

# Generalized Nonlinear Master Equations for Local Fluctuations: Dimensionality Expansions and Augmented Mean Field Theory

M. DelleDonne<sup>1</sup> and P. Ortoleva<sup>1</sup>

*Received April 19, 1977; revised August 19, 1977*

---

By application of a projection operator technique we derive a formally exact generalization of the nonlinear mean field master equation introduced recently for the study of local fluctuations in a reacting medium. Our starting point is a phenomenological cell master equation. The results of our theory are applicable to the theory of a fluctuating hydrodynamic reacting system. The mean field equation is placed on a firm theoretical foundation by showing it to be the lowest order approximation in an expansion in the dimensionality of the physical space keeping the product of the number of nearest neighbors (an increasing function of dimensionality) and the typical diffusion coefficient constant. A more accurate nonlinear master equation that allows for the correlation and fluctuations in the environment of a given volume element is derived in the form of an augmented mean field equation.

---

**KEY WORDS :** Master equations; fluctuations in chemical reactions; mean field theory; critical behavior; projection operators.

## 1. INTRODUCTION

Recently a nonlinear master equation has been used to study fluctuations in reacting diffusing systems.<sup>(1,2)</sup> The derivations presented there are heuristic, being based on the conjecture that the environment of a given subvolume of the system may be replaced by an averaged or mean environment.<sup>(1,2)</sup> It is the purpose of the present paper to both generalize this idea and to put these equations on a well-formulated theoretical basis as the lowest order approximation in a perturbation theory.

---

Work supported in part by a grant from the National Science Foundation.

<sup>1</sup> Department of Chemistry, Indiana University, Bloomington, Indiana.

The theory of projection operators developed by Zwanzig<sup>(3,4)</sup> has been used to study a variety of systems on the basis of rigorous statistical mechanics starting from a Hamiltonian and the Liouville equation. The projection operator formalism is devised to naturally separate the system into a subsystem of "interest" and the "remainder." Typically, if the part of interest interacts weakly with the remainder, then one may formulate a useful perturbation scheme. Alternatively, other schemes involve breaking the Hamiltonian into two parts (the free-particle kinetic part and the interparticle interaction, for example) and if one part is characterized by a smallness parameter (the case of weak interparticle potentials, say), then again a well-defined perturbation scheme arises in the projection operator theory. It is noteworthy that the projection operator formalism avoids the complexities of diagrammatic resummation techniques that arise in straightforward perturbation schemes in the smallness parameter.

In the present paper we use a projection operator formalism to carry out the separation of the system into a small subvolume of interest and its environment. We use the earlier work of Malek-Mansour and Nicolis (MN)<sup>(1)</sup> and Gardiner *et al.*<sup>(2)</sup> to guide our choice of a projection operator. In the work of MN the system is divided into a subvolume of "interest"  $\Delta V$  and the remainder and it is conjectured that the joint probability of the composition in  $\Delta V$  and its surroundings could be factorized. In the treatment of Ref. 2 the system is divided up into an array of  $N$  cells of relatively small dimensions and an  $N$ -cell probability function is introduced, giving the probability of the composition of each chemical species concentration in each cell. With this it is conjectured that the  $N$ -cell probability function may be approximated as a product of single-cell (i.e., reduced) concentration probability functions. The analogy with many-body theory would lead one to expect that each cell in this approximation would interact with an averaged environment. This is in fact the result of the calculations of Ref. 2. Thus the type of projection operator we introduce in order to map onto this mean field picture is one that projects the  $N$ -cell probability distribution onto the subspace of products of single-cell probability functions. With this we derive a generalized nonlinear master equation, which is an exact formal contraction of the phenomenological multicell master equation. The equation is valid for general transport and local processes, including convection, thermal conduction, and local heat production.

