/DERIVATION AND APPLICATIONS OF THE GENERALIZED MASTER EQUATION/

by

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CHAPTER 1

INTRODUCTION

The introduction of stochastic evolution equations as models for real physical systems offers a more general formulation when compared with the more traditional description involving ordinary or partial differential equations. A very general stochastic formulation with wide applicability to systems described by random vectors evolving through interactions among entities in the population is known as the master equation (Gradiner, 1983; Van Kampen, 1981). In this formulation it is assumed that individual entities change atate with a certain probability per unit time. This is in contrast to the deterministic approach where entities change state at an exact, predetermined moment in time. The stochastic formulation is therefore more general, encompassing deterministic motion as a special case.

The justification for the introduction of stochastic kinetics is best found in the increasing complexity of macroscopic systems involving many degrees of microscopic freedom. Although it is assumed that the fundamental laws of physics apply to microscopic entities, in principal, these laws leave room for a wide range of macroscopic behavior which, although in theory predictable, will contain some degree of unpredictability. (The prediction of the behavior of an individual droplet in a swarm of similar droplets whose motion, although governed by the fundamental laws of conservation of momentum and energy, is erratic, offers an example of a situation where an exact deterministic description is bound by immense difficulties. Such obstacles can, however, be eluded by employing a atochastic description as was recognized by physicists, in particular Albert Einstein, in the now classical description of Brownian

motion.) There are, of course, numerous situations where stochastic kinetics are inappropriate and should be avoided. These systems are characterized by their simplicity and relatively few degrees of freedom. However, even these well understood systems can become "chaotic", leaving only the possibility of a probabilistic interpretation. The transition from laminar to turbalent flow is such an example.

A second class of systems for which the stochastic formulation is known to be superfluous in an engineering sense, although entirely applicable, are those involving an extremely large number of independent entities. These systems are usually described by the thermostatic state variables of temperature, pressure, or volume which are the net average result of the complicated motion of fundamental entities governed by the laws of physics expressed through the equations of quantum mechanics. The methods of Statistical Mechanics, which are based partly on probabilitic assumptions, have shown that for a large number of independent entities, the fluctuations away from the thermostatic quantities will be negligibly small; thus allowing for a deterministic treatment of the system. Such behavior is also to be expected in systems described by population balance equations such as the master equation. Indeed, it is this fact upon which the successful application of approximation techniques such as the System Size Expansion (which is to be introduced in the following chapter) is predicated. Therefore, a second characteristics (in addition to the random behavior of the fundamental entities) possessed by systems to which the master equation formulation shall be applied is that of having a relatively low number of fundamental entities (low being any number which one could actually count in a reasonable span of time). There is, however, no theoretical restric-

tion to auch systems. In fact, the master equation formulation has been successfully applied to molecular systems involving an Avagadro's number of fundamental entities.

In the following chapters, the master equation shall be derived and applied to specific syatems of interest to chemical engineering. An approximation method will allow for the solution of the master equation to yield the mean, covariances, and correlation functions of the random variables. The last two of these quantities are of particular interest since they allow for an extended description of the system beyond the deterministic mean value equations. In particular, the correlation function offers a way of deriving rate constants from the steady state data which would prove important when applying the models to real systems.

Mention shall also be made of stochastic differential equations. These equations find extensive use in describing system embedded in a noisy environment subject to externally driven fluctuations. However, they can also be uaed in connection with the coefficients found from the master equation to describe systems subject to internal fluctuations due to diacrete changes in size of the random variables. It is important to note that only by first deriving the master equation can the noise term in the stochastic differential equation be found. The stochastic differential equation with an arbitrary noise term has no direct physical interpretation in terms of the parameters of the system whereas the master equation does. Combining the two allows one to use simulation procedures designed for integration of stochastic differential equations with the noise terms uniquely determined from the master

equation. Simulating the behavior of a complex system such as a fluidized-bed reactor then reduces to the simulation of a vector stochastic differential equation with uniquely determined noise terms.

CHAPTER 2

DERIVATION OF A GENERALIZED MASTER EQUATION FOR DISCRETE POPULATIONS

It will be assumed that a population of discrete entities exists and evolves through interaction between entities; that the entities possess certain characteristics, such as size, temperature and chemical makeup, which distinguish groups of entities from other groups; and that the entities exist in a Euclidian space of zero or higher degree. A stochastic model for this population can be derived based on the concepts of probability theory. The resultant expression for the joint probability of the random variables designating the distinct groups of entities in the population is known as the master equation (see, e.g., Van Kampen, 1981; Gardiner, 1983). The master equation arises directly from the assumption that the interactions between entities possess the Markov property, depending solely on the present state of the population, and not on its past states. Populations whose interactions do not possess this property can be successfully described, however, by a Markovian model if states can be combined in such a way that the explicit dependence on past states vanishes. Such processes are sometimes called Multiple-Markov processes, since multiple states are combined to form new Markovian states.

In the following, the random variable N will be used to denote the number of entities in a specific group in the population. Subscripts will be used to denote to which group N refers, i.e., $\{N_j : j \in \{1,2,3,\ldots\}\}$ could be used to denote the number of entities possessing characteristic j, where each characteristic has been assigned a positive integer. Similarly, multi-

ple subscripts will be used when distinct groups of characteristics are to be denoted, i.e., $\{N_{i,j}: j \in \{1,2,3,\ldots\},\ i \in \{-\infty,\ldots,-1,-2,0,1,2,\ldots,+\infty\}\}$ could be used to denote the number of entities with characteristic j, located at point i on the real number line.

When a population possesses continuously distributed characteristics, or if the population is continuously distributed in the Euclidian space, the random variable denoting the number of entities possessing a certain attribute at a specific point in the space will be written in functional form, e.g., $\{N(r,x): r \in [a,b],\ x \in (-\infty,+\infty)\}$. Note, however, that the random variable may be both subscripted and in functional form, as in cases where the population possesses both discrete and continuous characteristics or is distributed in a discrete or continuous space.

The joint probability of the random variables $\{N\}$ will be denoted as $P(\{n\},t)$, or simply P, when $\{\{n\}: n \in (0,1,2,3,\ldots)\}$, i.e., when the state space of N consists of the positive integers. However, for convenience of mathematical manipulation, it will sometimes be desirable to approximate n as a positive real number, i.e., $\{\{n\}: n \in [0,+\infty)\}$, in which case the joint probability density function of $\{N\}$ will be denoted as $p(\{n\},t)$, or simply p. In both expressions t refers to time since the model describes a process evolving in time. $P(\{n\},t)$ is interpreted as $P(\{N_1=n_1,\ N_2=n_2,\ldots\},t)$ or $P(\{N_1(x_1)=n_1(x_1),\ N_2(x_2)=n_2(x_2),\ldots\},t)$, which is the joint probability that the random variable N_1 has a value of n_1, and the random variable N_2 has a value of n_2, etc., at time t. It is also necessary to define a conditional probability, $P(\{n\}_1,t_1|\{n\}_0,t_0)$, which is the probability that the random variable N_1 has a value of n_{11}, and the random variable N_2 has a value of n_{21}, etc., at time t_1, given that the random variable N_1 had a value of n_{10}, and the random variable N_2 had a value of n_{20}, etc., at time t_0.

2.1 DERIVATION OF MASTER EQUATION

Letting $t_0=t$ and $t_1=t+\tau$ where τ is a small time interval tending toward zero, the conditional probability $P(\{n\}_1,t+\tau|\{n\}_0,t)$ can be expanded in a Taylor series. Noting that

$$P(\{n\}_1,t|\{n\}_0,t) = \delta^k(\{n\}_1-\{n\}_0)$$

where

$\delta^k(\cdot)$ is the Kronecker delta; it has the property that

$$\delta^k(0)=1,\ \delta^k(x)=0 \text{ for all } x \in \{(-\infty,+\infty)-\{0\}\}$$

The Taylor expansion of

$$P(\{n\}_1,t+\tau|\{n\}_0,t)$$

yields

$$\begin{aligned} &P(\{n\}_1,t+\tau|\{n\}_0,t) \\ &= \delta^k(\{n\}_1-\{n\}_0) - \tau \sum_{\{n\}} W_t(\{n\}_0,\{n\})\,\delta^k(\{n\}_1-\{n\}_0) + \tau W_t(\{n\}_0,\{n\}_1) + O(\tau^2) \\ &= [1-\tau \sum_{\{n\}} W_t(\{n\}_0,\{n\})]\delta^k(\{n\}_1-\{n\}_0) + \tau W_t(\{n\}_0,\{n\}_1) + O(\tau^2) \end{aligned} \tag{2-1}$$

The quantity $W_t(\{n\}_0,\{n\}_1)$ is the transition probability per unit time that the population changes from state $\{n\}_0$ to $\{n\}_1$ in the time interval between t and $t+\tau$. The quantity $\tau \sum_{\{n\}} W_t(\{n\}_0,\{n\}) - \tau W_t(\{n\}_0,\{n\}_0)$ is the total probability of a transition from state $\{n\}_0$ to any other state during the time interval between t and $t+\tau$. Therefore, $\tau W_t(\{n\}_0,\{n\}_1)$ is the probability of a transition from $\{n\}_0$ to $\{n\}_1$ during the time interval between t and $t+\tau$, and $[1-\tau \sum_{\{n\}} W_t(\{n\}_0,\{n\})]\delta^k(\{n\}_1-\{n\}_0) + \tau W_t(\{n\}_0,\{n\}_0)$ is the probability that no transitions occur during the time interval between t and $t+\tau$.

Assuming that the states of the population possess the Markov property, $P(\{n\}_1,t+\tau)$ can be expressed as

$$P(\{n\}_1,t+\tau) = \sum_{\{n\}_0} P(\{n\}_1,t+\tau|\{n\}_0,t)P(\{n\}_0,t) \tag{2-2}$$

By resorting to Eq. 2-1, Eq. 2-2 can be written as

$$\frac{P(\{n\}_1,t+\tau) - P(\{n\}_1,t)}{\tau} = \sum_{\{n\}} \{W_t(\{n\},\{n\}_1)P(\{n\},t) - W_t(\{n\}_1,\{n\})P(\{n\}_1,t)\} \tag{2-3}$$

Taking the limit as $\tau \to 0$ yields

$$\frac{dP(\{n\}_1,t)}{dt} = \sum_{\{n\}} W_t(\{n\},\{n\}_1)P(\{n\},t) \tag{2-4}$$

where $W_t(\{n\}_1,\{n\}_1)$ is defined as

$$W_t(\{n\}_1,\{n\}_1) = -\sum_{\substack{\{n\} \\ \{n\}\neq\{n\}_1}} W_t(\{n\}_1,\{n\}) \tag{2-5}$$

Equation 2-4 is known as the master equation, and, as written, is valid for $\{\{n\} = \{n_i\}: i \in Z\}$. If the population possesses both discrete and continuous characteristics, i.e.,

$$\{\{n\} = \{n_i(x)\}: i \in Z, x \in (-\infty, +\infty)\}$$

the master equation can be expressed as

$$\frac{dP(\{n\}_1,t)}{dt} = \sum_i \int W_t(\{n\},\{n\}_1)P(\{n\},t)dx \tag{2-6}$$

where the summation is over all discrete characteristics and an integral is performed for each continuous characteristic.

To resort to the master equation to model the evolution of a population of entities, it is necessary to derive an expression for $W_t(\{n\},\{n\}_1)$ for the system under study. However, before proceding to specific examples, it is desirable to discuss methods of solving, albeit approximately, the master equation. In most cases, the exact solutions for Eq. 2-4 are not available. Therefore, approximation techniques have been developed to simplify the solution, or at least to find the moments of the random variables {N}. One such method is known as the System Size Expansion or simply the Master Equation Expansion (see e.g., Van Kampen, 1981; Gardiner, 1983).

2.2 MASTER EQUATION EXPANSION

The master equation, as given in Eq. 2-4, is in the form of an ordinary differential equation. Since $P(\{n\},t)$ appears only to the first power, the equation is linear. However, if the state space is large, Eq. 2-4 is one of a larger system of coupled equations - one for each possible state. For example, for the set of two random variables

$$\{\{n\}_i = \{n_{1i},n_{2i}\}:n_{ji}\varepsilon\{0,1\},\ i\varepsilon\{1,2,3,4\},\ j\varepsilon\{1,2\}\},$$

there are four possible events

$$\{n\}_1=\{0,0\},\ \{n\}_2=\{1,0\},\ \{n\}_3=\{0,1\},\ \{n\}_4=\{1,1\}$$

Note that the state space of either of the two random variables, n_{1i} and n_{2i} consists of two events, i.e., {0,1}. The resulting system of differential equations could consist of four coupled equations. In general, if the number of random variables is j, and k(j) is the number of events in the state space of the random variable j, then the number of coupled differential equations could be equal to $\prod_j k(j)$. Even if j=1, this could still result in a very large system of equations, if, for example, k(1) consisted of all the integers.

It is necessary, therefore, to develop an approximation procedure for the solution of such equations.

When the change in the random variable during a transition is relatively small compared to the value of the random variable, an approximation method known as the System Size Expansion can be employed (see, e.g., Gardiner, 1983). Most populations of entities fall into the category of systems to which the System Size Expansion can be successfully applied since the number of entities in a group tends to increase by one or a few entities during any given interaction. For example, during the coalescence of two bubbles of different sizes, denoted by sizes 1 and 2, the number of bubbles of size 1 decreases by one and that of size 2 also decreases by one; in contrast, the number of bubbles of size 3 increases by one. Similarly, if two bubbles of size 1 coalesce, the number of bubbles of size 1 decreases by two, while the number of size 2 bubbles increases by one. In both cases the change in the number of entities in any group increases or decreases by a small amount (one or two). If the population is large, the number of entities in each group will usually be much larger than two, and the System Size Expansion yields a valid approximation.

For a system where the System Size Expansion approximation is not valid due to the smallness of the population size, it is usually possible to solve the equation without approximation. If, however, the population is large, but the changes during the transitions are also large, it is sometimes possible to redefine the random variable. For example, a new random variable, N_i^*, could be defined as $s_i N_i^* = N_i$ where $s_i \in \{1,2,3,\ldots\}$. N_i^* is then the number of subgroups of the original group of N_i entities where each subgroup contains s_i individual entities. The number of entities that can participate in generating a given subgroup must be at least as small as the smallest change resulting

from an interaction in the population. For example, if group i changes by twenty during each interaction, s_i must be less than or equal to twenty. For the System Size Expansion to be valid, s_i must be chosen so that $s_i << \langle N_i \rangle$ where $\langle N_i \rangle$ is the average number of entities in group i. In the following, it shall be assumed that the System Size Expansion is valid for the system in question.

The use of the System Size Expansion is also predicated upon the fact that for most systems involving interactions between entities in a population, the magnitude of the change in the number of entities in a group following a transition is an extensive variable, e.g., the number of molecules, but the dependence of the rate of transition on the number of entities is expressed as an intensive variable, i.e., concentration of molecules. For first order dependence of the rate of transition on the number of entities, it is always possible to use either the extensive or intensive variable. For second or higher order interactions, it is almost always best to express the rate of transition as an intensive variable..

Consider a population consisting of groups A and B undergoing second order interactions between them in a system of volume Ω. Suppose that q entities are in group A and r entities are in group B, and that a transition takes place when an entity from group A meets an entity from group B. In most cases, the rate of such a transition will be not only proportional to q times r, but also inversely proportional to the volume squared. This follows intuitively from the image of the entities moving freely in the volume Ω. Decreasing Ω will increase the number of collisions between species A and B. The rate of transition is thus dependent on the density or concentration of entities in the system. For systems confined to a lower degree Euclidian space, the proper intensive variable can be defined by dividing the extensive

variable by ℓ^d where ℓ is the characteristic length of the system, and d is the spatial dimension. In all cases Ω will be used as the system size, i.e.,

$$\{\Omega = \ell^d: \ \ell \in (0, +\infty), \ d = \{1,2,3,\ldots\}\}$$

Under the assumption that the System Size Expansion is valid, the term representing the rate of transition, $W_t(\{n\},\{n\}_1)$, in the master equation, Eq. 2-4, is first rewritten as $W_t(\{n\};\{n_1\}-\{n\})$, where $\{n\}_1 - \{n\}$ is the size of the change in the random variable, $\{N\}$, during a transition. Letting $\{\xi\} = \{n\}_1 - \{n\}$, the rate of transition can be expressed as $W_t(\{n\};\{\xi\})$. It can further be rewritten as

$$W_t(\{n\};\{\xi\}) = \Omega\psi_t(\{\frac{n}{\Omega}\};\{\xi\}) \tag{2-7}$$

if it is assumed to be a homogeneous function of the random variable. The rate of transition is now a function of the intensive random variables $\{N/\Omega\}$, and the System Size Expansion can be introduced.

Making a change of variables and introducing the new random variables $\{Z\}$ and the deterministic variables $\{\phi\}$ such that

$$\{N\} = \Omega\{\phi(t)\} + \Omega^{1/2}\{Z\}$$

the rate of transition is written as

$$W_t(\{n\};\{\xi\}) = \Omega\psi_t(\{\phi(t) + \Omega^{-1/2}z\};\{\xi\}) \tag{2-8}$$

It will be seen later that the deterministic variables $\{\phi\}$ correspond to the macroscopic behavior of the system. The master equation is then of the form

$$\frac{dP(\{\phi(t)+\Omega^{-1/2}z\}_1,\ t)}{dt} = \sum_i \sum_{\xi_i} \Omega\psi_t(\{\phi(t)+\Omega^{-1/2}z\};\xi_i)P(\{\phi(t)+\Omega^{-1/2}z\},t) \tag{2-9}$$

To proceed with the expansion, it is useful to first define the first and second jump moments, A_i and B_{ij}, respectively, and $\tilde{A}_i$ and $\tilde{B}_{ij}$, as follows:

$$\begin{aligned} A_i(\{n\}) &= \sum_{n_{il}} (n_{il}-n_i) W_t(\{n\},\{n\}_l) \\ &= \sum_{\xi_i} \xi_i W_t(\{n\};\xi_i) \\ &= \Omega \sum_{\xi_i} \xi_i \psi_t(\{\phi(t)+\Omega^{-1/2}z\};\xi_i) \ , \end{aligned} \tag{2-10}$$

$$\tilde{A}_i(\{\phi(t)+\Omega^{-1/2}z\}) = \Omega^{-1} A_i(\{n\}) \ , \tag{2-11}$$

and

$$\begin{aligned} B_{ij}(\{n\}) &= \sum_{n_i} \sum_{n_j} (n_{il}-n_i)(n_{jl}-n_j) W_t(\{n\},\{n\}_l) \\ &= \sum_{\xi_i} \sum_{\xi_j} \xi_i \xi_j W_t(\{n\};\xi_i,\xi_j) \\ &= \Omega \sum_{\xi_i} \sum_{\xi_j} \xi_i \xi_j \psi_t(\{\phi(t)+\Omega^{-1/2}\};\xi_i,\xi_j) \ , \end{aligned} \tag{2-12}$$

$$\tilde{B}_{ij}(\{\phi(t)+\Omega^{-1/2}z\}) = \Omega^{-1} B_{ij}(\{n\})$$

The expression $W_t(\{n\};\xi_i,\xi_j)$ denotes the dependence of the rate of transition on both n_i and n_j. If no such dependency exists, $W_t(\{n\};\xi_i,\xi_j)$ is identically zero. The master equation, Eq. 2-4, can then be expanded to yield

$$\frac{\partial p(\{z\},t)}{\partial t} - \Omega^{1/2}\sum_i \frac{d\phi_i}{dt}\frac{\partial p(\{z\},t)}{\partial z_i}$$

$$= -\Omega^{1/2}\sum_i \frac{\partial}{\partial z_i}[\tilde{A}_i(\{\phi(t)+\Omega^{-1/2}z\})p(\{z\},t)]$$

$$+ \frac{1}{2}\sum\sum_{ij}\frac{\partial^2}{\partial z_i \partial z_j}[\tilde{B}_{ij}(\{\phi(t)+\Omega^{-1/2}z\})p(\{z\},t)]$$

$$+ O(\Omega^{-1}) \qquad (2\text{-}14)$$

where $p(\{z\},t)$ is the probability density function of the new random variables $\{Z\}$, and $O(\Omega^{-1})$ represents terms of order Ω^{-1} and smaller.

To proceed further, the expansions of $\tilde{A}_i$ and $\tilde{B}_{ij}$ in powers of $\Omega^{-1/2}$ must be performed; they yield

$$\tilde{A}_i(\{\phi(t)+\Omega^{-1/2}z\}) = \tilde{A}_i(\{\phi(t)\}) + \Omega^{-1/2}\sum_j z_j \tilde{A}_{ij}(\{\phi(t)\}) + O(\Omega^{-1}) \qquad (2\text{-}15)$$

$$\tilde{B}_{ij}(\{\phi(t)+\Omega^{-1/2}z\}) = \tilde{B}_{ij}(\{\phi(t)\}) + O(\Omega^{-1/2}) \qquad (2\text{-}16)$$

The expanded master equation is then of the form

$$\frac{\partial p}{\partial t} - \Omega^{1/2} \sum_i \frac{d\phi_i}{dt} \frac{\partial p}{\partial z_i}$$

$$= -\Omega^{1/2} \sum_i \tilde{A}_i \frac{\partial p}{\partial z_i} - \sum\sum_{ij} \tilde{A}_{ij} \frac{\partial}{\partial z_i}[z_j p]$$

$$+ \frac{1}{2} \sum\sum_{ij} \tilde{B}_{ij} \frac{\partial^2 p}{\partial z_i \partial z_j} + O(\Omega^{-1/2}) \qquad (2\text{-}17)$$

The term of order $\Omega^{1/2}$ on both sides of this expression cancel if ϕ_i obeys

$$\frac{d\phi_i}{dt} = \tilde{A}_i(\{\phi(t)\}) \qquad (2\text{-}18)$$

Letting Ω approach infinity, the last term on the right-hand side of Eq. 2-17 vanishes and the System Size Expansion yields

$$\frac{\partial p}{\partial t} = -\sum\sum_{ij} \tilde{A}_{ij} \frac{\partial}{\partial z_i}[z_j p] + \frac{1}{2} \sum\sum_{ij} \tilde{B}_{ij} \frac{\partial^2 p}{\partial z_i \partial z_j} \qquad (2\text{-}19)$$

where $\tilde{A}_i$, $\tilde{A}_{ij}$, and $\tilde{B}_{ij}$ are given by Eqs. 2-15 and 2-16.

Even in the form given by Eq. 2-19, the master equation for the system may still involve a large number of variables $\{z\}$, since the number of random variables is equal to the number of distinct groups in the population which may be large. However, Eq. 2-19 is a linear Fokker-Planck equation whose solution yields a multinomial, normal distribution. The linearity of a Fokker-Planck equation is in reference to the coefficients $\tilde{A}_{ij}$ and $\tilde{B}_{ij}$. A Fokker-Planck equation is said to be linear if it can be written in the form shown in Eq. 2-19, and the coefficients do not depend on the random variables $\{z\}$. In the case of the master equation, the coefficients, although linear, are time dependent through the dependence on $\{\phi\}$ which obey the system of coupled, possibly non-linear, differential equations given by Eq. 2-18. To solve Eq. 2-19, it is necessary to first solve Eq. 2-18 for $\{\phi\}$, and then to solve the Fokker-Planck equation using $\{\phi\}$. Solving Eq. 2-18 for $\{\phi\}$ can itself be a non-trivial problem, especially if the equations are non-linear. Methods for solving Fokker-Planck equations with constant coefficient matrices, $\tilde{A}_{ij}$ and $\tilde{B}_{ij}$, are available, but the addition of a time dependence quickly increases the complexity of the problem.

Such problems can be circumvented in cases where a complete expression for $p(\{z\},t)$ can be substituted by expressions for its moments; in particular, the means, $\langle Z_i \rangle$, and the cross-moments $\langle Z_i Z_j \rangle$. This is done by multiplying Eq. 2-19 by z_i or $z_i z_j$, respectively, and integrating over all variables from $-\infty$ to $+\infty$. Doing so, integration by parts yields,

$$\frac{d}{dt} \langle Z_i \rangle = \sum_j \tilde{A}_{ij} \langle Z_j \rangle \qquad (2\text{-}20)$$

and

$$\frac{d}{dt}\langle Z_i Z_j\rangle = \sum_k [\tilde{A}_{ik}\langle Z_k Z_j\rangle + \tilde{A}_{jk}\langle Z_k Z_i\rangle] + \tilde{B}_{ij} \tag{2-21}$$

Using Eqs. 2-20 and 2-21, the covariances of {Z} can be shown to be,

$$\frac{d}{dt}\mathrm{Cov}[Z_i Z_j] = \sum_k \{\mathrm{Cov}[Z_k Z_j]\tilde{A}_{ik} + \mathrm{Cov}[Z_k Z_i]\tilde{A}_{jk}\} + \tilde{B}_{ij} \tag{2-22}$$

Returning to the original random variables, {N}, expressions for their means and covariances in terms of Eqs. 2-11 and 2-22 can be found to be

$$\begin{aligned}\frac{d}{dt}\langle N_i\rangle &= \frac{d\phi_i}{dt} + \Omega^{1/2}\frac{d}{dt}\langle Z_i\rangle \\ &= \Omega\tilde{A}_i + \Omega^{1/2}\sum_j \tilde{A}_{ij}\langle Z_j\rangle \\ &= \Omega\tilde{A}_i\left(\frac{\langle N_i\rangle}{\Omega}\right)\end{aligned} \tag{2-23}$$

and

$$\frac{d}{dt}\mathrm{Cov}[N_i N_j] = \Omega\frac{d}{dt}\mathrm{Cov}[Z_i Z_j] \tag{2-24}$$

Letting $\rho_i = \langle N_i\rangle/\Omega$, Eq. 2-23 reduces to

$$\frac{d\rho_i}{dt} = \underset{\sim}{A}_i(\rho_i) \tag{2-25}$$

which is an equation involving the population density of each of the specific groups as predestined for the successful use of the Systems Size Expansion. Equation 2-24 can also be written in terms of intensive variables. Doing so yields

$$\frac{d}{dt}\,\mathrm{Cov}\left[\frac{N_i}{\Omega}\,\frac{N_j}{\Omega}\right] = \frac{1}{\Omega}\,\frac{d}{dt}\,\mathrm{Cov}[Z_i Z_j] \tag{2-26}$$

2.3 DERIVATION OF CORRELATION FUNCTIONS

Thus far, expressions for the means and the covariances of the random variables have been derived, but these yield little information about the dynamic character of the fluctuations. Quantities known as the auto- and cross-correlation functions can, however, provide this information. These functions provide a measure of the influence of a value of a random variable at time t on the values of the random variables at time t+τ. For a Markov process the auto- and cross-correlation functions can easily be derived (see Gardiner, 1983), and obey the same equations as $\langle Z_i \rangle$, Eq. 2-20. Defining the correlation matrix as

$$K_{ij}(\tau) = \langle Z_i(0) Z_j(\tau) \rangle \tag{2-27}$$

the following set of differential equations can be derived relating $K_{ij}(\tau)$ to $\mathrm{Cov}[Z_i Z_j]$:

$$\frac{d}{d\tau} K_{ij}(\tau) = \sum_k \bar{A}^s_{jk} K_{ik}(\tau) \tag{2-28}$$

with $K_{ij}(0) = \mathrm{Cov}[Z_i Z_j]$

where $\bar{A}^s_{jk} = \bar{A}_{jk}(\{\phi^s\})$

$\{\phi^s\}$ = steady-state values

$\mathrm{Cov}[Z_i Z_j]$ = steady-state covariance

Equation 2-28 is a direct result of the linear nature of Eq. 2-20 and the fact that the process is Markovian. It also follows from Eqs. 2-27 and 2-28 and the relationship between the random variables {Z} and the original random variables {N}, that the correlation functions for the random variables {N} can be found from Eq. 2-28 using the initial conditions,

$$K_{ij}(0) = \mathrm{Cov}[N_i N_j]$$

where

$\mathrm{Cov}[N_i N_j]$ = steady-state convariance

2.4 CHANGING TO A NEW RANDOM VARIABLE

For many systems under study, direct information about the random variables $\{N\}$ themselves is not sufficient. Instead, the desired variables may be some function of $\{N\}$, and therefore it is necessary to derive the means and correlation functions of these variables from the available information on $\{N\}$. When the new random variable is a linear combination of $\{N\}$, e.g.,

$$S = \sum_i s_i N_i \tag{2-29}$$

where

S = new random variable

s_i = constant coefficient relating N_i to S

its mean and correlation function can be shown to be,

$$\langle S \rangle = \sum_i s_i \langle N_i \rangle \tag{2-30}$$

$$K(\tau) = \langle S(0)S(\tau) \rangle - \langle S(0) \rangle \langle S(\tau) \rangle$$

$$= \sum_{ij} \sum s_i s_j K_{ij} \tag{2-31}$$

Therefore, for systems where the rate of transition can be formulated and behaves according to the conditions set forth, the master equation can be solved approximately for the means and the correlation functions of the random variables of interest. Thus, it is possible to study the effects of stochastic kinectics on the evolution of the population and its effects on the behavior of the system; a possibility not available using the conventiona deterministic approach which yields equations only for the means, i.e., Eq. 2-25.

The master equation with the attendant System Size Expansion offers advantages over other stochastic formulations. For example, for non-linear systems, there is the well-known problem of coupling between moments of differing orders. In most formulations this problem is circumvented by assuming independence between random variables, or some other ad hoc procedure. By using a power series expansion, the System Size Expansion follows a more rational pathway; retaining a linear coupling between the means and the fluctuating components of the random variables - a coupling which is ignored or distorted when using an ad hoc approach. In situations where the System Size Expansion is not applicable, most ad hoc procedures are also invalid, and the system is best handled by a simulation procedure such as a Monte Carlo method.

NOTATION

A_i	=	First jump moment.
$\tilde{A}_i$	=	A_i/Ω
$\tilde{A}_{ij}$	=	coefficient in the expansion of $\tilde{A}_i$
B_{ij}	=	second jump moment
$\tilde{B}_{ij}$	=	B_{ij}/Ω
$Cov[N_iN_j]$	=	$\langle N_iN_j\rangle - \langle N_i\rangle\langle N_j\rangle$
$Cov[Z_iZ_j]$	=	$\langle Z_iZ_j\rangle - \langle Z_i\rangle\langle Z_j\rangle$
$K(\tau)$	=	correlation function for S.
$K_{ij}(\tau)$	=	correlation matrix defined as $\langle Z_i(0)Z_j(\tau)\rangle$ for Z_i and Z_j, or as $\langle N_i(0)N_j(\tau)\rangle - \langle N_i(0)\rangle\langle N_j(\tau)\rangle$ for N_i and N_j.
N_j	=	number of entities possessing characteristic j.
$N_{i,j}$	=	number of entities possessing characteristic i and characteristic j.
$N(r,x)drdx$	=	number of entities possessing characteristic r and characteric x, where r and x are continuous variables.
$\langle N_i\rangle$	=	expected value of random variable N_i.
$p(\{n\},t)$	=	joint density function of continuous random variables $\{N\}$.
$P(\{n\},t)$	=	joint probability of random variables $\{N\}$.
$P(\{n\}_1,t,\|\{n\}_0,t_0)$	=	conditional probability of random variables $\{N\}_1$ at time t_1 given the value of the random variables $\{N\}_0$ and time t_0.
s_i	=	constant coefficient relating N_i to S.
S	=	new random variable.
$\langle S\rangle$	=	expected value of S.
$W_t(\{n\}_0,\{n\}_1)$	=	intensity of transition function from state $\{n\}_0$ to state $\{n\}_1$.
Z_i	=	fluctuating component of the random variable N_i.

$\langle Z_i \rangle$ = expected value of the random variable Z_i.

$\langle Z_i Z_j \rangle$ = expected value of the product of the random variables Z_i and Z_j.

Greek Letters

$\delta^k(x)$ = Kronecker delta where $\delta^k(0)=1$ and $\delta^k(x)=0$ for $x \neq 0$.

ξ_i = Size of the change in the random variable N_i.

ρ_i = $\langle N_i \rangle / \Omega$

τ = small time interval tending toward zero.

ϕ_i = deterministic variable corresponding to the macroscopic behavior of N_i.

$\psi_t(\{\frac{n}{\Omega}\};\{\xi\})$ = homogeneous intensity of transition function.

Ω = system size

CHAPTER 3

APPLICATION OF GENERALIZED MASTER EQUATION TO BUBBLE POPULATION IN A BUBBLING FLUIDIZED BED

Suppose that the bubble population in a fluidized bed possesses the necessary characteristics, e.g., the Markov property and the necessary information, e.g., the dependence of interactions on bubble density, is available. Then a stochastic model based on the master equation can be formulated and successfully solved. In modelling the fluidized bed, the bed is traditionally divided into vertical compartments and each compartment is modelled as an individual reactor. Following this tradition, it is first assumed that bubbles coalesce only inside each compartment, and transfer only to the succeeding compartment above it - both actions taking place at a rate dependent on the volume of an individual bubble. It also must be assumed that coalescence between the bubbles is proportional to their number density in the compartment.

