

It is evident from (5) that if $\sum_i M_i{}^p$ and $\sum_i N_i{}^p$ are not greater than two, i.e., if (3) involves only bimolecular steps (which is almost always the case in realistic situations), then the Fokker–Planck equation (5) involves derivatives of no more than second order and may be written as

$$
\frac{\partial f(\boldsymbol{\alpha}, t)}{\partial t} = -\sum_{i=1}^{n} \frac{\partial}{\partial \alpha_i} \left[\sum_p A_i{}^p J_p(\boldsymbol{\alpha}) \right] f(\boldsymbol{\alpha}, t)
$$

$$
+ \frac{1}{2} \sum_{i,j=1}^{n} \frac{\partial^2}{\partial \alpha_i \, \partial \alpha_j} B_{ij}[\mathbf{J}(\boldsymbol{\alpha})] f(\boldsymbol{\alpha}, t) \tag{7}
$$

where

$$A_i^p = M_i^p - N_i^p \tag{8}$$

$$B_{ij}[\mathbf{J}(\boldsymbol{\alpha})] = \delta_{ij} \sum_p [M_i^p(M_i^p - 1) - N_i^p(N_i^p - 1)]J_p(\boldsymbol{\alpha})$$
$$+ (1 - \delta_{ij}) \sum_p [M_i^p M_j^p - N_i^p N_j^p]J_p(\boldsymbol{\alpha}) \tag{9}$$

From the point of view of calculations, rather than working with the Fokker–Planck equation (7), it proves much more convenient to work with the equivalent stochastic differential equation (which we use in the Itô[7] form)

$$d\alpha_i/dt = \sum_p A_i^p J_p(\boldsymbol{\alpha}) + \sum_j c_{ij}[\mathbf{J}(\boldsymbol{\alpha})]\xi_j(t) \tag{10}$$

where

$$c_{ij}[\mathbf{J}(\alpha)] = [\{B[\mathbf{J}(\boldsymbol{\alpha})]\}^{1/2}]_{ij} \tag{11}$$

and $\xi_j(t)$ are Gaussian stochastic noise sources, with

$$\langle \xi_j(t) \rangle = 0, \qquad \langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\,\delta(t - t') \tag{12}$$

For calculating quantities of interest from (10) in the inverse powers of the system size, it is convenient to define

$$\boldsymbol{\eta} = \boldsymbol{\alpha}/V \tag{13}$$

and

$$\kappa_p^F = k_p^F(V)^{-\Sigma_i N_i^p + 1}, \qquad \kappa_p^B = k_p^B(V)^{-\Sigma_i M_i^p + 1} \tag{14}$$

and thereby explicitly exhibit the volume dependence of various quantities involved. Equation (10) then becomes

$$d\eta_i/dt = \sum_p A_i^p J_p(\boldsymbol{\eta}) + \epsilon \sum_j c_{ij}[\mathbf{J}(\boldsymbol{\eta})]\xi_j(t) \tag{15}$$

where

$$\epsilon = 1/\sqrt{V}$$

Perturbative calculations then proceed through expanding thus

$$\boldsymbol{\eta}(t) = \boldsymbol{\eta}_0(t) + \epsilon\boldsymbol{\eta}_1(t) + \epsilon^2\boldsymbol{\eta}_2(t) + \cdots \tag{16}$$

Since we are using Itô definition of a stochastic differential equation in such perturbative calculations, certain rules have to be kept in mind. These have been discussed in I.

3. BASIC FORMULAS FOR TWO-TIME CORRELATION FUNCTIONS

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

$$\langle X_r(t) X_s(t') \rangle = \sum_{\mathbf{X}\mathbf{X}'} X_r X_s P(\mathbf{X}, t | \mathbf{X}', t') P(\mathbf{X}', t') \tag{17}$$

where $P(\mathbf{X}', t')$ is the unconditional probability that the system is in a state $\mathbf{X}'$ at time t' and $P(\mathbf{X}, t | \mathbf{X}', t')$ is the conditional probability that the system is in state $\mathbf{X}$ at time t given that it was in state $\mathbf{X}'$ at time t'.

Both $P(\mathbf{X}', t')$ and $P(\mathbf{X}, t | \mathbf{X}', t')$ will obey a master equation over respectively the variables $\mathbf{X}'$, t' and $\mathbf{X}$, 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

$$P(\mathbf{X}', t') = \int d\boldsymbol{\alpha} \left[\prod_k e^{-\alpha_k}(\alpha_k')^{X_{k'}} / X_{k'}! \right] f(\boldsymbol{\alpha}', t') \tag{18}$$

which defines $f(\boldsymbol{\alpha}', t')$. We now define $f(\boldsymbol{\alpha}, t | \mathbf{X}, t)$ by

$$P(\mathbf{X}, t | \mathbf{X}', t') = \int d\boldsymbol{\alpha} \left[\prod_i e^{-\alpha_i}(\alpha_i)^{X_i} / X_i! \right] f(\boldsymbol{\alpha}, t | \mathbf{X}', t') \tag{19}$$

Thus $f(\boldsymbol{\alpha}, t | \mathbf{X}', t')$ is the quasiprobability in $\boldsymbol{\alpha}$ space arising from an initially sharp $\mathbf{X}$ space state. Noting that

$$P(\mathbf{X}, t' | \mathbf{X}', t') = \delta_{\mathbf{X}, \mathbf{X}'} \tag{20}$$

we see that

$$f(\boldsymbol{\alpha}, t' | \mathbf{X}', t') = \prod_j [e^{\alpha_j}(-1)^{X_{j'}} \delta^{X_{j'}}(\alpha_j)] \tag{21}$$

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

$$f(\boldsymbol{\alpha}, t' | \boldsymbol{\alpha}', t') = \delta(\boldsymbol{\alpha} - \boldsymbol{\alpha}') \tag{22}$$