We turn next to the question of how the MN theory arises as an approximation to our exact formal master equation. To determine this we first note the topological fact that as the dimensionality  $\delta$  of the space increases, the number of nearest neighbor cells  $n(\delta)$  of a given cell increases. For a cubic lattice of dimension  $\delta$  the number of nearest neighbors  $n(\delta)$  is  $2\delta$ . For more closely packed lattices  $n(\delta)$  is larger. As  $\delta \rightarrow \infty$  each cell experiences the effect

of so many neighbors that one would expect the net result to be essentially that of an averaged environment. However, as  $\delta$  increases (with  $d$ , the cell-to-cell jump rate, held constant), the effect of diffusion eventually dominates the contribution of chemical reaction. Thus, to arrive at a theory that retains reaction and diffusion on an equal footing we expect that the MN mean field theory arises in the limit of infinite dimensions and vanishing jump rate with the product of  $n(\delta)$  and  $d$  held constant in the limiting process. This is in fact found to be the case. Indeed, one might have expected this from the wealth of experience in equilibrium phase transitions, where mean field theories are found to be essentially exact in four or greater dimensions. For our problem we find that the corrections to mean field theory enter as the square of the fluctuations in the environment and that the latter vanish as  $n(\delta)^{-1}$  in the limit  $\delta \rightarrow \infty$ ,  $n(\delta)d = \text{const.}$

The formal projection operator development is carried out in Section 2. A mean field expansion in the fluctuation of the environment from the mean is introduced in Section 3 and the relation of the scheme to the dimensionality expansion is shown explicitly for reaction–diffusion systems in Section 4. Conclusions and a discussion of further developments are given in Section 5.

## 2. PROJECTION OPERATOR FORMULATION

We formulate our theory in terms of the cell description of Gardiner *et al.*<sup>(2)</sup> and use the projection operator formalism of Zwanzig.<sup>(3,4)</sup> We wish to focus on a particular cell, denoted  $r$ , and in lowest order treat its environment in a mean field way. We know from earlier work that this intuitive picture is a consequence of the approximation of the  $N$ -cell probability distribution  $P(t)$  by a product of single-cell reduced distributions. Let  $\tilde{J}_r$  be the operator that sums over all particle numbers  $\psi_i^\alpha$  of species  $\alpha = (1, 2, \dots, s)$  in cell  $i = (1, 2, \dots, r - 1, r + 1, \dots, N)$ ,

$$\tilde{J}_r = \prod_{i \neq r} \prod_{\alpha} \sum_{\psi_i^\alpha} \quad (1)$$

For continuous variables like temperature or fluid velocity, (1) is appropriately augmented. Then the reduced distribution  $P_r(\psi_r, t)$  for cell  $r$  is given by

$$P_r = \tilde{J}_r P \quad (2)$$

With the  $P_r$  we form the product  $F$ ,

$$F = \prod_i P_i \quad (3)$$

and to lowest order in our theory we wish to map onto this product function, i.e.,

$$P \underset{\epsilon \rightarrow 0}{\sim} F \quad (4)$$

where  $\epsilon$  is a smallness parameter, which we shall relate to the dimensionality  $\delta$  of the space at a later stage in the development.

As it stands,  $\tilde{J}_r$  is not a projection operator, since the necessary property  $\tilde{J}_r^2 = \tilde{J}_r$  is not obeyed. However, if we introduce the operator  $J_r$  such that

$$J_r(t) = [F(t)/P_r(t)]\tilde{J}_r \quad (5)$$

then we see that

$$J_r^2 = J_r \quad (6)$$

and since  $J_r$  is a linear operator in the probability function space in which  $P$  is a member, it is indeed a projection operator.<sup>(8)</sup> We note that  $J_r$  depends on time, but the slight complications that this introduces over the usual time-independent projection operator formalism do not present major technical problems, but in fact are an essential part of our theory leading to nonlinear equations for the  $P_r$ . Indeed, the  $P_i$  are not initially known and hence  $J_r$  is not either. However, the resulting nonlinear equations resolve this ambiguity when expressed explicitly as equations for  $P_r$ , as we shall see. We now use this projection operator to derive a formal closed equation in the single-cell distribution function following the methods of Zwanzig.

The master equation for the  $N$ -cell probability distribution may be formally written in the operator notation

$$\partial P/\partial t = (D + R)P \quad (7)$$

where the effects of diffusion or other transport and reaction and other local processes are embodied in the  $D$  and  $R$  operators, respectively. For example, for an isothermal system at rest these operators may be written in terms of particle-number raising and lowering operators, as we shall see in Section 4.