3.1 DERIVATION OF MODEL

Following the notation developed in the preceding section, a set of random variables can be defined as

$$\{N_{ij}: \ i \in \{1,2,\ldots,M\}, \ j \in \{1,2,3,\ldots\}\}$$

where

N_{ij} = number of bubbles in compartment i with volume $j\Delta V$.

M = number of compartments.

ΔV = small unit of volume which is usually taken to be equal to the volume of the smallest bubble.

An additional assumption is that all coalescence events involve only two bubbles.

Letting A_{ij} represent a bubble of size $j\Delta V$ in compartment i, it is seen that the interaction during coalescence can be represented by the following equations;

$$\prod_{i=1}^{M} \prod_{j=1}^{\infty} \prod_{k=1}^{j} [A_{ij} + A_{ik} \rightarrow A_{i(j+k)}]$$

where Π is taken to mean "for all".
Similarly, equations for the movement of bubbles between compartments can be represented by

$$\prod_{i=1}^{M-1} \prod_{j=1}^{\infty} [A_{ij} \rightarrow A_{(i+1)j}]$$

In addition to these events, bubbles are added to the bed in the first compartment and leave the bed from the last; equations for these events are, respectively,

$$\prod_{j=1}^{\infty} [X_j \rightarrow A_{1j}]$$

and

$$\prod_{j=1}^{\infty} [A_{Mj} \rightarrow Y_j]$$

where X_j and Y_j are dummy symbols representing the inlet and outlet environments.

As previously, the set of random variables will be denoted by $\{N\}$, and the volume of the system by Ω. However, since the rates of transition are assumed to be dependent on the number density of bubbles in an individual compartment, the reduced volumes

$$F_i = V_i/\Omega \qquad \text{for all } i \tag{3-1}$$

need be introduced; in this expression V_i is the volume of compartment i.

Expressions for the rates of transition due to coalescence can now be derived. Letting $\beta_i(j,k)$ be the rate constant for the coalescence between bubbles of size j and size (k-j) to form bubbles of size k in compartment i, the rates of transition can be written as

$$W_t(\{n_{i(k-j)}, n_{ij}, n_{ik}\}, \{n_{i(k-j)}-1, n_{ij}-1, n_{ik}+1\})$$

$$= \beta_i(j,k) \frac{n_{ij} n_{ik-i}}{F_i \Omega} \qquad \text{for all } i,j,k;\ k \neq 2j \qquad (3\text{-}2)$$

$$W_t(\{n_{ij}, n_{ik}\}, \{n_{ij}-2, n_{ik}+1\})$$

$$= \beta_i(j,k) \frac{n_{ij}(n_{ij}-1)}{F_i \Omega} \qquad \text{for all } i,j,k;\ k = 2j \qquad (3\text{-}3)$$

where all random variables which remain constant during a transition have been omitted from the notation for {n}.

Similarly, letting $\gamma_i(j)$ be the rate at which bubbles of size j leave compartment i and enter into compartment (i+1), the rates of transition can be written as

$$W_t(\{n_{ij}, n_{(i+1)j}\}, \{n_{ij}-1, n_{(i+1)j}+1\})$$

$$= \gamma_i(j) n_{ij} \qquad \text{for all } i,j;\ i < M \qquad (3\text{-}4)$$

For bubbles exiting from the bed through compartment M, the rates of transition are

$$W_t(\{n_{Mj}\}, \{n_{Mj}-1\}) = \gamma_M(j) n_{Mj} \qquad \text{for all } j \qquad (3\text{-}5)$$

Finally, for bubbles entering the bed through the first compartment, i.e., compartment 1, immediately above the distributor plate at a rate of $\Omega f(j)$ bubbles of size j per unit time the rates of transition are

$$W_t(\{n_{1j}\},\{n_{1j}+1\}) = \Omega f(j) \qquad \text{for all } j \tag{3-6}$$

Given the rates of transition, the master equation for the system is now determined and the System Size Expansion can be applied to solve for the means and the correlation functions of $\{N\}$. The first step is to rewrite the expressions for the rates of transition in terms of $\{n\}$ and $\{\xi\}$ which yields the following expressions:

$$W_t(\{n_{ik-j},n_{ij},n_{ik}\};\{-1,-1,1\}) = \beta_i(j,k)\frac{n_{ij}n_{ik-j}}{F_i\Omega} \qquad \text{for all } i,j,k;\ k\neq 2j \tag{3-7}$$

$$W_t(\{n_{ij},n_{ik}\};\{-2,1\}) = \beta_i(j,k)\frac{n_{ij}(n_{ij}-1)}{F_i\Omega} \qquad \text{for all } i,j,k;\ k=2j$$

$$W_t(\{n_{ij},n_{i+1j}\};\{-1,1\}) = \gamma_i(j)n_{ij} \qquad \text{for all } i,j;\ i<M \tag{3-8}$$

$$W_t(\{n_{Mj}\};\{-1\}) = \gamma_M(j)n_{Mj} \qquad \text{for all } j \tag{3-9}$$

$$W_t(\{n_{1j}\};\{1\}) = \Omega f(j) \qquad \text{for all } j \tag{3-10}$$

where all null elements in the set $\{\xi\}$ are omitted, and the remaining elements correspond to those in $\{n\}$, e.g.,

$$(\{n_{ij}\};\{1\}) \rightarrow (\{n_{ij}\};\{\xi_{ij}=1\}). \tag{3-11}$$

Note that the two sets of subscripts are identical, thereby indicating the correspondence.

The next step is to calculate the jump moments, A_ℓ and $B_{\ell m}$, but first an arrangement must be made to account for the double subscript on the random variables $\{N\}$. This can be accomplished by changing to a single subscript ℓ defined as

$$\ell = j+\varepsilon(i-1) \tag{3-12}$$

where

j = subscript denoting the bubble size

i = subscript denoting the compartment number

$\varepsilon = \max\{ \sum_{i=1}^{M} (V_i/\Delta V)\}$

the variable n_{ij} now appears as

$$n_{j+\varepsilon(i-1)}$$

Rewriting the expressions for the rates of transition using this notation yields

$$W_t(\{n_{k-j+\varepsilon(i-1)}, n_{j+\varepsilon(i-1)}, n_{k+\varepsilon(i-1)}\};\{-1,-1,1\})$$
$$= \beta_i(j,k) \frac{n_{j+\varepsilon(i-1)} n_{k-j+\varepsilon(i-1)}}{F_i \Omega} \qquad \text{for all } i,j,k:\ k \neq 2j \tag{3-13}$$

$$W_t(\{n_{j+\varepsilon(i-1)}, n_{k+\varepsilon(i-1)}\};\{-2,1\})$$
$$= \beta_i(j,k) \frac{n_{j+\varepsilon(i-1)} (n_{n+\varepsilon(i-1)}-1)}{F_i \Omega} \qquad \text{for all } i,j,k:\ k=2j \tag{3-14}$$

$$W_t(\{n_{j+\varepsilon(i-1)}; n_{j+\varepsilon i}\};\{-1,1\})$$
$$= \gamma_i(j) n_{j+\varepsilon(i-1)} \qquad \text{for all } i,j:\ i < M \tag{3-15}$$

$$W_t(\{n_{j+\varepsilon(M-1)}\};\{-1\}) = \gamma_M(j) n_{j+\varepsilon(M-1)} \qquad \text{for all } j \tag{3-16}$$

$$W_t(\{n_j\};\{1\}) = \Omega f(j) \qquad \text{for all } j \tag{3-17}$$

Expressions for A_ℓ and $B_{\ell m}$ are now derived as follows:

$$A_\ell = \sum_i^M \sum_j^\epsilon \{ \sum_k^\epsilon \frac{1}{2}[-\delta^k(\ell-k+j-\epsilon i+\epsilon) - \delta^k(\ell-j-\epsilon i+\epsilon) + \delta^k(\ell-k-\epsilon i+\epsilon)][1-\delta^k(k-2j)]\beta_i(j,k)\frac{n_{j+\epsilon(i-1)}n_{k-j+\epsilon(i-1)}}{F_i\Omega}$$

$$+ \sum_k^\epsilon [-2\delta^k(\ell-j-\epsilon i+\epsilon) + \delta^k(\ell-k-\epsilon i+\epsilon)] \cdot \delta^k(k-2j)\beta_i(j,k)\frac{n_{j+\epsilon(i-1)}(n_{j+\epsilon(i-1)}-1)}{F_i\Omega}$$

$$+ [-\delta^k(\ell-j-\epsilon i+\epsilon) + \delta^k(\ell-j-\epsilon i)][1-\delta^k(i-M)]\gamma_i(j)n_{j+\epsilon(i-1)}\}$$

$$- \sum_j^\epsilon \delta^k(\ell-j-\epsilon M+\epsilon)\gamma_M(j)n_{j+\epsilon(M-1)}$$

$$+ \sum_j^\epsilon \delta^k(\ell-j)\Omega f(j) \qquad (3\text{-}18)$$

$$B_{\ell m} = \sum_i^M \sum_j^\epsilon \{ \sum_k^\epsilon \frac{1}{2}[-\delta^k(\ell-k+j-\epsilon i+\epsilon) - \delta^k(\ell-j-\epsilon i+\epsilon) + \delta^k(\ell-k-\epsilon i+\epsilon)][-\delta^k(m-k+j-\epsilon i+\epsilon) - \delta^k(m-j-\epsilon i+\epsilon) + \delta^k(m-k+\epsilon i+\epsilon)] \cdot [1-\delta^k(k-2j)]\beta_i(j,k)\frac{n_{j+\epsilon(i-1)}n_{k-j+\epsilon(i-1)}}{F_i\Omega}$$

$$+ \sum_k^\epsilon [-2\delta^k(\ell-j-\epsilon i+\epsilon) + \delta^k(\ell-k-\epsilon i+\epsilon)][-2\delta^k(m-j-\epsilon i+\epsilon) + \delta^k(m-k-\epsilon i+\epsilon)]\,\delta^k(k-2j)\beta_i(j,k)\frac{n_{j+\epsilon(i-1)}(n_{j+\epsilon(i-1)}-1)}{F_i\Omega}$$

$$+ [-\delta^k(\ell-j-\epsilon i+\epsilon) + \delta^k(\ell-j-\epsilon i)][-\delta^k(m-j-\epsilon i+\epsilon) + \delta^k(m-j-\epsilon i)][1-\delta^k(i-m)] \cdot \gamma_i(j)n_{j+\epsilon(i-1)}\}$$

$$+ \sum_j^\epsilon \delta^k(\ell-j-\epsilon M+\epsilon)\delta^k(\ell-m)\gamma_M(j)n_{j+\epsilon(M-1)}$$

$$+ \sum_j^\epsilon \delta^k(\ell-j)\delta^k(\ell-m)\Omega f(j) \qquad (3\text{-}19)$$

with the first of these expressions, Eq. 2-18 can be used to find

$$\frac{d\phi_{\ell}}{dt} = \sum_{i}^{M}\sum_{j}^{\varepsilon}\sum_{k}^{\varepsilon}\{\frac{1}{2}[-\delta^{k}(\ell-k+j-\varepsilon i+\varepsilon) - \delta^{k}(\ell-j-\varepsilon i+\varepsilon) + \delta^{k}(\ell-k-\varepsilon i+\varepsilon)]$$

$$\cdot[1 - \delta^{k}(k-2j)]\frac{\beta_i(j,k)}{F_i}\phi_{j+\varepsilon(i-1)}\phi_{k-j+\varepsilon(i-1)}$$

$$+ \sum_{k}^{\varepsilon}[-2\delta^{k}(\ell-j-\varepsilon i+\varepsilon) + \delta^{k}(\ell-k-\varepsilon i+\varepsilon)]\delta^{k}(k-2j)\frac{\beta_i(j,k)}{F_i}$$

$$\cdot\phi_{j+\varepsilon(i-1)}\phi_{k-j+\varepsilon(i+1)}$$

$$+ [-\delta^{k}(\ell-j-\varepsilon i+\varepsilon) + \delta^{k}(\ell-j-\varepsilon i)][1 - \delta^{k}(i-M)]\gamma_i(j)\phi_{j+\varepsilon(i-1)}\}$$

$$- \sum_{j}^{\varepsilon}\delta^{k}(\ell-j-\varepsilon M+\varepsilon)\gamma_M(j)\phi_{j+\varepsilon(M-1)} + \sum_{j}^{\varepsilon}\delta^{k}(\ell-j)f(j) \qquad (3\text{-}20)$$

Since it is no longer necessary to use a single subscript, this expression can be simplified by returning to double subscripts, yielding

$$\frac{d\phi_{\ell m}}{dt} = -\sum_{j=1}^{\varepsilon-m}\frac{\beta_{\ell}(m,j+m)}{F_{\ell}}\phi_{\ell m}\phi_{\ell j} + \sum_{j=1}^{\frac{m}{2}}\frac{\beta_{\ell}(j,m)}{F_{\ell}}\phi_{\ell j}\phi_{\ell m-j}$$

$$- \frac{\beta_{\ell}(m,2m)}{F_{\ell}}\phi_{\ell m}^{2} - \gamma_{\ell}(m)\phi_{\ell m} + \gamma_{\ell-1}(m)\phi_{\ell-1\,m}[1 - \delta^{k}(\ell-1)]$$

$$+ f(m)\delta^{k}(\ell-1) \qquad (3\text{-}21)$$

where ℓ corresponds to the compartment and m to the size.

To calculate the moments of the fluctuating component, it is necessary to identify $\tilde{A}_{\ell m}$ as given in Eq. 2-15. This gives rise to

$$\tilde{A}_{\ell m} = \sum_{i}^{M}\sum_{j}^{\varepsilon}\sum_{k}^{\varepsilon}[\frac{1}{2}[-\delta^{k}(\ell-k+j-\varepsilon i+\varepsilon) - \delta^{k}(\ell-j-\varepsilon i+\varepsilon)$$

$$+ \delta^{k}(\ell-k-\varepsilon i+\varepsilon)][1 - \delta^{k}(k-2j)]\frac{\beta_i(j,k)}{F_i}$$

$$\cdot[\phi_{j+\varepsilon(i-1)}\delta^k(m-k+j-\varepsilon i+\varepsilon) + \phi_{k-j+\varepsilon(i-1)}\delta^k(m-j-\varepsilon i+\varepsilon)]$$

$$+ \sum_k^{\varepsilon}[-2\delta^k(\ell-j-\varepsilon i+\varepsilon)+\delta^k(\ell-k-\varepsilon i+\varepsilon)]\delta^k(k-2j)\frac{\beta_i(j,k)}{F_i}$$

$$\cdot 2\phi_{j+\varepsilon(i-1)}\delta^k(m-j-\varepsilon i+\varepsilon)$$

$$+[-\delta^k(\ell-j-\varepsilon i+\varepsilon) + \delta^k(\ell-j-\varepsilon i)][1-\delta^k(i-M)]$$

$$\cdot\gamma_i(j)\delta^k(m-j-\varepsilon i+\varepsilon)\}$$

$$- \sum_j \delta^k(\ell-j-\varepsilon m+\varepsilon)\gamma_M(j)\delta^k(m-J-\varepsilon M+\varepsilon) \qquad (3\text{-}22)$$

Changing again to double subscripts, this expression in conjunction with Eq. 2-20 leads to

$$\frac{d\langle Z_{\ell m}\rangle}{dt} = -\sum_{j=1}^{\varepsilon-m}\frac{\beta_\ell(m,j+m)}{F_\ell}[\phi_{\ell m}\langle Z_{\ell j}\rangle + \langle Z_{\ell m}\rangle\phi_{\ell j}]$$

$$+\sum_{j=1}^{\frac{m}{2}}\frac{\beta_\ell(j,m)}{F_\ell}[\phi_{\ell m}\langle Z_{\ell m-j}\rangle + \langle Z_{\ell j}\rangle\phi_{\ell m-j}]$$

$$-2\frac{\beta_\ell(m,2m)}{F_\ell}\phi_{\ell m}\langle Z_{\ell m}\rangle - \gamma_\ell(m)\langle Z_{\ell m}\rangle$$

$$+\gamma_{\ell-1}(m)\langle Z_{\ell-1m}\rangle[1-\delta^k(\ell-1)] \qquad (3\text{-}23)$$

To calculate $\mathrm{Cov}[Z_{ij}Z_{\ell m}]$ from Eq. 2-21, it is first necessary to find $\tilde{B}_{ij\ell m}$ from $B_{\ell m}$ in Eq. 3-19 this yields

$$\tilde{B}_{ij\ell m} = \delta^k(\ell-i)\{\beta_i(m,j+m)\frac{\phi_{im}\phi_{ij}}{F_i} - \beta_i(j,m)\frac{\phi_{im-j}\phi_{ij}}{F_i}$$

$$-\beta_i(m,j)\frac{\phi_{ij-m}\phi_{im}}{F_i} + \delta^k(j-m)\sum_{k=1}^{\varepsilon-j}\beta_i(j,j+k)\frac{\phi_{ik}\phi_{ij}}{F_i}$$

$$+ \delta^k(j-m) \sum_{k=1}^{[\frac{j}{2}]} \beta_i(k,j) \frac{\phi_{ik}\phi_{ij-k}}{F_i}$$

$$+ 2\delta^k(j-m)\beta_i(j,2j)\frac{\phi_{ij}^2}{F_i} - \delta^k(j-2m)\beta_i(m,j)\frac{\phi_{im}^2}{F_i}$$

$$- \delta^k(2j-m)\beta_i(j,m)\frac{\phi_{ij}^2}{F_i} + \delta^k(j-m)\gamma_i(j)\phi_{ij}$$

$$+ \delta^k(j-m)[1-\delta^k(i-1)]\gamma_{i-1}(j)\phi_{i-1j}$$

$$+ \delta^k(j-m)\delta^k(i-1)f(j)\}$$

$$- \delta^k(\ell-1+i)\delta^k(j-m)\gamma_{i-1}(j)\phi_{i-1j}$$

$$- \delta^k(\ell-i-1)\delta^k(j-m)\gamma_i(j)\phi_{ij} \qquad (3\text{-}24)$$

Using this expression and an expression for $\check{A}_{\ell m}$ in double subscripts, Eq. 2-22 yields the following equation for the rate of change of $\mathrm{Cov}[Z_{ij}Z_{\ell m}]$:

$$\frac{d}{dt}\mathrm{Cov}[Z_{ij}Z_{\ell m}] = - \sum_{k=1}^{\varepsilon-j} \frac{\beta_i(j,j+k)}{F_i} \{\phi_{ik}\mathrm{Cov}[Z_{ij}Z_{\ell m}] + \phi_{ij}\mathrm{Cov}[Z_{ik}Z_{\ell m}]\}$$

$$- \sum_{k=1}^{\varepsilon-m} \frac{\beta_\ell(m,m+k)}{F_\ell} \{\phi_{\ell k}\mathrm{Cov}[Z_{ij}Z_{\ell m}] + \phi_{\ell m}\mathrm{Cov}[Z_{ij}Z_{\ell k}]\}$$

$$+ \sum_{k=1}^{[\frac{j}{2}]} \frac{\beta_i(k,j)}{F_i} \{\phi_{ik}\mathrm{Cov}[Z_{ij-k}Z_{\ell m}] + \phi_{ij-k}\mathrm{Cov}[Z_{ik}Z_{\ell m}]\}$$

$$+ \sum_{k=1}^{[\frac{m}{2}]} \frac{\beta_\ell(k,m)}{F_\ell} \{\phi_{\ell k}\mathrm{Cov}[Z_{\ell m-k}Z_{ij}] + \phi_{\ell m-k}\mathrm{Cov}[Z_{ij}Z_{\ell k}]\}$$

$$
\begin{aligned}
&- 2\left[\frac{\beta_i(j,2j)}{F_i}\phi_{ij} + \frac{\beta_\ell(m,2m)}{F_\ell}\phi_{\ell m}\right]\mathrm{Cov}[Z_{ij}Z_{\ell m}] \\
&- [\gamma_i(j) + \gamma_\ell(m)]\ \mathrm{Cov}[Z_{ij}Z_{\ell m}] \\
&+ [1-\delta^k(i-1)]\gamma_{i-1}(j)\ \mathrm{Cov}[Z_{i-1j}Z_{\ell m}] \\
&+ [1-\delta^k(\ell-1)]\gamma_{\ell-1}(m)\ \mathrm{Cov}[Z_{ij}Z_{\ell-1m}] \\
&+ \delta^k(\ell-i)\{\delta^k(j-m)\Big[\sum_{k=1}^{\varepsilon-j}\frac{\beta_i(m,m+k)}{F_i}\phi_{ik}\phi_{im} + \frac{\beta_i(j,2j)}{F_i}\phi_{ij}^2 \\
&\qquad + \sum_{k=1}^{[\frac{j}{2}]}\frac{\beta_i(k,j)}{F_i}\phi_{ik}\phi_{ij-k} + \gamma_i(j)\phi_{ij} \\
&\qquad + [1-\delta^k(i-1)]\gamma_{i-1}(j)\phi_{i-1j} + \delta^k(i-1)f(j)] \\
&\qquad + \frac{\beta_i(m,j+m)}{F_i}\phi_{im}\phi_{ij} - \frac{\beta_i(j,m)}{F_i}\phi_{im-j}\phi_{ij} - \frac{\beta_i(m,j)}{F_i}\phi_{ij-m}\phi_{im} \\
&\qquad - \delta^k(j-2m)\frac{\beta_i(m,j)}{F_i}\phi_{im}^2 - \delta^k(m-2j)\frac{\beta_i(j,m)}{F_i}\phi_{ij}^2\ \} \\
&- \delta^k(j-m)\{\delta^k(\ell-i+1)\gamma_{i-1}(j)\phi_{i-1j} + \delta^k(\ell-i-1)\gamma_i(j)\phi_{ij}\}
\end{aligned}
\qquad (3\text{-}25)
$$

Using this expression with Eq. 2-24 then yields the rate of change of the $\mathrm{Cov}[N_{ij}N_{\ell m}]$ which are the random variables representing the number of entities in each group of the population. The size of Eq. 3-25 is evidence as to the tenuous nature of an assumption of independence between random variables. Such an assumption would lead to covariances of zero between all pairs of unequal random variables. With Eq. 3-25 it is possible to calculate these covariances in a rational manner without resorting to ad hoc assumptions of independence.

Furthermore, using Eq. 3-23 with Eq. 2-28, expressions for the correlation functions of the random variables {N} can now be derived, and are as follows:

$$\frac{d}{d\tau}K_{ij\ell m}(\tau) = -\sum_{k=1}^{\varepsilon-m}\frac{\beta_\ell(m,k+m)}{F_\ell}[\phi^s_{\ell m}K_{ij\ell k} + \phi^s_{\ell k}K_{ij\ell m}]$$
$$+\sum_{k=1}^{\frac{m}{2}}\frac{\beta_\ell(k,m)}{F_\ell}[\phi^s_{\ell k}K_{ij\ell m-l} + \phi^s_{\ell m-k}K_{ij\ell k}]$$
$$-2\frac{\beta_\ell(m,2m)}{F_\ell}\phi^s_{\ell m}K_{ij\ell m}$$
$$-\gamma_\ell(m)K_{ij\ell m} + \gamma_{\ell-1}(m)[1-\delta^k(\ell-1)]K_{ij\ell-1m} \qquad (3\text{-}26)$$

with

$$K_{ij\ell m}(0) = \mathrm{Cov}[N_{ij}N_{\ell m}]$$

where

$\phi^s_{\ell m}$ = steady-state value of $\phi_{\ell m}$

$\mathrm{Cov}[N_{ij}N_{\ell m}]$ = steady-state covariances

The system can now be characterized by the means found from Eq. 3-21 and the correlation functions found from Eq. 3-26 of the random variable representing the number of bubbles of a given volume in a given compartment. In contrast to the deterministic study of this system, where only the means of the random variables are studied, the correlation functions allow for the study of the effects of dynamic variations from the means on the behavior of the fluidized bed. These effects have been previously

studied by using a Langevin approach with fluctuations represented by the ad hoc addition of a noise term. With the information gsined from Eq. 3-26 about the correlation functions of the random variables, this Langevin approsch could be improved by using these correlation functions, or correlation functions derived for the random variable of interest, to specify the behavior of the sdded noise term; thus plscing an otherwise ad hoc procedure on a more rational basis. Such a project could however introduce substantial difficulties since the correlation functions would no longer necessarily behave in a mathematically simple fashion. Knowledge of the correlation functions found from Eq. 3-26 could however lead to better assumptions about the type of noise term to employ when an approximation is deemed necessary.

3.2 DETERMINATION OF RATE-OF-COALESCENCE FUNCTION

The rate of coalescence function $\beta_k(j,k)$, should possess certain properties in order for it to properly model the phenomenon of bubble coalescence. Some of these properties are:

i) $\beta_k(i,j)$ should be equal to zero for i=0 or for j-i=0

ii) $\beta_k(i,j)$ should have a maximum at 2i=j

iii) $\beta_k(i,j)$ should approach infinity as $j\Delta V$ approaches V_k

iv) $\beta_k(i,j)$ should be approximately linear for small i for a given j

Property i) follows from the intuitive picture of two bubbles coslescing in a volume of V_k upon collision. Property i) thus states that as the sizes (volumes) of the bubbles become smaller and approach zero, the probability of a collision in a compsrtment with constant volume also approaches zero, thereby rendering the rate of coalescence to approach zero. Property ii) follows from property i), the property of symmetry with respect to i snd j-i which $\beta_k(i,j)$ must possess, i.e.,

$$\beta_k(i,j) = \beta_k(j-i,j)$$

and the intuitive picture of colliding bubbles, suggesting that $\beta_k(i,j)$ should be continuous and possess no local minimum in the interval $i \in (0,j)$. Property iii) is a result of the finite volume of the compartment. When two bubbles are in a compartment of volume V_k and the combined volume of the two bubbles is close to V_k, it would be expected that the two bubbles coalesce almost instantaneously, thereby giving rise to

$$\beta_k(i,j) \to +\infty \qquad \text{as} \qquad j\Delta V \to V_k$$

Property iv) resulta from similar reasoning applied to the other extreme. If two small bubbles are in a large compartment, they should feel no restriction due to the finiteness of the compartment size and behave as if they were in an infinite space. In this extreme it could be expected that the rate of coalesence would be linearly proportional to i for a given j.

There are many possible candidates for a function which possess properties i) through iv); one of the simplest of such functions is

$$\beta_k(i,j) = B_k V_k \Delta V \left(\frac{i}{j}\right)\left[\frac{j-i}{V_k - j\Delta V}\right] \tag{3-27}$$

where B_k is a parameter which can be recovered by fitting the model to the observed population distribution data. Other functions are possible for $\beta_k(i,j)$, and the optimal functional form for $\beta_k(i,j)$ can be selected based on a detailed study of the phenomenon incorporating known bubble behavior. However, use of Eq. 3-21 will allow for preliminary characterization of the effects of the fluctuations in the bubble size distribution in a fluidized bed.

3.3 DETERMINATION OF OTHER RATES OF THANSITION FUNCTIONS

Besides the rate of coalesence function, two further functions remain to be specified; these are $\gamma_k(j)$ and $f(j)$. The first of these functions can be approximated by considering the velocity of bubbles of volume $j\Delta V$ in a fluidized bed, $u(j)$, and the height of compartment k, h_k. The velocity of a bubble in a fluidized bed has been shown to be approximately

$$u(j) = 0.7908\sqrt{g}\ (j\Delta V)^{1/6} \tag{3-28}$$

Using this expression, the rate at which bubbles of size $j\Delta V$ leave compartment k can be approximated as

$$\gamma_k(j) = \frac{0.7908\sqrt{g}\ (j\Delta V)^{1/6}}{h_k} \tag{3-29}$$

Determination of the rate of entrance of bubbles of size $j\Delta V$ into the first compartment, $\Omega f(j)$, requires some knowledge as to the size distribution of the bubbles entering into the bed, and of the volumetric rate at which gas enters into the bubble phase at the distributor plate, G. If it is assumed that all bubbles entering into the first compartment are approximately of the same size, the distribution of bubble sizes can be written as

$$\delta^k(j-1)$$

and f(j) as

$$f(j) = \delta^{k}(j-1)\,\frac{G}{\Omega\Delta V} = f_0\,\delta^{k}(j-1) \qquad (3\text{-}30)$$

where

$G = (U - U_{mf})S$

U = superficial gas velocity

U_{mf} = minimum superficial gas velocity for fluidization

S = cross-sectional area of the fluidized-bed

Darton et al. (1977) have given the expression for ΔV as

$$\Delta V = 2.2676\{(U - U_{mf})\,\frac{S}{N_0 g^{1/2}}\}^{6/5} \qquad (3\text{-}31)$$

where N_0 is the number of orifices in the distributor plate; f_0 in Eq. 3-24 can thus be seen to be

$$f_0 = \frac{1}{\Omega}\,[\frac{g^3\,N_0^6}{60(U - U_{mf})S}]^{1/5} \qquad (3\text{-}32)$$

Equations 3-21, 3-23, 3-25 and 3-26 specify the rates of transition functions in the present stochastic model of the bubble population..

3.4 DETERMINATION OF COMPARTMENT HEIGHT

When using a compartmental model of a fluidized bed, it is common to base the compartment height on the average bubble volume in the compartment. In this model, however, the compartment height appears in the transition rates and can therefore be used to control the relative probability of coalescence versus exiting from the compartment. This results from the fact that h_k appears in Eq. 3-23 to the inverse one power. Increasing h_k will thus decrease the rate of transition without much effect on the rate of coalesence. In a larger compartment it would be possible, therefore, to effect a large number of coalescence events involving a single volume element.

By decreasing h_k it is possible to reduce the probability that a single volume element will coalesce and thus to control the possible bubble sizes which can be formed in a given compartment. For example, by reducing h_1 it is possible to control the probability that a single bubble entering the compartment is involved in one or two, or more coalescence events. If h_1 is properly chosen, it would be safe to assume that only bubbles formed by a maximum of two coalescence events are present in the first compartment. This would restrict the possible bubble sizes in the first compartment to $j \in \{1, 2, 3, 4\}$; all other sizes being of very low probability.

To determine which values of h_k should be used in order to safely assume that the probability of coalescence is less than the probability of exiting from the compartment, the ratio of the rate of coalescence to the rate of exit must be considered. If it is desired to limit the maximum number of coalescence events to two per compartment, the maximum bubble size in the compartment k is

$4^k \Delta V$

Equation 3-23 for a bubble of this size yields

$$\gamma_k(4^k) = \frac{0.7988\sqrt{g}(4^k \Delta V)^{1/6}}{h_k} \tag{3-33}$$

which is the rate of exit.

The rate of coalescence depends not only on size of the largest bubble, but also on the size and number density of the bubbles with which it can coalesce. Since, in general, knowledge of the number density of the bubbles requires a solution of the model, a more conservative estimate can be used. The most conservative estimate available is found by using the number of bubbles of size 1 in compartment 1. Calling this estimate ϕ^*, it is found that

$$\phi^* = \frac{f_0}{\gamma_1(1)} \tag{3-34}$$

Using the maximum value of $\beta_k(4^k, j)$, the ratio of probability of coalescence to probability of exit is found to be

$$\frac{\beta_k(4^k, 4^{k+\frac{1}{2}})\phi^*}{\gamma_k(4^k)F_k} = \frac{B_k h_k(\Delta V)^{2/3}\left[\frac{4^k}{h_k S - 4^{k+\frac{1}{2}}\Delta V}\right] f_0 \Omega}{2(0.7098)^2 g\, 4^{k/6}} \tag{3-35}$$

Setting this expression equal to a constant, C, which can be controlled so that the ratio is less than one by a derived percentage, yields the following expression for h_k,

$$h_k = \frac{4C\,\Delta V\,(0.7908)^2 g\, 4^k}{2SC(0.7908)^2 g - B_k(\Delta V)^{2/3} f_0 \Omega\, 4^{5k/6}} \tag{3-36}$$

Equation 3-29 can now be used to determine the height and thus the volume of each compartment.

3.5 EXAMPLE CALCULATION FOR THE FIRST COMPARTMENT

As an example of using the stochastic model, a calculation will be carried out using the following parameters:

$$U - U_{mf} = 2 \text{ cm/s}$$

$$N_0 = 10$$

$$S = 314 \text{ cm}^2$$

$$g = 980 \text{ cm}^2/\text{s}^2$$

$$\Delta V = 5.23 \text{ cm}^3$$

$$\Omega f_0 = 120.1 \text{ s}^{-1}$$

$$B_1 = 330.5 \text{ s}^{-1}$$

$$C = 1$$

$$h_1 = 9.90 \text{ cm}$$

$$V_1 = 3108.6 \text{ cm}^3$$

where h_1 was found using Eq. 3-36.