Since the Fokker–Planck equation is linear, we find that

$$f(\boldsymbol{\alpha}, t | \mathbf{X}', t') = \int d\boldsymbol{\alpha}' \prod_j [e^{\alpha_{j'}}(-1)^{X_{j'}} \delta^{X_{j'}}(\alpha_{j'})] f(\boldsymbol{\alpha}, t | \boldsymbol{\alpha}', t') \tag{23}$$

we now substitute (23), (19), and (18) into (17). In the resulting expression, the sum over $\mathbf{X}$ is trivial. It merely replaces X_r by α_r. Summing over $\mathbf{X}'$ and noting that

$$\sum_{X_{s'}} (-1)^{X_{s'}} \delta^{X_{s'}}(\alpha_s'')(\alpha_s')^{X_{s'}} / X_{s'}! = \delta(\alpha_s'' - \alpha_s') \tag{24a}$$

the lhs of (24a) being the Taylor expansion of $\delta(\alpha_s'' - \alpha_s')$, and similarly

$$\sum_{X_{s'}} X_{s'}(-1)^{X_{s'}} \delta^{X_{s'}}(\alpha_s'')(\alpha_s')^{X_{s'}} / X_{s'}! = \alpha_s'(\partial/\partial\alpha_s')\delta(\alpha_s'' - \alpha_s') \tag{24b}$$

we find that

$$\langle X_r(t) X_s(t') \rangle$$

$$= \int d\boldsymbol{\alpha}\, d\boldsymbol{\alpha}'\, d\boldsymbol{\alpha}''\, \alpha_r \left\{ \exp\left[\sum_i (\alpha_i'' - \alpha_i') \right] \right\} \alpha_s'$$

$$\times [\partial \delta(\boldsymbol{\alpha}'' - \boldsymbol{\alpha}')/\partial\alpha_s'] f(\boldsymbol{\alpha}, t \,|\, \boldsymbol{\alpha}'', t') f(\boldsymbol{\alpha}', t') \tag{25}$$

and integrating by parts

$$= \int d\boldsymbol{\alpha}\, d\boldsymbol{\alpha}'\, \alpha_r \alpha_s' f(\boldsymbol{\alpha}, t \,|\, \boldsymbol{\alpha}', t') f(\boldsymbol{\alpha}', t')$$

$$+ \int d\boldsymbol{\alpha}' \left[\alpha_s' \frac{\partial}{\partial\alpha_s'} \int d\boldsymbol{\alpha}\, \alpha_r f(\boldsymbol{\alpha}, t \,|\, \boldsymbol{\alpha}', t') \right] f(\boldsymbol{\alpha}', t') \tag{26}$$

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 $f(\boldsymbol{\alpha}', t')$ of the response function to a variation of the initial condition. Thus, writing

$$\int d\boldsymbol{\alpha}\, \alpha_r f(\boldsymbol{\alpha}, t \,|\, \boldsymbol{\alpha}', t') \equiv \langle \alpha_r(t) | [\boldsymbol{\alpha}', t'] \rangle \tag{27}$$

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

$$\int d\boldsymbol{\alpha}'\, \alpha_s'(\partial/\partial\alpha_s')\langle \alpha_r(t) | [\boldsymbol{\alpha}', t'] \rangle f(\boldsymbol{\alpha}', t')$$

$$\equiv \langle\langle \alpha_s'(\partial/\partial\alpha_s')\langle \alpha_r(t) | [\boldsymbol{\alpha}', t'] \rangle \rangle\rangle \tag{28}$$

Thus the second term is the average over the initial quasiprobability of a response function.

Remembering that the $\boldsymbol{\alpha}$-space mean $\langle \alpha_r(t) \rangle$ is equal to $\langle X_r(t) \rangle$ for all t, we derive

$$\langle X_r(t), X_s(t') \rangle = \langle \alpha_r(t), \alpha_s(t') \rangle + \langle \alpha_s'(\partial/\partial\alpha_s')\langle \alpha_r(t)|[\boldsymbol{\alpha}', t'] \rangle\rangle \qquad (29)$$

Here we have introduced the notation

$$\langle a, b \rangle = \langle ab \rangle - \langle a \rangle\langle b \rangle \qquad (29a)$$

for the correlation function $\langle a, b \rangle$.

Modifications to these formulas when the indices r, s refer to continuous labeling of spatial position are treated in Section 5.

3.1. Application to Equilibrium Systems

We showed in I that in equilibrium situations, the unconditional quasiprobability (in a grand canonical ensemble) is

$$f(\boldsymbol{\alpha})_{eq} = \delta(\boldsymbol{\alpha} - \boldsymbol{\alpha}(eq)) \qquad (30)$$

so that the X-space distribution is Poissonian: There are then two results of this.

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

$$\langle \alpha_r(t), \alpha_s(t') \rangle_{eq} = 0 \qquad (31)$$

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

$$\langle X_r(t), X_s(t') \rangle = \left[\alpha_s' \frac{\partial}{\partial\alpha_s'} \langle \alpha_r(t')|[\boldsymbol{\alpha}', t'] \rangle \right]_{\boldsymbol{\alpha}' = \boldsymbol{\alpha}(eq)} \qquad (32)$$

This result is in fact exactly that of Bernard and Callen,[2,3] which relates a two-time correlation function to a derivative of the mean of a quantity with respect to a thermodynamically conjugate variable. The proof of the result is so simple that we shall explain it here, in a form suitable for our work. Consider a system in which the numbers of molecules of chemical species X_1, X_2,... corresponding to a configuration I of the system are $X_1(I)$, $X_2(I)$,... and it is understood that these chemical species may react with each other. Then in a grand canonical ensemble, as demonstrated in I, the equilibrium distribution function is

$$Z^{-1}(\boldsymbol{\mu}) \exp\left\{ (1/kT)\left[\sum_i \mu_i X_i(I) - E(I) \right] \right\} \qquad (33)$$

where $Z(\boldsymbol{\mu})$ is the grand canonical partition function. As pointed out in I, the chemical potentials μ_i for a reacting system cannot be chosen arbitrarily,

but must be related by the stoichiometric constraints of the allowable reactions.

Now we further define the quantities

$$\langle X_i, t | [I, t'] \rangle \tag{34}$$

to be the mean values of the quantities X_i at time t under the condition that the system was in a configuration I at time t'. Then a quantity of interest is the mean value of (34) over the distribution (33) of initial conditions, namely

$$\langle X_i, t | [\mu, t'] \rangle = \sum_J \langle X_i, t | [J, t'] \rangle Z^{-1}(\mu)$$

$$\times \exp\left\{ (1/kT) \left[\sum_j \mu_j X_j(J) - E(J) \right] \right\} \tag{35}$$

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

$$\left[kT \frac{\partial}{\partial \mu_j} \langle X_i, t | [\mu, t'] \rangle \right]_{\mu = \mu(eq)} = \langle X_i(t), X_j(t') \rangle_{eq} \tag{36}$$

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 correlation function in equilibrium, is a measure of fluctuations.

This is a different form of fluctuation-dissipation theorem from that most often considered, in which the response is to an impressed external field introduced into the Hamiltonian, and the relationship to the generalized susceptibility thus defined involves the imaginary part of the Fourier transform of the two-time correlation function (see, e.g., Ref. 4). However, the result (36) follows as a special case, in which the external field has a step-function time dependence.