In accordance with the usual projection operator methodology we derive separate equations for  $J_r P$  and  $(1 - J_r)P$  and combine them to get a closed equation for the single-cell product function  $F (=J_r P)$  or alternatively for  $P_r$  itself. Since  $J_r$  depends on  $t$ , there are some changes in the usual derivation, so we present it here. First we multiply (7) by  $J_r$ ,

$$J_r(\partial P/\partial t) = J_r(D + R)(F + Q) \quad (8)$$

where

$$Q \equiv (1 - J_r)P = P - F \quad (9)$$

The operator  $R$  is a "single-cell" operator since it can be written as a sum of terms  $R_i$  operating only on the variables of cell  $i$ . For example, for chemical reaction  $R_i$  has for each reaction a positive term that increases the number of products and decreases the number of reactants to the state of interest and an equivalent negative contribution that decreases the probability of the state of interest. Then the sum over all species numbers  $\psi_i^\alpha$  of species of type  $\alpha$  in cell  $i$  of  $R_i A$  yields zero. Hence

$$J_r R A = R_r J_r A \quad (10)$$

where  $A$  is an arbitrary function,  $R_r$  denotes the reaction (local process) operator for cell  $r$ , and

$$R = \sum_r R_r \tag{11}$$

Noting that

$$J_r R Q = R_r J_r Q = R_r J_r (1 - J_r) P = 0 \tag{12}$$

and that

$$J_r \partial P / \partial t = (F/P_r) \partial P_r / \partial t \tag{13}$$

we obtain

$$\partial P_r / \partial t = (\langle D \rangle_r + R_r) P_r + \tilde{J}_r D Q \tag{14}$$

where the “mean field transport operator”  $\langle D \rangle_r$  for cell  $r$  is defined by

$$\langle D \rangle_r = \tilde{J}_r D (F/P_r) \tag{15}$$

Note that if we neglect the excess correlation  $Q$  in (14), then we obtain a generalized nonlinear master equation analogous to the mean field results derived earlier in Refs. 1 and 2.

The next part of the calculation is to derive an equation for  $Q$ , solve it formally, and put the result in (14) to get a closed equation for the  $P_r$ . Multiplying (7) by  $1 - J_r$  and rearranging terms in analogy to the first part of the derivation, we obtain

$$\partial Q / \partial t = \hat{L} Q + (1 - J_r)(D + R - \partial / \partial t) F \tag{16}$$

where

$$\hat{L}(t) \equiv (1 - J_r)(D + R) \tag{17}$$

To solve the equation for  $Q$  we introduce an evolution operator  $\mathcal{K}$  such that

$$\partial \mathcal{K} / \partial t = \hat{L}(t) \mathcal{K} \tag{18}$$

$$\mathcal{K}(0) = I \tag{19}$$

where  $I$  is the identity operator. One obtains

$$Q(t) = \mathcal{K}(t) Q(0) + \int_0^t dt' K(t, t') [1 - J_r(t')](D + R - \partial / \partial t) F \tag{20}$$

We have introduced the notation  $\mathcal{K}(t)[\mathcal{K}(t')]^{-1} = K(t, t')$ .

At this point we assume that the cells are initially uncorrelated and hence

$$Q(0) = 0 \tag{21}$$

Although not strictly required for our further developments, this assumption leads to simplified equations and for many physical situations (i.e., rapid

stirring of the solution for  $t < 0$  and then stopping the fluid motion at  $t = 0$  and following the isothermal reacting fluid at rest) this is probably a reasonable assumption. Putting (20) and (21) into (14), we obtain

$$\begin{aligned} \partial P_r / \partial t = & (\langle D \rangle_r + R_r) P_r \\ & + \bar{J}_r D \int_0^t dt' K(t, t') [1 - J_r(t')] (D + R - \partial / \partial t) F \end{aligned} \quad (22)$$

Since  $F$  is a product of  $P_i$ 's and  $J_r$ , and  $\mathcal{K}$  may be expressed in terms of the latter, we see that (22) is the desired closed formal equation for the single-cell probability distribution function  $P_r$ ,  $r = 1, 2, \dots, N$ . This equation shall serve as the basis of our analysis.