The choice of h_1 has been made such that the maximum size bubble in compartment one is $4\Delta V$, which results from two coalescence events starting from bubbles of size ΔV. Since the maximum number of coalescence events is restricted to two, the following coalescence events are possible:

$$A_{11} + A_{11} \rightarrow A_{12}$$

$$A_{11} + A_{12} \rightarrow A_{13}$$

$$A_{12} + A_{13} \rightarrow A_{14}$$

All other coalescence events are considered to occur with very low probability and thus can be neglected. Equation 3-21 can now be used to find

$$\frac{d\phi_{11}}{dt} = -2 \frac{\beta_1(1,2)}{F_1} \phi_{11}^2 - \frac{\beta_1(1,3)}{F_1} \phi_{11} \phi_{12} - \gamma_1(1)\phi_{11} + f_0 \qquad (3\text{-}37)$$

$$\frac{d\phi_{12}}{dt} = -\frac{\beta_1(2,3)}{F_1}\phi_{12}\phi_{11} + \frac{\beta_1(1,2)}{F_1}\phi_{11}^2 - 2\frac{\beta_1(2,4)}{F_1}\phi_{12}^2 - \gamma_i(2)\phi_{12} \tag{3-38}$$

$$\frac{d\phi_{13}}{dt} = \frac{\beta_1(1,3)}{F_1}\phi_{12}\phi_{11} - \gamma_1(3)\,\phi_{13} \tag{3-39}$$

$$\frac{d\phi_{14}}{dt} = \frac{\beta_1(2,4)}{F_1}\phi_{12}^2 - \gamma\,(4)\phi_{14} \tag{3-40}$$

Assuming steady-state behavior for

$$\langle N_{1i}\rangle = \Omega\phi_{1i},\ i \in \{1, 2, 3, 4\},$$

Eqs. 3-37 through 3-40 reduce, respectively, to the following expressions;

$$2\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle^2 + \frac{\beta_1(1,3)}{V_1}\langle N_{11}\rangle\langle N_{12}\rangle + \gamma_1(1)\,\langle N_{11}\rangle = \Omega f_0 \tag{3-41}$$

$$\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle^2 - \frac{\beta_1(2,3)}{V_1}\langle N_{12}\rangle\,\langle N_{11}\rangle - 2\frac{\beta_1(2,4)}{V_1}\langle N_{12}\rangle^2 - \gamma_1(2)\langle N_{12}\rangle = 0 \tag{3-42}$$

$$\langle N_{13}\rangle = \frac{\beta_1(1,3)}{\gamma_1(3)V_1}\,\langle N_{12}\rangle\,\langle N_{11}\rangle \tag{3-43}$$

$$\langle N_{14} \rangle = \frac{\beta_1(2,4)}{\gamma_1(4)V_1} \langle N_{12} \rangle^2 \qquad (3\text{-}44)$$

Solving Eqs. 3-41 through 3-44 with the assumed parameters yields

$$\langle N_{11} \rangle = 11.333$$

$$\langle N_{12} \rangle = 3.116$$

$$\langle N_{13} \rangle = 3.245$$

$$\langle N_{14} \rangle = 1.277$$

Noting that

$$\mathrm{Cov}[N_{ij}N_{ij}] = \mathrm{Var}[N_{ij}], \qquad (3\text{-}45)$$

Eq. 3-25 in conjunction with Eq. 2-24 leads to the following expressions;

$$\begin{aligned}\frac{d}{dt}\mathrm{Var}[N_{11}] = &-8\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle \mathrm{Var}[N_{11}] \\ &-2\frac{\beta_1(1,3)}{V_1}\{\langle N_{12}\rangle \mathrm{Var}[N_{11}] + \langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}]\} \\ &-2\gamma_1(1)\,\mathrm{Var}[N_{11}] + 4\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle^2 \\ &+\frac{\beta_1(1,3)}{V_1}\langle N_{11}\rangle\langle N_{12}\rangle + \gamma(1)\langle N_{11}\rangle + \Omega f(1)\end{aligned} \qquad (3\text{-}46)$$

$$\begin{aligned}\frac{d}{dt}\mathrm{Cov}[N_{11}\,N_{12}] = &-\frac{\beta_1(1,3)}{V_1}\{\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}] + \langle N_{12}\rangle \mathrm{Var}[N_{11}]\} \\ &-4\left[\frac{\beta_1(2,4)}{V_1}\langle N_{12}\rangle + \frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle\right]\mathrm{Cov}[N_{11}\,N_{12}] \\ &-\frac{\beta_1(1,3)}{V_1}\{\langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}] + \langle N_{11}\rangle \mathrm{Var}[N_{12}]\} \\ &+2\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle \mathrm{Var}[N_{11}] - [\gamma_1(1) + \gamma_1(2)]\mathrm{Cov}[N_{11}N_{12}] \\ &+\frac{\beta_1(1,3)}{V_1}\langle N_{11}\rangle\langle N_{12}\rangle - 2\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle^2\end{aligned} \qquad (3\text{-}47)$$

$$\frac{d}{dt}\,\mathrm{Cov}[N_{11}N_{13}] = -4\,\frac{\beta_1(1,2)}{V_1}\,\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{13}]$$
$$-\frac{\beta_1(1,3)}{V_1}\,\{\langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{13}] + \langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{13}]\}$$
$$+2\,\frac{\beta_1(1,3)}{V_1}\,\{\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}] + \langle N_{12}\rangle \mathrm{Var}[N_{11}]\}$$
$$-[\gamma_1(1) + \gamma_1(3)]\,\mathrm{Cov}[N_{11}N_{13}]$$
$$-\frac{\beta_1(1,3)}{V_1}\,\langle N_{11}\rangle\,\langle N_{12}\rangle \qquad (3\text{-}48)$$

$$\frac{d}{dt}\,\mathrm{Cov}[N_{11}N_{14}] = -4\,\frac{\beta_1(1,2)}{V_1}\,\langle N_{11}\rangle\,\mathrm{Cov}[N_{11}N_{14}]$$
$$-\frac{\beta_1(1,3)}{V_1}\,\{\langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{14}] + \langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{14}]\}$$
$$+2\,\frac{\beta_1(2,4)}{V_1}\,\langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}]$$
$$-[\gamma_1(1) + \gamma_1(4)]\,\mathrm{Cov}[N_{11}N_{14}] \qquad (3\text{-}49)$$

$$\frac{d}{dt}\,\mathrm{Var}[N_{12}] = -2\,\frac{\beta_1(1,3)}{V_1}\,\{\langle N_{11}\rangle \mathrm{Var}[N_{12}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}]\}$$
$$-8\,\frac{\beta_1(2,4)}{V_1}\,\langle N_{12}\rangle \mathrm{Var}[N_{12}]$$
$$+4\,\frac{\beta_1(1,2)}{V_1}\,\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}] - 2\gamma_1(2)\,\mathrm{Var}[N_{12}]$$
$$+\frac{\beta_1(1,3)}{V_1}\,\langle N_{11}\rangle\,\langle N_{12}\rangle + 4\,\frac{\beta_1(2,4)}{V_1}\,\langle N_{12}\rangle^2$$
$$+\frac{\beta_1(1,2)}{V_1}\,\langle N_{11}\rangle^2 + \gamma_1(2)\,\langle N_{12}\rangle \qquad (3\text{-}50)$$

$$\frac{d}{dt}\,\mathrm{Cov}[N_{12}N_{13}] = -\frac{\beta_1(1,3)}{V_1}\{\langle N_{11}\rangle\,\mathrm{Cov}[N_{12}N_{13}] + \langle N_{12}\rangle\,\mathrm{Cov}[N_{11}N_{13}]\}$$
$$- 4\,\frac{\beta_1(2,4)}{V_1}\langle N_{12}\rangle\,\mathrm{Cov}[N_{12}N_{13}]$$
$$+ 2\,\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle\,\mathrm{Cov}[N_{11}N_{13}]$$
$$+ 2\,\frac{\beta_1(1,3)}{V_1}\{\langle N_{11}\rangle\mathrm{Var}[N_{12}] + \langle N_{12}\rangle\,\mathrm{Cov}[N_{11}N_{12}]\}$$
$$- [\gamma_1(2) + \gamma_1(3)]\,\mathrm{Cov}[N_{12}N_{13}]$$
$$- \frac{\beta_1(1,3)}{V_1}\langle N_{11}\rangle\langle N_{12}\rangle \qquad (3\text{-}51)$$

$$\frac{d}{dt}\,\mathrm{Cov}[N_{12}N_{14}] = -\frac{\beta_1(1,3)}{V_1}\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{14}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{14}]\}$$
$$- 4\,\frac{\beta_1(2,4)}{V_1}\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{14}]$$
$$+ 2\,\frac{\beta_1(1,2)}{V_1}\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{14}]$$
$$+ 2\,\frac{\beta_1(2,4)}{V_1}\langle N_{12}\rangle\mathrm{Var}[N_{12}]$$
$$- [\gamma_1(2) + \gamma_1(4)]\,\mathrm{Cov}[N_{12}N_{14}]$$
$$- 2\,\frac{\beta_1(2,4)}{V_1}\langle N_{12}\rangle^2 \qquad (3\text{-}52)$$

$$\frac{d}{dt}\,\mathrm{Var}[N_{13}] = 2\,\frac{\beta_1(1,3)}{V_1}\,\{\langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{13}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{13}]\}$$
$$- 2\gamma_1(3)\,\mathrm{Var}[N_{13}] + 2\,\frac{\beta_1(1,3)}{V_1}\,\langle N_{11}\rangle\,\langle N_{12}\rangle$$
$$+ \gamma_1(3)\,\langle N_{13}\rangle \qquad (3\text{-}53)$$

$$\frac{d}{dt}\,\mathrm{Cov}[N_{13}N_{14}] = 2\,\frac{\beta_1(1,3)}{V_1}\,\{N_{11}\,\mathrm{Cov}[N_{12}N_{14}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{14}]\}$$
$$+ 2\,\frac{\beta_1(2,4)}{V_1}\,\langle N_{12}\rangle\,\mathrm{Cov}[N_{12}N_{14}]$$
$$- [\gamma_1(3) + \gamma_1(4)]\,\mathrm{Cov}[N_{13}N_{14}] \qquad (3\text{-}54)$$

$$\frac{d}{dt}\,\mathrm{Var}[N_{14}] = 4\,\frac{\beta_1(2,4)}{V_1}\,\langle N_{12}\rangle\,\mathrm{Cov}[N_{12}N_{14}]$$
$$- 2\gamma_1(4)\,\mathrm{Var}[N_{14}] + \frac{\beta_1(2,4)}{V_1}\,\langle N_{12}\rangle^2$$
$$+ \gamma_1(4)\,\langle N_{14}\rangle \qquad (3\text{-}55)$$

Solving Eqs. 3-46 through 3-55, again under steady-state conditions and with the assumed parameters, yields

$\mathrm{Var}[N_{11}] = 9.405$	$\mathrm{Cov}[N_{12}N_{13}] = -1.067$
$\mathrm{Cov}[N_{11}N_{12}] = -0.643$	$\mathrm{Cov}[N_{12}N_{14}] = -0.082$
$\mathrm{Cov}[N_{11}N_{13}] = 0.366$	$\mathrm{Var}[N_{13}] = 2.855$
$\mathrm{Cov}[N_{11}N_{14}] = -0.088$	$\mathrm{Cov}[N_{13}N_{14}] = -0.143$
$\mathrm{Var}[N_{12}] = 2.532$	$\mathrm{Var}[N_{14}] = 1.210$

These values of the covariances can now be used as the initial conditions for solving Eq. 3-26 for the correlation functions which are of the form,

$$\frac{d}{d\tau} K_{1j11} = -[4 \frac{\beta_1(1,2)}{V_1} \langle N_{11} \rangle + \frac{\beta_1(1,3)}{V_1} \langle N_{12} \rangle + \gamma_1(1)]K_{1j11} - \frac{\beta_1(1,2)}{V_1} \langle N_{11} \rangle K_{1j12} \quad (3\text{-}56)$$

$$\frac{d}{d\tau} K_{1j12} = [2 \frac{\beta_1(1,2)}{V_1} \langle N_{11} \rangle - \frac{\beta_1(1,3)}{V_1} \langle N_{12} \rangle] K_{1j11} - [\frac{\beta_1(1,3)}{V_1} \langle N_{11} \rangle + 4 \frac{\beta_1(2,4)}{V_1} \langle N_{12} \rangle + \gamma_1(2)]K_{1j12} \quad (3\text{-}57)$$

$$\frac{d}{d\tau} K_{1j13} = 2 \frac{\beta_1(1,3)}{V_1} \langle N_{12} \rangle K_{1j11} + 2 \frac{\beta_1(1,3)}{V_1} \langle N_{11} \rangle K_{1j12} - \gamma_1(3)K_{1j13} \quad (3\text{-}58)$$

$$\frac{d}{d\tau} K_{1j14} = 2 \frac{\beta_1(2,4)}{V_1} \langle N_{12} \rangle K_{1j12} - \gamma_1(4)K_{1j14} \quad (3\text{-}59)$$

where

$j = 1,2,3,4$

$\langle N_{1j} \rangle$ = steady-state value

Solving these equations with the initial conditions and the assumed parameters yields the following expressions:

$$K_{1111}(\tau) = e^{-\theta_1\tau}[9.4052\cos(\phi\tau) - 2.8715\sin(\phi\tau)] \quad (3\text{-}60)$$

$$K_{1112}(\tau) = e^{-\theta_1\tau}[-0.6416\cos(\phi\tau) - 10.8546\sin(\phi\tau)] \quad (3\text{-}61)$$

$$K_{1113}(\tau) = e^{-\theta_1\tau}[1.504\cos(\phi\tau) + 7.6055\sin(\phi\tau)] - 1.1385e^{-\theta_2\tau} \quad (3\text{-}62)$$

$$K_{1114}(\tau) = e^{-\theta_1\tau}[0.8575\cos(\phi\tau) + 2.2990\sin(\phi\tau)] - 0.9457e^{-\theta_2\tau} \quad (3\text{-}63)$$

$$K_{1211}(\tau) = e^{-\theta_1\tau}[-0.6416\cos(\phi\tau) + 2.5111\sin(\phi\tau)] \quad (3\text{-}64)$$

$$K_{1212}(\tau) = e^{-\theta_1\tau}[2.5320\cos(\phi\tau) + 1.3423\sin(\phi\tau)] \quad (3\text{-}65)$$

$$K_{1213}(\tau) = e^{-\theta_1\tau}[-1.9186\cos(\phi\tau) - 0.7030\sin(\phi\tau)] + 0.8519e^{-\theta_2\tau} \quad (3\text{-}66)$$

$$K_{1214}(\tau) = e^{-\theta_1\tau}[-0.6351\cos(\phi\tau) - 0.1218\sin(\phi\tau)] + 0.5530e^{-\theta_3\tau} \quad (3\text{-}67)$$

$$K_{1311}(\tau) = e^{-\theta_1\tau}[0.3657\cos(\phi\tau) - 1.0809\sin(\phi\tau)] \quad (3\text{-}68)$$

$$K_{1312}(\tau) = e^{-\theta_1\tau}[-1.0666\cos(\phi\tau) - 0.6739\sin(\phi\tau)] \quad (3\text{-}69)$$

$$K_{1313}(\tau) = e^{-\theta_1\tau}[0.8187\cos(\phi\tau) + 0.3728\sin(\phi\tau)] + 2.0359e^{-\theta_2\tau} \quad (3\text{-}70)$$

$$K_{1314}(\tau) = e^{-\theta_1\tau}[0.2747\cos(\phi\tau) + 0.0747\sin(\phi\tau)] - 0.4173e^{-\theta_3\tau} \quad (3\text{-}71)$$

$$K_{1411}(\tau) = e^{-\theta_1\tau}[-.0882\cos(\phi\tau) - 0.0551\sin(\phi\tau)] \quad (3\text{-}72)$$

$$K_{1412}(\tau) = e^{-\theta_1\tau}[-.0821\cos(\phi\tau) - 0.4358\sin(\phi\tau)] \quad (3\text{-}73)$$

$$K_{1413}(\tau) = e^{-\theta_1\tau}[0.0502\cos(\phi\tau) - 0.0648\sin(\phi\tau)] - 0.1928e^{-\theta_2\tau} \quad (3\text{-}74)$$

$$K_{1414}(\tau) = e^{-\theta_1\tau}[0.0124\cos(\phi\tau) - 0.0228\sin(\phi\tau)] + 1.1977e^{-\theta_3\tau} \quad (3\text{-}75)$$

In these expressions,

$$\theta_1 = 15.6971,\ \theta_2 = 3.9565,\ \theta_3 = 1.2775,\ \phi = 4.4283$$

As mentioned earlier, it is often the case that the variables of interest are not the number of bubbles, but some other characteristics, e.g., the total surface area of the bubble phase in a compartment. In this case, the surface area of the bubble phase in compartment 1, S_1, can be related to the number of bubbles of size $j\Delta V$ in compartment 1, N_{1j}, through Eq. 2-29. With s_j equal to the surface area of a bubble having a volume of $j\Delta V$, Eq. 2-29 yields

$$S_1 = \sum_{i=1}^{4} s_i N_i \tag{3-76}$$

Assuming spherical bubbles, the assumed parameters yield the following values for s_i;

$$s_1 = 14.570 \text{ cm}^2$$

$$s_2 = 23.130 \text{ cm}^2$$

$$s_3 = 30.308 \text{ cm}^2$$

$$s_4 = 36.716 \text{ cm}^2$$

It then follows from Eq. 2-30 that

$$\langle S_1 \rangle = 382.431 \text{ cm}^2$$

and from Eq. 2-31 that

$$K_1(\tau) = e^{-\theta_1 \tau}[2584.679 \cos(\phi\tau) + 263.483 \sin(\phi\tau)] + 1749.778\, e^{-\theta_2 \tau} + 1113.733\, e^{-\theta_3 \tau} \tag{3-77}$$

where

$$\theta_1 = 15.6971, \ \theta_2 = 3.9565, \ \theta_3 = 1.2775, \ \phi = 4.4283$$

Setting $\tau = 0$ in Eq. 3-77 yields

$$\text{Var}[S_1] = 5448.190$$

$$\text{Sd}[S_1] = 73.812$$

This indicates that fluctuations in the total surface area of the bubble phase are relatively large since the standard deviation is 19.30 percent of the mean.

A dimensionless correlation function can be found by dividing $K_1(\tau)$ by $Var[S_1]$ yielding

$$\rho_1(\tau) = e^{-\theta_1\tau}[0.4744\cos(\phi\tau) + 0.0484\sin(\phi\tau)] + 0.3212e^{-\theta_2\tau} + 0.2044e^{-\theta_3\tau} \qquad (3\text{-}78)$$

NOTATION

A_ℓ = first jump moment.

$\tilde{A}_\ell$ = A_ℓ/Ω

$\tilde{A}_{\ell m}$ = coefficient matrix from the expansion of $\tilde{A}_\ell$.

B_k = constant appearing in the expression for the rate of coalescence in compartment k.

$\tilde{B}_{\ell m}$ = second jump moment.

C = constant used to set compartment height.

$Cov[N_{ij}N_{\ell m}]$ = $\langle N_{ij}N_{\ell m}\rangle - \langle N_{ij}\rangle\langle N_{\ell m}\rangle$

$Cov[Z_{ij}Z_{\ell m}]$ = $\langle Z_{ij}Z_{\ell m}\rangle - \langle Z_{ij}\rangle\langle Z_{\ell m}\rangle$

F_i = V_i/Ω

g = gravitational constant.

G = $(U - U_{mf})S$

h_k = height of compartment k.

$K_1(\tau)$ = correlation function of S_1.

$K_{ij\ell m}(\tau)$ = $\langle N_{ij}(0)N_{\ell m}(\tau)\rangle - \langle N_{ij}(0)\rangle\langle N_{\ell m}(\tau)\rangle$

M = number of compartments.

N_0 = number of orifices in the distributor plate.

N_{ij} = number of bubbles in compartment i with volume $j\Delta V$.

$\langle N_{ij}\rangle$ = expected value of N_{ij}.

s_j = surface area of a bubble of volume $j\Delta V$.

S = cross-sectional area of fluidized-bed.

S_1 = surface area of the bubble phase in compartment 1.

$\langle S_1\rangle$ = expected value of S_1.

$Sd[S_1]$ = $(Var[S_1])^{1/2}$

u(j) = linear velocity of a bubble of volume $j\Delta V$.

U = superficial gas velocity

U_{mf} = minimum superficial gas velocity for fluidization.

V_i = volume of compartment i.

$Var[S_1]$ = $\langle S_1^2 \rangle - \langle S_1 \rangle^2$

$W_t(\{\cdot\},\{\cdot\})$ = intensity of transition function.

$\langle Z_{\ell m} \rangle$ = expected value of the fluctuating component of $N_{\ell m}$.

Greek Letters

$\beta_i(j,k)$ = rate constant for the coalescence between bubbles of size j and size (k-j) in compartment i.

$\gamma_i(j)$ = rate at which bubble of size j leave compartment i.

$\delta^k(\cdot)$ = Kronecker delta where $\delta^k(0)=1$ and $\delta^k(x)=0$ for all $x \neq 0$.

ΔV = small unit of volume which is usually taken to be equal to the volume of the smallest bubble.

ε = volume of largest compartment divided by ΔV.

$\theta_1, \theta_2, \theta_3$ = constants appearing in correlation functions.

ξ_{ij} = size of change in random variable N_{ij}.

$\rho_1(\tau)$ = dimensionless correlation function.

ϕ = constant appearing in correlation functions.

$\phi_{\ell m}$ = $\langle N_{\ell m} \rangle / \Omega$

ϕ^* = number of bubbles of size 1 in compartment 1.

Ω = system size.

$\Omega f(j)$ = rate at which bubbles of size j enter the bed into compartment 1.

CHAPTER 4

APPLICATION OF GENERALIZED MASTER EQUATION TO COALESCENCE AND DISPERSION PHENOMENA

Suppose that a population of entities, or synonymously particles, exists and evolves through coalescence and dispersion of individual entities. Also suppose that the interactions amoung the entities in this population possess the Markov property, and information on the rates of the interactions is available. A stochastic model based on the master equation can be developed by extending and modifying the model established in the previous section for pure coalescence. For simplicity a system containing only one compartment will be considered. Extension to two or more compartments is straightforward; this can be accomplished by adding a subscript denoting the compartment number and deriving transition rates similar to those defined in the previous chapter. It will again be assumed that entities coalesce at a rate dependent on their sizes, and that a single incident of coalescence involves only two entities.

The rate of dispersion of an entity will be assumed to be dependent on its size, and furthermore, it will be assumed that a breakage event produces only two smaller entities. The latter assumption, though it appears tenuous, can be strengthened by including a variable to account for the "distance" of an entity from its formation. In this way, particles which have just been formed can have a higher breakage rate, thus accounting for the experimental observation that particles appear to form many daughter particles after breakup. The words "distance" is intentionally somewhat vague and could refer to distance in space, time, or any other factor which would increase the probability of the entity to breakup after it has been formed. Intuitively, the

breakage rate of the entity as a function of the distance from its formation should decrease to an asymptotic value as the distance increases. Thus the assumption of binary breakage can be retained, but at the expense of the addition of a new variable.

4.1 DERIVATION OF MODEL

Following the previous notation, a set of random variables is defined as

$$\{N_{ij} : i \in \{1,2,\ldots,M\},\ j \in \{1,2,3,\ldots\}\}$$

where

N_{ij} = number of entities of size $j\Delta V$ at a "distance" of $i\Delta S$ from formation

$M\Delta S$ = "distance" at which the breakage rate equals its asymptotic value

ΔV = small unit of size corresponding to the smallest possible entity

Letting A_{ij} represent an entity of size $j\Delta V$ at a "distance" of $i\Delta S$ from its formation, the interactions during coalescence can be represented by

$$\prod_{i=1}^{M}\prod_{m=1}^{M}\prod_{j=1}^{\infty}\prod_{k=1}^{\infty}\left[A_{ij} + A_{mk} \longrightarrow A_{\ell(j+k)}\right]$$

where

$$\ell = \frac{ij + mk}{j+k} \text{ with } \ell \text{ rounded to the nearest integer}$$

Note that in the summation as indicated, all interactions are counted twice, except those where both i=m and j=k. This must be taken into account when the master equation is derived. Note also that ℓ is set equal to the size weighted "distances" of the two coalescing entities. Other conventions could be used to simplify the resulting equation if desired.

Similarly, the interactions during breakage can be represented by

$$\prod_{i=1}^{M}\prod_{j=2}^{\infty}\prod_{k=1}^{[\frac{i}{2}]}\left[A_{ij} \longrightarrow A_{lk} + A_{l(j-k)}\right]$$

Scattering, i.e., the movement of entities to a greater "distance" from formation can be represented by

$$\prod_{i=1}^{M-1} [A_{ij} \longrightarrow A_{(i+1)j}]$$

In addition, the entities can be added to or leave from the compartment. These events can be represented, respectively, by

$$\prod_{j=1}^{\infty} [X_j \longrightarrow A_{Mj}]$$

and

$$\prod_{i=1}^{M} \prod_{j=1}^{\infty} [A_{ij} \longrightarrow Y_{ij}]$$

where X_j and Y_{ij} are dummy symbols representing the inlet and outlet environments, respectively. Note that the entities entering the compartment are assigned a value of $M\Delta S$ to their distance variable. This follows from an assumption that the entering entities breakup at the asymptotic breakage rate.

The set of random variables will be denoted as $\{N\}$ and the volume of the compartment as Ω. As in the previous section, the rates of transition due to the various interactions can now be derived. Let $\beta_{im}(j,k)$ be the rate constant for the coalescence between entities of size $j\Delta V$ a distance $i\Delta S$ from formation and entities of size $(k-j)\Delta V$ a distance $m\Delta S$ from formation to form entities of size $k\Delta V$ with an average distance $\ell\Delta S$ from formation. Then, the rates of transition due to coalescence can be written as

$$W_t(\{n_{ij}, n_{mk-j}, n_{\ell k}\}, \{n_{ij}-1, n_{mk-j}-1, n_{\ell k}+1\}) \qquad (4\text{-}1)$$
$$= \beta_{im}(j,k) \frac{n_{ij} n_{mk-j}}{\Omega}$$

for all i, j, m, k, ℓ: $i \neq m$ or $k \neq 2j$, $\ell = [\frac{ij+m(k-j)}{k}]$

and

$$W_t(\{n_{ij},n_{ik}\},\ \{n_{ij}-2,\ n_{ik}+1\}) = \beta_{ii}(j,k)\ \frac{n_{ij}(n_{ij}-1)}{\Omega} \qquad (4\text{-}2)$$

for all i, j, k: i=m and k=2j

In these expressions, all random variables which remain constant during a transition have been omitted from the notation for {n} for simplicity.

Let $\alpha_i(j,k)$ be the rate at which entities of size $j\Delta V$, having a "distance' $i\Delta S$ from formation, break apart to form entities of size $k\Delta V$ and $(j-k)\Delta V$. Then the rates of transition due to breakage can be written as

$$W_t(\{n_{ij},\ n_{lk},\ n_{l(j-k)}\},\ \{n_{ij}-1,\ n_{lk}+1,\ n_{l(j-k)}+1\}) \qquad (4\text{-}3)$$

$$= \alpha_i(j,k)n_{ij}$$

for all i,j,k: j≠2k

$$W_t(\{n_{ij},n_{lk}\},\ \{n_{ij}-1,\ n_{ik}+2\}) = \alpha_i(j,k)n_{ij} \qquad (4\text{-}4)$$

for all i,j,k: j=2k

Letting $\kappa_i(j)$ be the rate at which entities of size $j\Delta V$ and a "distance" $i\Delta S$ from formation move to a "distance" $(i+1)\Delta S$, the rates of transition for scattering can be written as

$$W(\{n_{ij},n_{(i+1)j}\},\ \{n_{ij}-1,\ n_{(i+1)j}+1\}) = \kappa_i(j)n_{ij} \qquad (4\text{-}5)$$

for all i,j: i≠m

Similarly, letting $\Omega f(j)$ be the rate at which entities of size $j\Delta V$ are added to the compartment from the environment, the rates of transition for entrance of entities can be written as

$$W(\{n_{ij}\}, \{n_{ij}+1\}) = \Omega f(j) \quad \text{for all } j \tag{4-6}$$

Finally, let $\gamma_i(j)$ be the rate at which entities of size $j\Delta V$ and "distance" $i\Delta S$ from formation exit from the compartment. Then the rates of transition due to exiting can be written as

$$W(\{n_{ij}\}, \{n_{ij}-1\}) = \gamma_i(j)n_{ij} \qquad \text{for all } i,j \tag{4-7}$$

With the rates of transition known, the master equation is specified, and the System Size Expansion can be applied to solve it for the means and correlation functions of the random variables. The first step in this approach is to rewrite the equations for the rates of transition, Eqs. (4-1) through (4-7), in terms of $\{n\}$ and $\{\xi\}$, respectively, as follows:

$$W_t(\{n_{ij}, n_{m(k-j)}, n_{\ell k}\}; \{-1, -1, 1\}) = \beta_{im}(j,h) \frac{n_{ij} n_{mj-k}}{\Omega} \tag{4-8}$$

$$\text{for all } i,j,m,k,\ell: \; i \neq m \text{ or } k \neq 2j, \; \ell = \left[\frac{ij + m(k-j)}{k}\right]$$

$$W_t(\{n_{ij}, n_{ik}\}; \{-2, 1\}) = \beta_{ii}(j,k) \frac{n_{ij}(n_{ij}-1)}{\Omega} \tag{4-9}$$

$$\text{for all } i,j,k: \; i=m \text{ and } k=2j$$

$$W_t(\{n_{ij}, n_{lk}, n_{l(j-k)}\}; \{-1, 1, 1\}) = \alpha_i(j,k)n_{ij} \tag{4-10}$$

$$\text{for all } i,j,k: \quad j \neq 2k$$

$$W_t(\{n_{ij}, n_{lk}\}; \{-1, 2\}) = \alpha_i(j,k)n_{ij} \tag{4-11}$$

$$\text{for all } i,j,k: \quad j=2k$$

$$W_t(\{n_{ij}, n_{(i+1)j}\};\ \{-1,\ 1\}) = \kappa_i(j)n_{ij} \qquad (4\text{-}12)$$

for all i,j: $i \neq M$

$$W_t(\{n_{Mj}\};\ \{1\}) = \Omega f(j)n_{ij} \quad \text{for all } j \qquad (4\text{-}13)$$

$$W_t(\{n_{ij}\};\ \{-1\}) = \gamma_i(j)n_{ij} \quad \text{for all } i,j \qquad (4\text{-}14)$$

where, as in the previous chapter, all null elements in the set $\{\xi\}$ are omitted, and the remaining elements correspond to those in $\{n\}$.