To make contact with the Poisson representation result (32), we note that the chemical potentials μ_j in ideal solution theory (which we have shown in I to be equivalent to our form of the master equation) are given by

$$\mu_i[\langle X \rangle] = kT \log\langle X_i \rangle + \text{const} \tag{37}$$

Using (37), we find that (36) becomes

$$\langle X_i(t), X_j(t') \rangle = \left[\langle X_j \rangle \frac{\partial}{\partial \langle X_r \rangle} \langle X_i, t | [\mu[\langle X \rangle], t'] \rangle \right]_{\langle X \rangle = \langle X \rangle_{eq}} \tag{38}$$

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

$$\langle X_i, t | [\mu[\langle \mathbf{X} \rangle], t'] \rangle = \langle \alpha_i, t | [\alpha', t'] \rangle \tag{39}$$

with $\alpha' = \langle \mathbf{X} \rangle$. Thus (38) becomes

$$\langle X_i(t), X_j(t') \rangle = \left[\alpha_j' \frac{\partial}{\partial \alpha_j'} \langle \alpha_i, t | [\alpha', t] \rangle \right]_{\alpha' = \alpha(\mathrm{eq})} \tag{40}$$

Thus (32) is the ideal solution limit of the general result (36). Thus, the general formula (29) can be considered as a generalization of the Bernard–Callen result to systems that are not in thermodynamic equilibrium.

3.2. Nonequilibrium Steady States

The general formula (29) 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 α-space states. The first term is the contribution from the α-space fluctuations themselves and is not directly related to a response function. It represents the fluctuations in excess of equilibrium.

By integrating the second term in (26) by parts we may also derive a slightly different formula

$$\langle X_r(t), X_s(t') \rangle = \langle \alpha_r(t), \alpha_s(t') \rangle - \langle \alpha_r(t) \rangle$$

$$- \left\langle \alpha_r(t) \alpha_s(t') \frac{\partial}{\partial \alpha_s} \log f(\alpha', t') \right\rangle \tag{41}$$

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

4. RESULTS FOR LINEARIZED SYSTEMS

If (15) is linearized by putting

$$\eta(t) = \eta(\mathrm{ss}) + \epsilon \eta_1(t) \tag{42}$$

where $\eta(\mathrm{ss})$ are the macroscopic steady-state values given by

$$\sum A_i{}^p J_p(\eta(\mathrm{ss})) = 0, \qquad p = 1, ..., s \tag{43}$$

then in the lowest order in ϵ this gives a linear stochastic differential equation for η_1,

$$d\eta_1/dt = -F\eta_1(t) + B\xi(t) \tag{44}$$

Then

$$\langle \alpha_r(t), \alpha_s(t') \rangle = \sum_{r'} V\{\exp[-F(t - t')]\}_{rr'}\langle \eta_{r',1}(t'), \eta_{s,1}(t') \rangle \qquad (45)$$

and

$$\frac{\partial}{\partial \alpha_s'} \langle \alpha_r, t | [\boldsymbol{\alpha}', t'] \rangle = \frac{\partial}{\partial \eta_{s,1}'} \langle \eta_{r,1}, t | [\boldsymbol{\eta}_1', t'] \rangle = \{\exp[-F(t - t')]\}_{rs}$$

$$(46)$$

Thus by using the statistical properties (12) of the Langevin source $\xi(t)$ and substituting in (29), we derive

$$\langle X_r(t), X_s(t') \rangle = V \sum_{r'} \{\exp[-F(t - t')]\}_{rr'}[\langle \eta_{r',1}(t'), \eta_{s,1}(t') \rangle + \delta_{r',s}\eta_s(\text{ss})]$$

$$= \sum_{r'} \{\exp[-F(t - t')]\}_{rr'}\langle X_{r'}(t'), X_s(t') \rangle \qquad (47)$$

where we have used the fact that in the lowest order

$$\langle X_r(t'), X_s(t') \rangle = \langle \alpha_r(t'), \alpha_s(t') \rangle + \delta_{rs}\langle \alpha_s(t') \rangle$$
$$= V[\langle \eta_{r,1}(t'), \eta_{s,1}(t') \rangle + \delta_{r,s}\eta_s(\text{ss})] \qquad (48)$$

This result is the same as that obtained by Kitahara,[8] Kubo et al.,[9] and Keizer[10] using various different approaches. When specialized to systems in thermodynamic equilibrium, the Poissonian nature of the variance matrix $\langle X_r(t'), X_s(t') \rangle$ gives the simpler result

$$\langle X_r(t), X_s(t') \rangle_{\text{eq}} = (\exp[-F(t - t')])_{rs}\langle X_s \rangle_{\text{eq}} \qquad (49)$$

5. APPLICATIONS: HIGHER ORDER CORRECTIONS

In this section we shall calculate next higher order corrections to the results obtained in Section 4. Higher order corrections in a specific case have also been calculated by van Kampen[11] using his system size expansion. We shall consider three examples, each chosen to bring out a special feature. Our first example is a simple nonlinear reaction with a Poissonian steady state and serves to illustrate the technique. The second one is a simple two-variable equilibrium reaction with a conservation law. Finally, we consider the second-order phase transition mode,[12–15] including spatial diffusion, and discuss the effect the corrections have on the analytic structure of the two-time correlations.

5.1. A Nonlinear Reaction with a Poissonian Steady State

Consider the reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X \qquad (50)$$

the stochastic differential equation for which is

$$d\eta/dt = (\kappa_1 - \kappa_2\eta^2) + \epsilon[2(\kappa_1 - \kappa_2\eta^2)]^{1/2}\xi(t) \tag{51}$$

Because we hold the total quantity of A fixed, (50) is not a genuine equilibrium reaction. However, it has a Poissonian steady state, as a consequence of which we have

$$\kappa_1 - \kappa_2\eta^2(\text{ss}) = 0 \tag{52}$$

exactly. To solve (51) perturbatively we expand $\eta(t)$ thus

$$\eta(t) = \eta_0(t) + \epsilon\eta_1(t) + \epsilon^2\eta_2(t) + \cdots \tag{53}$$

Substituting (53) in (51) and equating like powers of ϵ, we get

$$\frac{d\eta_0(t)}{dt} = \kappa_1 - \kappa_2\eta_0^2(t) \tag{53a}$$

$$\frac{d\eta_1(t)}{dt} = -2\kappa_2\eta_0(t)\eta_1(t) + \{2[\kappa_1 - \kappa_2\eta_0^2(t)]\}^{1/2}\xi(t) \tag{53b}$$

$$\frac{d\eta_2(t)}{dt} = -2\kappa_2\eta_0(t) - \kappa_2\eta_0^2(t) - \frac{2\kappa_2\eta_0(t)\eta_1(t)\xi(t)}{\{2[\kappa_1 - \kappa_2\eta_0^2(t)]\}^{1/2}} \tag{53c}$$

Note that if we put $\eta_0(t) = \eta(\text{ss})$, 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 fluctuations vanish.