### 3. MEAN FIELD PERTURBATION THEORY

#### 3.1. Formulation of the Theory

In this section we introduce a formal expansion procedure which allows for an orderly correction scheme to the mean field equation. The generalized mean field equation in our present notation is obtained by neglecting the excess correlation term  $Q$  in (14). Denoting this approximation by a superscript (0), we obtain

$$\partial P_r^{(0)} / \partial t = (\langle D \rangle_r^{(0)} + R_r) P_r^{(0)} \quad (23)$$

Alternatively, from its definition (3) the factor function  $F$  obeys the equation

$$\partial F^{(0)} / \partial t = (\langle D \rangle^{(0)} + R) F^{(0)} \quad (24)$$

where

$$\langle D \rangle \equiv \sum_r \langle D \rangle_r \quad (25)$$

Comparison of (24) with the full equation (7) for the exact  $N$ -cell probability distribution  $P$  suggests rewriting the latter in the form

$$\partial P / \partial t = (\langle D \rangle + R + \epsilon \Delta) P \quad (26)$$

where the "perturbation"  $\epsilon \Delta$  is defined by

$$\epsilon \Delta \equiv D - \langle D \rangle \quad (27)$$

The formal smallness parameter  $\epsilon$  is introduced for the purpose of conveniently ordering the perturbation theory. At the end of a calculation one sets  $\epsilon = 1$  and presumably the natural system smallness parameter will have manifested itself. In Section 4 we show that this is related to the dimensionality of the space.

Let us investigate this scheme via the formal single-cell equation (22). To start the procedure we introduce expansions in terms of  $\epsilon$ ; for example,

$$P_\tau = \sum_{n=0}^{\infty} P_\tau^{(n)} \epsilon^n \quad (28)$$

Since  $\langle D \rangle_\tau$  (and hence  $\langle D \rangle$ ) is a functional of  $P_i$  ( $i = 1, 2, \dots, N$ ), we must also calculate the contributions to  $\langle D \rangle_\tau$  to various orders. We write

$$\langle D \rangle_\tau = \sum_{n=0}^{\infty} \langle D \rangle_\tau^{(n)} \epsilon^n \quad (29)$$

The  $\langle D \rangle_\tau^{(n)}$  are related to the  $P_i^{(n)}$  through the functional derivatives of  $\langle D \rangle_\tau$  with respect to  $P_i$  evaluated at  $P_i^{(0)}$ . We now show that the kernel term in (22) brings in corrections to order  $\epsilon^2$  only, a result commonly found in the projection operator formulation.

From (24) we note that to lowest order

$$\begin{aligned} (1 - J_\tau)(D + R - \partial/\partial t)F &\sim \epsilon(1 - J_\tau^{(0)})[(\Delta^{(0)} + \langle D \rangle^{(1)})F^{(0)} \\ &\quad + (\langle D \rangle^{(0)} + R - \partial/\partial t)F^{(1)}] \\ &= \epsilon(1 - J_\tau^{(0)})\Delta^{(0)}F^{(0)} \end{aligned} \quad (30)$$

We shall show that the first nonvanishing contribution from the  $F^{(0)}$  term in (30) actually arises in order  $\epsilon^2$  and  $\langle D \rangle^{(1)}$  and  $F^{(1)}$  terms will be dropped since  $P_\tau^{(1)}$  vanishes, i.e.,  $P_\tau - P_\tau^{(0)} \sim O(\epsilon^2)$  as  $\epsilon \rightarrow 0$ .

### 3.2. Properties of $K^{(0)}$

We now derive some properties of  $K^{(0)}$  useful for our later calculations. First we note that  $K$  obeys the same equation as  $\mathcal{X}$ , i.e., (18), with initial condition  $K(t', t') = I$ . Thus, multiplying this equation by  $\tilde{J}_\tau$ , we obtain the following equation for  $\tilde{J}_\tau K^{(0)}$ :

$$\partial \tilde{J}_\tau K^{(0)} / \partial t = \tilde{J}_\tau (1 - J_\tau^{(0)}) (\langle D \rangle^{(0)} + R) K^{(0)} \quad (31)$$