As previously, the next step is to calculate the jump moments, A_h and B_{hn}, after arranging to change the double subscript to a single one, denoted as h; for convenience, it is defined as

$$h = j+\varepsilon(i-1) \qquad (4\text{-}15)$$

where

j = subscript denoting the size of an entity

i = subscript denoting the "distance" from formation

$$\varepsilon = \frac{\text{size of the largest possible entity}}{\Delta V}$$

The variable n_{ij} now appears as

$$n_{j+\varepsilon(i-1)}$$

Introducing this notation into the expressions for the rates of transition gives rise to

$$W_t(\{n_{j+\varepsilon(i-1)}, n_{k-j+\varepsilon(m-1)}, n_{k+\varepsilon(\ell-1)}\};\{-1,-1,1\})$$

$$= \beta_{im}(j,k)\frac{n_{j+\varepsilon(i-1)}n_{k-j+\varepsilon(m-1)}}{\Omega} \qquad (4\text{-}16)$$

for all i,j,m,k,ℓ: $i\neq m$ or $k\neq 2j$, $\ell=[\frac{ij+m(k-j)}{k}]$

$$W_t(\{n_{j+\varepsilon(i-1)}, n_{k+\varepsilon(i-1)}\};\{-2,1\}) = \beta_m(j,k)\frac{n_{j+\varepsilon(i-1)}(n_{j+\varepsilon(i-1)}-1)}{\Omega} \qquad (4\text{-}17)$$

for all i,j,k: i=m and k=2j

$$W_t(\{n_{j+\varepsilon(i-1)}, n_k, n_{j-k}\};\{-1,1,1\}) = \alpha_i(j,k)n_{j+\varepsilon(i-1)} \qquad (4\text{-}18)$$

for all i,j,k: $j\neq 2k$

$$W_t(\{n_{j+\varepsilon(i-1)}, n_k\};\{-1,2\}) = \alpha_i(j,k)n_{j+\varepsilon(i-1)} \qquad (4\text{-}19)$$

for all i,j,k: j=2k

$$W_t(\{n_{j+\varepsilon(i-1)}, n_{j+\varepsilon i}\};\{-1,1\}) = \kappa_i(j)n_{j+\varepsilon(i-1)} \qquad (4\text{-}20)$$

for all i,j: $i\neq m$

$$W_t(\{n_{j+\varepsilon(M-1)}\};\{1\}) = \Omega f(j) \qquad \text{for all } j \qquad (4\text{-}21)$$

$$W_t(\{n_{j+\varepsilon(i-1)}\};\{-1\}) = \gamma_i(j)n_{j+\varepsilon(i-1)} \qquad \text{for all } i,j \qquad (4\text{-}22)$$

Expressions for A_h and B_{hn} are now derived, respectively, as follows:

$$A_h = \sum_{\ell}\sum_{i}\sum_{m}\sum_{j}\sum_{k}\frac{1}{2}[-\delta^k(h-k+j-\varepsilon i+\varepsilon) - \delta^k(h-j-\varepsilon i+\varepsilon)$$

$$+ \delta^k(h-k-\varepsilon\ell+\varepsilon)][1-\delta^k(i-m)\delta^k(k-2j)]$$

$$\cdot \delta^k(\ell-[(ij+m(k-j))/k])\beta_{im}(j,k)\frac{n_{j+\varepsilon(i-1)}n_{k-j+\varepsilon(m-1)}}{\Omega}$$

$$+ \sum_{i}\sum_{j}[-2\delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-2j-\varepsilon i+\varepsilon)]\beta_{ii}(j,2j)\frac{n_{j+\varepsilon(i-1)}(n_{j+\varepsilon(i-1)}-1)}{\Omega}$$

$$+ \sum_{i}\sum_{j}\sum_{k}\frac{1}{2}[-\delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-k) + \delta^k(h-j+k)][1-\delta^k(j-2k)]\alpha_i(j,k)n_{j+\varepsilon(i-1)}$$

$$+ \sum_{i}\sum_{j}[-\delta^k(h-2j-\varepsilon i+\varepsilon) + 2\delta^k(h-j)]\alpha_i(2j,j)n_{2j+\varepsilon(i-1)}$$

$$+ \sum_{i}\sum_{j}[-\delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-j-\varepsilon i)][1-\delta^k(i-M)]\kappa_i(j)n_{j+\varepsilon(i-1)}$$

$$+ \sum_{j}\delta^k(h-j-\varepsilon M+\varepsilon)\Omega f(j)$$

$$- \sum_{i}\sum_{j}\delta^k(h-j-\varepsilon i+\varepsilon)\gamma_i(j)n_{j+\varepsilon(i-1)} \qquad (4\text{-}23)$$

$$
\begin{aligned}
\beta_{hn} = {} & \sum_{\ell}^{M}\sum_{i}^{M}\sum_{m}^{M}\sum_{j}^{\varepsilon}\sum_{k}^{\varepsilon}\frac{1}{2}[-\delta^k(h-k+j-\varepsilon i+\varepsilon) - \delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-k-\varepsilon\ell+\varepsilon)][-\delta^k(n-k+j-\varepsilon i+\varepsilon) \\
& - \delta^k(n-j-\varepsilon i+\varepsilon) + \delta^k(n-k-\varepsilon\ell+\varepsilon)][1-\delta^k(i-m)\delta^k(k-2j)] \\
& \cdot \delta^k(\ell-1(ij+m(k-j))/k])\,\beta_{im}(j,k)\frac{n_{j+\varepsilon(i-1)}n_{k-j+\varepsilon(m-1)}}{\Omega} \\
& + \sum_{i}^{M}\sum_{j}^{\varepsilon}[-2\delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-2j-\varepsilon i+\varepsilon)][-2\delta^k(n-j-\varepsilon i+\varepsilon) \\
& + \delta^k(n-2j-\varepsilon i+\varepsilon)]\beta_{ii}(j,2j)\frac{n_{j+\varepsilon(i-1)}(n_{j+\varepsilon(i-1)}-1)}{\Omega} \\
& + \sum_{i}^{M}\sum_{j}^{\varepsilon}\sum_{k}^{\varepsilon}\frac{1}{2}[-\delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-k) + \delta^k(h-j+k)][-\delta^k(n-j-\varepsilon i+\varepsilon) \\
& + \delta^k(n-k) + \delta^k(n-j+k)][1-\delta^k(j-2k)]\alpha_i(j,k)n_{j+\varepsilon(i-1)} \\
& + \sum_{i}^{M}\sum_{k}^{\varepsilon}[-\delta^k(h-2k-\varepsilon i+\varepsilon) + 2\delta^k(h-k)][-\delta^k(n-2k-\varepsilon i+\varepsilon) + 2\delta^h(n-k)] \\
& \cdot \alpha_i(2k,k)n_{2k+\varepsilon(i-1)} \\
& + \sum_{i}^{M}\sum_{j}^{\varepsilon}[-\delta^k(h-j-\varepsilon i+\varepsilon) + \delta^k(h-j-\varepsilon i)][-\delta^k(n-j-\varepsilon i+\varepsilon) + \delta^k(n-j-\varepsilon i)] \\
& \cdot [1-\delta^k(i-m)]\kappa_i(j)n_{j+\varepsilon(i-1)} \\
& + \sum_{j}^{\varepsilon}\delta^k(h-j-\varepsilon M+\varepsilon)\delta^k(h-n)\Omega r(j) \\
& + \sum_{i}^{M}\sum_{j}^{\varepsilon}\delta^k(h-j-\varepsilon i+\varepsilon)\delta^k(h-n)\gamma_i(j)n_{j+\varepsilon(i-1)}
\end{aligned}
\tag{4-24}
$$

The first of these expressions together with Eq. (2-18) gives

$$\frac{d\phi_h}{dt} = \sum_{i}^{M} \sum_{j}^{\varepsilon} \{ \sum_{\ell}^{M} \sum_{m}^{M} \sum_{k}^{\varepsilon} \frac{1}{2} [-\delta^{K}(h-k+j-\varepsilon i+\varepsilon) - \delta^{K}(h-j-\varepsilon i+\varepsilon) + \delta^{h}(h-k-\varepsilon\ell+\varepsilon)]$$

$$\cdot [1-\delta^{k}(i-m)\delta^{k}(k-2j)]\delta^{k}(\ell-[(ij+m(k-j))/k])$$

$$\beta_{im}(j,k)\phi_{j+\varepsilon(i-1)}\phi_{k-j+\varepsilon(m-1)}$$

$$+ [-2\delta^{k}(h-j+\varepsilon i+\varepsilon) + \delta^{k}(h-2j-\varepsilon i+\varepsilon)]\beta_{ii}(j,2j)\phi^{2}_{j+\varepsilon(i-1)}$$

$$+ \sum_{k}^{\varepsilon} \frac{1}{2} [-\delta^{k}(h-j-\varepsilon i+\varepsilon) + \delta^{k}(h-K) + \delta^{k}(h-j+k)][1-\delta^{k}(j-2k)]\alpha_{i}(j,k)\phi_{j+\varepsilon(i-1)}$$

$$+ [-\delta^{k}(h-2j-\varepsilon i+\varepsilon) + 2\delta^{k}(h-j)]\alpha_{i}(2j,j)\phi_{2j+\varepsilon(i-1)}$$

$$+ [-\delta^{k}(h-j-\varepsilon i+\varepsilon) + \delta^{k}(h-j-\varepsilon i)][1-\delta^{k}(i-M)]\kappa_{i}(j)\phi_{j+\varepsilon(i-1)}$$

$$- \delta^{k}(h-j-\varepsilon i+\varepsilon)\gamma_{i}(j)\phi_{j+\varepsilon(i-1)}\}$$

$$+ \sum_{j}^{\varepsilon} \delta^{k}(h-j-\varepsilon M+\varepsilon)\Omega f(j) \qquad (2\text{-}25)$$

Simplifying this expression by returning to double subscripts yields

$$\frac{d\phi_{\ell m}}{dt} = -\frac{1}{2}\sum_{i}^{M}\sum_{j}^{\varepsilon}\beta_{\ell i}(m,m+j)[\phi_{\ell j}\phi_{im}+\phi_{\ell m}\phi_{im}] - \beta_{\ell\ell}(m,2m)\phi_{\ell m}^{2}$$

$$+\frac{1}{2}\sum_{i}^{M}\sum_{k}^{M}\sum_{j}^{m-1}[1+\delta^{k}(i-k)\delta^{k}(m-2j)]\delta^{k}(\ell-[(ij+k(m-j))/m])\beta_{ik}(j,m)\phi_{ij}\phi_{km-j}$$

$$-\sum_{k}^{[\frac{m}{2}]}\alpha_{\ell}(m,k)\phi_{\ell m}+\sum_{i}^{M}\sum_{j}^{\varepsilon}\delta^{k}(\ell-1)[1+\delta^{k}(j-2m)]\alpha_{i}(j,m)\phi_{ij}$$

$$-[1-\delta^{k}(\ell-M)]\kappa_{\ell}(m)\phi_{\ell m}+[1-\delta^{k}(\ell-1)]\kappa_{\ell-1}(m)\phi_{\ell-1m}$$

$$-\gamma_{\ell}(m)\phi_{\ell m}+\delta^{k}(\ell-M)f(m) \qquad (4\text{-}26)$$

where

$$\delta^{k}(\ell-[(ij+k(m-j))/m]) = 1 \quad \text{if} \quad \ell = [(ij+k(m-j))/m]$$

$[(ij+k(m-j))/m]$ = $(ij+k(m-j)/m)$ rounded to the nearest integer

The moments of the fluctuating component can be found from the following expression for $\tilde{A}_{hn}$;

$$\tilde{A}_{hn} = \frac{1}{2}\sum_{\ell}^{M}\sum_{i}^{M}\sum_{m}^{M}\sum_{j}^{\varepsilon}\sum_{k}^{\varepsilon}[-\delta^{k}(h-k+j-\varepsilon i+\varepsilon) - \delta^{k}(h-j-\varepsilon i+\varepsilon) + \delta^{k}(h-k-\varepsilon\ell+\varepsilon)][1-\delta^{k}(i-m)\delta^{k}(k-2j)]$$

$$\cdot\delta^{k}(\ell-[(ij+m(k-j))/k])\beta_{im}(j,k)[\phi_{j+\varepsilon(i-1)}\delta^{k}(n-k+j-\varepsilon m+\varepsilon)$$

$$+\phi_{k-j+\varepsilon(m-1)}\delta^{k}(n-j-\varepsilon i+\varepsilon)]$$

$$+ 2\sum_{i}^{M}\sum_{j}^{\varepsilon}[-2\delta^{k}(h-j-\varepsilon i+\varepsilon) + \delta^{k}(h-2j-\varepsilon i+\varepsilon)]\beta_{ii}(j,2j)\phi_{j+\varepsilon(i-1)}\delta^{k}(n-j-\varepsilon i+\varepsilon)$$

$$+ \frac{1}{2}\sum_{i}^{M}\sum_{j}^{\varepsilon}\sum_{k}^{\varepsilon}[-\delta^{k}(h-j-\varepsilon i+\varepsilon) + \delta^{k}(h-k) + \delta^{k}(h-j+k][1-\delta^{k}(j-2k)]\alpha_{i}(j,k)\delta^{k}(n-j-\varepsilon i+\varepsilon)$$

$$+ \sum_{i}^{M}\sum_{j}^{\varepsilon}[-\delta^{k}(h-2j-\varepsilon i+\varepsilon) + 2\delta^{k}(h-j)]\ \alpha_{i}(2j,j)\delta^{k}(n-2j-\varepsilon i+\varepsilon)$$

$$+ \sum_{i}^{M}\sum_{j}^{\varepsilon}[-\delta^{k}(h-j-\varepsilon i+\varepsilon) + \delta^{k}(h-j-\varepsilon i)][1-\delta^{k}(i-M)]\kappa_{i}(j)\delta^{k}(n-j-\varepsilon i+\varepsilon)$$

$$+ \sum_{i}^{M}\sum_{j}^{\varepsilon}\delta^{k}(h-j-\varepsilon i+\varepsilon)\ \gamma_{i}(j)\ \delta^{k}(n-j-\varepsilon i+\varepsilon) \qquad (4\text{-}27)$$

Changing to double subscripts, this expression in conjunction with Eq. 2-20 yields

$$\frac{d\langle Z_{\ell m}\rangle}{dt} = -\frac{1}{2}\sum_{i}^{M}\sum_{j}^{\varepsilon-m}\beta_{\ell i}(m,m+j)\ [\phi_{\ell j}\langle Z_{im}\rangle + \langle Z_{\ell j}\rangle\phi_{im} + \phi_{\ell m}\langle Z_{ij}\rangle + \phi_{\ell m}\langle Z_{ij}\rangle]$$

$$- 2\ \beta_{\ell\ell}(m,2m)\ \ \phi_{\ell m}\langle Z_{\ell m}\rangle$$

$$+ \frac{1}{2}\sum_{i}^{M}\sum_{k}^{M}\sum_{j}^{m-1}[1+\delta^{k}(i-k)\delta^{k}(m-2j)]\delta^{k}(1-[(ij+k(m-j))/m])$$

$$\cdot\beta_{ik}(j,m)\ [\phi_{ij}\langle Z_{km-j}\rangle + \langle Z_{ij}\rangle\phi_{km-j}]$$

$$- \sum_{k}^{[\frac{m}{2}]}\alpha_{\ell}(m,k)\langle Z_{\ell m}\rangle + \sum_{i}^{M}\sum_{j}^{\varepsilon}\delta^{k}(\ell-1)[1+\delta^{k}(j-2m)]\alpha_{i}(j,m)\langle Z_{ij}\rangle$$

$$- [1-\delta^{k}(\ell-M)]\kappa_{\ell}(m)\langle Z_{\ell m}\rangle + [1-\delta^{k}(\ell-1)]\kappa_{\ell-1}(m)\langle Z_{\ell-1m}\rangle$$

$$- \gamma_{\ell}(m)\ \langle Z_{\ell m}\rangle \qquad (4\text{-}28)$$

Expressions for the rate of change of $\mathcal{C}ov[Z_{\ell m} Z_{pq}]$ can be found from Eq. 4-27 for $\tilde{A}_{hn}$, Eq. 4-24 for $\tilde{B}_{hn}$ and Eq. 2-21 after changing to double subscripts; this yields

$$\frac{d}{dt} Cov[Z_{\ell m} Z_{pq}] = -\frac{1}{2}\sum_{i}^{M}\sum_{j}^{\varepsilon-m} \beta_{\ell i}(m,m+j)\{\phi_{\ell j} \mathcal{C}ov[Z_{im} Z_{pq}] + \phi_{im} Cov[Z_{\ell j} Z_{pq}]$$

$$+ \phi_{\ell m} Cov[Z_{ij} Z_{pq}] + \phi_{ij} Cov[Z_{\ell m} Z_{pq}]\}$$

$$-\frac{1}{2}\sum_{i}^{M}\sum_{j}^{\varepsilon-q} \beta_{pi}(q,q+j)\{\phi_{pj} Cov[Z_{\ell m} Z_{iq}] + \phi_{iq} Cov[Z_{\ell m} Z_{pj}]$$

$$+ \phi_{pq} Cov[Z_{\ell m} Z_{ij}] + \phi_{ij} Cov[Z_{\ell m} Z_{pq}]\}$$

$$- 2[\beta_{\ell\ell}(m,2m)\,\phi_{\ell m} + \beta_{pp}(q,2q)\,\phi_{pq}] Cov[Z_{\ell m} Z_{pq}]$$

$$+\frac{1}{2}\sum_{i}^{M}\sum_{k}^{M}\sum_{j}^{m-1}[1+\delta^{k}(i-k)\delta^{k}(m-2j)]\delta^{k}(\ell-[(ij+k(m-j))/m])$$

$$\cdot \beta_{ik}(j,m)\{\phi_{ij} Cov[Z_{km-j} Z_{pq}] + \phi_{km-j} Cov[Z_{ij} Z_{pq}]\}$$

$$+\frac{1}{2}\sum_{i}^{M}\sum_{k}^{M}\sum_{j}^{q-1}[1+\delta^{k}(i-k)\delta^{k}(q-2j)]\delta^{k}(p-[(ij\pm k(q-j))/q])$$

$$\cdot \beta_{ik}(j,q)\{\phi_{ij} Cov[Z_{\ell m} Z_{kq-j}] + \phi_{km-j} Cov[Z_{\ell m} Z_{ij}]\}$$

$$-\left[\sum_{k}^{[\frac{m}{2}]} \alpha_{\ell}(m,k) + \sum_{k}^{[\frac{q}{2}]} \alpha_{p}(q,k)\right] Cov[Z_{\ell m} Z_{pq}]$$

$$+ \sum_{i}^{M} \sum_{j}^{\varepsilon} \delta^{k}(\ell-1)[1+\delta^{k}(j-2m)]\alpha_{i}(j,m)\mathrm{Cov}[Z_{ij}Z_{pq}]$$

$$+ \sum_{i}^{M} \sum_{j}^{\varepsilon} \delta^{k}(p-1)[1+\delta^{k}(j-2q)]\alpha_{i}(j,q)\mathrm{Cov}[Z_{\ell m}Z_{ij}]$$

$$- [1-\delta^{k}(\ell-M)]\kappa_{\ell}(m)\,\mathrm{Cov}[Z_{\ell m}Z_{pq}]$$

$$- [1-\delta^{k}(p-M)]\kappa_{p}(q)\mathrm{Cov}[Z_{\ell m}Z_{pq}]$$

$$+ [1-\delta^{k}(\ell-1)]\kappa_{\ell-1}(m)\,\mathrm{Cov}[Z_{\ell-1m}Z_{pq}]$$

$$+ [1-\delta^{k}(p-1)]\kappa_{p-1}(q)\mathrm{Cov}[Z_{\ell m}Z_{p-1q}]$$

$$- [\gamma_{\ell}(m) + \gamma_{p}(q)]\,\mathrm{Cov}\,[Z_{\ell m}Z_{pq}]$$

$$+ \frac{1}{2}\,\delta^{k}(\ell-p)\delta^{k}(m-q)\sum_{i}^{M\varepsilon-m}\sum_{j}[1+\delta^{k}(\ell-i)\delta^{k}(m-j)]\beta_{\ell i}(m,m+j)$$

$$\cdot[\phi_{\ell q}\phi_{im} + \phi_{\ell m}\phi_{ij}]$$

$$+ \frac{1}{2}\,\delta^{k}(\ell-p)\sum_{i}^{M}[1+\delta^{k}(\ell-i)\delta^{k}(m-q)]\beta_{\ell i}(q,m+q)$$

$$\cdot[\phi_{\ell m}\phi_{im} + \phi_{\ell m}\phi_{iq}]$$

$$- \frac{1}{2}\sum_{i}^{M}[1+\delta^{k}(i-\ell)\delta^{k}(2m-q)]\beta_{i\ell}(m,q)[\delta^{k}(p-[(\ell q-\ell m+im)/q])$$

$$\cdot\,\phi_{\ell q-m}\phi_{im} + \delta^{k}(p-[(\ell m+iq-im)/q])\phi_{\ell m}\phi_{iq-m}]$$

$$
\begin{aligned}
&- \frac{1}{2}\sum_{i}^{M}[1+\delta^k(p-i)\delta^k(m-2q)]\beta_{pi}(q,m)i\delta^k(\ell-[(pm-pq+iq)/m])\\
&\qquad\cdot\phi_{pm-q}\phi_{iq} + \delta^k(\ell-[(pq+im-iq)/m])\phi_{pq}\phi_{im-q}]\\
&+ \frac{1}{2}\delta^k(m-q)\delta^k(\ell-p)\sum_{i}^{M}\sum_{k}^{M}\sum_{j}^{\varepsilon}[1+\delta^k(k-i)\delta^k(m-2j)]\\
&\qquad\cdot\delta^k(\ell-[kj+im-ij/m])\beta_{ki}(j,m)\phi_{kj}\phi_{im-j}\\
&+\delta^k(p-\ell)\delta^k(m-q)\sum_{k}^{[\frac{m}{2}]}\alpha_\ell(m,k)\phi_{\ell m}\\
&- \delta^k(p-1)[1+\delta^k(m-2q)]\alpha_\ell(m,k)\phi_{\ell m}\\
&- \delta^k(\ell-1)[1+\delta^k(q-2m)]\alpha_p(q,m)\phi_{pq}\\
&+ \delta^k(\ell-1)\delta^k(q-m)\delta^k(\ell-p)\sum_{i}^{M}\sum_{k}^{\varepsilon-m}[1+\delta^k(k-m)]\alpha_i(m+k,m)\phi_{im+k}\\
&+ \delta^k(\ell-1)\delta^k(\ell-p)\sum_{i}^{M}[1+\delta^k(q-m)]\alpha_i(q+m,q)\phi_{iq+m}\\
&+ \delta^k(q-m)\{\delta^k(p-\ell)[1-\delta^k(\ell-M)]\kappa_\ell(m)\phi_{\ell m}\\
&\qquad\div\delta^k(p-\ell)[1-\delta^k(p-M+1)]\kappa_{p+1}(m)\phi_{p+1m}\\
&\qquad-\delta^k(p-\ell+1)[1-\delta^k(\ell-M)]\kappa_\ell(m)\phi_{\ell m}\\
&\qquad+\delta^k(\ell-p+1)[1-\delta^k(p-M)]\kappa_p(m)\phi_{pm}\}\\
&+\delta^k(p-\ell)\delta^k(m-q)\{\delta^k(\ell-M)f(m)+\gamma_\ell(m)\phi_{\ell m}\}
\end{aligned}
\tag{4-29}
$$

Finally, Eq. 4-28 in conjunction with Eq. 2-28 yields the following expressions for the correlation functions of the random variables {N};

$$\frac{d}{d\tau} K_{pq\ell m}(\tau) = -\frac{1}{2}\sum_{i}^{M}\sum_{j}^{\varepsilon-m,} \beta_{\ell i}(m,m+j)\left[\phi^{s}_{\ell j}K_{pqim} + \phi^{s}_{im}K_{pq\ell j} + \phi^{s}_{\ell m}K_{pqij} + \phi^{s}_{ij}K_{pq\ell m}\right]$$

$$- 2\beta_{\ell\ell}(m,2m)\ \phi^{s}_{\ell m}K_{pq\ell m}$$

$$+ \frac{1}{2}\sum_{i}^{M}\sum_{k}^{M}\sum_{j}^{m-1}\left[1+\delta^{k}(i-k)\delta^{k}(m-2j)\right]\delta^{k}(\ell-[(ij+k(m-j)/m])$$

$$\cdot\beta_{ik}(j,m)\left[\phi^{s}_{ij}K_{pqkm-j} + \phi^{s}_{km-j}K_{pqij}\right]$$

$$- \sum_{k}^{[\frac{m}{2}]}\alpha_{\ell}(m,k)K_{pq\ell m}$$

$$+ \sum_{i}^{M}\sum_{j}^{\varepsilon}\delta^{k}(\ell-1)\left[1+\delta^{k}(j-2m)\right]\alpha_{i}(j,m)K_{pqij}$$

$$-\left[1-\delta^{k}(\ell-M)\right]\kappa_{\ell}(m)K_{pq\ell m}$$

$$+\left[1-\delta^{k}(\ell-1)\right]\kappa_{\ell-1}(m)K_{pq\ell-1m}$$

$$-\gamma_{\ell}(m)K_{pq\ell m} \qquad (4\text{-}30)$$

with the initial condition

$$K_{pq\ell m}(0) = \mathrm{Cov}[N_{\ell m}N_{pq}]$$

where

$\phi^{s}_{\ell m}$ = steady-state value of $\phi_{\ell m}$

$Cov[N_{\ell m} N_{pq}]$ = steady-state covariances

Equations 4-26, 4-29, and 4-30 respectively, for the means, the covariances and the correlation functions thus provide a viable description of the stochastic evolution of the coalescence-dispersion system. It is however, possible, to consider the variables denoting the size of entities as continuous. This can be effected by redefining the functions $\alpha(\cdot)$, $\beta(\cdot,\cdot)$, $f(\cdot)$, $\gamma(\cdot)$ and $\kappa(\cdot)$ as continuous functions. The continuous size variable will be denoted as v or v'. Transformation to continuous functions proceeds as follows:

$$\beta_{\ell i}(m,m+j) \longrightarrow \beta_{\ell i}(v,v+v')dv'$$

$$\alpha_{\ell}(m,k) \longrightarrow \alpha_{\ell}(v,v')dv'$$

$$\gamma_{\ell}(m) \longrightarrow \gamma_{\ell}(v)$$

$$\kappa_{\ell}(m) \longrightarrow \kappa_{\ell}(v)$$

$$f(m) \longrightarrow f(v)$$

Equation 4-26 can now be written in continuous form as

$$\frac{\partial \phi_{\ell}(v)}{\partial t} = -\frac{1}{2}\sum_{i}^{M}\int_{0}^{v_{max}-v} \beta_{\ell i}(v,v+v')[\phi_{\ell}(v')\phi_{i}(v) + \phi_{\ell}(v)\phi_{i}(v')]dv'$$

$$+ \frac{1}{2}\sum_{i}^{M}\int_{0}^{v} \beta_{ik*}(v',v)\phi_{i}(v')\phi_{k*}(v-v')dv'$$

$$
\begin{aligned}
&- \int_0^{\frac{v}{2}} \alpha_\ell(v,v')\phi_\ell(v)dv' \\
&+ \sum_i^M \delta^{k^*(\ell-1)} \int_v^{v_{max}} \alpha_i(v',v)\phi_i(v')dv' \\
&- [1-\delta^{k^*(\ell-M)}]\kappa_\ell(v)\phi_\ell(v) \\
&+ [1-\delta^{k^*(\ell-1)}]\kappa_{\ell-1}(v)\phi_{\ell-1}(v) \\
&- \gamma_\ell(v)\phi_\ell(v) \\
&+ \delta^{k^*(\ell-M)}f(v)
\end{aligned}
\qquad (4\text{-}31)
$$

where

$$k^* = \left[\frac{\ell v - iv'}{v - v'}\right] \text{ with } k^* \text{ rounded to the nearest integer.}$$

Note that several terms, e.g.,

$$\beta_{\ell\ell}(m,2m)\phi_{\ell m}^2$$

which are in Eq. 4-26, no longer appear in Eq. 4-31 in continuous form. This results from the limiting process where $\Delta V \to 0$. In such a limit, the expression $\beta_{\ell\ell}(m,2m)$ describes the transition between two points, m and 2m, and since the area under a point approaches zero as $\Delta V \to 0$, this term offers no contribution. This always occurs in transforming a discrete variable to a continuous one whenever a point discontinuity exists in an otherwise continuous variable. This indicates that caution must be taken when describing a discrete system

by a continuous function. It is not possible to transform the continuous function back to the discrete description unless the behavior at every discontinuity is known.

Equation 4-29 can now be written in continuous form as

$$\frac{\partial}{\partial t}\,\mathrm{Cov}[Z_\ell(v)Z_p(v^*)] = -\frac{1}{2}\sum_i^M \int_0^{v_{max}-v} \beta_{\ell i}(v,v+v')\{\phi_\ell(v')\mathrm{Cov}[Z_1(v')Z_p(v^*)]$$

$$+ \phi_i(v)\mathrm{Cov}[Z_\ell(v')Z_p(v^*)] + \phi_\ell(v)\mathrm{Cov}[Z_i(v')Z_p(v^*)]$$

$$+ \phi_i(v')\mathrm{Cov}[Z_\ell(v')Z_p(v^*)]\}dv'$$

$$-\frac{1}{2}\sum_i^M \int_0^{v_{max}-v^*} \beta_{pi}(v^*,v^*+v')\{\phi_p(v')\mathrm{Cov}[Z_\ell(v)Z_i(v^*)]$$

$$+ \phi_i(v^*)\mathrm{Cov}[Z_\ell(v)Z_p(v')] + \phi_p(v^*)\mathrm{Cov}[Z_\ell(v)Z_i(v')]$$

$$+ \phi_i(v')\mathrm{Cov}[Z_\ell(v)Z_p(v^*)]\}dv'$$

$$+\frac{1}{2}\sum_i^M \int_0^{v} \beta_{ik^*}(v',v)\{\phi_i(v')\mathrm{Cov}[Z_{k^*}(v-v')Z_p(v^*)]$$

$$+ \phi_{k^*}(v-v')\mathrm{Cov}[Z_i(v')Z_p(v^*)]\}dv'$$

$$+ \frac{1}{2}\sum_{i}^{M} \int_{0}^{v^*} \beta_{ik'}(v',v^*)\{\phi_i(v')\mathrm{Cov}[Z_\ell(v)Z_{k'}(v^*-v')]$$

$$+ \phi_{k'}(v^*-v')\mathrm{Cov}[Z_\ell(v)Z_i(v')]\}dv'$$

$$- [\int_{0}^{\frac{v}{2}} \alpha_\ell(v,v')dv' + \int_{0}^{\frac{v^*}{2}} \alpha_p(v^*,v')dv']\mathrm{Cov}[Z_\ell(v)Z_p(v^*)]$$

$$+ \sum_{i}^{M}\delta^k(\ell-1) \int_{v}^{v_{max}} \alpha_i(v',v)\mathrm{Cov}[Z_i(v')Z_p(v^*)]dv'$$

$$+ \sum_{i}^{M}\delta^k(p-1) \int_{v^*}^{v_{max}} \alpha_i(v',v^*)\mathrm{Cov}[Z_\ell(v)Z_i(v')]dv'$$

$$- [1-\delta^k(\ell-M)]\kappa_\ell(v)\ \mathrm{Cov}[Z_\ell(v)Z_p(v^*)]$$

$$- [1-\delta^k(p-M)]\kappa_p(v^*)\mathrm{Cov}[Z_\ell(v)Z_p(v^*)]$$

$$+ [1-\delta^k(\ell-1)]\kappa_{\ell-1}(v)\mathrm{Cov}[Z_{\ell-1}(v)Z_p(v^*)]$$

$$+ [1-\delta^k(p-1)]\kappa_{p-1}(v^*)\mathrm{Cov}[Z_\ell(v)Z_{p-1}(v^*)]$$

$$- [\gamma_\ell(v) + \gamma_p(v^*)]\mathrm{Cov}[Z_\ell(v)Z_p(v^*)]$$

$$+ \frac{1}{2}\delta^k(\ell-1)\delta^k(v-v^*)\sum_{i}^{M} \int_{0}^{v_{max}-v} \beta_{\ell i}(v,v+v')[\phi_\ell(v')\phi_i(v)$$

$$+ \phi_\ell(v)\phi_i(v')]dv'$$

$$+ \frac{1}{2}\delta^k(\ell-p)\delta^k(v-v^*)\sum_{i}^{M}\int_{0}^{v}\beta_{\ell i}(v',v)\phi_\ell(v')\phi_i(v-v')dv'$$

$$+ \delta^k(\ell-p)\delta^k(v-v^*)\int_{0}^{\frac{v}{2}}\alpha_\ell(v,v')\phi_\ell(v)dv'$$

$$+ \delta^k(\ell-1)\delta^k(v-v^*)\delta^k(\ell-p)\sum_{i}^{M}\int_{0}^{v_{max}-v}\alpha_i(v+v',v)\phi_i(v+v')dv'$$

$$+ \delta^k(v-v^*)\{\delta^k(p-\ell)[1-\delta^k(\ell-M)]\kappa_\ell(v)\phi_\ell(v)$$

$$+ \delta^k(p-\ell)[1-\delta^k(p-M+1)]\kappa_{p+1}(v)\phi_{p+1}(v)$$

$$- \delta^k(p-\ell+1)[1-\delta^k(\ell-M)]\kappa_\ell(v)\phi_\ell(v)$$

$$+ \delta^k(\ell-p+1)[1-\delta^k(p-M)]\kappa_p(v)\phi_\ell(v)\}$$

$$+ \delta^k(p-\ell)\delta^k(v-v^*)\{\delta^k(m-M)f(v) + \gamma_\ell(v)\phi_\ell(v)\} \qquad (4\text{-}32)$$

where both

$$k^* = [\frac{\ell v - iv'}{v - v'}]$$

$$k' = [\frac{pv^* - iv'}{v^* - v'}]$$

are rounded to their respective nearest integers. The number of terms in Eq. 4-32 is substantially smaller that that of Eq. 4-29 because of numerous point discontinuities in the latter.

Finally, Eq. 4-30 in continuous form yields

$$\frac{\partial}{\partial\tau} K_{p\ell}(v^*,v,\tau) = -\frac{1}{2}\sum_{i}^{M}\int_{0}^{v_{max}-v} \beta_{\ell i}(v,v+v')[\phi_{\ell}^{s}(v')K_{pi}(v^*,v,\tau)$$

$$+ \phi_{i}^{s}(v)K_{p\ell}(v^*,v',\tau) + \phi_{\ell}^{s}(v)K_{pi}(v^*,v',\tau)$$

$$+ \phi_{i}^{s}(v')K_{p\ell}(v^*,v,\tau)]dv'$$

$$+ \frac{1}{2}\sum_{i}^{M}\int_{0}^{v} \beta_{ik^*}(v',v)[\phi_{i}^{s}(v')K_{pk^*}(v^*,v-v',\tau)$$

$$+ \phi_{k^*}^{s}(v-v')K_{pi}(v^*,v',\tau)]dv'$$

$$- \int_{0}^{\frac{v}{2}} \alpha_{\ell}(v,v')K_{p\ell}(v^*,v,\tau)dv'$$

$$+ \delta^{k}(\ell-1)\sum_{i}^{M}\int_{v}^{v_{max}} \alpha_{i}(v',v)K_{pi}(v^*,v',\tau)dv'$$

$$- [1-\delta^{k}(\ell-M)]\kappa_{\ell}(v)K_{p\ell}(v^*,v,\tau)$$

$$+ [1-\delta^{k}(\ell-1)]\kappa_{\ell-1}(v)K_{p\ell-1}(v^*,v,\tau)$$

$$- \gamma_{\ell}(v)K_{p\ell}(v^*,v,\tau) \qquad (4\text{-}33)$$

with the initial condition

$$K_{p\ell}(v^*,v,0) = \mathrm{Cov}[N_{\ell}(v)N_{p}(v^*)]$$

where

$$\phi_{\ell}^{s}(v) = \text{steady-state value of } \phi_{\ell}(v)$$

$$\text{Cov}[N_{\ell}(v)N_{p}(v^*)] = \text{steady-state covariances}$$

$$k^* = \left[\frac{\ell v - i v'}{v - v'}\right] \text{ rounded to the nearest integer}$$

Returning to Eq. 4-31 and considering the special case of M = 1 (all entities disperse at their steady-state rate), or the equivalent case where $\beta(.,.)$, $\alpha(.,.)$ and $\gamma(.)$ do not depend on the "distance" from formation, the balance equation reduces to

$$\begin{aligned}
\frac{\partial \phi(v)}{\partial t} = & -\int_{0}^{v_{max}-v} \beta(v, v+v')\phi(v')\phi(v)dv' \\
& + \frac{1}{2}\int_{0}^{v} \beta(v', v)\sum_{\ell}^{M}\sum_{i}^{M} \phi_{i}(v')\phi_{k^*}(v-v')dv' \\
& - \int_{0}^{\frac{v}{2}} \alpha(v,v')\phi(v)dv' \\
& + \int_{v}^{v_{max}} \alpha(v',v)\phi(v')dv' \\
& - \gamma(v)\phi(v) \\
& + f(v)
\end{aligned} \tag{4-34}$$

where

$$\phi(v) = \sum_{\ell}^{M} \phi_{\ell}(v) \quad , \quad \phi(v') = \sum_{i}^{M} \phi_{i}(v')$$

This expression is of the same form as other expressions which have been used to model coalescence and dispersion (see, e.g., Tavlavides and Bapat, 1983).