Defining

$$G(t, t') = \exp\left[-2\kappa_2 \int_{t'}^{t} dt'' \, \eta_0(t'')\right] \tag{54}$$

and solving (53a)–(53c) subject to the initial condition

$$\eta_i(0) = 0, \quad i \geqslant 1$$

(henceforth we shall choose the initial time to be zero) we obtain

$$\eta_1(t) = \int_0^t dt' \, G(t, t')\{2[\kappa_1 - \kappa_2\eta_0^2(t')]\}^{1/2}\xi(t') \tag{55a}$$

$$\langle\eta_1^2(t)\rangle = \int_0^t dt' \, G^2(t, t')\{2[\kappa_1 - \kappa_2\eta_0^2(t')]\}^{1/2} \tag{55b}$$

$$\langle\eta_2(t)\rangle = -\kappa_2 \int_0^t dt' \, G(t, t')\langle\eta_1^2(t')\rangle$$

$$= -\kappa_2 \int_0^t dt' \, G(t, t') \int_0^{t'} dt'' \, G^2(t', t'')[2(\kappa_1 - \kappa_2\eta_0^2(t''))] \tag{55c}$$

Now

$$\frac{\partial \langle \eta(t) \rangle}{\partial \eta(0)} \bigg|_{\eta(0) = \eta(\text{ss})} = \frac{\partial \eta_0(t)}{\partial \eta_0(0)} \bigg|_{\eta_0(0) = \eta(\text{ss})} + \epsilon^2 \frac{\partial \langle \eta_2(t) \rangle}{\partial \eta_0(0)} \bigg|_{\eta_0(0) = \eta(\text{ss})} \tag{56}$$

where we have used the abbreviated notation

$$\frac{\partial \langle \eta(t) \rangle}{\partial \eta(0)} \equiv \frac{\partial \langle \eta(t) | [\eta(0), 0] \rangle}{\partial \eta(0)} \tag{57}$$

For the response function, we have simply to carry out the appropriate differentiation in (56) and evaluate those at the steady state. It is clear that

$$\frac{\partial \eta_0(t)}{\partial \eta_0(0)} \bigg|_{\eta_0(0) = \eta(\text{ss})} = G(t, 0) \big|_{\eta_0(0) = \eta(\text{ss})} = \exp[-2\kappa_2 \eta(\text{ss})t] \tag{58}$$

The next term involves the derivative of (55c) with respect to $\eta_0(0)$, but since the final factor is zero when $\eta_0(0) = \eta(\text{ss})$, only the term in which it is differentiated is nonzero 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

$$\langle X(t), X(0) \rangle = V\eta(\text{ss})e^{-2\kappa_2 \eta(\text{ss})t} \left\{ 1 + \frac{1}{V} \left[\frac{\kappa_2}{2} \left(t - \frac{1}{2\kappa_2 \eta(\text{ss})} \right) \right. \right.$$

$$\left. \left. + \frac{1}{2\kappa_2 \eta(\text{ss})} e^{-2\kappa_2 \eta(\text{ss})t} \right] \right\} \tag{59}$$

5.2. An Equilibrium Reaction with a Conserved Quantity

We now consider a genuine equilibrium reaction with a conservation law

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Y \tag{60}$$

the stochastic differential equations for which are

$$d\eta_1(t)/dt = -[\kappa_1 \eta_1(t) - \kappa_2 \eta_2^2(t)] \tag{61a}$$

$$d\eta_2(t)/dt = 2[\kappa_1 \eta_1(t) - \kappa_2 \eta_2^2(t)]$$
$$+ \epsilon\{2[\kappa_1 \eta_1(t) - \eta_2^2(t)]\}^{1/2}\xi(t) \tag{61b}$$

To display the conserved quantity, we define

$$X_1(t) = \eta_1(t) \tag{62a}$$

$$X_3(t) = 2\eta_1(t) + \eta_2(t) \tag{62b}$$

which gives

$$dX_1/dt = -(\kappa_1 - \kappa_2 X_3^2 + 4\kappa_2 X_3 X_1 - 4\kappa_2 X_1^2) \tag{63a}$$

$$dX_3/dt = \epsilon[2(\kappa_1 - \kappa_2 X_3^2 + 4\kappa_2 X_3 X_1 - 4\kappa_2 X_1^2)]^{1/2}\xi(t) \tag{63b}$$

It follows from (63b) and Itô rules that

$$d\langle X_3(t)\rangle/dt = 0 \tag{64}$$

i.e.,

$$X_3(\text{eq}) = \langle X_3(0)\rangle = \langle 2X + Y\rangle \tag{65}$$

The equilibrium value of $X_1(\text{eq}) = \eta_1(\text{eq})$ is given in terms of $X_3(\text{eq})$ by

$$\kappa_1 - \kappa_2 X_3^2(\text{eq}) + 4X_3(\text{eq})X_1(\text{eq}) - 4\kappa_2 X_1^2(\text{eq}) = 0 \tag{66}$$

exactly. $\eta_2(\text{eq})$ may be deduced by using the conservation law. In terms of X_1 and X_3 the two-time correlations may be written as

$$\langle 2X(t) + Y(t), X(0)\rangle = X_1(\text{eq}) \tag{67a}$$

$$\langle 2X(t) + Y(t), Y(0)\rangle = X_3(\text{eq}) - 2X_1(\text{eq}) \tag{67b}$$

$$\langle X(t), X(0)\rangle = X_1(\text{eq})\left[\frac{\partial\langle X_1(t)\rangle}{\partial X_1(0)} + 2\frac{\partial\langle X_1(t)\rangle}{\partial X_3(0)}\right]_{\mathbf{X}=\mathbf{X}(\text{eq})} \tag{67c}$$

$$\langle X(t), Y(0)\rangle = X_3(\text{eq})\left[\frac{\partial\langle X_1(t)\rangle}{\partial X_1(0)}\right]_{\mathbf{X}=\mathbf{X}(\text{eq})} \tag{67d}$$