It is easy to show from the definitions of  $\tilde{J}_\tau$  and  $J_\tau(t)$ , (1) and (5), that

$$\tilde{J}_\tau (1 - J_\tau) = 0 \quad (32)$$

Hence  $\tilde{J}_\tau K^{(0)}$  is a constant and from its value  $\tilde{J}_\tau$  at  $t = t'$  [i.e.,  $K^{(0)}(t', t') = I$ ] we have

$$\tilde{J}_\tau K^{(0)} = \tilde{J}_\tau \quad (33)$$

With this result we can determine other properties of  $K^{(0)}$ . From its definition  $K^{(0)}$  obeys the equation

$$\partial K^{(0)} / \partial t = (1 - J_\tau^{(0)}) L^{(0)} K^{(0)} \quad (34)$$

$$L^{(0)} = \langle D \rangle^{(0)} + R \quad (35)$$

Since  $L^{(0)}$  is a single-cell operator

$$J_r^{(0)}L^{(0)}K^{(0)} = (\langle D \rangle_r^{(0)} + R_r)J_r^{(0)}K^{(0)} \tag{36}$$

Thus, using (33), we obtain

$$\partial K^{(0)}/\partial t(t, t') = L^{(0)}(t)K^{(0)}(t, t') - (\langle D \rangle(t)_r^{(0)} + R_r)J_r^{(0)}(t) \tag{37}$$

where we have explicitly displayed the time dependence of all operators. From (22) it is clear that the quantity  $K(t, t')[1 - J_r(t')]$  is of great importance in evaluating the kernel term. Multiplying both sides of (37) into  $[1 - J_r^{(0)}(t')]$ , we obtain

$$\begin{aligned} \partial B(t, t')/\partial t &= L^{(0)}B \\ B(t, t') &\equiv K^{(0)}(t, t')[1 - J_r^{(0)}(t')] \end{aligned} \tag{38}$$

where we have used (32) to show that the contribution to  $B$  from the second term in (37) is zero. From the initial data

$$B(t', t') = 1 - J_r^{(0)}(t') \tag{39}$$

and since  $L^{(0)}$  is a sum of single-cell operators, one may verify that  $B$  is given by

$$B(t, t') = \prod_{i=1}^N k_i(\psi_i; t, t')[1 - J_r^{(0)}(t')] \tag{40}$$

$$\partial k_i/\partial t = (\langle D \rangle_i^{(0)} + R_i)k_i, \quad k_i(\psi_i; t', t') = 1 \tag{41}$$

The results (33) and (40) will now be used to aid in the study of the structure of the mean field expansion.

### 3.3. Evaluation of the Corrections to the Mean Field Theory

Writing  $D = \langle D \rangle + \epsilon\Delta$ , the lowest order contribution from the kernel term takes the form (neglecting the  $F^{(1)}$  and  $\langle D \rangle^{(1)}$  terms)

$$\epsilon \tilde{J}_r \langle D \rangle^{(0)} \int_0^t dt' B(t, t') \Delta^{(0)} F^{(0)} \tag{42}$$

Since  $\langle D \rangle$  is a single-cell operator,  $\tilde{J}_r \langle D \rangle = \langle D \rangle_r \tilde{J}_r$ , and using (32) and (33), one finds that (34) vanishes. Thus from (22) and (27) we see that to lowest order the kernel term takes the form

$$\epsilon^2 \tilde{J}_r \Delta^{(0)}(t) \int_0^t dt' B(t, t') \Delta^{(0)}(t') F^{(0)}(t') \tag{43}$$



and contributes only to order  $\epsilon^2$ . Since the corrections to the mean field theory (23) are thus found to arise in order  $\epsilon^2$ , we note that the dropping of the  $\langle D \rangle^{(1)}$  and  $F^{(1)}$  terms done earlier is justified.

Using the result (43), we may write an equation for  $P_r$  which is valid to terms of order  $\epsilon^2$ . Dropping the superscript (0), we obtain an "augmented mean field approximation" as follows:

$$\partial P_r / \partial t = (\langle D \rangle_r + R_r) P_r + \epsilon^2 \bar{J}_r \Delta(t) \int_0^t dt' B(t, t') \Delta(t') F(t') \quad (44)$$

Since  $J_r$  and  $K^{(0)}$  involve  $P_r$ , this equation is a highly nonlinear integro-differential equation. Its solution agrees with those of the formal exact equation (22) to order  $\epsilon^2$ . We now turn to the important task of relating the formal parameter  $\epsilon$  to the natural smallness parameter for the system.