The first two terms on the right-hand side represent, respectively, loss and formation of entities of size v due to coalescence. The third and fourth terms are the corresponding terms for dispersion. The fifth term represents the exit of entities from the compartment. The last term represents the entrance of entities into the compartment.

It is also possible to transform the "distance" variable into continuous form by introducing the following transformed functions;

$$\beta_{\ell i}(v,v+v') \rightarrow \beta(s,s',v,v+v')ds'$$

$$\alpha_{\ell}(v,v') \rightarrow \alpha(s,v,v')$$

$$\alpha_{i}(v',v) \rightarrow \alpha(s',v',v)ds'$$

$$\kappa_{\ell-1}(v)\phi_{\ell-1}(v)-\kappa_{\ell}(v)\phi_{\ell}(v) \rightarrow -\frac{\partial}{\partial s}[\kappa(s,v)\phi(s,v)]$$

$$\gamma_{\ell}(v) \rightarrow \gamma(s,v)$$

$$\delta^{k}(\ell-M)\Omega f(v) \rightarrow f(M,v)$$

Transforming Eq. 4-31 to continuous form using these functions yields

$$\frac{\partial\phi(s,v)}{\partial t} = -\frac{1}{2}\int_0^M \int_0^{v_{max}-v} \beta(s,s',v+v')[\phi(s,v')\phi(s',v) + \phi(s,v)\phi(s',v')]dv'ds'$$

$$+\frac{1}{2}\int_0^M \int_0^v \beta(s',s^*,v',v)\phi(s',v')\phi(s^*,v-v')dv'ds'$$

$$-\int_0^{\frac{v}{2}} \alpha(s,v,v')\phi(s,v)dv'$$

$$+\delta^{k}(s)\int_0^M \int_v^{v_{max}} \alpha(s',v',v)\phi(s',v')dv'ds'$$

$$-\frac{\partial}{\partial s}[\kappa(s,v)\phi(s,v)]$$

$$- \gamma(s,v)\phi(s,v)$$

$$+ f(M,v) \qquad (4\text{-}35)$$

where

$$s^* = \frac{(sv - s'v')}{(v - v')}$$

The governing equations in continuous form would appear to be much simplier and, therefore, preferable for application; however, it is usually necessary to revert them back into discrete form for computation. As noted earlier, care must be taken since terms have been dropped in the limiting process for obtaining the continuous form. Therefore, a rigorous application of the population balance approach to a discrete population should resort to the discrete governing equations, i.e., Eqs. 4-26, 4-29 and 4-30 at the onset.

4.2 DETERMINATION OF THE RATE-OF-COALESCENCE FUNCTION

The rate-of-coalescence function for two droplets in the dispersed phase, one with size v and the other with size v', to form a droplet of size (v+v') where the rate of coalescence does not depend on the "distance" variable, has been given by Tavlavidas and Bapat (1983) to be a function of two separate parts.

$$\beta(v,v+v') = h(v,v')\lambda(v,v') \qquad (4\text{-}36)$$

where

$h(v,v')$ = collision frequency of a droplet pair

$\lambda(v,v')$ = coalescence efficiency function (the probability of coalescence between two droplets given that they have collided.)

For liquid droplets in a turbulent flow field, Coulaloglou and Tavlavides (1977) have derived the following expression for the collision frequency;

$$h(v,v') = C_3 \frac{\varepsilon^{1/3}}{1+\phi} (v^{2/3} + v'^{2/3})(v^{2/9} + v'^{2/9}) \qquad (4\text{-}37)$$

where

C_3 = constant

ε = power dissipation per unit mass

ϕ = dispersed phase holdup

They have also derived the following expression for the coalescence efficiency function;

$$\lambda(v,v') = \exp[-C_4 (\frac{\mu_c \rho_c \varepsilon}{\sigma^2 (1+\phi)^3}) (\frac{v^{1/3} v'^{1/3}}{v^{1/3} + v'^{1/3}})^4] \qquad (4\text{-}38)$$

where

C_4 = constant

μ_c = dynamic viscosity of the continuous phase

ρ_c = density of the continuous phase

σ = interfacial tension

Following Howarth's (1964) observation that the energy of collision is the controlling factor in the coalescence process, Sovova (1981) has derived the following expression for the coalescence efficiency function;

$$\lambda(v,v') = \exp\left[-C_5 \frac{\sigma}{\rho_c \varepsilon^{2/3} D_I^{4/3}} \frac{(v^{2/3}+v'^{2/3})(v+v')}{vv'(v^{2/3}+v'^{2/3})}\right] \quad (4\text{-}39)$$

where

C_5 = constant

D_I = impeller diameter

According to Tavlarides and Bapat (1983), this expression predicts that the coalescence efficiency decreases with a decreasing droplet size, in contrast to Eq. 4-38. They also note that both functions are valid, each in a certain energy range - Eq. 4-38 for low energy collisions, and Eq. 4-39 for high energy collisions.

The present model includes the "distance" from formation as a parameter; naturally it can be incorporated into the rate of coalescence function. Intuitively a recently formed droplet would possess a higher energy, and thus would be best described by a function of the form of Eq. 4-39. A droplet whose "distance" variable is much greater than 1 (i.e., close to the asymptotic rate where the "distance variable is equal to M) would be expected to have a lower energy and could be described by a function similar to Eq. 4-38. In this way a natural distinction between high and low energy droplets can be incorporated into the description of the system.

4.3 DETERMINATION OF THE RATE-OF-BREAKAGE FUNCTION

It would seem logical to divide the rate-of-breakage function into two distinct parts, the first corresponding to the frequency of breakage, and the second corresponding to the probability of forming a daughter droplet of a certain volume. The rate-of-breakage function thus would be of the following form;

$$\alpha_{\ell}(v,v') = \alpha^1(v,v')\alpha_{\ell}^2(v) \tag{4-40}$$

where

$\alpha^1(v,v')$ = probability of forming a daughter droplet of size v' given that a droplet of size v has broken apart

$\alpha_{\ell}^2(v)$ = frequency at which a droplet of volume v and a "distance" $\ell\Delta S$ from formation breaks apart.

Note that it is also likely that $\alpha^1(v,v')$ would depend on the "distance" from formation, in this case it would be written as $\alpha_{\ell}^1(v,v')$.

Coulaloglou and Tavlarides (1977) have derived an expression for the breakage frequency as a function of the volume of a droplet in a dispersed phase system; it is

$$\alpha^2(v) = C_6 \frac{\varepsilon^{1/3}}{v^{2/9}} \exp\left(- \frac{C_7\sigma}{\rho_d v^{5/9}\varepsilon^{2/3}}\right) \tag{4-41}$$

where

C_6, C_7 = constants

The effect of the "distance" from formation can be included in the breakage frequency expression, $\alpha_{\ell}^2(v)$, by assuming that the power-dissipation per unit mass, ε, is dependent on the distance from formation. This follows from the intuitive notion of droplets breaking in regions of high energy, and thereafter migrating into regions of low energy. The resultant expression then would be of the form

$$\alpha_{\ell}^2(v) = C_6 \frac{\varepsilon_{\ell}^{1/3}}{v^{2/9}} \exp\left(- \frac{C_7\sigma}{\rho_d v^{5/9}\varepsilon_{\ell}^{2/3}}\right) \tag{4-42}$$

where ε_{ℓ}, unlike ε, depends on the "distance" from formation.

To arrive at an expression for probability of forming a daughter droplet of size v' given that a droplet of size v has broken apart, $\alpha^1(v,v')$,

it is best to first define the random variables of interest. For clarity, discrete droplet sizes will be used in what follows. Let $i\Delta V$ be the volume of a droplet of size v. From the conservation of volume and the assumption of binary breakage it follows that the daughter droplets will have volumes $j\Delta V$ and $(i-j)\Delta V$ where

$$j \in \{1,2,\ldots,i-1\}$$

Thus, letting

Z = volume of the original droplet

X = volume of the smallest droplet

and

Y = volume of the largest droplet,

breakage of a droplet results in the ordered pairs (X,Y), i.e.,

$$\{(Z) \rightarrow (X,Y);\ x \in \{1, 2, 3, \ldots, [\tfrac{z}{2}]\},$$

$$y \in \{[\tfrac{z}{2}], [\tfrac{z}{2}]+1, [\tfrac{z}{2}]+2, \ldots, z-1\}\}$$

$$X \leq Y$$

where each ordered pair has a joint conditional probability

$$f_{X,Y|Z}(x,y|z) = P(X=x,\ Y=y|Z=z) \tag{4-43}$$

In deriving an expression for $\alpha^1(i,j)$, the event of interest is the one where X is equal to j. Consequently, $\alpha^1(i,j)$ can be found by summing over all possible values of x and y in Eq. 4-43 with z=i, under the constraint that x is equal to j, i.e.,

$$\alpha^1(i,j) = \sum_{x=1}^{[\frac{i}{2}]} \sum_{y=[\frac{i}{2}]}^{i-1} \delta^k(x-j)\delta^k(y+x-z)P(X=x,Y=y|Z=i)$$

$$= P(X=j,\ Y=z-j|Z=i) \tag{4-44}$$

Note that from the definition of the event space of X, the following must be true

$$\sum_{j=1}^{[\frac{i}{2}]} \alpha^1(i,j) = 1 \tag{4-45}$$

Common practice is to normalize $\alpha^1(i,j)$ (see, e.g., Tavlarides and Bapat, 1983) as

$$\sum_{j=1}^{i-1} \alpha^1(i,j) = 1 \tag{4-46}$$

and then to include a constant of 2 in the final expression for $\alpha_\ell(i,j)$. This practice is entirely in line with the derivation of Eq. 4-45, because of the following symmetry;

$$\sum_{j=i}^{[\frac{i}{2}]} \alpha^1(i,j) = \sum_{[\frac{i}{2}]+1}^{i-1} \alpha^1(i,j) \quad ; \quad i \text{ odd} \tag{4-47}$$

$$\sum_{j=1}^{\frac{i}{2}} \alpha^1(i,j) = \sum_{j=[\frac{i}{2}]}^{i-1} \alpha^1(i,j) \quad ; \quad i \text{ even} \tag{4-48}$$

where

$[\frac{i}{2}]$ = integer part of $\frac{i}{2}$

A disadvantage of this practice is that when i is even and volumes are discrete, the point $[\frac{i}{2}]$ must be included in both summations. To circumvent this difficulty, it is best to normalize $\alpha^1(i,j)$ only on the interval $\{1, [\frac{i}{2}]\}$, as in Eq, 4-45. This eliminates the necessity of including the constant factor of 2 in the derivation. Note, however, that if this convention is used [Eq. 4-46], the breakage terms in line 3 of Eq. 4-26 must be modified as follows:

$$- \sum_{k}^{\frac{m}{2}} [1 - \frac{1}{2}\delta^{k}(m-2k)]\alpha_{\ell}(m,k)\phi_{\ell m} + \sum_{i}^{M} \sum_{j}^{\varepsilon} \delta^{k}(\ell-1)\alpha_{i}(j,m)\phi_{ij}$$

Similar modifications must be made in Eqs. 4-28, 4-29, 4-30. The resultant equations will hereafter be refered to as the modified forms of the governing equations.

It should be emphasized that all the results derived in this section strongly depend on the assumption of binary breakage, since all symmetry arguments loose their validity when other cases are considered. For example, the assumption that the number of daughter droplets is either two or three leads to the ordered triplet

$$(X_1, X_2, X_3)$$

where

$$X_1 \leq X_2 \leq X_3$$

The resulting breakage distribution function will then contain three variables, i.e.,

$\alpha_1(i,j,k)$ = probability that a droplet of size $i\Delta V$ breaks apart to form droplets of sizes $j\Delta V$, $k\Delta V$, and $(i-j-k)\Delta V$ where $j \leq k \leq i - j - k$

where

$$j \in \{0,1,2,3,\ldots,[\tfrac{i}{3}]\}$$

$$k \in \{j, j+1, j+2, \ldots, [\tfrac{i-j}{2}]\} \quad \text{for } j \neq 0$$

or

$$k \in \{1,2,3,\ldots,[\tfrac{i}{2}]\} \quad \text{for } j = 0$$

By the definition of ordered triplet, $\alpha_1(i,j,k)$ normalizes as follows:

$$\sum_{j=1}^{[\frac{i}{3}]} \sum_{k=j}^{[\frac{i-j}{2}]} \alpha_1(i,j,k) + \sum_{k=1}^{[\frac{i}{2}]} \alpha_1(i,0,k) = 1 \qquad (4\text{-}49)$$

By defining $\alpha(i,0,0,) = 0$, it normalizes as

$$\sum_{j=0}^{[\frac{i}{3}]} \sum_{k=j}^{[\frac{i-j}{2}]} \alpha_1(i,j,k) = 1 \qquad (4\text{-}50)$$

For a given i and j, $\alpha(i,j,k)$ possesses a symmetry about the point $[(i-j)/2]$, i.e.,

$$\sum_{k=j}^{[\frac{i-j}{2}]} \alpha_1(i,j,k) = \sum_{k=[\frac{i-j}{2}]+1}^{i-j-1} \alpha_1(i,j,k) \; ; \text{ for } \frac{i-j}{2} \neq [\frac{i-j}{2}] \qquad (4\text{-}51)$$

$$\sum_{k=j}^{\frac{i-j}{2}} \alpha_1(i,j,k) = \sum_{k=\frac{i-j}{2}}^{i-j-1} \alpha_1(i,j,k) \; ; \text{ for } \frac{i-j}{2} = [\frac{i-j}{2}] \qquad (4\text{-}52)$$

It is obvious, therefore, that with this definition of the breakage distribution it will be impossible, in general, to reduce the expression to the form $3\alpha^1(i,j)$ as is usually done (see, e.g., Tavlarides and Bapat, 1983).

It is possible, however, to derive a breakage function of the form $3\alpha^1(i,j):j \in \{1,2,3,\ldots,i-1\}$, from the expression for $\alpha(i,j,k)$ for the case where three daughter droplets are formed. Noting again that

$$\alpha_1(i,j,k) = P(X_1=j,\ X_2=k,\ X_3=i-j-k \mid Z=i) \qquad (4\text{-}53)$$

the expected number of daughter droplets of size $\ell\Delta V$, $E[N(\ell)]$, can be found as follows:

$$E[N(\ell)] = \sum_{j=1}^{[\frac{i}{3}]} \sum_{n=j}^{[\frac{i-j}{2}]} \{\delta^k(\ell-j) + \delta^k(\ell-n) + \delta^k(\ell-i+j+n)\}\alpha_1(i,j,n) \qquad (4\text{-}54)$$

Note that, because of the restriction to ternary breakage,

$$\sum_{\ell=1}^{i-1} E[N(\ell)] = 3 \tag{4-55}$$

Therefore, the following distribution function can be defined;

$$\alpha^1(i,\ell) = E[N(\ell)]\left\{\sum_{\ell=1}^{i-1} E[N(\ell)]\right\}^{-1}$$

$$= \frac{1}{3} E[N(\ell)] \tag{4-56}$$

where

$$\sum_{\ell=1}^{i-1} \alpha^1(i,\ell) = 1$$

indicating that $\alpha^1(i,\ell)$ normalizes to one on the interval $\{1,i-1\}$. This definition of the breakage function can be extended to cases where any number of daughter droplets is formed. Similar to the derivation of Eq. 4-54, $E[N(\ell)]$ can be found for cases where combinations of two or more daughter droplets are formed. It is also evident from Eq. 4-54 that, in general, the breakage function will be unsymmetrical about the mid-point, $[\frac{i}{2}]$, except in the special case where the number of daughter cells is equal to two. Therefore, it is not possible to use the same breakage distribution for every case by simply multiplying the binary breakage distribution by the number of daughter droplets formed.

A more rational approach to finding the distribution of daughter droplets could start with the probabilities of the ordered sets. Each ordered set represents a set of droplets of differing sizes, and thus differing energy per unit volume relative to the starting droplet; the smaller droplets usually have the highest energy per unit volume due to increased surface tension.

Consequently, probabilities could thus be assigned according to the relative energy per unit volume of ordered set i.

One possible assignment of probability for binary breakage could start with the distribution of the excess surface energy per unit volume amoung the volume elements in the original droplet. The surface energy of a droplet of volume v_0 is essentially equal to $\sigma v_0^{2/3}$ where σ is the surface tension. If this energy is distributed evenly amoung the volume elements in the original droplet, a sub-volume with volume v_1 will have a surface energy of

$$\sigma v_0^{2/3} \frac{v_1}{v_0} \tag{4-57}$$

or a surface energy per unit volume of $\sigma v_0^{-1/3}$. Furthermore, if during breakage two droplets are formed, one with volume v_1, the other with volume (v_0-v_1), the surface energies per unit volume of these droplets relative to the original droplets are, respectively, proportional to

$$\sigma[v_1^{-1/3} - v_0^{-1/3}] \tag{4-58}$$

and

$$\sigma[(v_0-v_1)^{-1/3} - v_0^{-1/3}] \tag{4-59}$$

If v_1 is small, the excess surface energy of v_1 relative to that of v_0 is very large (Eq. 4-58). This excess energy is poorly distributed since it resides in the small volume element v_1. The rest of the volume element, $(v_0 - v_1)$, has a very low excess surface energy relative to v_0 (Eq. 4-59) . A normalized distribution of the excess energy per unit volume can be defined as a function of v_0 and v_1 using Eqs. 4-58 and 4-59 as follows:

$$f(v) = \frac{(v_0 - v_1)^{1/3}\left[(v_0)^{1/3} - (v_1)^{1/3}\right]}{(v_0 - v_1)^{1/3}\left(v_0^{1/3} - 2v_1^{1/3}\right) + v_0^{1/3}v_1^{1/3}} \qquad (4\text{-}60)$$

$$\text{for } -\frac{v_1}{2} \leq v \leq \frac{v_1}{2}$$

$$f(v) = \frac{v_1^{1/3}\left[v_0^{1/3} - (v_0 - v_1)^{1/3}\right]}{(v_0 - v_1)^{1/3}\left(v_0^{1/3} - 2v_1^{1/3}\right) + v_0^{1/3}v_1^{1/3}} \qquad (4\text{-}61)$$

$$\text{for } -\frac{v_0}{2} < v < -\frac{v_1}{2} \text{ and } \frac{v_1}{2} < v < \frac{v_0}{2}$$

$$f(v) = 0 \text{ for } -\infty < v \leq -\frac{v_0}{2} \text{ and } \frac{v_0}{2} \leq v < +\infty \qquad (4\text{-}62)$$

where

$$0 < v_1 \leq \frac{v_0}{2}$$

Note that $f(v)$ is a piecewise uniform distribution on the interval $(-v_0/2,\ v_0/2)$ with the mean of zero and the variance of

$$\sigma^2(v_0, v_1) = \frac{v_1^{1/3}v_0^{1/3}}{12}\left[\frac{v_0^3 - v_1^3 - (v_0^{8/3} - v_1^{8/3})(v_0 - v_1)^{1/3}}{(v_0^{1/3} - 2v_1^{1/3})(v_0 - v_1)^{1/3} + v_1^{1/3}v_0^{1/3}}\right] \qquad (4\text{-}63)$$

where

$$0 < v_1 \leq \frac{v_0}{2}$$

The variance, σ^2, is a measure of the distribution of the excess energy among the volume elements in the daughter droplets. When $v_1 = v_0/2$, the variance is a maximum, indicating that the excess energy is evenly spread amoung the volume elements. As v_1 approaches zero, σ^2 also approaches zero, indicating that the excess energy is poorly distributed among the volume elements, i.e., that all the excess energy resides in the small droplet of volume v_1 while the other droplet of volume $(v_0 - v_1)$ has very little excess energy relative to the original droplet.

If it is assumed that the probability of a specific pair of droplets is directly proportional to the distribution of excess energy, i.e.,

$$P[(v_1, v_0 - v_1)] \propto \sigma^2(v_0, v_1) \tag{4-64}$$

where

$$0 < v_1 \leq \frac{v_0}{2},$$

then the probability of a specific pair can be calculated as follows:

$$P[(v_1, v_0 - v_1)] = \sigma^2(v_0, v_1) \left[\sum_{v_i}^{[\frac{v_0}{2}]} \sigma^2(v_0, v_i) \right]^{-1} \tag{4-65}$$

where the summation is over all droplets, each with a volume less that or equal to $v_0/2$. For example, given that $v_0 = 4\Delta V$, the possible pairs are (1,3) and (2,2), and therefore, $v_i = i\Delta V$: where $i\varepsilon\{1,2\}$. The probabilites in this case are thus

$$P[(1,3)] = \frac{\sigma^2(4,1)}{\sigma^2(4,1) + \sigma^2(4,2)} \tag{4-66}$$

$$P[(2,2)] = \frac{\sigma^2(4,2)}{\sigma^2(4,1) + \sigma^2(4,2)} \tag{4-67}$$

or, using the notation defined in Eq. 4-53

$$\alpha_1(4,1) = \frac{\sigma^2(4,1)}{\sigma^2(4,1) + \sigma^2(4,2)} \tag{4-68}$$

$$\alpha_1(4,2) = \frac{\sigma^2(4,2)}{\sigma^2(4,1) + \sigma^2(4,2)} \tag{4-69}$$

To find the expected number of daughter droplets of size $\ell\Delta V$, Eq. 4-54 can be employed in the form corresponding to binary breakage, i.e.,

$$E[N(\ell)] = \sum_{j=1}^{[\frac{i}{2}]} \{\delta^k(\ell-j) + \delta^k(\ell-i+j)\}\alpha_1(i,j) \tag{4-70}$$

Furthermore, Eq. 4-70 give rise to the following expressions;

$$E[N(1)] = \sum_{j=1}^{2} \{\delta^k(1-j) + \delta^k(j-3)\}\alpha_1(4,j)$$

$$= \alpha_1(4,1) \tag{4-71}$$

$$E[N(2)] = \sum_{j=1}^{2} \{\delta^k(2-j) + \delta^k(j-2)\}\alpha_1(4,j)$$

$$= 2\alpha_1(4,2) \tag{4-72}$$

$$E[N(3)] = \sum_{j=1}^{2} \{\delta^k(3-j) + \delta^k(j-1)\}\alpha_1(4,j)$$

$$= \alpha_1(4,1) \tag{4-73}$$

These expressions together with Eq. 4-56 , in turn, yield the distribution function, i.e.,

$$\alpha^1(4,1) = \frac{1}{2}\alpha_1(4,1) \tag{4-74}$$

$$\alpha^1(4,2) = \alpha_1(4,2) \tag{4-75}$$

$$\alpha^1(4,3) = \frac{1}{2}\alpha_1(4,1) \tag{4-76}$$

or, by resorting to $\alpha_1(4,1)$ and $\alpha_1(4,2)$ as defined, respectively, by Eqs. 4-68 and 4-69,

$$\alpha^1(4,1) = \alpha^1(4,3) = \frac{1}{2}\left[\frac{\sigma^2(4,1)}{\sigma^2(4,1) + \sigma^2(4,2)}\right] \tag{4-77}$$

$$\alpha^1(4,2) = \frac{\sigma^2(4,2)}{\sigma^2(4,1) + \sigma^2(4,2)} \tag{4-78}$$

These expressions in conjunction with Eq. 4-63 yield

$$\alpha^1(4,1) = \alpha^1(4,3) = 0.1197 \tag{4-79}$$

$$\alpha^1(4,2) = 0.7606 \tag{4-80}$$

According to Eq. 4-46 , these expressions normalize to one and, therefore, a constant of 2 must be included in the final expression of $\alpha(i,j)$ as indicated earlier. The modified forms of the governing equations must also be used.

With additional information on the distribution of energy containing eddies in the turbulent flow field which initiates the breakup, it may be possible to further refine the expressions for the probability which are assigned to the ordered sets (cf. Narsimhan et al, 1979). For example, given a certain eddy with a specific energy content, if is plausible that the ordered set resulting from the interaction between this eddy and the original droplet will have a relative energy less than or equal to the energy content of the eddy; the remainder of the energy is transformed into the kinetic mode. To determine the unconditional droplet distribution, the distribution of the energy content of the eddies in the flow field need be used in conjuction with the conditional probability of a specific droplet

distribution, given that the droplets have been formed by an eddy with a specific energy content. Letting $P[(X)_i|Z]$ be the conditional probability of the ordered set $(X)_i$ given that it was formed through the interaction of the original droplet with an eddy of energy content Z, and f(z) be the probability density function for eddies with energy content Z, the unconditional distribution would then be

$$P[(X)_i] = \int_0^{+\infty} P[(X)_i|Z]f(z)dz \tag{4-81}$$

Note that $P[(X)_i]$ for ternary breakage is equivalent to $P(X_1=j, X_2=k, X_3=i-j-k|Z=i)$ which appears in Eq. 4-53.

4.4 DETERMINATION OF OTHER RATES OF TRANSITION FUNCTIONS

The rates of transition functions yet to be specified are those corresponding to the rate of change in the "distance" variable, $\dot{\kappa}_i(v)$, the rate of exit, $\gamma_i(v)$, and the rate of entrance, $\Omega f(v)$. The last of these can be determined from the volumetric flow rate into the compartment, q, and a factor equal to the number of droplets of size v per unit volume of inlet flow, $f_0(v)$, i.e.,

$$\Omega f(v) = f_0(v)q \tag{4-82}$$

The rate of exit, $\gamma_i(v)$, can be determined from the flow pattern in the compartment. For completely mixed flow,

$$\gamma_i(v) = \frac{q}{\Omega} \tag{4-83}$$

Determination of the rate-of-transition function corresponding to the change in the "distance" variable, $\kappa_i(v)$, requires some knowledge of the processes leading to the rate of droplet breakage after the droplet is sufficiently far from its formation. If it is assumed that the principal factor is the movement of the droplet away from its point of formation, then the quantity of interest is the velocity of the droplet. If a droplet with a volume of v and a density of ρ receives kinetic energy from the continuous phase in proportion to its surface area, then it will have a velocity inversely proportional to its density and volume; more specifically,

$$u \propto \frac{1}{\rho^{1/2} v^{1/6}} \tag{4-84}$$

Under the assumption that $\kappa_i(v)$ is proportional to this velocity, it can be expressed as

$$\kappa_i(v) = \frac{C_i}{\rho^{1/2} v^{1/6}} \tag{4-85}$$

where

C_i = constant

Naturally, this expression can be further refine by including additional information on the mechanisms of breakage.

4.5 EXAMPLE CALCULATION

In the present example, the parameters will be chosen so that only the following interactions need be considered;

$$A_{i1} + A_{i1} \longrightarrow A_{i2} \quad , \quad i=1,2$$

$$A_{i2} + A_{i1} \longrightarrow A_{i3} \quad , \quad i=1,2$$

$$A_{i2} + A_{i2} \longrightarrow A_{i4} \quad , \quad i = 1,2$$
$$A_{i3} + A_{i1} \longrightarrow A_{i4} \quad , \quad i = 1,2$$

$$A_{i4} \longrightarrow A_{i3} + A_{11} \quad , \quad i = 1,2$$
$$A_{i4} \longrightarrow A_{i2} + A_{12} \quad , \quad i = 1,2$$
$$A_{i3} \longrightarrow A_{i2} + A_{11} \quad , \quad i = 1,2$$
$$A_{i2} \longrightarrow A_{11} + A_{11} \quad , \quad i = 1,2$$

$$A_{1j} \longrightarrow A_{2j} \quad , \quad j = 1,2$$
$$X_2 \longrightarrow A_{22} \text{ (entrance)}$$
$$A_{ij} \longrightarrow Y_{ij} \text{ (exit)} \quad , \quad i,j = 1,2$$

Note that M = 2 and that coalescence is assumed to take place only between entities whose "distance" variables, i, have the same value. Also note that only entities of size 2 exist in the entrance stream.

The transition functions used-found using arbitrary constants and Eqs. 4-65, 4-37, and 4-85 - are ;

$$\gamma_i(j) = 0.1$$
$$\Omega f(j) = 10\delta^k(j-2)$$

$\alpha_1(4,1) = 4.658$ $\qquad$ $\alpha_2(4,1) = 0.9316$

$\alpha_1(4,2) = 7.929$ $\qquad$ $\alpha_2(4,2) = 1.5860$

$\alpha_1(3,1) = 5.809$ $\qquad$ $\alpha_2(3,1) = 1.1618$

$\alpha_1(2,1) = 10.128$ $\qquad$ $\alpha_2(2,1) = 2.0256$

$\Omega^{-1}\beta(1,4) = 0.0427$ $\qquad$ $\kappa_1(1) = 10.0$

$\Omega^{-1}\beta(2,4) = 0.0584$ $\qquad$ $\kappa_1(2) = 8.909$

$\Omega^{-1}\beta(1,3) = 0.0271$ $\qquad$ $\kappa_1(3) = 8.327$

$\Omega^{-1}\beta(1,2) = 0.0125$ $\qquad$ $\kappa_1(4) = 7.937$

Since the breakage function used here normalizes on the interval $[1,[\frac{i}{2}]]$, the governing equations in the original or unmodified form, Eqs. 4-26 4-29, and 4-30, apply.