Thus, to evaluate the various two-time correlations, one only needs to calculate the response functions $[\partial\langle X_1(t)\rangle/\partial X_1(0)]|_{\text{eq}}$ and $[\partial\langle X_1(t)\rangle/\partial X_3(0)]|_{\text{eq}}$. Following the procedure outlined above, the results are found to be

$$\langle X(t), X(0)\rangle = X_1(\text{eq})\left[\frac{2b}{a} + \left(1 - \frac{2b}{a}\right)e^{-at} + \frac{1}{V}\left(\frac{2b}{a} + 1\right)H(t)\right] \tag{68}$$

$$\langle X(t), Y(0)\rangle = X_3(\text{eq})\left[\frac{b}{a}(1 - e^{-at}) + \frac{1}{V}\frac{b}{a}H(t)\right] \tag{69}$$

where

$$a = \kappa_1 + 4\kappa_2 X_3(\text{eq}) - 8\kappa_2 X_1(\text{eq}) \tag{70}$$

$$b = 2\kappa_2 X_3(\text{eq}) - 4\kappa_2 X_1(\text{eq}) = (a - \kappa_1)/2 \tag{71}$$

and

$$H(t) = (2\kappa_2/a)[1 - e^{-at}(1 + at)]$$
$$- (8\kappa_2 b/a^2)[1 - e^{-at}(1 + at + \tfrac{1}{2}a^2t^2)]$$
$$+ (16\kappa_2 b^2/a^3)[1 + e^{-at}(1 - 2at - \tfrac{1}{2}a^2t^2) - e^{-2at}(2 + at)] \tag{72}$$

Notice the nondecaying terms in these results, which are 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. This means that when spatial dependence is omitted, the canonical and grand canonical ensembles give very different results.

When diffusion is included (as shown for a linear system in Ref. 14) there is very little difference between the two ensembles. The two-time correlation function between conserved quantities is then damped in time by the process of diffusion.

5.3. Nonlinear Reaction with Diffusion: Second-Order Phase Transition Model

We shall now investigate a nonequilibrium reaction which exhibits a second-order phase transition behavior[12-15]

$$A + X \underset{k_4}{\overset{k_2}{\rightleftarrows}} 2X, \qquad B + X \underset{k_3}{\overset{k_1}{\rightleftarrows}} C \tag{73}$$
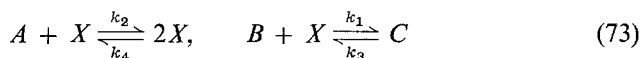
including spatial diffusion, viewing the process of diffusion as an exchange of one particle at a time between cells in which the system is assumed to be divided. The master equation for reaction-diffusion systems has been treated thoroughly in Refs. 8, 14, and 16. The equivalent stochastic differential equation in this case is (as derived in I)

$$\frac{d\eta_i}{dt} = \sum_j D_{ij}\eta_j + \kappa_3 + (\kappa_2 - \kappa_1)\eta_i - \eta_i^2 + \left[\frac{2(\kappa_2\eta_i - \eta_i^2)}{\Delta V}\right]^{1/2}\xi_i(t) \tag{74}$$

where i, j, etc. are the cell labels, ΔV is the cell volume, and

$$\eta_i = \alpha_i/\Delta V, \quad \kappa_3 \Delta V = k_3 C, \quad \kappa_2 = k_2 A, \quad \kappa_1 = k_1 B, \quad \kappa_4 \Delta V^{-1} = k_4 \tag{75}$$

and

$$D_{ij} = d_{ij} - \sum_k d_{ik} \, \delta_{ij} \tag{76}$$

with

$$d_{ij} = \begin{cases} d, & i, j \text{ nearest neighbors} \\ 0, & \text{otherwise} \end{cases} \tag{77}$$

In the continuum notation (74) becomes

$$d\eta(\mathbf{r}, t)/dt = D \, \nabla^2 \eta(\mathbf{r}, t) + \kappa_3 + (\kappa_2 - \kappa_1)\eta(\mathbf{r}, t) - \eta_1{}^2(\mathbf{r}, t)$$
$$+ \{2[\kappa_2 \eta(\mathbf{r}, t) - \eta^2(\mathbf{r}, t)]\}^{1/2} \xi(\mathbf{r}, t) \tag{78}$$

Also in the continuum notation the relation

$$\langle X_r(t), X_s(0) \rangle = \langle \alpha_r(t), \alpha_3(0) \rangle + \langle \alpha_s(0) \, \partial \langle \alpha_r(t) | [\boldsymbol{\alpha}(0), 0] \rangle / \partial \alpha_s(0) \rangle \tag{79}$$

becomes

$$\langle \rho(\mathbf{r}, t), \rho(\mathbf{r}', 0) \rangle = \langle \eta(\mathbf{r}, t), \eta(\mathbf{r}', 0) \rangle + \langle \eta(\mathbf{r}', 0) \, \delta \langle \eta(\mathbf{r}, t) \rangle / \delta \eta(\mathbf{r}', 0) \rangle$$
$$\tag{80}$$

where $\rho(\mathbf{r}, t)$ corresponds to the density variable and $\delta \langle \eta(\mathbf{r}, t) \rangle / \delta \eta(\mathbf{r}', 0)$ denotes the functional derivative of $\eta(\mathbf{r}, t)$ with respect to its initial value.

In the limit $\kappa_3 \to 0$ and $\kappa_2 - \kappa_1 > 0$ the homogeneous steady-state solution of the nonfluctuating part of (78) is

$$\eta(\text{ss}) = \kappa_2 - \kappa_1 \tag{81}$$

Putting

$$\eta = \eta(\text{ss}) + \hat{\eta} \tag{82}$$

in (78) and (80), we have

$$d\hat{\eta}(\mathbf{r}, t)/dt = [D \, \nabla^2 - \eta(\text{ss})]\hat{\eta} - \hat{\eta}^2$$
$$+ \lambda\{2[\kappa_1 \eta(\text{ss}) + (2\kappa_1 - \kappa_2)\hat{\eta} - \hat{\eta}^2]\}^{1/2} \xi(\mathbf{r}, t) \tag{83}$$

and

$$T(\mathbf{r}, t; \mathbf{r}', 0) = \langle \hat{\eta}(\mathbf{r}, t), \hat{\eta}(\mathbf{r}', 0) \rangle + \langle [\eta(\text{ss}) + \hat{\eta}(r', 0)] \langle \hat{R}(\mathbf{r}, t; r', 0) \rangle \rangle \tag{84}$$

where we have introduced the following abbreviations:

$$T(\mathbf{r}, t; \mathbf{r}', 0) = \langle \rho(\mathbf{r}, t), \rho(\mathbf{r}', 0) \rangle \tag{85a}$$

$$\hat{R}(\mathbf{r}, t, \mathbf{r}', 0) = \delta\hat{\eta}(\mathbf{r}, t)/\delta\hat{\eta}(\mathbf{r}, 0) \tag{85b}$$

Also note that, as in I, we have introduced a formal expansion parameter in order to carry out a perturbative solution of the lhs of (83) and hence that of (84). We set $\lambda = 1$ at the end of the calculation.