#### 4. RELATION OF THE MEAN FIELD EXPANSION TO THE DIMENSION OF THE SPACE

We now show that the formal expansion parameter  $\epsilon$  may be related to the dimensionality of the space. We focus on the case of isothermal reaction and diffusion in a convection-free system. For this case we may write

$$D = \sum_{i \neq j} D_{ij} \quad (45)$$

$$D_{ij} = \sum_{\alpha} d_{ij}^{\alpha} (a_{i\alpha}^+ a_{j\alpha}^- - 1) \psi_i^{\alpha} \quad (46)$$

$$a_{i\alpha}^{\pm} = \exp(\pm \partial / \partial \psi_i^{\alpha}) \quad (47)$$

Here  $\psi_i^{\alpha}$  is the concentration of species  $\alpha$  in cell  $i$  and  $d_{ij}^{\alpha}$  is the diffusion jump transition rate for the molecule of species  $\alpha$  to jump from cell  $i$  to cell  $j$ .<sup>(2)</sup> Note that  $a_{i\alpha}^+$  and  $a_{i\alpha}^-$  are particle-number raising and lowering operators. Similarly, we can write the reaction term  $R$  in the form

$$R = \sum_i R_i \quad (48)$$

where  $R_i$  is a function of  $a_{i\alpha}^+$  and  $a_{i\alpha}^-$ . As noted earlier,  $R$  is a single-cell operator since it may be written as a sum of terms  $R_i$  each of which only operates on one cell. In contrast to this,  $D$  is a two-cell operator, since we have written it as a sum of terms each of which involves simultaneous operations on two cells. In general  $d_{ij}^{\alpha}$  will fall off rapidly as the distance between cell  $i$  and  $j$  increases and for simplicity we assume that  $d_{ij}^{\alpha}$  is nonzero only if  $i$  and  $j$  are nearest neighbors.

#### 4.1. Recovering the Mean Field Equation

In Section 3 we have stated that in the limit as  $\epsilon \rightarrow 0$ , (43) reduces to the generalization of the mean field equation of Refs. 1 and 2. For the case of reaction and diffusion considered in (45)–(48) one obtains from (15) that

$$\langle D \rangle_r = \sum_{\alpha} \sum_{i \neq r} [d_{ir}^{\alpha} \langle \psi_i^{\alpha} \rangle (a_{r\alpha}^- - 1) + d_{ri}^{\alpha} (a_{r\alpha}^+ - 1) \psi_r^{\alpha}] \quad (49)$$

where

$$\langle \psi_i^{\alpha} \rangle = \sum_{\psi_i^{\alpha}} \psi_i^{\alpha} P_i(\psi_i, t) \quad (50)$$

and  $\psi_i \equiv \text{col}\{\psi_i^1, \psi_i^2, \dots, \psi_i^s\}$  for a system of  $s$  species,  $\alpha = 1, 2, \dots, s$ . Inserting (49) to zeroth order into (23), we obtain the mean field equation as a special case of the generalized nonlinear master equation (23).

#### 4.2. Calculation of the First Correction

Let us now use (36) and (37) to calculate the first correction term to the mean field theory. For simplicity we limit our derivation to the case of a homogeneous ensemble, although the more general case appears to hold no major technical problems. The quantity  $\Delta$ , defined in (27) as the fluctuation from the mean field transport term, may be written

$$\Delta = \sum_{\alpha} d^{\alpha} \sum_{\substack{i \neq j \\ (\text{nn})}} (a_{i\alpha}^+ \psi_i^{\alpha} - \langle \psi_i^{\alpha} \rangle) (a_{j\beta}^- - 1) \quad (51)$$

Since we have taken nearest neighbor diffusion only, we write

$$d_{ij}^{\alpha} = \begin{cases} d^{\alpha}, & i, j \text{ nearest neighbors} \\ 0, & i, j \text{ not nearest neighbors} \end{cases} \quad (52)$$

and the symbol (nn) below the summation indicates that  $i$  and  $j$  must be nearest neighbors.