For the interactions included in this example, Eq. 4-26 reduces to

$$\frac{d\phi_{11}}{dt} = -2\beta(1,2)\phi_{11}\phi_{11} - \beta(1,3)\phi_{11}\phi_{12} - \beta(1,4)\phi_{11}\phi_{13}$$

$$+ 2\alpha_1(2,1)\phi_{12} + \alpha_1(3,1)\phi_{13} + \alpha_1(4,1)\phi_{14}$$

$$+ 2\alpha_2(2,1)\phi_{22} + \alpha_2(3,1)\phi_{23} + \alpha_2(4,1)\phi_{24}$$

$$- \kappa_1(1)\phi_{11} - \gamma_1(1)\phi_{11} \qquad (4\text{-}86)$$

$$\frac{d\phi_{12}}{dt} = -2\beta(2,4)\phi_{12}\phi_{12} - \beta(1,3)\phi_{11}\phi_{12} + \beta(1,2)\phi_{11}\phi_{11}$$

$$- \alpha_1(2,1)\phi_{12} + 2\alpha_1(4,2)\phi_{14} + 2\alpha_2(4,2)\phi_{24}$$

$$+ \alpha_1(3,1)\phi_{13} + \alpha_2(3,1)\phi_{23}$$

$$- \kappa_1(2)\phi_{12} - \gamma_1(2)\phi_{12} \qquad (4\text{-}87)$$

$$\frac{d\phi_{13}}{dt} = -\beta(1,4)\phi_{11}\phi_{13} + \beta(1,3)\phi_{11}\phi_{12}$$

$$- \alpha_1(3,1)\phi_{13} + \alpha_1(4,1)\phi_{14} + \alpha_2(4,1)\phi_{24}$$

$$- \kappa_1(3)\phi_{13} - \gamma_1(3)\phi_{13} \qquad (4\text{-}88)$$

$$\frac{d\phi_{14}}{dt} = \beta(2,4)\phi_{12}\phi_{12} + \beta(1,4)\phi_{11}\phi_{13} - \alpha_1(4,1)\phi_{14}$$

$$- \alpha_1(4,2)\phi_{14} - \kappa_1(4)\phi_{14} - \gamma_1(4)\phi_{14} \qquad (4\text{-}89)$$

$$\frac{d\phi_{21}}{dt} = -2\beta(1,2)\phi_{21}\phi_{21} - \beta(1,3)\phi_{21}\phi_{22} - \beta(1,4)\phi_{21}\phi_{23}$$

$$+ \kappa_1(1)\phi_{11} - \gamma_2(1)\phi_{21} \qquad (4\text{-}90)$$

$$\frac{d\phi_{22}}{dt} = -2\beta(2,4)\phi_{22}\phi_{22} - \beta(1,3)\phi_{21}\phi_{22} + \beta(1,2)\phi_{21}\phi_{21}$$

$$- \alpha_2(2,1)\phi_{22} + \kappa_1(2)\phi_{12} - \gamma_2(2)\phi_{22} + f(2) \qquad (4\text{-}91)$$

$$\frac{d\phi_{23}}{dt} = -\beta(1,4)\phi_{21}\phi_{23} + \beta(1,3)\phi_{21}\phi_{22} - \alpha_2(3,1)\phi_{23}$$

$$+ \kappa_1(3)\phi_{13} - \gamma_2(3)\phi_{23} \qquad (4\text{-}92)$$

$$\frac{d\phi_{24}}{dt} = \beta(2,4)\phi_{22}\phi_{22} + \beta(1,4)\phi_{21}\phi_{23} - \alpha_2(4,1)\phi$$

$$- \alpha_2(4,2)\phi_{24} + \kappa_1(4)\phi_{14} - \gamma_2(4)\phi_{24} \qquad (4\text{-}93)$$

At steady state, these equations reduce, respectively, to

$$0 = -0.025\langle N_{11}\rangle^2 - 0.0271\langle N_{11}\rangle\langle N_{12}\rangle - 0.0427\langle N_{11}\rangle\langle N_{13}\rangle$$

$$+ 20.236\langle N_{12}\rangle + 5.809\langle N_{13}\rangle + 4.658\langle N_{14}\rangle$$

$$+ 4.0512\langle N_{22}\rangle + 1.1618\langle N_{23}\rangle + 0.9316\langle N_{24}\rangle - 10.1\langle N_{11}\rangle \qquad (4\text{-}94)$$

$$0 = -0.1167\langle N_{12}\rangle^2 - 0.0271\langle N_{11}\rangle\langle N_{12}\rangle + 0.0125\langle N_{11}\rangle^2$$

$$- 19.137\langle N_{12}\rangle + 15.858\langle N_{14}\rangle + 3.1720\langle N_{24}\rangle$$

$$+ 5.809\langle N_{13}\rangle + 1.1618\langle N_{23}\rangle \qquad (4\text{-}95)$$

$$0 = -0.0427\langle N_{11}\rangle\langle N_{13}\rangle + 0.0271\langle N_{11}\rangle\langle N_{12}\rangle - 14.236\langle N_{13}\rangle$$

$$+ 4.658\langle N_{14}\rangle + 0.9316\langle N_{24}\rangle \qquad (4\text{-}96)$$

$$0 = 0.0584\langle N_{12}\rangle^2 + 0.0427\langle N_{11}\rangle\langle N_{13}\rangle - 20.624\langle N_{14}\rangle \qquad (4\text{-}97)$$

$$0 = -0.025\langle N_{21}\rangle^2 - 0.0271\langle N_{21}\rangle\langle N_{22}\rangle - 0.0427\langle N_{21}\rangle\langle N_{23}\rangle$$

$$+ 10.0\langle N_{11}\rangle - 0.1\langle N_{21}\rangle \qquad (4\text{-}98)$$

$$0 = -0.1167\langle N_{22}\rangle^2 - 0.0271\langle N_{21}\rangle\langle N_{22}\rangle + 0.0125\langle N_{21}\rangle^2 - 2.1256\langle N_{22}\rangle + 8.909\langle N_{12}\rangle + 10.0 \quad (4\text{-}99)$$

$$0 = -0.0427\langle N_{21}\rangle\langle N_{23}\rangle + 0.0271\langle N_{21}\rangle\langle N_{22}\rangle - 1.2618\langle N_{23}\rangle + 8.327\langle N_{13}\rangle \quad (4\text{-}100)$$

$$0 = 0.0584\langle N_{22}\rangle^2 + 0.0427\langle N_{21}\rangle\langle N_{22}\rangle + 7.937\langle N_{14}\rangle - 2.6176\langle N_{24}\rangle \quad (4\text{-}101)$$

Solving these equations yields the following values for the average number of droplets in the compartment at steady-state,

$\langle N_{11}\rangle = 14.830$ $\qquad$ $\langle N_{21}\rangle = 61.271$

$\langle N_{12}\rangle = 3.239$ $\qquad$ $\langle N_{22}\rangle = 15.371$

$\langle N_{13}\rangle = 0.994$ $\qquad$ $\langle N_{23}\rangle = 8.723$

$\langle N_{14}\rangle = 0.060$ $\qquad$ $\langle N_{24}\rangle = 14.159$

Since eight random variables are involved in the present problems, Eq. 4-29 for the covariances of the random variables yields 36 coupled equations. These equations are

$$\frac{d}{dt}\mathrm{Var}[N_{11}] = -8\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Var}[N_{11}]$$

$$- 2\Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Var}[N_{11}] + \langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{12}]\}$$

$$-2\Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle \mathrm{Var}[N_{11}] + \langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{13}]\}$$

$$+ 4\alpha_1(2,1)\mathrm{Cov}[N_{11}N_{12}] + 4\alpha_2(2,1)\ \mathrm{Cov}[N_{12}N_{21}]$$

$$+ 2\alpha_1(3,1)\mathrm{Cov}[N_{11}N_{13}] + 2\alpha_2(3,1)\mathrm{Cov}[N_{11}N_{23}]$$

$$+ 2\alpha_1(4,1)\mathrm{Cov}[N_{11}N_{14}] + 2\alpha_2(4,1)\mathrm{Cov}[N_{11}N_{24}]$$

$$- 2[\kappa_1(1) + \gamma_1(1)]\mathrm{Var}[N_{11}]$$

$$+ 4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle^2 + \Omega^{-1}\beta(1,3)\langle N_{11}\rangle\langle N_{12}\rangle + \Omega^{-1}\beta(1,4)\langle N_{11}\rangle\langle N_{13}\rangle$$

$$+ 4\alpha_1(2,1)\langle N_{12}\rangle + \alpha_1(3,1)\langle N_{13}\rangle + \alpha_1(4,1)\langle N_{14}\rangle$$

$$+ 4\alpha_2(2,1)\langle N_{22}\rangle + \alpha_2(3,1)\langle N_{23}\rangle + \alpha_2(4,1)\langle N_{24}\rangle$$

$$+ [\kappa_1(1) + \gamma_1(1)]\langle N_{11}\rangle \qquad (4\text{-}102)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{12}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}] - 4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}] + \langle N_{11}\rangle \mathrm{Var}[N_{12}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle \mathrm{Cov}[N_{11}N_{12}] + \langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{13}]\}$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}] + \langle N_{12}\rangle \mathrm{Var}[N_{11}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle \mathrm{Var}[N_{11}]$$

$$- \alpha_1(2,1)\mathrm{Cov}[N_{11}N_{12}]$$

$$+ 2\alpha_1(2,1)\mathrm{Var}[N_{12}] + 2\alpha_2(2,1)\mathrm{Cov}[N_{12}N_{22}]$$

$$+ 2\alpha_1(4,2)\mathrm{Cov}[N_{11}N_{14}] + 2\alpha_2(4,2)\mathrm{Cov}[N_{11}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{12}N_{13}] + \alpha_2(3,1)\mathrm{Cov}[N_{12}N_{23}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{11}N_{13}] + \alpha_2(3,1)\mathrm{Cov}[N_{11}N_{23}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{12}N_{14}] + \alpha_2(4,1)\mathrm{Cov}[N_{12}N_{24}]$$

$$- [\kappa_1(1) + \kappa_1(2) + \gamma_1(1) + \gamma_1(2)]\mathrm{Cov}[N_{11}N_{12}]$$

$$+ \Omega^{-1}\beta(1,3)\langle N_{11}\rangle\langle N_{12}\rangle - 2\Omega^{-1}\beta(1,3)\langle N_{11}\rangle^2 - 2\alpha_1(2,1)\langle N_{12}\rangle$$

$$+ \alpha_1(3,1)\langle N_{13}\rangle + \alpha_2(3,1)\langle N_{23}\rangle \qquad (4\text{-}103)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{13}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{13}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{13}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{13}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{13}] + \langle N_{11}\rangle\mathrm{Var}[N_{13}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{13}] + \langle N_{13}\rangle\mathrm{Var}[N_{11}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{12}] + \langle N_{12}\rangle\mathrm{Var}[N_{11}]\}$$

$$- \alpha_1(3,1)\mathrm{Cov}[N_{11}N_{13}]$$

$$+ 2\alpha_1(2,1)\mathrm{Cov}[N_{12}N_{13}] + 2\alpha_2(2,1)\mathrm{Cov}[N_{13}N_{22}]$$

$$+ \alpha_1(3,1)\mathrm{Var}[N_{13}] + \alpha_2(3,1)\mathrm{Cov}[N_{13}N_{23}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{13}N_{14}] + \alpha_2(4,1)\mathrm{Cov}[N_{13}N_{24}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{11}N_{14}] + \alpha_2(4,1)\mathrm{Cov}[N_{11}N_{24}]$$

$$- [\kappa_1(1) + \kappa_1(3) + \gamma_1(1) + \gamma_1(3)]\mathrm{Cov}[N_{11}N_{13}]$$

$$+ \Omega^{-1}\beta(1,4)\langle N_{11}\rangle\langle N_{13}\rangle - \Omega^{-1}\beta(1,3)\langle N_{11}\rangle\langle N_{12}\rangle$$

$$+ \alpha_1(4,1)\langle N_{14}\rangle + \alpha_2(4,1)\langle N_{24}\rangle - \alpha_1(3,1)\langle N_{13}\rangle \qquad (4\text{-}104)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{14}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N14]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{14}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{14}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{14}] + \langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{14}]\}$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{13}] + \langle N_{13}\rangle\mathrm{Var}[Z_{11}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{12}]$$

$$- [\alpha_1(4,1) + \alpha_1(4,2)]\mathrm{Cov}[N_{11}N_{14}]$$

$$+ 2\alpha_1(2,1)\mathrm{Cov}[N_{12}N_{14}] + 2\alpha_2(2,1)\mathrm{Cov}[N_{14}N_{22}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{14}] + \alpha_2(3,1)\mathrm{Cov}[N_{14}N_{23}]$$

$$+ \alpha_1(4,1)\mathrm{Var}[N_{14}] + \alpha_2(4,1)\mathrm{Cov}[N_{14}N_{24}]$$

$$- [\kappa_1(1) + \kappa_1(4) + \gamma_1(1) + \gamma_1(4)]\mathrm{Cov}[N_{11}N_{14}]$$

$$- \Omega^{-1}\beta(1,4)\langle N_{11}\rangle\langle N_{13}\rangle - \alpha_1(4,1)\langle N_{14}\rangle \qquad (4\text{-}105)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{21}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{21}] - 4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{21}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{21}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{21}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{21}] + \langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{21}]\}$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle\mathrm{Cov}[N_{11}N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{22}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle\mathrm{Cov}[N_{11}N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{23}]$$

$$+ 2\alpha_1(2,1)\mathrm{Cov}[N_{12}N_{21}] + 2\alpha_2(2,1)\mathrm{Cov}[N_{21}N_{22}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{21}] + \alpha_2(3,1)\mathrm{Cov}[N_{21}N_{23}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{14}N_{21}] + \alpha_2(4,1)\mathrm{Cov}[N_{21}N_{24}]$$

$$- [\kappa_1(1) + \gamma_1(1) + \gamma_2(1)]\mathrm{Cov}[N_{11}N_{21}] + \kappa_1(1)\mathrm{Var}[N_{11}] \qquad (4\text{-}106)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{22}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{22}] - 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{11}N_{22}]$$
$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{22}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{22}]\}$$
$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{22}] + \langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{22}]\}$$
$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$
$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{21}] - \alpha_2(2,1)\mathrm{Cov}[N_{11}N_{22}]$$
$$+ 2\alpha_1(2,1)\mathrm{Cov}[N_{12}N_{22}] + 2\alpha_2(2,1)\mathrm{Var}[N_{22}]$$
$$+ \alpha_1(3,1)\mathrm{Cov}[N_1\ N_{22}] + \alpha_2(3,1)\mathrm{Cov}[N_{22}N_{23}]$$
$$+ \alpha_2(4,1)\mathrm{Cov}[N_{14}N_{22}] + \alpha_2(4,1)\mathrm{Cov}[N_{22}N_{24}]$$
$$- [\kappa_1(1) + \gamma_1(1) + \gamma_2(2)]\mathrm{Cov}[N_{11}N_{22}]$$
$$+ \kappa_1(2)\mathrm{Cov}[N_{11}N_{12}] - 2\alpha_2(2,1)\langle N_{22}\rangle \qquad (4\text{-}107)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{23}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{23}]$$
$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{23}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{23}]\}$$
$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{23}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{23}]\}$$
$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$
$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$
$$- \alpha_2(3,1)\mathrm{Cov}[N_{11}N_{23}]$$
$$+ 2\alpha_1(2,1)\mathrm{Cov}[N_{12}N_{23}] + 2\alpha_2(2,1)\mathrm{Cov}[N_{22}N_{23}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{23}] + \alpha_2(3,1)\mathrm{Var}[N_{23}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{14}N_{23}] + \alpha_2(4,1)\mathrm{Cov}[N_{23}N_{24}]$$

$$- [\kappa_1(1) + \gamma_1(1) + \gamma_2(3)]\mathrm{Cov}[N_{11}N_{23}]$$

$$+ \kappa_1(3)\mathrm{Cov}[N_{11}N_{13}] \qquad (4\text{-}108)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{11}N_{24}] = -4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{24}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{24}] + \langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{24}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{24}] + \langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{24}]\}$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{11}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{11}N_{22}]$$

$$- [\alpha_2(4,1) + \alpha_2(4,2)]\mathrm{Cov}[N_{11}N_{24}]$$

$$+ 2\alpha_1(2,1)\mathrm{Cov}[N_{12}N_{24}] + 2\alpha_2(2,1)\mathrm{Cov}[N_{21}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{24}] + \alpha_2(3.1)\mathrm{Cov}[N_{23}N_{24}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{14}N_{24}] + \alpha_2(4,1)\mathrm{Var}[N_{24}]$$

$$- [\kappa_1(1) + \gamma_1(1) + \gamma_2(4)]\mathrm{Cov}[N_{11}N_{24}]$$

$$+ \kappa_1(4)\mathrm{Cov}[N_{11}N_{14}] - \alpha_2(4,1)\langle N_{24}\rangle \qquad (4\text{-}109)$$

$$\frac{d}{dt}\mathrm{Var}[N_{12}] = -8\Omega^{-1}\beta(2,4)\langle N_{12}\rangle \mathrm{Var}[N_{12}]$$

$$- 2\Omega^{-1}\beta(1,3)\ \{\langle N_{11}\rangle \mathrm{Var}[N_{12}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}]\}$$

$$+ 4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{12}]$$

$$- 2\alpha_1(2,1)\mathrm{Var}[N_{12}] + 4\alpha_1(4,2)\mathrm{Cov}[N_{12}N_{14}] + 4\alpha_2(4,2)\mathrm{Cov}[N_{12}N_{24}]$$

$$+ 2\alpha_1(3,1)\mathrm{Cov}[N_{12}N_{13}] + 2\alpha_2(3,1)\mathrm{Cov}[N_{12}N_{23}]$$

$$- 2[\kappa_1(2) + \gamma_1(2)]\mathrm{Var}[N_{12}] + 2\Omega^{-1}\beta(1,3)\langle N_{11}\rangle\langle N_{12}\rangle + 4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle^2$$
$$+ \Omega^{-1}\beta(1,2)\langle N_{11}\rangle^2 + \alpha_1(2,1)\langle N_{12}\rangle + \alpha_1(3,1)\langle N_{13}\rangle$$

$$+ 4\alpha_1(4,2)\langle N_{14}\rangle + \alpha_2(3,1)\langle N_{23}\rangle + 4\alpha_2(4,2)\langle N_{24}\rangle$$

$$+ \kappa_1(2)\langle N_{12}\rangle + \gamma_1(2)\langle N_{12}\rangle \qquad (4\text{-}110)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{12}N_{13}] = -4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle \mathrm{Cov}[N_{12}N_{13}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{13}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{13}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{13}] + \langle N_{13}\rangle \mathrm{Cov}[N_{11}N_{12}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle \mathrm{Cov}[N_{11}N_{13}]$$

$$+ 2\Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle \mathrm{Var}[N_{12}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{12}]\}$$

$$- [\alpha_1(2,1) + \alpha_1(3,1)]\mathrm{Cov}[N_{12}N_{13}]$$

$$+ 2\alpha_1(4,2)\mathrm{Cov}[N_{14}N_{13}] + 2\alpha_2(4,2)\mathrm{Cov}[N_{13}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Var}[N_{13}] + \alpha_2(3,1)\mathrm{Cov}[N_{13}N_{23}]$$

$$+ \alpha_1(4,1)\mathrm{Cov}[N_{12}N_{14}] + \alpha_2(4,1)\mathrm{Cor}[N_{12}N_{24}]$$

$$- [\kappa_1(2) + \kappa_1(3) + \gamma_1(2) + \gamma_1(3)]\mathrm{Cov}[N_{12}N_{13}]$$

$$- \Omega^{-1}\beta(1,3)\langle N_{11}\rangle\langle N_{12}\rangle - \alpha_1(3,1)\langle N_{13}\rangle \qquad (4\text{-}111)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{12}N_{14}] = -4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{14}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{14}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{14}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{14}]$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{13}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{12}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\{\langle N_{12}\rangle\mathrm{Var}[N_{12}] + \langle N_{22}\rangle\mathrm{Cov}[N_{12}N_{22}]\}$$

$$- [\alpha_1(4,1) + \alpha_1(4,2) + \alpha_1(2,1)]\mathrm{Cov}[N_{12}N_{14}]$$

$$+ 2\alpha_1(4,2)\mathrm{Var}[N_{14}] + 2\alpha_2(4,2)\mathrm{Cov}[N_{14}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{14}] + \alpha_2(3,1)\mathrm{Cov}[N_{14}N_{23}]$$

$$- [\kappa_1(2) + \kappa_1(4) + \gamma_1(2) + \gamma_1(4)]\mathrm{Cov}[N_{12}N_{14}]$$

$$- 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle^2 - 2\alpha_1(4,2)\langle N_{14}\rangle \qquad (4\text{-}112)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{12}N_{21}] = -4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{21}] - 4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{21}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{21}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle\mathrm{Cov}[N_{12}N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{22}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle\mathrm{Cov}[N_{12}N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{23}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{21}]$$

$$- \alpha_1(2,1)\mathrm{Cov}[N_{12}N_{21}]$$

$$+ 2\alpha_1(4,2)\mathrm{Cov}[N_{14}N_{21}] + 2\alpha_2(4,2)\mathrm{Cov}[N_{21}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{21}] + \alpha_2(3,1)\mathrm{Cov}[N_{21}N_{23}]$$

$$- [\kappa_1(2) + \gamma_1(2) + \gamma_2(1)]\mathrm{Cov}[N_{12}N_{21}]$$

$$+ \kappa_1(1)\mathrm{Cov}[N_{11}N_{12}] \qquad (4\text{-}113)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{12}N_{22}] = -4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{22}] - 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{12}N_{22}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{22}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{22}]\}$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{12}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{22}]$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{21}]$$

$$- [\alpha_1(2,1) + \alpha_2(2,1)]\mathrm{Cov}[N_{12}N_{22}]$$

$$+ 2\alpha_1(4,2)\mathrm{Cov}[N_{14}N_{22}] + 2\alpha_2(4,2)\mathrm{Cov}[N_{22}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{22}] + \alpha_2(3,1)\mathrm{Cov}[N_{22}N_{23}]$$

$$- [\kappa_1(2) + \gamma_1(2) + \gamma_2(2)]\mathrm{Cov}[N_{12}N_{22}]$$

$$+ \kappa_1(2)\mathrm{Var}[N_{12}] - \alpha_2(3,1)\langle N_{23}\rangle \qquad (4\text{-}114)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{12}N_{23}] = -4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{23}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{23}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{23}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{12}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{23}]$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{12}N_{21}]\}$$

$$- [\alpha_1(2,1) + \alpha_2(3,1)]\mathrm{Cov}[N_{12}N_{23}]$$

$$+ 2\alpha_1(4,2)\mathrm{Cov}[N_{14}N_{23}] + 2\alpha_2(4,2)\mathrm{Cov}[N_{23}N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{23}] + \alpha_2(3,1)\mathrm{Var}[N_{23}]$$

$$- [\kappa_1(2) + \gamma_1(2) + \gamma_2(3)]\mathrm{Cov}[N_{12}N_{23}]$$

$$+ \kappa_1(3)\mathrm{Cov}[N_{12}N_{13}] - \alpha_2(3,1)\langle N_{23}\rangle \qquad (4\text{-}115)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{12}N_{24}] = -4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{24}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{24}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{24}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{11}\rangle\mathrm{Cov}[N_{11}N_{24}]$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{12}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{12}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle \mathrm{Cov}[N_{12}N_{22}]$$

$$- [\alpha_1(2,1) + \alpha_2(4,2) + \alpha_2(4,1)]\mathrm{Cov}[N_{12}N_{24}]$$

$$+ 2\alpha_1(4,2)\mathrm{Cov}[N_{14}N_{24}] + 2\alpha_2(4,2)\mathrm{Var}[N_{24}]$$

$$+ \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{24}] + \alpha_2(3,1)\mathrm{Cov}[N_{23}N_{24}]$$

$$- [\kappa_1(2) + \gamma_1(2) + \gamma_2(4)]\mathrm{Cov}[N_{12}N_{24}]$$

$$+ \kappa_1(4)\mathrm{Cov}[N_{12}N_{14}] - 2\alpha_2(4,2)\langle N_{24}\rangle \qquad (4\text{-}116)$$

$$\frac{d}{dt}\mathrm{Var}[N_{13}] = -2\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle \mathrm{Var}[N_{13}] + \langle N_{13}\rangle \mathrm{Cov}[N_{11}N_{13}]\}$$

$$+ 2\Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle \mathrm{Cov}[N_{12}N_{13}] + \langle N_{12}\rangle \mathrm{Cov}[N_{11}N_{13}]\}$$

$$- 2\alpha_1(3,1)\mathrm{Var}[N_{13}]$$

$$+ 2\alpha_1(4,1)\mathrm{Cov}[N_{13}N_{14}] + 2\alpha_2(4,1)\mathrm{Cov}[N_{13}N_{24}]$$

$$- 2[\kappa_1(3) + \gamma_1(3)]\mathrm{Var}[N_{13}] + \Omega^{-1}\beta(1,4)\langle N_{11}\rangle\langle N_{13}\rangle$$

$$+ \Omega^{-1}\beta(1,3)\langle N_{11}\rangle\langle N_{12}\rangle + \alpha_1(3,1)\langle N_{13}\rangle$$

$$+ \alpha_1(4,1)\langle N_{14}\rangle + \alpha_2(4,1)\langle N_{24}\rangle$$

$$+ \kappa_1(3)\langle N_{13}\rangle + \gamma_1(3)\langle N_{13}\rangle \qquad (4\text{-}117)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{13}N_{14}] = -\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{14}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{14}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{14}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{14}]\}$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Var}[N_{13}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{13}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{13}]$$

$$- [\alpha_1(3,1) + \alpha_1(4,2) + \alpha_1(4,1)]\mathrm{Cov}[N_{13}N_{24}]$$

$$+ 2\alpha_1(4,1)\mathrm{Var}[N_{14}] + 2\alpha_2(4,1)\mathrm{Cov}[N_{14}N_{24}]$$

$$- [\kappa_1(3) + \kappa_1(4) + \gamma_1(3) + \gamma_1(4)]\mathrm{Cov}[N_{13}N_{14}]$$

$$- \beta(1,4)\langle N_{11}\rangle\langle N_{13}\rangle - \alpha_1(4,1)\langle N_{14}\rangle \qquad (4\text{-}118)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{13}N_{21}] = -\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{21}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{21}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{21}]\}$$

$$- 4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{21}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle\mathrm{Cov}[N_{13}N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{22}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle\mathrm{Cov}[N_{13}N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{23}]\}$$

$$- \alpha_1(3,1)\mathrm{Cov}[N_{13}N_{21}]$$

$$+ 2\alpha_1(4,1)\mathrm{Cov}[N_{14}N_{21}] + 2\alpha_2(4,1)\mathrm{Cov}[N_{21}N_{24}]$$

$$- [\kappa_1(3) + \gamma_1(3) + \gamma_2(1)]\mathrm{Cov}[N_{13}N_{21}]$$

$$+ \kappa_1(1)\mathrm{Cov}[N_{11}N_{13}] \qquad (4\text{-}119)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{13}N_{22}] = -\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{22}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{22}]\}$$

$$\pm \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{22}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{22}]\}$$

$$- 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{13}N_{22}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{13}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{21}]$$

$$- [\alpha_1(3,1) + \alpha_2(2,1)]\mathrm{Cov}[N_{13}N_{22}]$$

$$+ 2\alpha_1(4,1)\mathrm{Cov}[N_{14}N_{22}] + 2\alpha_2(4,1)\mathrm{Cov}[N_{22}N_{24}]$$

$$- [\kappa_1(3) + \gamma_1(3) + \gamma_2(2)]\mathrm{Cov}[N_{13}N_{22}]$$

$$+ \kappa_1(2)\mathrm{Cov}[N_{12}N_{13}] \qquad (4\text{-}120)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{13}N_{23}] = -\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{23}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{23}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{23}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{23}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{13}N_{21}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{13}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{13}N_{21}]\}$$

$$- [\alpha_1(3,1) + \alpha_2(3,1)]\mathrm{Cov}[N_{13}N_{23}]$$

$$+ 2\alpha_1(4,1)\mathrm{Cov}[N_{14}N_{23}] + 2\alpha_2(4,1)\mathrm{Cov}[N_{23}N_{24}]$$

$$- [\kappa_1(3) + \gamma_1(3) + \gamma_2(3)]\mathrm{Cov}[N_{13}N_{23}]$$

$$+ \kappa_1(3)\mathrm{Var}[N_{13}] \qquad (4\text{-}121)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{13}N_{24}] = -\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{24}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{24}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{11}\rangle\mathrm{Cov}[N_{12}N_{24}] + \langle N_{12}\rangle\mathrm{Cov}[N_{11}N_{24}]\}$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{12}\rangle\mathrm{Cov}[N_{13}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{13}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{13}N_{22}]$$

$$- [\alpha_1(3,1) + \alpha_2(4,2) + \alpha_2(4,1)]\mathrm{Cov}[N_{13}N_{24}]$$

$$+ 2\alpha_1(4,1)\mathrm{Cov}[N_{14}N_{24}] + 2\alpha_2(4,1)\mathrm{Var}[N_{24}]$$

$$- [\kappa_1(3) + \gamma_1(3) + \gamma_2(4)]\mathrm{Cov}[N_{13}N_{24}]$$

$$+ \kappa_1(4)\mathrm{Cov}[N_{13}N_{14}] - \alpha_2(4,1)\langle N_{24}\rangle \qquad (4\text{-}122)$$

$$\frac{d}{dt}\mathrm{Var}[N_{14}] = 2\Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle \mathrm{Cov}[N_{13}N_{14}] + \langle N_{13}\rangle \mathrm{Cov}[N_{11}N_{14}]\}$$

$$+ 4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle \mathrm{Cov}[N_{12}N_{14}]\}$$

$$- 2[\alpha_1(4,2) + \alpha_1(4,1)]\mathrm{Var}[N_{14}]$$

$$+ 2[\kappa_1(4) + \gamma_1(4)]\mathrm{Var}[N_{14}]$$

$$+ \Omega^{-1}\beta(1,4)\langle N_{11}\rangle\langle N_{13}\rangle + \Omega^{-1}\beta(2,4)\langle N_{12}\rangle^2$$

$$+ [\alpha_1(4,1) + \alpha_1(4,2)]\langle N_{14}\rangle + \kappa_1(4)\langle N_{14}\rangle + \gamma_1(4)\langle N_{14}\rangle \qquad (4\text{-}123)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{14}N_{21}] = \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle \mathrm{Cov}[N_{13}N_{21}] + \langle N_{13}\rangle \mathrm{Cov}[N_{11}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle \mathrm{Cov}[N_{12}N_{21}]$$

$$- 4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle \mathrm{Cov}[N_{14}N_{21}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle \mathrm{Cov}[N_{14}N_{21}] + \langle N_{21}\rangle \mathrm{Cov}[N_{14}N_{22}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle \mathrm{Cov}[N_{14}N_{21}] + \langle N_{21}\rangle \mathrm{Cov}[N_{14}N_{23}]\}$$

$$- [\alpha_1(4,1) + \alpha_1(4,2)]\mathrm{Cov}[N_{14}N_{21}]$$

$$- [\kappa_1(4) + \gamma_1(4) + \gamma_2(1)]\mathrm{Cov}[N_{14}N_{21}] \qquad (4\text{-}124)$$

$$+ \kappa_1(1)\mathrm{Cov}[N_{11}N_{14}]$$

$$\frac{d}{dt}\mathrm{Cov}[N_{14}N_{22}] = \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{22}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{22}]\}$$
$$+ 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{22}]$$
$$- 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{14}N_{22}]$$
$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{14}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{14}N_{21}]$$
$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{14}N_{21}]$$
$$- [\alpha_1(4,1) + \alpha_1(4,2) + \alpha_2(2,1)]\mathrm{Cov}[N_{14}N_{22}]$$
$$- \kappa_1(4) + \gamma_1(4) + \gamma_2(2)]\mathrm{Cov}[N_{14}N_{22}]$$
$$+ \kappa_1(2)\mathrm{Cov}[N_{12}N_{14}] \qquad (4\text{-}125)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{14}N_{23}] = \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{23}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{23}]\}$$
$$+ 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{23}]$$
$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{14}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{14}N_{21}]\}$$
$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{14}N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{14}N_{21}]\}$$
$$- [\alpha_1(4,1) + \alpha_1(4,2) + \alpha_2(3,1)]\mathrm{Cov}[N_{14}N_{23}]$$
$$- [\kappa_1(4) + \gamma_1(4) + \gamma_2(4)]\mathrm{Cov}[N_{14}N_{23}]$$
$$+ \kappa_1(3)\mathrm{Cov}[N_{13}N_{14}] \qquad (4\text{-}126)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{14}N_{24}] = \Omega^{-1}\beta(1,4)\{\langle N_{11}\rangle\mathrm{Cov}[N_{13}N_{24}] + \langle N_{13}\rangle\mathrm{Cov}[N_{11}N_{24}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{12}\rangle\mathrm{Cov}[N_{12}N_{24}]$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{14}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{14}N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{14}N_{22}]$$

$$- [\alpha_1(4,1) + \alpha_1(4,2) + \alpha_2(4,1) + \alpha_2(4,2)]\mathrm{Cov}[N_{14}N_{24}]$$

$$- [\kappa_1(4) + \gamma_1(4) + \gamma_2(4)]\mathrm{Cov}[N_{14}N_{24}]$$

$$+ \kappa_1(4)\mathrm{Var}[N_{14}] \qquad (4\text{-}127)$$

$$\frac{d}{dt}\mathrm{Var}[N_{21}] = -8\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Var}[N_{21}]$$

$$- 2\Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle\mathrm{Var}[N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{22}]\}$$

$$- 2\Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle\mathrm{Var}[N_{21}] + \langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{23}]\}$$

$$- 2\Omega_2(1)\mathrm{Var}[N_{21}] + 2\kappa_1(1)\mathrm{Cov}[N_{11}N_{21}]$$

$$+ 4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle^2 + \Omega^{-1}\beta(1,3)\langle N_{21}\rangle\langle N_{22}\rangle$$

$$+ \Omega^{-1}\beta(1,4)\langle N_{21}\rangle\langle N_{23}\rangle + \gamma_2(1)\langle N_{21}\rangle \qquad (4\text{-}128)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{21}N_{22}] = -4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{22}]$$

$$-4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{22}]$$

$$-\Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{22}] + \langle N_{21}\rangle\mathrm{Var}[N_{22}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle \mathrm{Cov}[N_{21}N_{22}] + \langle N_{21}\rangle \mathrm{Cov}[N_{22}N_{23}]\}$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle \mathrm{Cov}[N_{21}N_{22}] + \langle N_{22}\rangle \mathrm{Var}[N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle \mathrm{Var}[N_{21}]$$

$$- \alpha_2(2,1)\mathrm{Cov}[N_{21}N_{22}] - [\gamma_2(1) + \gamma(2)]\mathrm{Cov}[N_{21}N_{22}]$$

$$+ \kappa_1(1)\mathrm{Cov}[N_{11}N_{22}] + \kappa_1(2)\mathrm{Cov}[N_{12}N_{21}]$$

$$+ \Omega^{-1}\beta(1,3)\langle N_{21}\rangle\langle N_{22}\rangle - 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle^2 \qquad (4\text{-}129)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{21}N_{23}] = -4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle \mathrm{Cov}[N_{21}N_{23}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle \mathrm{Cov}[N_{21}N_{23}] + \langle N_{21}\rangle \mathrm{Cov}[N_{22}N_{23}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle \mathrm{Cov}[N_{21}N_{23}] + \langle N_{21}\rangle \mathrm{Var}[N_{23}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle \mathrm{Cov}[N_{21}N_{23}] + \langle N_{23}\rangle \mathrm{Var}[N_{21}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle \mathrm{Cov}[N_{21}N_{22}] + \langle N_{22}\rangle \mathrm{Var}[N_{21}]\}$$