It follows from (62) that $\hat{R}(\mathbf{r}, t; \mathbf{r}', 0)$ obeys

$$\frac{d\hat{R}(\mathbf{r}, t; \mathbf{r}', 0)}{dt} = [D \nabla^2 - \eta(\mathrm{ss})]\hat{R}(\mathbf{r}, t; \mathbf{r}', 0) - 2\hat{\eta}(\mathbf{r}, t)\hat{R}(\mathbf{r}, t; \mathbf{r}', 0)$$

$$+ \frac{\lambda[(2\kappa_1 - \kappa_2) - 2\hat{\eta}(\mathbf{r}, t)]\hat{R}(\mathbf{r}, t; r', 0)\xi(\mathbf{r}, t)}{[2\kappa_1\eta(\mathrm{ss}) + (2\kappa_1 - \kappa_2)\hat{\eta}(\mathbf{r}, t) - \hat{\eta}^2(\mathbf{r}, t)]^{1/2}} \tag{86}$$

We now expand $\hat{\eta}(\mathbf{r}, t)$ and $\hat{R}(\mathbf{r}, t; \mathbf{r}', 0)$:

$$\hat{\eta} = \lambda\eta_1 + \lambda^2\eta_2 + \cdots, \qquad \hat{R} = R_0 + \lambda R_1 + \lambda^2 R_2 + \cdots \tag{87}$$

Substituting (87) in (83) and (84) and equating like powers of λ on both sides, we obtain

$$\frac{d\eta_1(\mathbf{r}, t)}{dt} = [D \nabla^2 - \eta(\mathrm{ss})]\eta_1(\mathbf{r}, t) + [2\kappa_1\eta(\mathrm{ss})]^{1/2}\xi(\mathbf{r}, t) \tag{88a}$$

$$\frac{d\eta_2(\mathbf{r}, t)}{dt} = [D \nabla^2 - \eta(\mathrm{ss})]\eta_2(\mathbf{r}, t) - \eta_1^2(\mathbf{r}, t)$$

$$+ \frac{(2\kappa_1 - \kappa_2)\eta_2(\mathbf{r}, t)\xi(\mathbf{r}, t)}{[2\kappa_1\eta(\mathrm{ss})]^{1/2}} \tag{88b}$$

$$\frac{d\eta_3(\mathbf{r}, t)}{dt} = [D \nabla^2 - \eta(\mathrm{ss})]\eta_3(\mathbf{r}, t) - 2\eta_1(\mathbf{r}, t)\eta_2(\mathbf{r}, t)$$

$$+ \frac{(2\kappa_1 - \kappa_2)\eta_2(\mathbf{r}, t)\xi(\mathbf{r}, t)}{[2\kappa_1\eta(\mathrm{ss})]^{1/2}} - \frac{\kappa_2^2\eta_1^2(\mathbf{r}, t)\xi(\mathbf{r}, t)}{2[2\kappa_1\eta(\mathrm{ss})]^{3/2}} \tag{88c}$$

$$\frac{dR_0(\mathbf{r}, t; \mathbf{r}', 0)}{dt} = [D \nabla^2 - \eta(\mathrm{ss})]R_0(\mathbf{r}, t; \mathbf{r}', 0) \tag{89a}$$

$$\frac{dR_1(\mathbf{r}, t; \mathbf{r}', 0)}{dt} = [D \nabla^2 - \eta(\mathrm{ss})]R_1(\mathbf{r}, t; \mathbf{r}', 0) - 2\eta_1(\mathbf{r}, t)R_0(\mathbf{r}, t; \mathbf{r}', 0)$$

$$+ \frac{2\kappa_1 - \kappa_2}{[2\kappa_1\eta(\mathrm{ss})]^{1/2}} R_0(\mathbf{r}, t; \mathbf{r}', 0)\xi(\mathbf{r}, t) \tag{89b}$$

The expansions for the first and second terms on the lhs of (84) are

$$\langle \hat{\eta}(\mathbf{r}, t), \hat{\eta}(\mathbf{r}', 0) \rangle = \lambda^2 \langle \eta_1(\mathbf{r}, t), \eta_1(\mathbf{r}', 0) \rangle + \lambda^4 [\langle \eta_2(\mathbf{r}, t), \eta_2(\mathbf{r}', 0) \rangle$$
$$+ \langle \eta_1(\mathbf{r}, t), \eta_3(\mathbf{r}', 0) \rangle + \langle \eta_3(\mathbf{r}, t), \eta_1(r', 0) \rangle]$$
$$(90a)$$

$$\langle [\eta(ss) + \hat{\eta}(r', 0)] \langle \hat{R}(\mathbf{r}, t; \mathbf{r}', 0) \rangle \rangle$$
$$= \eta(ss) \langle R_0(\mathbf{r}, t; \mathbf{r}', 0) \rangle + \lambda^2 [\langle \eta_2(r', 0) \langle R_0(\mathbf{r}, t, \mathbf{r}', 0) \rangle \rangle$$
$$+ \langle \eta_1(\mathbf{r}', 0) \langle R_1(\mathbf{r}, t, \mathbf{r}', 0) \rangle \rangle]$$
$$(90b)$$

Terms of $O(\lambda)$ and $O(\lambda^3)$ vanish identically because they involve averages of odd numbers of factors of $\xi(\mathbf{r}, t)$. Also note that although the terms in the expansion (90a) differ from the corresponding terms in (90b) by a factor of λ^2, they are really of the same order in terms of the actual expansion parameter $(\Delta V)^{-1}$, which reappears as a cutoff on the q-integrals in the evaluation of the Fourier transforms of the various terms. This point has been explained at length in I.

Keeping this in mind while grouping the terms on the lhs of (84), one finds that the lowest order contributions to the two-time correlation function $\langle \rho(\mathbf{r}, t), \rho(\mathbf{r}', 0) \rangle$ are given by

$$T_0(\mathbf{r}, t; \mathbf{r}', 0) = \langle \eta_1(\mathbf{r}, t), \eta_2(\mathbf{r}', 0) \rangle + \eta(ss) \langle R_0(\mathbf{r}, t; \mathbf{r}', 0) \rangle \qquad (91)$$

and the next order corrections are

$$T_1(\mathbf{r}, t; \mathbf{r}', 0) = \langle \eta_2(\mathbf{r}, t), \eta_2(\mathbf{r}', 0) \rangle + \langle \eta_1(\mathbf{r}, t), \eta_3(\mathbf{r}', 0) \rangle$$
$$+ \langle \eta_3(\mathbf{r}, t), \eta_1(\mathbf{r}', 0) \rangle$$
$$+ \langle \eta_2(\mathbf{r}', 0) \langle R_0(\mathbf{r}, t; \mathbf{r}', 0) \rangle \rangle$$
$$+ \langle \eta_1(r', 0) \langle R_1(\mathbf{r}, t; \mathbf{r}', 0) \rangle \rangle \qquad (92)$$