Because we are working with a homogeneous ensemble,  $\langle \psi_i^{\alpha} \rangle$  is independent of  $i$ , and we have

$$\langle \psi_i^{\alpha} \rangle = \bar{\psi}^{\alpha}(t) \quad (53)$$

With this the correction term,  $\epsilon^2 C$  may be written

$$C = \int_0^t dt' \sum_{\substack{i \neq j \\ (\text{nn})}} \sum_{\substack{l \neq m \\ (\text{nn})}} \sum_{\alpha, \beta} d^{\alpha} d^{\beta} \bar{J}_r [a_{i\alpha}^+ \psi_i^{\alpha} - \bar{\psi}^{\alpha}(t')] (a_{j\alpha}^- - 1) B(t, t') \\ \times (a_{i\beta}^+ \psi_i^{\beta} - 1) (a_{m\beta}^- - 1) F(t') \quad (54)$$

Note that if  $j \neq r$ , then everything to the right of the  $a_{j\alpha}^- - 1$  factor, which we denote  $A(\dots, \psi_j^{\alpha}, \dots)$ , makes no contribution since

$$\sum_{\psi_j^{\alpha}} (a_{j\alpha}^- - 1) A(\dots, \psi_j^{\alpha}, \dots) = \sum_{\psi_j^{\alpha}} [A(\dots, \psi_j^{\alpha} - 1, \dots) - A(\dots, \psi_j^{\alpha}, \dots)] \quad (55)$$

which, neglecting the vanishing contribution  $A(\dots, \infty, \dots)$ , is zero. Thus we obtain

$$C = \int_0^t dt' \sum_{i=\text{nn}(r)} \sum_l \sum_{m=\text{nn}(l)} \sum_{\alpha, \beta} d^\alpha d^\beta \prod_\gamma \sum_{\psi_i^\gamma} [a_{i\alpha}^+ \psi_i^\alpha - \bar{\psi}^\alpha(t)] \times (a_{r\alpha}^- - 1) k_r(t, t') k_i(t, t') U_{il}^\beta(t') \tag{56}$$

$$U_{il}^\beta(t') = \prod_{k \neq i, r} \prod_\alpha \sum_{\psi_k^\alpha} [1 - J_r(t')] [a_{i\beta}^+ \psi_i^\beta - \bar{\psi}^\beta(t')] (a_{m\beta}^- - 1) F^{(0)}(t') \tag{57}$$

We have used (40) and (41). Note that the  $J_r$  term in  $U$  vanishes since it contributes only if  $l = m = r$ , but  $l \neq m$ . Also, if  $m \neq i$  or  $r$ , then the operator  $U_{il}^\beta$  must vanish and similarly if  $l \neq i$  or  $r$ . Thus since  $l \neq m$  we have in the expression for  $C$

$$U_{il}^\beta \rightarrow U_{iir}^\beta \delta_{ii} \delta_{mr} + U_{iri}^\beta \delta_{ir} \delta_{mi} \tag{58}$$

With this we obtain

$$C = \int_0^t dt' \sum_{i=\text{nn}(r)} \sum_{\alpha, \beta} d^\alpha d^\beta \prod_\gamma \sum_{\psi_i^\gamma} [a_{i\alpha}^+ \psi_i^\alpha - \bar{\psi}^\alpha(t)] \times (a_{r\alpha}^- - 1) k_r(t, t') k_i(t, t') [U_{iir}^\beta(t') - U_{iri}^\beta(t')] \tag{59}$$

Note that in  $C$  we have two factors of diffusion coefficients and only one sum over nearest neighbors. Thus, letting  $n(\delta)$  be the number of nearest neighbors and  $d$  be a characteristic diffusion coefficient, we have

$$C = O[n(\delta)d^2] = O[n(\delta)^{-1}] \tag{60}$$

in our mean field limit, where  $n(\delta)d$  is kept constant. As our physical intuition dictated, the corrections to the mean field theory vanish as the number of nearest neighbors increases and the interaction per neighbor decreases.

As a technical point we note that  $k_r$  is not an unknown functional of  $P$  but is the solution of (32) involving the zeroth-order value of  $P$ , determined from mean field theory (23) only.

It is clear that the result of this section generalizes appropriately to inhomogeneous systems and furthermore to systems with flow or energy transport and production. We thus conclude that the earlier mean field theory and our generalized nonlinear master equation (23) is probably a fairly good approximation for three-dimensional systems but may not be particularly good for one- and two-dimensional systems. These systems of lower dimensionality should be more reasonably handled by the augmented mean field theory (36) and (37). In addition, the augmented theory is an improvement for three dimensions since it allows for fluctuations in the environment.