$$- [\alpha_2(3,1) + \gamma_2(1) + \gamma_2(3)]\mathrm{Cov}[N_{21}N_{23}]$$

$$+ \kappa_1(1)\mathrm{Cov}[N_{11}N_{23}] + \kappa_1(3)\mathrm{Cov}[N_{13}N_{21}]$$

$$+ \Omega^{-1}\beta(1,4)\langle N_{21}\rangle\langle N_{23}\rangle - \beta(1,3)\langle N_{21}\rangle\langle N_{22}\rangle \qquad (4\text{-}130)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{21}N_{24}] = -4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{24}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{24}] + \langle N_{21}\rangle\mathrm{Cov}[N_{22}N_{24}]\}$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{23}\rangle\mathrm{Cov}[N_{21}N_{24}] + \langle N_{21}\rangle\mathrm{Cov}[N_{23}N_{24}]\}$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{23}N_{24}] + \langle N_{23}\rangle\mathrm{Var}[N_{21}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{22}]$$

$$- [\alpha_2(4,1) + \alpha_2(4,2) + \gamma_2(1) + \gamma_2(4)]\mathrm{Cov}[N_{21}N_{24}]$$

$$+ \kappa_1(1)\mathrm{Cov}[N_{11}N_{24}] + \kappa_1(4)\mathrm{Cov}[N_{14}N_{21}]$$

$$- \Omega^{-1}\beta(1,4)\langle N_{21}\rangle\langle N_{23}\rangle - 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle^2 \qquad (4\text{-}131)$$

$$\frac{d}{dt}\mathrm{Var}[N_{22}] = -8\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Var}[N_{22}]$$

$$- 2\Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Var}[N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{22}]\}$$

$$+ 4\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{22}]$$

$$- 2\alpha_2(2,1)\mathrm{Var}[N_{22}] + 2\kappa_1(2)\mathrm{Cov}[N_{12}N_{22}]$$

$$- 2\gamma_2(2)\mathrm{Var}[N_{22}] + \Omega^{-1}\beta(1,3)\langle N_{21}\rangle\langle N_{22}\rangle + 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle^2$$

$$+ \Omega^{-1}\beta(1,2)\langle N_{21}\rangle^2 + \alpha_2(2,1)\langle N_{22}\rangle + \Omega f(2) + \gamma_2(2)\langle N_{22}\rangle \qquad (4\text{-}132)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{22}N_{23}] = -4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{22}N_{23}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{22}N_{23}] + \langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{23}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{23}]$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{22}N_{23}] + \langle N_{23}\rangle\mathrm{Cov}[N_{21}N_{22}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Var}[N_{22}] + \langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{22}]\}$$

$$- [\alpha_2(2,1) + \alpha_2(3,1) + \gamma_2(2) + \gamma_2(3)]\mathrm{Cov}[N_{22}N_{23}]$$

$$+ \kappa_1(2)\mathrm{Cov}[N_{12}N_{23}] + \kappa_1(3)\mathrm{Cov}[N_{13}N_{22}]$$

$$- \Omega^{-1}\beta(1,3)\langle N_{21}\rangle\langle N_{22}\rangle \qquad (4\text{-}133)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{22}N_{24}] = -4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Cov}[N_{22}N_{24}]$$

$$- \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle\mathrm{Cov}[N_{22}N_{24}] + \langle N_{22}\rangle\mathrm{Cov}[N_{21}N_{24}]\}$$

$$+ 2\Omega^{-1}\beta(1,2)\langle N_{21}\rangle\mathrm{Cov}[N_{21}N_{24}]$$

$$+ \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle\mathrm{Cov}[N_{23}N_{24}] + \langle N_{23}\rangle\mathrm{Cov}[N_{21}N_{23}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle\mathrm{Var}[N_{22}]$$

$$- [\alpha_2(2.1) + \alpha_2(4,1) + \alpha_2(4,2) + \gamma_2(2) + \gamma_2(4)]\mathrm{Cov}[N_{22}N_{24}]$$

$$+ \kappa_1(2)\mathrm{Cov}[N_{12}N_{24}] + \kappa_1(4)\mathrm{Cov}[N_{14}N_{22}]$$

$$- 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle^2 \qquad (4\text{-}134)$$

$$\frac{d}{dt}\mathrm{Var}[N_{23}] = -2\Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle \mathrm{Var}[N_{23}] + \langle N_{23}\rangle \mathrm{Cov}[N_{21}N_{23}]\}$$

$$+ 2\Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle \mathrm{Cov}[N_{22}N_{23}] + \langle N_{22}\rangle \mathrm{Cov}[N_{21}N_{23}]\}$$

$$- 2[\alpha_2(3,1) + \gamma_2(3)]\mathrm{Var}[N_{23}] + \kappa_1(3)\mathrm{Cov}[N_{13}N_{23}]$$

$$+ \Omega^{-1}\beta(1,4)\langle N_{21}\rangle\langle N_{23}\rangle + \Omega^{-1}\beta(1,3)\langle N_{21}\rangle\langle N_{22}\rangle$$

$$+ \alpha_2(3,1)\langle N_{23}\rangle + \gamma_2(3)\langle N_{23}\rangle \qquad (4\text{-}135)$$

$$\frac{d}{dt}\mathrm{Cov}[N_{23}N_{24}] = \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle \mathrm{Var}[N_{23}] + \langle N_{23}\rangle \mathrm{Cov}[N_{21}N_{23}]\}$$

$$+ 2\Omega^{-1}\beta(2,4)\langle N_{22}\rangle \mathrm{Cov}[N_{23}N_{22}]$$

$$- \Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle \mathrm{Cov}[N_{23}N_{24}] + \langle N_{23}\rangle \mathrm{Cov}[N_{21}N_{24}]\}$$

$$+ \Omega^{-1}\beta(1,3)\{\langle N_{21}\rangle \mathrm{Cov}[N_{22}N_{24}] + \langle N_{22}\rangle \mathrm{Cov}[N_{21}N_{24}]\}$$

$$- [\alpha_2(3,1) + \alpha_2(4,1) + \alpha_2(4,2) + \gamma_2(3) + \gamma_2(4)]\mathrm{Cov}[N_{23}N_{24}]$$

$$+ \kappa_1(3)\mathrm{Cov}[N_{13}N_{24}] + \kappa_1(4)\mathrm{Cov}[N_{14}N_{23}]$$

$$- \Omega^{-1}\beta(1,4)\langle N_{21}\rangle\langle N_{23}\rangle \qquad (4\text{-}136)$$

$$\frac{d}{dt}\mathrm{Var}[N_{24}] = 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle \mathrm{Cov}[N_{22}N_{24}]$$

$$+ 2\Omega^{-1}\beta(1,4)\{\langle N_{21}\rangle \mathrm{Cov}[N_{23}N_{24}] + \langle N_{23}\rangle \mathrm{Cov}[N_{21}N_{24}]$$

$$- 2[\alpha_2(4,1] + \alpha_2(4,2) + \gamma_2(4)]\mathrm{Var}[N_{24}]$$

$$+ 2\kappa_1(4)\mathrm{Cov}[N_{14}N_{24}]$$

$$+\Omega^{-1}\beta(1,4)\langle N_{21}\rangle\langle N_{23}\rangle + \Omega^{-1}\beta(2,4)\langle N_{22}\rangle^2$$

$$+ [\alpha_2(4,1) + \alpha_2(4,2)]\langle N_{24}\rangle + \gamma_2(4)\langle N_{24}\rangle \qquad (4\text{-}137)$$

From the assumed values of the transition functions and the steady-state values for $\langle N_{ij}\rangle$, the following values for the steady-state covariances have been obtained from the steady-state solution of Eqs. 4-102 through 4-137;

$\text{Var}[N_{11}] = 24.6553$ $\quad$ $\text{Cov}[N_{11}N_{21}] = 17.9258$

$\text{Cov}[N_{11}N_{12}] = 1.9747$ $\quad$ $\text{Cov}[N_{11}N_{22}] = -2.0765$

$\text{Cov}[N_{11}N_{13}] = 0.8728$ $\quad$ $\text{Cov}[N_{11}N_{23}] = 0.5485$

$\text{Cov}[N_{11}N_{14}] = 0.1223$ $\quad$ $\text{Cov}[N_{11}N_{24}] = 1.3126$

$\text{Var}[N_{12}] = 4.5873$ $\quad$ $\text{Cov}[N_{12}N_{21}] = 0.9555$

$\text{Cov}[N_{12}N_{13}] = 0.2335$ $\quad$ $\text{Cov}[N_{12}N_{22}] = 0.9462$

$\text{Cov}[N_{12}N_{14}] = 0.0891$ $\quad$ $\text{Cov}[N_{12}N_{23}] = -0.0822$

$\text{Cov}[N_{12}N_{24}] = 0.4948$

$\text{Var}[N_{13}] = 1.0495$ $\quad$ $\text{Cov}[N_{13}N_{22}] = 0.0336$

$\text{Cov}[N_{13}N_{14}] = 0.0235$ $\quad$ $\text{Cov}[N_{13}N_{23}] = 0.4810$

$\text{Cov}[N_{13}N_{21}] = 0.3745$ $\quad$ $\text{Cov}[N_{13}N_{24}] = 0.9966$

$\text{Var}[N_{14}] = 0.0830$ $\quad$ $\text{Cov}[N_{14}N_{23}] = 0.0232$

$\text{Cov}[N_{14}N_{21}] = 0.0996$ $\quad$ $\text{Cov}[N_{14}N_{24}] = 0.0735$

$\text{Cov}[N_{14}N_{22}] = 0.0427$

$\mathrm{Var}[N_{21}] = 76.7055$ $\quad\quad$ $\mathrm{Cov}[N_{21}N_{23}] = -1.0200$

$\mathrm{Cov}[N_{21}N_{22}] = -0.0960$ $\quad\quad$ $\mathrm{Cov}[N_{21}N_{24}] = -0.9034$

$\mathrm{Var}[N_{22}] = 6.0388$ $\quad\quad$ $\mathrm{Cov}[N_{22}N_{24}] = -1.3060$

$\mathrm{Cov}[N_{22}N_{23}] = -1.5183$

$\mathrm{Var}[N_{23}] = 7.5051$ $\quad\quad$ $\mathrm{Cov}[N_{23}N_{24}] = -0.0015$

$\mathrm{Var}[N_{24}] = 15.0449$

Furthermore, Eq. 4-130 yields the following set of coupled linear differential equations for the correlation functions;

$$\begin{aligned}\frac{d}{d\tau}K_{pq11}(\tau) = &-4\Omega^{-1}\beta(1,2)\langle N_{11}\rangle K_{pq11} \\ &- \Omega^{-1}\beta(1,3)[\langle N_{12}\rangle K_{pq11} + \langle N_{11}\rangle K_{pq12}] \\ &- \Omega^{-1}\beta(1,4)[\langle N_{13}\rangle K_{pq11} + \langle N_{11}\rangle K_{pq13}] \\ &+ 2\alpha_1(2,1)K_{pq12} + \alpha_1(3,1)K_{pq13} + \alpha_1(4,1)K_{pq14} \\ &+ 2\alpha_2(2,1)K_{pq22} + \alpha_2(3,1)K_{pq23} + \alpha_2(4,1)K_{pq24} \\ &- [\kappa_1(1) + \gamma_1(1)]K_{pq11}\end{aligned} \tag{4-138}$$

$$\begin{aligned}\frac{d}{d\tau}K_{pq12}(\tau) = &-\Omega^{-1}\beta(1,3)[\langle N_{11}\rangle K_{pq12} + \langle N_{12}\rangle K_{pq11}] \\ &- 4\Omega^{-1}\beta(2,4)\langle N_{12}\rangle K_{pq12} \\ &+ 2\beta(1,2)\langle N_{11}\rangle K_{pq11}\end{aligned}$$

$$+ \alpha_1(3,1)K_{pq13} + 2\alpha_1(4,2)K_{pq14}$$

$$+ \alpha_2(3,1)K_{pq23} + 2\alpha_2(4,2)K_{pq24}$$

$$- [\alpha_1(2,1) + \kappa_1(2) + \gamma_1(2)]K_{pq12} \qquad (4\text{-}139)$$

$$\frac{d}{d\tau} K_{pq13}(\tau) = -\Omega^{-1}\beta(1,4)[\langle N_{11}\rangle K_{pq13} + \langle N_{13}\rangle K_{pq11}]$$

$$+ \Omega^{-1}\beta(1,3)[\langle N_{11}\rangle K_{pq12} + \langle N_{12}\rangle K_{pq11}]$$

$$+ \alpha_1(4,1)K_{pq14} + \alpha_2(4,1)K_{pq24}$$

$$- [\alpha_1(3,1) + \kappa_1(3) + \gamma_1(3)]K_{pq13} \qquad (4\text{-}140)$$

$$\frac{d}{d\tau}K_{pq14}(\tau) = \Omega^{-1}\beta(1,4)[\langle N_{11}\rangle K_{pq13} + \langle N_{13}\rangle K_{pq11}$$

$$+ \Omega^{-1}\beta(2,4)\langle N_{12}\rangle K_{pq12}$$

$$- [\alpha_1(4,1) + \alpha_1(4,2) + \kappa_1(4) + \gamma_1(4)]K_{pq14} \qquad (4\text{-}141)$$

$$\frac{d}{d\tau}K_{pq21}(\tau) = -4\beta(1,2)\langle N_{21}\rangle K_{pq21}$$

$$-\Omega^{-1}\beta(1,3)[\langle N_{22}\rangle K_{pq21} + \langle N_{21}\rangle K_{pq22}]$$

$$-\Omega^{-1}\beta(1,4)[\langle N_{23}\rangle K_{pq21} + \langle N_{21}\rangle K_{pq23}]$$

$$+ \kappa_1(1)K_{pq11} - \gamma_2(1)K_{pq21} \qquad (4\text{-}142)$$

$$\frac{d}{d\tau}K_{pq22}(\tau) = -\Omega^{-1}\beta(1,3)[\langle N_{21}\rangle K_{pq22} + \langle N_{22}\rangle K_{pq21}]$$
$$- 4\Omega^{-1}\beta(2,4)\langle N_{22}\rangle K_{pq22} + 2\beta(1,2)\langle N_{21}\rangle K_{pq21}$$
$$- [\alpha_2(2,1) + \gamma_2(2)]K_{pq22}$$
$$+ \kappa_1(2)K_{pq12} \qquad (4\text{-}143)$$

$$\frac{d}{d\tau}K_{pq23}(\tau) = -\Omega^{-1}\beta(1,4)[\langle N_{21}\rangle K_{pq23} + \langle N_{23}\rangle K_{pq21}]$$
$$+ \Omega^{-1}\beta(1,3)[\langle N_{21}\rangle K_{pq22} + \langle N_{22}\rangle K_{pq21}]$$
$$- [\alpha_2(3,1) + \gamma_2(3)]K_{pq23}$$
$$+ \kappa_1(3)K_{pq13} \qquad (4\text{-}144)$$

$$\frac{d}{d\tau}K_{pq24}(\tau) = \Omega^{-1}\beta(1,4)[\langle N_{21}\rangle K_{pq23} + \langle N_{23}\rangle K_{pq21}]$$
$$+ \Omega^{-1}\beta(2,4)\langle N_{22}\rangle K_{pq22}$$
$$- [\alpha_2(4,1) + \alpha_2(4,2) + \gamma_1(4)]K_{pq24}$$
$$+ \kappa_1(4)K_{pq14} \qquad (4\text{-}145)$$

where

$p = 1, 2$

$q = 1, 2, 3, 4$

These equations are solved with the steady-state covariances as the initial conditions to yield

$$K_{pqij}(\tau) = C_{pq}^{(1)}A_{ij}^{(1)}e^{-\theta_1\tau} + C_{pq}^{(2)}[A_{ij}^{(2)}\cos\phi_1\tau - A_{ij}^{(3)}\sin\phi_1\tau]e^{-\theta_2\tau}$$

$$+ C_{pq}^{(3)}[A_{ij}^{(2)}\sin\phi_1\tau + A_{ij}^{(3)}\cos\phi_1\tau]e^{-\theta_2\tau} + C_{pq}^{(4)}A_{ij}^{(4)}e^{-\theta_3\tau}$$

$$+ C_{pq}^{(5)}[A_{ij}^{(5)}\cos\phi_2\tau - A_{ij}^{(6)}\sin\phi_2\tau]e^{-\theta_4\tau}$$

$$+ C_{pq}^{(6)}[A_{ij}^{(5)}\sin\phi_2\tau + A_{ij}^{(6)}\cos\phi_2\tau]e^{-\theta_4\tau} + C_{pq}^{(7)}A_{ij}^{(7)}e^{-\theta_5\tau}$$

$$+ C_{pq}^{(8)}A_{ij}^{(8)}e^{-\theta_6\tau} \qquad (4\text{-}146)$$

where

$p,i = 1$ or 2 $\qquad$ $j,q = 1,2,3$, or 4

$\theta_1 = 14.5268$ $\qquad$ $\phi_1 = 0.5219$

$\theta_2 = 2.0515$ $\qquad$ $\phi_2 = 2.4904$

$\theta_3 = 11.3521$

$\theta_4 = 6.1783$

$\theta_5 = 20.2468$

$\theta_6 = 21.9965$

and

p,q	$C_{pq}^{(1)}$	$C_{pq}^{(2)}$	$C_{pq}^{(3)}$	$C_{pq}^{(4)}$	$C_{pq}^{(5)}$	$C_{pq}^{(6)}$	$C_{pq}^{(7)}$	$C_{pq}^{(8)}$
1,1	-1.1445	-11.9487	-17.1291	24.8540	-4.8996	15.9469	0.5158	0.7295
1,2	2.2622	1.1439	-1.8366	8.3904	-3.4186	4.0196	-4.1754	2.8924
1,3	13.1044	4.0402	1.3626	4.5022	-0.3078	0.6363	1.7219	0.0227
1,4	0.8948	0.2687	-0.0070	0.5543	-0.1467	0.1375	-0.8344	-0.6935
2,1	4.3093	-37.3867	-38.9760	10.5224	-2.0704	28.0984	-0.3319	0.5775
2,2	4.9450	0.0958	0.2731	-2.2766	-2.5689	1.6161	-1.6065	0.6496
2,3	8.2620	17.5966	10.9301	3.4241	4.4369	1.0462	1.2100	-0.4386
2,4	-2.1216	26.4637	7.2148	-8.8367	-0.5992	-12.2610	1.6101	-2.2211

i,j	$A_{ij}^{(1)}$	$A_{ij}^{(2)}$	$A_{ij}^{(3)}$	$A_{ij}^{(4)}$	$A_{ij}^{(5)}$	$A_{ij}^{(6)}$	$A_{ij}^{(7)}$	$A_{ij}^{(8)}$
1,1	-0.3312	0.3533	-0.3044	0.4508	-0.7394	0.5443	0.9408	-0.9711
1,2	0.0401	0.1315	-0.1920	0.0789	0.0190	-0.1100	-0.4964	0.6106
1,3	0.0554	0.0461	-0.0776	0.0374	-0.0180	-0.0562	0.0607	0.0058
1,4	0.0047	0.0036	-0.0054	0.0062	-0.0030	-0.0018	-0.0416	-0.0569
2,1	0.3062	0.9790	-2.5180	-0.6981	2.0530	0.8883	-0.5599	0.5137
2,2	0.0335	-0.0786	0.6079	-0.5189	-1.4848	0.8243	0.2588	-0.3036
2,3	-0.0498	0.1866	0.0846	0.0777	0.7089	0.3589	-0.0556	0.0239
2,4	-0.0043	0.5859	-0.9171	0.0542	0.0251	-0.5428	0.0256	0.0243

It is also possible to redefine the random variables such that only the size is included as a parameter. Doing so yields a new set of random variables

$$\{N_j: \; j\varepsilon\{1,2,3,4\}\}$$

where

$$N_j = N_{1j} + N_{2j} \tag{4-147}$$

The expected values of the new random variables, $\langle N_j \rangle$, can be found from the expected values of the original random variables

$$\langle N_j \rangle = \langle N_{1j} \rangle + \langle N_{2j} \rangle \tag{4-148}$$

or

$$\langle N_1 \rangle = 76.1007$$

$$\langle N_2 \rangle = 18.6131$$

$$\langle N_3 \rangle = 9.7161$$

$$\langle N_4 \rangle = 14.2191$$

The correlation functions of the new random variables, $K_{qj}(\tau)$, can be found from Eq. 4-146 using the following relationship;

$$K_{qj}(\tau) = \sum_{p=1}^{2} \sum_{i=1}^{2} K_{pqij}(\tau) \tag{4-149}$$

This expressions then, in turn, yields

$$K_{qj}(\tau) = B_{qj}^{(1)} e^{-\theta_1 \tau} + [B_{qj}^{(2)} \cos\phi_1 \tau + B_{qj}^{(3)} \sin\phi_1 \tau] e^{-\theta_2 \tau}$$

$$+ B_{ij}^{(4)} e^{\theta_3 \tau} + [B_{ij}^{(5)} \cos\phi_2 \tau + B_{ij}^{(6)} \sin\phi_2 \tau] e^{-\theta_4 \tau}$$

$$+ B_{ij}^{(7)} e^{-\theta_5 \tau} + B_{ij}^{(8)} e^{-\theta_6 \tau} \qquad (4\text{-}150)$$

where

$q,j = 1,2,3,$ or 4

$$B_{qj}^{(1)} = \sum_p \sum_i C_{pq}^{(1)} A_{ij}^{(1)}$$

$$B_{qj}^{(2)} = \sum_p \sum_i [C_{pq}^{(2)} A_{ij}^{(2)} + C_{pq}^{(3)} A_{ij}^{(3)}]$$

$$B_{qj}^{(3)} = \sum_p \sum_i [C_{pq}^{(3)} A_{ij}^{(2)} - C_{pq}^{(2)} A_{ij}^{(3)}]$$

$$B_{qj}^{(4)} = \sum_p \sum_i C_{pq}^{(4)} A_{ij}^{(4)}$$

$$B_{qj}^{(5)} = \sum_p \sum_i [C_{pq}^{(5)} A_{ij}^{(5)} + C_{pq}^{(6)} A_{ij}^{(6)}]$$

$$B_{qj}^{(6)} = \sum_p \sum_i [C_{pq}^{(6)} A_{ij}^{(5)} - C_{pq}^{(5)} A_{ij}^{(6)}]$$

$$B_{qj}^{(7)} = \sum_p \sum_i C_{pq}^{(7)} A_{ij}^{(7)}$$

$$B_{qj}^{(8)} = \sum_p \sum_i C_{pq}^{(8)} A_{ij}^{(8)}$$

or

$$B_{qj}^{(1)} = \begin{bmatrix} -0.0794 & 0.2328 & 0.0177 & 0.0013 \\ -0.1808 & 0.5302 & 0.0403 & 0.0030 \\ -0.5359 & 1.5717 & 0.1194 & 0.0090 \\ 0.0308 & -0.0902 & -0.0069 & -0.0005 \end{bmatrix}$$

$$B_{qj}^{(2)} = \begin{bmatrix} 92.6251 & -25.9451 & -11.8717 & 22.6798 \\ 6.0645 & -0.5848 & 0.2774 & 2.1731 \\ -5.8694 & 6.2573 & 5.1201 & 1.4125 \\ 15.2713 & 4.4118 & 6.2699 & 9.1070 \end{bmatrix}$$

$$B_{qj}^{(3)} = \begin{bmatrix} -213.9932 & 17.5527 & -12.7065 & -78.5822 \\ 1.4157 & -0.5983 & -0.3725 & 0.2220 \\ 77.4456 & -8.3492 & 2.7080 & 27.2060 \\ 85.0532 & -10.7376 & 1.4892 & 28.9097 \end{bmatrix}$$

$$B_{qj}^{(4)} = \begin{bmatrix} -8.7493 & -15.5642 & 4.0725 & 2.1360 \\ -1.5121 & -2.6898 & 0.7038 & 0.3692 \\ -1.9603 & -3.4873 & 0.9125 & 0.4786 \\ 2.0484 & 3.6440 & -0.9535 & -0.5001 \end{bmatrix}$$

$$B_{qj}^{(5)} = \begin{bmatrix} 53.9435 & 41.6767 & 8.5176 & -24.1405 \\ 0.2084 & 12.0821 & -2.4306 & -3.2014 \\ 7.8345 & -4.8510 & 3.3620 & -0.8250 \\ -18.3480 & -7.5660 & -4.1852 & 6.5858 \end{bmatrix}$$

$$B_{qj}^{(6)} = \begin{bmatrix} 67.8447 & -59.5853 & 32.5494 & -2.8228 \\ 15.9811 & -3.9846 & 5.7060 & -3.1362 \\ -3.7053 & -5.4155 & -0.0876 & 2.2858 \\ -14.8573 & 18.3039 & -8.1500 & -0.6740 \end{bmatrix}$$

$$B_{qj}^{(7)} = \begin{bmatrix} 0.0700 & -0.0437 & 0.0009 & -0.0029 \\ -2.2023 & 1.3735 & -0.0295 & 0.0923 \\ 1.1167 & -0.6965 & 0.0150 & -0.0468 \\ 0.2955 & -0.1843 & 0.0040 & -0.0124 \end{bmatrix}$$

$$B_{qj}^{(8)} = \begin{bmatrix} -0.5979 & 0.4012 & 0.0388 & -0.0426 \\ -1.6202 & 1.0873 & 0.1051 & -0.1155 \\ 0.1902 & -0.1277 & -0.0123 & 0.0136 \\ 1.3332 & -0.8947 & -0.0865 & 0.0951 \end{bmatrix}$$

Setting $\tau=0$ in Eq. 4-150 yields the following expressions for the covariances of the new random variables;

$$\text{Var}[N_1] = 137.2124 \quad \text{Cov}[N_2N_3] = -1.3335$$
$$\text{Cov}[N_1N_2] = 0.7577 \quad \text{Cov}[N_2N_4] = -0.6794$$
$$\text{Cov}[N_1N_3] = 0.7758 \quad \text{Var}[N_3] = 9.5166$$
$$\text{Cov}[N_1N_4] = 0.6311 \quad \text{Cov}[N_3N_4] = 1.0418$$
$$\text{Var}[N_2] = 12.5185 \quad \text{Var}[N_4] = 15.2749$$

Furthermore, since the total surface area of the dispersed phase is an important parameter in determination of the interphase mass transfer, an expression for the dispersed phase surface area, S, can be derived as follows:

$$S = \sum_{j=1}^{4} s_j N_j \tag{4-151}$$

where

s_j = surface area of a droplet of size j

For spherical droplets, the following relationship for s_j can be found;

s_1 = C = surface area of the smallest droplet

s_2 = 1.5874C

s_3 = 2.0801C

s_4 = 2.5198C

From these values, the expected value of the total surface area of the dispersed phase can be found as

$$\langle S \rangle = 161.6869C$$

The correlation function for the random variable S, $K(\tau)$, can be found from Eq. 4-150 as

$$K(\tau) = \sum_{q}^{4}\sum_{j}^{4} s_q s_j K_{qj}(\tau)$$

$$= B_1 e^{-\theta_1 \tau} + [B_2 \cos\phi_1\tau + B_3 \sin\phi_1\tau]e^{-\theta_2\tau}$$

$$+ B_4 e^{-\theta_3\tau} + [B_5 \cos\phi_2\tau + B_6 \sin\phi_2\tau]e^{-\theta_4\tau}$$

$$+ B_7 e^{-\theta_5\tau} + B_8 e^{-\theta_6\tau} \qquad (4\text{-}152)$$

where

$$B_k = \sum_{q}^{4}\sum_{j}^{4} s_q s_j B_{qj}^{(k)}$$

or

$B_1 = 5.8407C^2$ $\qquad$ $B_5 = 42.6324C^2$

$B_2 = 286.4792C^2$ $\qquad$ $B_6 = 30.2486C^2$

$B_3 = 240.3999C^2$ $\qquad$ $B_7 = 0.0243C^2$

$B_4 = -22.5513C^2$ $\qquad$ $B_8 = -0.0120C^2$

Setting $\tau=0$ in Eq. 4-152 yields the following value for the variance of the total surface area of the dispersed phase;

$$\text{Var}[S] = 312.4133\,C^2 \qquad \text{or} \qquad \text{Sd}[S] = 17.6752C$$

The standard deviation of the mean is thus 10.93 percent of the mean total surface area of the dispersed phase. A dimensionless correlation function, $\rho(\tau)$, is found by dividing $K(\tau)$ by Var[S] yielding

$$\rho(\tau) = 0.0187e^{-\theta_1\tau} + [0.9170\cos\phi_1\tau + 0.7695\sin\phi_1\tau]e^{-\theta_2\tau}$$

$$- 0.0722\,e^{-\theta_3\tau} + [0.1365\cos\phi_2\tau + 0.0968\sin\phi_2\tau]e^{-\theta_4\tau} \qquad (4\text{-}153)$$

where

$\theta_1 = 14.5269$ $\qquad$ $\phi_1 = 0.5219$

$\theta_2 = 2.0515$ $\qquad$ $\phi_2 = 2.4904$

$\theta_3 = 11.3521$

$\theta_4 = 6.1783$

Note that the correlation functions given by Eq. 4-30 could be found experimentally from, for example, continuous observation of the steady-state bubble population using a photographic technique combined with a method to determine the size and number of bubbles in each image. This would necessarily require a large number of images taken at known time intervals (i.e., a movie camera), and thus a systematic method of image analysis would be highly desirable.

NOTATION

A_h = first jump moment.

$\tilde{A}_h$ = A_h/Ω

$\tilde{A}_{hn}$ = coefficient matrix in the expansion of $\tilde{A}_h$.

$A_{ij}^{(\cdot)}$ = constants appearing in the correlation functions.

B_k = constants appearing in the correlation function of S.

B_{hn} = second jump moment.

$\tilde{B}_{hn}$ = B_{hn}/Ω

$B_{qj}^{(\cdot)}$ = constants appearing in the correlation functions.

C = surface area of the smallest droplet.

$C_i, C_3, C_4, C_5, C_6, C_7$ = constants.

$C_{pq}^{(\cdot)}$ = constants appearing in the correlation functions.

$Cov[N_{im}N_{pq}]$ = $\langle N_{\ell m}N_{pq}\rangle - \langle N_{\ell m}\rangle\langle N_{pq}\rangle$

$Cov[Z_{im}Z_{pq}]$ = $\langle Z_{\ell m}Z_{pq}\rangle - \langle Z_{\ell m}\rangle\langle Z_{pq}\rangle$

D_I = impeller dimeter.

$f(v)$ = distribution function for excess energy.

$f(z)$ = distribution function for energy in eddies.

$f_{x,y|z}(x,y|z)$ = probability of X and Y conditioned on Z.

$h(v,v')$ = collision frequency of a droplet pair.

$K(\tau)$ = $\langle S(0)S(\tau)\rangle - \langle S(0)\rangle\langle S(\tau)\rangle$

$K_{qj}(\tau)$ = $\langle N_q(0)N_j(\tau)\rangle - \langle N_q(0)\rangle\langle N_j(\tau)\rangle$

$K_{iq\ell m}(\tau)$ = $\langle N_{pq}(0)N_{\ell m}(\tau)\rangle - \langle N_{pq}(0)\rangle\langle N_{\ell m}(\tau)\rangle$

$K_{p\ell}(v^*,v,\tau)$ = continuous form of $K_{pq\ell m}(\tau)$.

$M\Delta S$ = "distance" at which the breakage rate equals its asymptotic value

N_j = number of entities of size $j\Delta V$.

$N(\ell)$ = number of droplets of size $\ell\Delta V$ formed upon breakage.

N_{ij} = number of entities of size $j\Delta V$ at a "distance" of $j\Delta S$.

$\langle N_{ij} \rangle$ = expected value of N_{ij}.

q = volumetric flow rate.

s_j = surface area of a droplet of size $j\Delta V$.

S = surface area of the dispersed phase.

$\langle S \rangle$ = expected value of S.

$Sd[S]$ = $(Var[S])^{1/2}$

v_0 = volume of original droplet.

v_1 = volume of smallest droplet formed by binary breakage.

$Var[S]$ = $K(0)$

$W_t(\cdot,\cdot)$ = intensity of transition function.

X = volume of the smallest droplet formed.

Y = volume of the largest droplet formed.

Z = volume of the original droplet.

$\langle Z_{\ell m} \rangle$ = expected value of fluctuating component of N_{ij}.

Greek Letters

$\alpha_i(j,k)$ = rate at which entities of size $j\Delta V$ and distance $i\Delta S$ from formation break apart to form entities of size $k\Delta V$ and $(j-k)\Delta V$.

$\alpha_i(v,v')$ = continuous form of $\alpha_i(j,k)$.

$\alpha(s,v,v')$ = continuous form of $\alpha_i(v,v')$.

$\alpha_1(i,j,k)$ = probability that a droplet of size $i\Delta V$ breaks apart to form droplets of sizes $j\Delta V$, $k\Delta V$ and $(i-j-k)\Delta V$.