To evaluate the expressions (91) and (92), one proceeds in two steps. The first step consists in solving (88a)–(88c) as a function of the initial values and (89a) and (89b) subject to the initial conditions

$$R_0(\mathbf{r}, 0; \mathbf{r}', 0) = \delta(\mathbf{r} - \mathbf{r}'), \qquad R_i(\mathbf{r}, 0; \mathbf{r}', 0) = 0, \qquad i \geqslant 1 \qquad (93)$$

This then enables one to express (91) and (92) 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 (88a)–(88c) and (89a)–(89b) with respect to the spatial variable. Here we shall merely

quote the results. The Fourier–Laplace transform of the lowest order contribution to the two-time correlation function turns out to be

$$\tilde{T}_0(\mathbf{q}, \mathbf{q}', s) = \frac{\delta(\mathbf{q} + \mathbf{q}')}{s + Dq^2 + \eta(\text{ss})} \left[\eta(\text{ss}) + \frac{\kappa_1 \eta(\text{ss})}{Dq^2 + \eta(\text{ss})} \right] \tag{94}$$

The next higher correction is found to have the following analytic structure:

$$\tilde{T}_1(\mathbf{q}, \mathbf{q}', s) = \delta(\mathbf{q} + \mathbf{q}') \left\{ \frac{a(q)}{s + Dq^2 + \eta(\text{ss})} + \frac{b(q)}{[s + Dq^2 + \eta(\text{ss})]^2} \right\}$$

$$+ \int_{Dq^2/2 + 2\eta(\text{ss})}^{\infty} \frac{c(q, s')}{s' + s} ds' + \int_{Dq^2 + 2\eta(\text{ss})}^{\infty} \frac{d(q, s')}{s' + s} ds' \tag{95}$$

[The full expression for $\tilde{T}_1(\mathbf{q}, \mathbf{q}', s)$ is rather involved and is presented in the appendix.]

It follows from (94) and (95) that $\tilde{T}_0(\mathbf{q}, \mathbf{q}', s)$ has a simple pole at $s = -[Dq^2 + \eta(\text{ss})]$. When the next higher correction is included, the two-time correlation acquires a double pole at $s = -[Dq^2 + 2\eta(\text{ss})]$, and branch cuts at $-[2\eta(\text{ss}) + Dq^2/2]$ and $-[Dq^2 + 2\eta(\text{ss})]$. As $\eta(\text{ss}) \to 0$, i.e., as the critical point is approached, and as $q \to 0$, all the singularities of $T(\mathbf{q}, \mathbf{q}', s)$ collapse to zero This gives rise to a very singular behavior near the critical point for long wavelengths, and is probably an indication of nonclassical behavior of the dynamic critical exponents.

6. POISSON REPRESENTATION AND ITS RELATION TO THE GLAUBER–SUDARSHAN *P*-REPRESENTATION

A well-known procedure in quantum optics for deriving *c*-number equations from the operator equations satisfied by the density operator makes use of the Glauber–Sudarshan *P*-representation [5,6]

$$\rho(a, a^\dagger) = \int \frac{d^2\beta}{\pi} |\beta\rangle\langle\beta| \bar{\rho}^{(a)}(\beta, \beta^*) \tag{96}$$

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

$$\rho(a, a^\dagger) = \sum_n P(n) |n\rangle\langle n| \tag{97}$$

Then from (96) we have the following representation for

$$P(n) = \int \frac{d^2\beta}{\pi} e^{-\beta\beta*} \frac{(\beta\beta*)^n}{n!} \bar{\rho}^{(a)}(\beta, \beta*) \tag{98}$$

Also, when (97) holds, $\bar{\rho}^{(a)}(\beta, \beta*)$ is a function of $\beta\beta*$ only. Hence, on introducing the variables

$$\beta = \sqrt{\alpha}\, e^{i\varphi} \tag{99}$$

in (98) and carrying out the trivial φ integral, we get

$$P(n) = \int d\alpha\, e^{-\alpha}(\alpha^n/n!)\bar{\rho}^{(a)}(\alpha) \tag{100}$$

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

$$P(n) \geqslant 0, \qquad \sum_n P(n) = 1 \tag{101}$$

and therefore (100) corresponds exactly to the expansion of a probability distribution in terms of Poisson distributions. Having thus seen how the Poisson representation arises from the Glauber–Sudarshan P-representation, we shall now investigate the relationship between the expressions for the two-time averages obtained from the two methods.

For a quantum Markovian system, it may be shown[17,18] that two-time operator averages may be expressed in the P-representation as

$$\langle M(a, a^\dagger, t)N(a, a^\dagger, 0)\rangle$$

$$= \int \frac{d^2\beta}{\pi} \frac{d^2\beta'}{\pi} \bar{\rho}^{(a)}(\beta, \beta*, t\,|\,\beta', \beta'*, 0)$$

$$\times \overline{M}^{(n)}(\beta, \beta*)\left[\overline{N}^{(n)}\left(\beta'* - \frac{\partial}{\partial\beta'}, \beta'\right)\bar{\rho}^{(a)}(\beta', \beta'*, 0)\right] \tag{102}$$

where

$$\langle M(a, a^\dagger, t)N(a, a^\dagger, 0)\rangle = \mathrm{Tr}[M(a, a^\dagger, t)N(a, a^\dagger, 0)\rho(a, a^\dagger, t)]$$

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

For the photon number correlation function, (102) gives

$$\langle a^\dagger(t)a(t)a^\dagger(0)a(0)\rangle = \int \frac{d^2\beta}{\pi} \frac{d^2\beta'}{\pi} \beta*\beta\bar{\rho}^{(a)}(\beta, \beta*, t\,|\,\beta', \beta'*, 0)$$

$$\times [(\beta'* - \partial/\partial\beta')\beta'\bar{\rho}^{(a)}(\beta', \beta'*, 0)] \tag{103}$$

We now assume that at time $t = 0$ 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 $\bar{\rho}^{(a)}(\beta', \beta'^*, 0)$ and $\bar{\rho}^{(a)}(\beta, \beta^*, t\,|\,\beta', \beta'^*, 0)$ are functions of $\beta'^*\beta'$ and $\beta^*\beta$ only. Under these assumptions, on introducing the variables

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

we find that (103) becomes

$$\langle n(t)n(0)\rangle = \int d\alpha\, d\alpha'\; \alpha\alpha'\, \bar{\rho}^{(a)}(\alpha, t\,|\,\alpha', 0)\bar{\rho}^{(a)}(\alpha', 0)$$

$$+ \int d\alpha'\, \frac{\partial}{\partial\alpha'}\left[\int d\alpha\; \alpha\bar{\rho}^{(a)}(\alpha, t\,|\,\alpha', 0)\right]\bar{\rho}^{(a)}(\alpha', 0) \qquad (104)$$

which is identical to the result (26) for a single-variable case.