## 5. CONCLUSIONS

The generalization of the nonlinear master equation and introduction of our perturbation scheme should be of great value in studying fluctuations in hydrodynamic systems. In particular, for an isothermal reaction–diffusion system without center-of-mass flow we have shown explicitly in Section 4 that the corrections to the earlier mean field theories<sup>(1,2)</sup> decrease inversely with the number of nearest neighbors and hence with the dimensionality of the space. This suggests a new perturbation method using the number of nearest neighbors as the asymptotic expansion parameter.

In Fig. 1 we show a parameter space plane of  $n(\delta)$  vs.  $d$ . Let us assume that we wish to study a three-dimensional system with a typical diffusion transition rate  $d^*$ . Then to carry out the mean field dimensionality expansion we expand all functions with respect to  $[n(\delta)]^{-1}$  via the mean field expansion along the curve  $n(\delta) = n(3)d^*/d$  that passes through the point  $(d^*, n(3))$  of interest. Truncation of the theory to order  $[n(\delta)]^{-1}$  leads to our augmented mean field nonlinear master equation (44).

In a sequel study we shall present further results on the application of the mean field dimensionality expansion to the study of critical fluctuations<sup>(6)</sup> and nucleation<sup>(6)</sup> of chemical instabilities. We shall also develop these ideas for application to systems with flow or energy exchange and production. A heuristically derived mean field nonlinear master equation has recently been applied to hydrodynamic systems by other authors.<sup>(7)</sup>

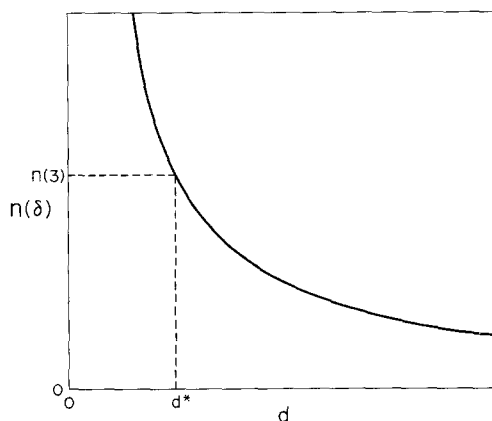


Fig. 1. Parameter plane showing number of nearest neighbors  $n(\delta)$  (for a space of dimension  $\delta$ ) vs. a typical diffusive transition rate parameter  $d$ . The mean field perturbation theory is an expansion with respect to  $[n(\delta)]^{-1}$  keeping the product  $n(\delta)d$  fixed at the value  $n(3)d^*$  of interest, i.e., along the curve  $n(\delta) = n(3)d^*/d$  shown for a three-dimensional system with diffusion transition rate  $d^*$ .

Since submission of this paper it has been brought to our attention that a projection operator closely related to the one used here has been introduced by Willis and Picard.<sup>(9)</sup> The projection operator used by these authors is symmetrized with respect to the reduced probabilities ( $P_i$  for our problem). The symmetrized projection operator leads to results similar to ours except that the  $\partial/\partial t$  term in the correlation term is accounted for by the presence of a different kernel term than the one arising in our theory. Choice between the two projection operators seems to be a matter of convenience, depending on the problem of interest. They applied their formalism to an optical system and to the derivation of a Boltzmann equation.

## REFERENCES

1. M. Malek-Mansour and G. Nicolis, *J. Stat. Phys.* **13**:197 (1975).
2. C. W. Gardiner, K. J. McNeil, D. F. Walls, and J. S. Matheson, *J. Stat. Phys.* **14**:307 (1976).
3. R. Zwanzig, in *Lecture in Theoretical Physics*, W. E. Britin *et al.*, eds. (Wiley—Interscience, 1961), Vol. 4, p. 106.
4. J. T. Hynes and M. Deutch, in *Physical Chemistry, an Advanced Treatise, Vol. XIB* (Academic Press, 1975), p. 729.
5. A. Nitzan, P. Ortoleva, J. Deutch, and J. Ross, *J. Chem. Phys.* **61**:1056 (1974).
6. A. Nitzan, P. Ortoleva, and J. Ross, *Faraday Symp. Chem. Soc.* **9**:241 (1974).
7. I. Brenig, M. Malek-Mansour, and W. Horsthemke, *Phys. Lett.* **59A**:341 (1976).
8. W. Rudin, *Functional Analysis* (McGraw-Hill, 1973), p. 126.
9. C. R. Willis and R. H. Picard, *Phys. Rev. A* **9**:1343 (1974).