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 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, as we have shown in I. A further major difference between the two representations is the role which the quasiprobabilities $\bar{\rho}^{(a)}(\beta, \beta^*)$ in the Glauber–Sudarshan P-representation and $f(\alpha)$ in the Poisson representation play in the description of the corresponding physical systems. $\bar{\rho}^{(a)}(\beta, \beta^*)$ is a measure of the deviation of the quantum optical system from the more interesting coherent behavior that occurs in a nonequilibrium situation, whereas $f(\alpha)$ is a measure of the deviation of the chemical systems from the uninteresting Poissonian behavior that arises in thermodynamic equilibrium.

7. CONCLUSIONS

We have managed in this paper to extend the Poisson representation methods to two-time correlation functions and have shown how the methods can be used to gain insight into the nature of fluctuation-dissipation theorems in equilibrium and away from equilibrium. The ability to calculate higher order corrections systematically and reasonably simply is an advantage which we feel the Poisson method has compared to other methods. Although

we can show that very singular behavior is expected at a critical point, we are still unable to provide a satisfactory perturbation theory valid in that neighborhood. Work along this direction is proceeding.

APPENDIX

The full expression for the next higher correction to the Fourier–Laplace transform of the two-time correlation function $\tilde{T}_1(\mathbf{q}, \mathbf{q}', s)$ is as follows

$$T_1(\mathbf{q}, \mathbf{q}', s) = \delta(\mathbf{q} + \mathbf{q}')\tilde{T}_1(\mathbf{q}, s)$$

$$\tilde{T}_1(\mathbf{q}, s) = \frac{1}{s + g(\mathbf{q})} \left[\frac{2\kappa_1\eta^2(ss)}{g(\mathbf{q})} \right.$$

$$\times \int \frac{d\mathbf{q}_1}{[g(\mathbf{q}_1) + g(\mathbf{q} - \mathbf{q}_1) + g(\mathbf{q})]g(\mathbf{q}_1)g(\mathbf{q} - \mathbf{q}_1)}$$

$$+ \frac{4\kappa_1\eta(ss)[\kappa_1\eta(ss) - (2\kappa_1 - \kappa_2)g(\mathbf{q})]}{g^2(\mathbf{q})}$$

$$\times \int \frac{d\mathbf{q}_1}{g(\mathbf{q}_1)[g(\mathbf{q}_1) + g(\mathbf{q}) + g(\mathbf{q} - \mathbf{q}_1)]}$$

$$- \frac{2\kappa_1\eta(ss)(2\kappa_1 - \kappa_2)}{g^2(\mathbf{q})} \int \frac{d\mathbf{q}_1}{g(\mathbf{q}_1) + g(\mathbf{q} - \mathbf{q}_1) + g(\mathbf{q})}$$

$$+ \left. \frac{2\kappa_1^2\eta(ss) - \kappa_1^2 g(\mathbf{q}) - \kappa_1(\mathbf{q})}{g^2(\mathbf{q})} \int \frac{d\mathbf{q}_1}{g(\mathbf{q}_1)} \right]$$

$$+ \frac{2\kappa_1^2\eta(ss)}{[s + g(\mathbf{q})]^2} \left[\int \frac{d\mathbf{q}_1}{g(\mathbf{q}_1)} \right] - \frac{2\kappa_1\eta(ss)(2\kappa_1 - \kappa_2)}{[s + g(\mathbf{q})][s - g(\mathbf{q})]g(\mathbf{q})}$$

$$\times \left[\int \frac{d\mathbf{q}_1[2g(\mathbf{q}) + g(\mathbf{q}_1)]}{g(\mathbf{q}) + g(\mathbf{q}_1) + g(\mathbf{q} - \mathbf{q}_1)} \right.$$

$$\left. - \int \frac{d\mathbf{q}_1[2g(\mathbf{q}) + g(\mathbf{q}_1)]}{s + g(\mathbf{q} - \mathbf{q}_1) + g(\mathbf{q}_1)} \right]$$

$$- \frac{2\kappa_1\eta(ss)}{s + g(\mathbf{q})} \int \frac{d\mathbf{q}_1}{[s + g(\mathbf{q}_1) + g(\mathbf{q} - \mathbf{q}_1)]g(\mathbf{q}_1)}$$

$$+ \frac{2\kappa_1\eta(ss)}{[s + g(\mathbf{q})]^2 g(\mathbf{q})} \int \frac{d\mathbf{q}_1 \, [2\kappa_1\eta(ss) - (2\kappa_1 - \kappa_2)g(\mathbf{q})]}{[s + g(\mathbf{q}_1) + g(\mathbf{q} - \mathbf{q}_1)]g(\mathbf{q}_1)} \tag{A1}$$

where

$$g(\mathbf{q}) = D\mathbf{q}^2 + \eta(ss) \tag{A2}$$

It is clear from the above that in the complex s plane $\tilde{T}_1(\mathbf{q}, \mathbf{q}', s)$ has a pole and a double pole at $s = -g(\mathbf{q})$. The pole at $s = g(\mathbf{q})$, which arises from the third term in (A1) is spurious, for its residue is zero. The last three terms in (A1) also give rise to cuts. All of these three terms contain an integral of the form

$$I = \int \frac{d\mathbf{q}_1 \, \phi(\mathbf{q}_1{}^2)}{s + g(\mathbf{q} - \mathbf{q}_1) + g(\mathbf{q}_1)} \tag{A3}$$

Doing the angular integrals, we find for I

$$I = \frac{\pi}{D} \int_0^\infty \frac{q_1 \, dq_1 \, \phi(q_1{}^2)}{q} \log \frac{s + 2\eta(\text{ss}) + Dq_1{}^2 + D(q + q_1)^2}{s + 2\eta(\text{ss}) + Dq_1{}^2 + D(q - q_1)^2}$$

which gives rise to the cuts at $s = -D[q^2 + 2\eta(\text{ss})]$ and $s = -[Dq^2/2 + 2\eta(\text{ss})]$.

Having thus determined the analytic structure of $\tilde{T}_1(\mathbf{q}, \mathbf{q}', s)$ in the complex s plane, we may write a dispersion relation for $\tilde{T}_1(\mathbf{q}, \mathbf{q}', s)$ as in (95). The residues $a(q)$ and $b(q)$ and the discontinuities across the cuts $c(q, s')$ and $d(q, s')$ in (95) may be calculated from (A1) if desired.

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