$\alpha^1(v,v')$ = probability of forming a daughter droplet of size v' given that a droplet of size v has broken apart.

$\alpha^2_\ell(v)$ = frequency at which a droplet of volume v and a distance $\ell\Delta S$ from formation breaks apart.

$\beta_{im}(j,k)$ = rate constant for the coalescence between entities of size $j\Delta V$ a distance $i\Delta S$ from formation and entities of size $(k-j)\Delta V$ a distance $m\Delta S$ from formation to form entities of size $k\Delta V$ with an average distance $\ell\Delta S$ from formation.

$\beta_{im}(v,v')$ = continuous form of $\beta_{im}(j,k)$.

$\beta(s,s',v,v')$ = continuous form of $\beta_{im}(v,v')$.

$\gamma_i(j)$ = rate at which entities of size $j\Delta V$ and distance $i\Delta S$ from formation exit from the compartment.

$\gamma_i(v)$ = continuous form of $\gamma_i(j)$

$\gamma(s,v)$ = continuous form of $\gamma_i(v)$.

$\delta^k(\cdot)$ = Kronecker delta where $\delta^k(0)=1$ and $\delta^k(x)=0$ for $x\neq 0$.

ΔV = small unit of size corresponding to the smallest possible entitiy.

ΔS = discrete unit of distance.

ε = size of largest possible entity divided by ΔV.

ε_ℓ = power dissipation per unit mass.

$\theta_1,\theta_2,\theta_3,\theta_4,\theta_5,\theta_6$ = constant appearing in tha correlation functions.

$\kappa_i(j)$ = rate at which entities of size $j\Delta V$ and a distance $i\Delta S$ from formation move to a distance $(i+1)\Delta S$.

$\kappa_i(v)$ = continuous form of $\kappa_i(j)$.

$\kappa(s,v)$ = continuous form of $\kappa_i(v)$.

$\lambda(v,v')$ = coalescence efficiency function.

μ_c = dynamic viscosity of the continuous phase.

ξ_{ij} = size of change of random variable N_{ij}.

ρ_c = density of the continuous phase.

ρ_d = density of dispersed phase.

$\rho(\tau)$ = dimensionless correlation function.

σ = interfacial tension.

$\sigma^2(v_0,v_1)$ = variance of excess energy distribution.

ϕ = dispersed phase holdup.

ϕ_1, ϕ_2 = constant appearing in the correlation functions.

$\phi(v)$ = total number of entities of size v divided by Ω.

$\phi_\ell(v)$ = continuous form of $\phi_{\ell m}$.

$\phi(s,v)$ = continuous form of $\phi_\ell(v)$.

$\phi_{\ell m}$ = $\langle N_{\ell m} \rangle / \Omega$

Ω = system size.

$\Omega f(j)$ = rate at which entities of size $j\Delta V$ are added to the compartment.

$\Omega f(v)$ = continuous form of $\Omega f(j)$.

CHAPTER 5

APPLICATION OF GENERALIZED MASTER EQUATION TO COALESCENCE AND REDISPERSION ON A TWO DIMENSIONAL LATTICE

Suppose that a population of entities, e.g. atoms, exists on a two dimensional lattice - positioned at lattice points - and evolves through coalescence and migration of individual entities and/or entire groups of entities. Also suppose that the interactions among the groups of entities in this population possess the Markov property, and information on the rates of interactions as a function of group size, relative position on the lattice, and other state variables is available. A stochastic model based on the master equation can be developed by extending the model established in the preceeding chapter for coalescence and dispersion. It, however, will be necessary to include two subscripts indicating the position on the 2-D lattice at which the groups of entities are located; thus modifying the definition of the random variable. In this chapter, the random variable will denote the number of entities (size of group) located at a particular lattice point. It will be assumed that individuals or groups of entities migrate across the lattice and coalesce with other individuals or groups at a rate dependent on the sizes of the groups involved, and their relative position on the lattice. It will also be assumed that a single incident of coalescence involves only two groups of entities from neighboring lattice points.

A physical example of such a system is that of sintering and redispersion in supported metal catalysis (see, e.g., Ruckenstein and

Dadyburjor, 1983, for a current review of the subject). Parameters which influence the direction and extent of sintering and redispersion include time, temperature, vapor phase composition, the presence of other species, and properties of the substrate and the metal. Several deterministic models have been used to describe the process including (1) migration of entire groups of atoms with coalescence, (2) migration of single atoms which are captured by large groups, and (3) a combination of both (1) and (2). The present stochastic model would fall into catagory (3). Most models consider one or both of two cases as the limiting rate process. In one case, diffusion across the substrate, i.e. surface diffusion, is the limiting step. The other case considers coalescense at the interface between groups as the limiting rate. In general, migration of larger groups is expected to be slower than that of smaller groups. Ruckstein and Dadyburjor (1983) note that the determining forces for the migration of large groups appears to be the liquid-like behavior of groups of atoms at temperatures near the Tamman temperature and/or a relatively weak metal-substrate interaction. They also present rate constants for coalescence of neighboring groups of atoms. This detailed information could be incorporated in the rate functions of the present stochastic model when applying it to the sintering and redispersion phenomenon.

5.1 DERIVATION OF MODEL

Following previous notation, a set of random variables is defined as

$$\{N_{ij} : i \in \{1,2,3,...\},\ j \in \{1,2,3,...\}\}$$

where

N_{ij} = number of entities in the group located at the point $\{i,j\}$ on the 2-dimensional lattice.

Migration of entities will be assumed to be one of two types. The first type is movement of individual entities from the group at point {i,j} to one of the eight surrounding lattice points, {i-1,j}, {i+1,j}, {i,j-1}, {i,j+1}, {i+1,j+1}, {i+1,j-1}, {i-1,j+1}, or {i-1,j-1}. The second type is movement of the entire group of entities at the point {i,j} to one of the eight surrounding lattice points. When the group at point {i,j} consists of only one entity, the distinction between the two types of motion is superfluous since both are identical.

In the following, let $\alpha(n_{pk},n_{ij})$ be the rate at which individual entities at the point {p,k} migrate to the point {i,j}. Note that, if there is a group of entities at the point {i,j}, then $\alpha(n_{pk},n_{ij})$ is also the rate of coalescence between the group at {p,k} and the group at {i,k}. By the assumption of migration occuring only between neighboring lattice points, the point {p,k} must be one of the eight points specified in the preceding paragraph. Note also that $\alpha(n_{pk},n_{ij})$ can be a function of the group distribution on the lattice, as well as other state variables. The rate of transition due to the migration of individual entities can then be written as

$$W_t((n_{ij},n_{pk}),(n_{ij}+1,n_{pk}-1)) = \alpha(n_{pk},n_{ij})H(n_{pk}-1) \qquad (5\text{-}1)$$

$$\text{for all } i,j,p,k : p \in \{i-1,i,i+1\},\ k \in \{j-1,j,j+1\},$$

$$\text{and } (p,k) \neq (i,j)$$

where

$$H(x) = \begin{cases} 0 & x \leq 0 \\ 1 & 0 < x \end{cases}$$

Let $\beta(n_{pk},n_{ij})$ be the rate at which the entire group of entities at the point $\{p,k\}$ migrates to the point $\{i,j\}$. Note, as with $\alpha(n_{pk},n_{ij})$, $\beta(n_{pk},n_{ij})$ can also represent the rate of coalescence when there is a group at the point $\{i,j\}$. Again, due to the assumption of migration to neighboring lattice points, the point $\{p,k\}$ must be one of the eight neighboring points of the point $\{i,j\}$. The functional dependence of $\beta(n_{pk},n_{ij})$ should be considered to include the entire group distribution on the lattice in addition to the other state variables. The rates of transition due to migration of entire groups of entities can now be written as

$$W_t(\{n_{ij},n_{pk}\},\{n_{ij}+n_{pk},0\}) = \beta(n_{pk},n_{ij}) \qquad (5\text{-}2)$$

$$\text{for all } i,j,p,k : p \in \{i-1,i,i+1\},\ k \in \{j-1,j,j+1\},$$

$$\text{and } (p,k) \neq (i,j)$$

Note that the inclusion of other processes, such as addition or disappearance of entities at lattice points from the environment, can be expressed through additional rate functions. These processes will be excluded for simplicity in the following discussion.

The transition rates given in Eqs. 5-1 and 5-2 determine the stochastic evolution of the system. Note, however, that the application of the System Size Expansion is hindered by the fact that the transition

represented by Eq. 5-2 involves changes in the random variable of a large relative magnitude. The discussion, however, shall proceed in ignorance of this fact in order to illustrate the resulting difficulties.

The first step in the application of the System Size Expansion is to rewrite the expressions for the rates of transition in terms of {n} and {ξ}, respectively, as follows:

$$W_t(\{n_{ij},n_{pk}\};\{1,-1\}) = \alpha(n_{pk},n_{ij})H(n_{pk}-1) \tag{5-3}$$

$$W_t(\{n_{ij},n_{pk}\};\{n_{pk},-n_{pk}\}) = \beta(n_{pk},n_{ij}) \tag{5-4}$$

$$\text{for all } i,j,p,k : p \in \{i-1,i,i+1\},\ k \in \{j-1,j,j+1\},$$
$$\text{and } (p,k) \neq (i,j)$$

Note that, as in previous chapters, all null elements in the set {ξ} are omitted, and the remaining elements correspond to those in {n}.

The next step is to calculate the jump moments, A_h, and B_{hn}, after arranging to change the double subscript to a single one, denoted as h; for convenience it is defined as

$$h = j+\epsilon(i-1) \tag{5-5}$$

where

i,j= coordinates of the point $\{i,j\}$

ϵ = maximum value of j

The variable n_{ij} now appears as

$$n_{j+\varepsilon(i-1)}$$

Using this notation in Eqs. 5-3 and 5-4 gives rise to

$$W_t(\{n_{j+\varepsilon(i-1)}, n_{k+\varepsilon(p-1)}\};\{1,-1\}) = \alpha(n_{k+\varepsilon(p-1)}, n_{j+\varepsilon(i-1)}) \cdot H(n_{k+\varepsilon(p-1)}-1) \tag{5-6}$$

$$W_t(\{n_{j+\varepsilon(i-1)}, n_{k+\varepsilon(p-1)}\};\{n_{k+\varepsilon(p-1)}, -n_{k+\varepsilon(p-1)}\}) = \beta(n_{k+\varepsilon(p-1)}, n_{j+\varepsilon(i-1)}) \tag{5-7}$$

for all $i,j,p,k : p \in \{i-1,i,i+1\}$, $k \in \{j-1,j,j+1\}$,

and $(p,k) \neq (i,j)$

Expressions for A_h and B_{hn} are now derived as follows:

$$A_h = \sum_i \sum_j \sum_p \sum_\ell \Delta(ijp\ell)[\delta^k(h-j-\varepsilon i+\varepsilon) - \delta^k(h-\ell-\varepsilon p+\varepsilon)] \cdot [\alpha(n_{\ell+\varepsilon(p-1)}, n_{j+\varepsilon(i-1)}) H(n_{\ell+\varepsilon(p-1)}-1) + n_{\ell+\varepsilon(p-1)} \beta(n_{\ell+\varepsilon(p-1)}, n_{j+\varepsilon(i-1)})] \tag{5-8}$$

$$B_{hn} = \sum_i \sum_j \sum_p \sum_\ell \Delta(ijp\ell)[\delta^k(h-j-\varepsilon i+\varepsilon) - \delta^k(h-\ell-\varepsilon p+\varepsilon)]$$
$$\cdot[\delta^k(n-j-\varepsilon i+\varepsilon) - \delta^k(n-\ell-\varepsilon p+\varepsilon)]$$
$$\cdot[\alpha(n_{\ell+\varepsilon(p-1)}, n_{j+\varepsilon(i-1)})H(n_{\ell+\varepsilon(p-1)}-1)$$
$$+ n_{\ell+\varepsilon(p-1)} n_{\ell+\varepsilon(p-1)} \beta(n_{\ell+\varepsilon(p-1)}, n_{j+\varepsilon(i-1)})] \qquad (5\text{-}9)$$

where

$$\Delta(ijp\ell) = \{\delta^k(p-i)[\delta^k(\ell-j-1) + \delta^k(\ell-j+1)]$$
$$+ \delta^k(\ell-j)[\delta^k(p-i-1) + \delta^k(p-i+1)]$$
$$+ \delta^k(p-i-1)[\delta^k(\ell-j-1) + \delta^k(\ell-j+1)]$$
$$+ \delta^k(p-i+1)[\delta^k(\ell-j-1) + \delta^k(\ell-j+1)]\}$$

Note that $\Delta(ijp\ell)$ restricts the summation to include only the eight surrounding lattice points. The first of these expressions can be used with Eq. 2-18 to find

$$\frac{d\phi_h}{dt} = \sum_i \sum_j \sum_p \sum_\ell \Delta(ijp\ell)[\delta^k(h-j-\varepsilon i+\varepsilon) - \delta^k(h-\ell-\varepsilon p+\varepsilon)]$$
$$\cdot[\Omega^{-1}\alpha(\Omega\phi_{\ell+\varepsilon(p-1)}, \Omega\phi_{j+\varepsilon(i-1)})H(\Omega\phi_{\ell+\varepsilon(p-1)}-1)$$
$$+ \phi_{\ell+\varepsilon(p-1)} \beta(\Omega\phi_{\ell+\varepsilon(p-1)}, \Omega\phi_{j+\varepsilon(i-1)})] \qquad (5\text{-}10)$$

This expression can be simplified by returning to double subscripts, i.e.,

$$\frac{d\phi_{ij}}{dt} = \sum_p \sum_\ell \Delta(ijp\ell)[\Omega^{-1}\alpha(\Omega\phi_{p\ell},\Omega\phi_{ij})H(\Omega\phi_{p\ell} - 1) - \Omega^{-1}\alpha(\Omega\phi_{ij},\Omega\phi_{pk})H(\Omega\phi_{ij}-1) + \phi_{p\ell}\beta(\Omega\phi_{p\ell},\Omega\phi_{ij}) - \phi_{ij}\beta(\Omega\phi_{ij},\Omega\phi_{p\ell})] \quad (5\text{-}11)$$

or, in terms of $\langle N_{ij}\rangle$ (the mean number of entities at the point $\{i,j\}$),

$$\frac{d}{dt}\langle N_{ij}\rangle = \sum_p \sum_\ell \Delta(ijp\ell)[\alpha(\langle N_{p\ell}\rangle,\langle N_{ij}\rangle)H(\langle N_{p\ell}\rangle-1) - \alpha(\langle N_{ij}\rangle,\langle N_{pk}\rangle)H(\langle N_{ij}\rangle-1) + \langle N_{p\ell}\rangle\beta(\langle N_{p\ell}\rangle,\langle N_{ij}\rangle) - \langle N_{ij}\rangle\beta(\langle N_{ij}\rangle,\langle N_{p\ell}\rangle)] \quad (5\text{-}12)$$

To proceed further, the expansion of Eq. 5-8, after a change of variables, as indicated in Eqs. 2-15 and 2-11, respectively, is necessary. However this step requires knowledge of the exact functional dependence of the transition rate functions, α and β, on the random variables $\{n\}$. To simplify the resulting discussion, it will be assumed in the following that α and β depend only on the number of entities located at the point of origin of the migration, i.e.,

$$\alpha(n_{p\ell},n_{ij}) = c_1 n_{p\ell} \quad (5\text{-}13)$$

$$\beta(n_{p\ell},n_{ij}) = c_2 n_{p\ell} \quad (5\text{-}14)$$

where c_1 and c_2 are constants depending only on state variables such as temperature and pressure, but not on the group distribution. With this assumption, $\tilde{A}_h$ can now be written as

$$\tilde{A}_h = \sum_i \sum_j \sum_p \sum_\ell \Delta(ijp\ell)[\delta^k(h-j-\varepsilon i+\varepsilon) - \delta^k(h-\ell-\varepsilon p+\varepsilon)]$$
$$\cdot[c_1(\phi_{\ell+\varepsilon(p-1)} + \Omega^{-1/2}z_{\ell+\varepsilon(p-1)})H(n_{\ell+\varepsilon(p-1)}-1)$$
$$+ (\phi_{\ell+\varepsilon(p-1)} + \Omega^{-1/2}z_{\ell+\varepsilon(p-1)})$$
$$\cdot\Omega c_2(\phi_{\ell+\varepsilon(p-1)} + \Omega^{-1/2}z_{\ell+\varepsilon(p-1)})] \qquad (5\text{-}15)$$

Expansion of this expression in powers of $\Omega^{-1/2}$ can now proceed as follows (only the terms appearing between the last pair of square brackets in Eq. 5-15 are shown. The other terms remain unchanged);

$$\Omega[c_2\phi_{\ell+\varepsilon(p-1)}\phi_{\ell+\varepsilon(p-1)}]$$
$$+ \Omega^{1/2}[2c_2 z_{\ell+\varepsilon(p-1)}\phi_{\ell+\varepsilon(p-1)}]$$
$$+ [c_1\phi_{\ell+\varepsilon(p-1)}H(n_{\ell+\varepsilon(p-1)}-1) + c_2 z_{\ell+\varepsilon(p-1)}z_{\ell+\varepsilon(p-1)}]$$
$$+ \Omega^{-1/2}[c_1 z_{\ell+\varepsilon(p-1)}H(n_{\ell+\varepsilon(p-1)}-1)] \qquad (5\text{-}16)$$

Note, that as expected, a problem has arisen. Comparison with Eq. 2-15 will reveal that two new terms are present in the expansion, i.e., terms to the powers Ω and $\Omega^{1/2}$. These terms result from the fact that the changes in the random variable are of the same order of magnitude as the random variable itself. In this case, separation of the mean and the fluctuating components is, strictly speaking,

invalid. Results obtained upon continuation of the expansion must be viewed with some skepticism, and accepted only if shown applicable by actual simulation of the process. In any case, the next step in the expansion would be to separate out those terms in Eq. 5-16 which only contain the mean ($\phi_{\ell+\epsilon(p-1)}$). This procedure yields the following expression [cf. Eq. 5-11];

$$\frac{d\phi_{ij}}{dt} = \sum_p \sum_\ell \Delta(ijp\ell)[c_1\phi_{p\ell}H(\Omega\phi_{p\ell}-1) - c_1\phi_{ij}H(\Omega\phi_{ij}-1) + \Omega c_2\phi_{p\ell}\phi_{p\ell} - \Omega c_2\phi_{ij}\phi_{ij}] \tag{5-17}$$

or, in terms of $\langle N_{ij}\rangle$ [cf. Eq. 5-12],

$$\frac{d}{dt}\langle N_{ij}\rangle = \sum_p \sum_\ell \Delta(ijp\ell)[c_1\langle N_{p\ell}\rangle H(\langle N_{p\ell}\rangle-1) - c_1\langle N_{ij}\rangle H(\langle N_{ij}\rangle-1) + c_2\langle N_{p\ell}\rangle^2 - c_2\langle N_{ij}\rangle^2] \tag{5-18}$$

Comparison of Eq. 5-16 with Eq. 2-15 leads to the following expression for $\tilde{A}_{hn}$;

$$\tilde{A}_{hn} = \sum_i \sum_j \sum_p \sum_\ell \Delta(ijp\ell)[\delta^k(h-j-\epsilon i+\epsilon) - \delta^k(h-\ell-\epsilon p+\epsilon)] \cdot \delta^k(n-\ell-\epsilon p+\epsilon)[2\Omega c_2\phi_{\ell+\epsilon(p-1)} + c_1H(\langle N_{\ell+\epsilon(p-1)}\rangle-1)] \tag{5-19}$$

Note that the fourth term in Eq. 5-16 does not have a corresponding term in either Eq. 5-17 or 5-19. This is in accordance with the linear noise approximation upon which the System Size Expansion is based. However, this term is of the same order of Ω as some of the terms appearing in Eq. 5-17 for the mean, and therefore cannot justifiably be excluded. However, continuing dauntlessly, Eq. 5-19 in conjunction with Eq. 2-20 yields

$$\frac{d\langle Z_{ij}\rangle}{dt} = \sum_p \sum_\ell \Delta(ijp\ell)[c_1\langle Z_{p\ell}\rangle H(\langle N_{p\ell}\rangle - 1) - c_1\langle Z_{ij}\rangle H(\langle N_{ij}\rangle - 1) + 2c_2\langle N_{p\ell}\rangle\langle Z_{p\ell}\rangle - 2c_2\langle N_{ij}\rangle\langle Z_{ij}\rangle] \tag{5-20}$$

Expressions for the rate of change of $\mathrm{Cov}[Z_{ij}Z_{p\ell}]$ can be found from Eq. 5-19 for $\tilde{A}_{hn}$, Eq. 5-9 for B_{hn} and Eq. 2-22, after changing to double subscripts; this yields

$$\begin{aligned}\frac{d}{dt}\mathrm{Cov}[Z_{ij}Z_{p\ell}] = \sum_h \sum_q \{&\Delta(ijhq)[c_1 H(\Omega\phi_{hq} - 1)\mathrm{Cov}[Z_{hq}Z_{p\ell}] \\ &- c_1 H(\Omega\phi_{ij} - 1)\mathrm{Cov}[Z_{ij}Z_{p\ell}] \\ &+ 2c_2\Omega\phi_{hq}\mathrm{Cov}[Z_{hq}Z_{p\ell}] - 2c_2\Omega\phi_{ij}\mathrm{Cov}[Z_{ij}Z_{p\ell}]] \\ &+ \Delta(p\ell hq)[c_1 H(\Omega\phi_{hq} - 1)\mathrm{Cov}[Z_{ij}Z_{hg}] \\ &- c_1 H(\Omega\phi_{p\ell} - 1)\mathrm{Cov}[Z_{ij}Z_{p\ell}] \\ &+ 2c_2\Omega\phi_{hq}\mathrm{Cov}[Z_{ij}Z_{hq}] - 2c_2\Omega\phi_{p\ell}\mathrm{Cov}[Z_{ij}Z_{p\ell}]] \\ &+ \delta^k(i-p)\delta^k(j-\ell)\Delta(ijhq)[c_1\phi_{hq}H(\Omega\phi_{hq} - 1) + c_2\Omega^2\phi_{hq}^3]\end{aligned}$$

$$+ \delta^k(i-p)\delta^k(j-\ell)\Delta(p\ell hq)[c_1\phi_{p\ell}H(\Omega\phi_{p\ell}-1) + c_2\Omega^2\phi_{p\ell}^3]\}$$

$$- \Delta(ijp\ell)[c_1\phi_{p\ell}H(\Omega\phi_{p\ell}-1) + c_1\phi_{ij}H(\Omega\phi_{ij}-1)$$

$$+ c_2\Omega^2\phi_{p\ell}^3 + c_2\Omega^2\phi_{ij}^3] \qquad (5\text{-}21)$$

or, in terms of $\mathrm{Cov}[N_{ij}N_{p\ell}]$,

$$\frac{d}{dt}\mathrm{Cov}[N_{ij}N_{p\ell}] = \sum_h \sum_q \{\Delta(ijhq)[c_1H(\langle N_{hq}\rangle-1)\mathrm{Cov}[N_{hq}N_{p\ell}]$$

$$- c_1H(\langle N_{ij}\rangle-1)\mathrm{Cov}[N_{ij}N_{p\ell}]$$

$$+ 2c_2\langle N_{hq}\rangle\mathrm{Cov}[N_{hq}N_{p\ell}]$$

$$- 2c_2\langle N_{ij}\rangle\mathrm{Cov}[N_{ij}N_{p\ell}]]$$

$$+ \Delta(p\ell hq)[c_1H(\langle N_{hq}\rangle-1)\mathrm{Cov}[N_{ij}N_{hq}]$$

$$- c_1H(\langle N_p\rangle -1)\mathrm{Cov}[N_{ij}N_{p\ell}]$$

$$+ 2c_2\langle N_{hq}\rangle\mathrm{Cov}\,[N_{ij}N_{p\ell}]]$$

$$+ \delta^k(i-p)\delta^k(j-\ell)\Delta(ijhq)\,[\,c_1\langle N_{hq}\rangle H(\langle N_{hq}\rangle-1) + c_2\langle N_{hq}\rangle^3]$$

$$+ \delta^k(i-p)\delta^k(j-\ell)\Delta(p\ell hq)[c_1\langle N_{p\ell}\rangle H(\langle N_{p\ell}\rangle-1) + c_2\langle N_{p\ell}\rangle^3]\}$$

$$- \Delta(ijp\ell)[c_1\langle N_{p\ell}\rangle H(\langle N_{p\ell}\rangle-1) + c_1\langle N_{ij}\rangle H(\langle N_{ij}\rangle-1)$$

$$+ c_2\langle N_{p\ell}\rangle^3 + c_2\langle N_{ij}\rangle^3] \qquad (5\text{-}22)$$

The correlation functions of the random variables {N} can be found from Eq. 5-20 in conjunction with Eq. 2-28, as

$$\frac{d}{d\tau} K_{ijp\ell}(\tau) = \sum_h \sum_q \Delta(p\ell hq)[c_1 H(<N_{hq}>-1)K_{ijhq} - c_1 H(<N_{p\ell}>-1)K_{ijp\ell} + 2c_2<N_{hq}>K_{ijhq} - 2c_2<N_{p\ell}>K_{ijp\ell}] \quad (5\text{-}23)$$

with

$$K_{ijp\ell}(0) = \mathrm{Cov}[N_{ij}N_{p\ell}]$$

where

$\mathrm{Cov}[N_{ij}N_{p\ell}]$ = steady-state covariances

The evolution of the population of entities on a 2-dimensional lattice can now be characterized according to the mean number of entities at a lattice point (Eq. 5-18) and the dynamic fluctuations about the mean (Eq. 5-22 with Eq. 5-23).

5.2 EXAMPLE CALCULATION FOR A SMALL LATTICE

To illustrate the application of the equations derived in the preceding section, an example calculation will be carried-out for a 2X2 lattice with the initial condition of 10 entities at each lattice point. For thia caae Eq. 5-18 yields

$$\frac{d}{dt}\langle N_{11}\rangle = c_1\langle N_{12}\rangle H(\langle N_{12}\rangle - 1) + c_1\langle N_{22}\rangle H(\langle N_{22}\rangle - 1)$$
$$+ c_1\langle N_{21}\rangle H(\langle N_{21}\rangle - 1) - 3c_1\langle N_{11}\rangle H(\langle N_{11}\rangle - 1)$$
$$+ c_2\langle N_{12}\rangle^2 + c_2\langle N_{22}\rangle^2 + c_2\langle N_{21}\rangle^2 - 3c_2\langle N_{11}\rangle^2 \qquad (5\text{-}24)$$

$$\frac{d}{dt}\langle N_{12}\rangle = c_1\langle N_{11}\rangle H(\langle N_{11}\rangle - 1) + c_1\langle N_{22}\rangle H(\langle N_{22}\rangle - 1)$$
$$+ c_1\langle N_{21}\rangle H(\langle N_{21}\rangle - 1) - 3c_1\langle N_{12}\rangle H(\langle N_{12}\rangle - 1)$$
$$+ c_2\langle N_{11}\rangle^2 + c_2\langle N_{22}\rangle^2 + c_2\langle N_{21}\rangle^2 - 3c_2\langle N_{12}\rangle^2 \qquad (5\text{-}25)$$

$$\frac{d}{dt}\langle N_{22}\rangle = c_1\langle N_{11}\rangle H(\langle N_{11}\rangle - 1) + c_2\langle N_{12}\rangle H(\langle N_{12}\rangle - 1)$$
$$+ c_1\langle N_{21}\rangle H(\langle N_{21}\rangle - 1) - 3c_1\langle N_{22}\rangle H(\langle N_{22}\rangle - 1)$$
$$+ c_2\langle N_{11}\rangle^2 + c_2\langle N_{12}\rangle^2 + c_2\langle N_{21}\rangle^2 - 3c_2\langle N_{22}\rangle^2 \qquad (5\text{-}26)$$

$$\frac{d}{dt}\langle N_{21}\rangle = c_1\langle N_{11}\rangle H(\langle N_{11}\rangle - 1) + c_1\langle N_{12}\rangle H(\langle N_{12}\rangle - 1)$$
$$+ c_1\langle N_{22}\rangle H(\langle N_{22}\rangle - 1) - 3c_1\langle N_{21}\rangle H(\langle N_{21}\rangle - 1)$$
$$+ c_2\langle N_{11}\rangle^2 + c_2\langle N_{12}\rangle^2 + c_2\langle N_{22}\rangle^2 - 3c_2\langle N_{21}\rangle^2 \qquad (5\text{-}27)$$

with

$$\langle N_{11}\rangle = \langle N_{12}\rangle = \langle N_{22}\rangle = \langle N_{21}\rangle = 10.0 \text{ at } t=0$$

By symmetry, it follows that the solution to Eqs. 5-24 through 5-27 is time invariant, and thus

$$\langle N_{11} \rangle = 10.0$$
$$\langle N_{12} \rangle = 10.0$$
$$\langle N_{22} \rangle = 10.0$$
$$\langle N_{21} \rangle = 10.0$$

Note, symmetry also requires that, at steady-state,

$$\text{Var}[N_{11}] = \text{Var}[N_{12}] = \text{Var}[N_{21}] = \text{Var}[N_{22}] = \text{Var}$$
$$\text{Cov}[N_{11}N_{12}] = \text{Cov}[N_{11}N_{21}] = \text{Cov}[N_{11}N_{22}] = \text{Cov}[N_{12}N_{21}]$$
$$= \text{Cov}[N_{12}N_{22}] = \text{Cov}[N_{21}N_{22}] = \text{Cov}$$

Thus, at steady state, Eq. 5-21 yields the following two expressions

$$0 = (c_1 + 20c_2)(\text{Cov} - \text{Var}) + 10(c_1 + 100c_2) \qquad (5\text{-}28)$$
$$0 = (c_1 + 20c_2)(\text{Var} - \text{Cov}) - 10(c_1 + 100c_2) \qquad (5\text{-}29)$$

which are identical, except for a constant of -1. Adding the two expressions found from Eq. 5-21 for <u>non</u>-steady state conditions yields the following identity;

$$\text{Var} + \text{Cov} = \text{constant} \qquad (5\text{-}30)$$

Assuming that the initial values of the lattice point group sizes are known exactly yields

$$\text{Var} + \text{Cov} = 0 \tag{5-31}$$

Solving Eqs. 5-28 and 5-31 yields the following values for Var and Cov;

$$\text{Var} = 5\left(\frac{c_1 + 100c_2}{c_1 + 20\ c_2}\right) \tag{5-32}$$

$$\text{Cov} = -5\left(\frac{c_1 + 100c_2}{c_1 + 20\ c_2}\right) \tag{5-33}$$

Equation 5-32 reveals the conditions under which the System Size Expansion is valid, i.e., when $c_1 >> c_2$ and thus Var $\simeq$ 5. This is of course the case when migration of individual entities is dominant. In the other extreme, $c_2 >> c_1$, the variance approaches 25, indicating that the fluctuations in the random variable are of the same order of magnitude as the mean. In this case the System Size Expansion loses its validity.

Continuing, the correlation function can be found from Eq. 5-23. Letting

$$K^* = K_{ijij}(\tau) \tag{5-34}$$

$$K = K_{ijp\ell}(\tau),\ i \neq p,\ j \neq \ell \tag{5-35}$$

results in the following two expressions;

$$\frac{dK^*}{d\tau} = 3(c_1 + 20c_2)(K - K^*) \tag{5-36}$$

$$\frac{dK}{d\tau} = (c_1 + 20c_2)(K + K^*) \tag{5-37}$$

with

$$K^*(0) = \text{Var}$$

$$K(0) = \text{Cov}$$

The solution of these equations yields

$$K^*(\tau) = \text{Var}[1.4449\ e^{-\theta_1\tau} - 0.4449\ e^{-\theta_2\tau}] \tag{5-38}$$

$$K(\tau) = \text{Cov}[0.3110\ e^{-\theta_1\tau} + 0.6890\ e^{-\theta_2\tau}] \tag{5-39}$$

where

$$\theta_1 = 3.6458\ (c_1 + 20c_2)$$

$$\theta_2 = 1.6458\ (c_1 + 20c_2)$$

Note that the final form of the correlation function suggests a method with which the constants c_1 and c_2 can be determined from experimental data. If the steady-state time series of the number of entities at a point on the lattice could be observed, and the correlation function determined, then the values of the correlation function at τ=0 and at any other point, say τ=1, uniquely determine the two constants, c_1 and c_2, i.e.,

$$K^*(0) = \text{Var} = 5\left(\frac{c_1 + 100c_2}{c_1 + 20\,c_2}\right) \tag{5-40}$$

$$K^*(1) = \text{Var}(1.4449\ e^{-\theta_1} - 0.4449\ e^{-\theta_2}) \tag{5-41}$$

where

$$\theta_1 = 3.6458(c_1 + 20c_2)$$
$$\theta_2 = 1.6458(c_1 + 20c_2)$$

Solution of Eqs. 5-40 and 5-41, given $K^*(0)$ and $K^*(1)$, then yields c_1 and c_2. For example, given $K^*(0) = 10$ and $K^*(1) = 5$, c_1 and c_2 are found to be

$$c_1 = 0.10905$$
$$c_2 = 1.8174 \times 10^{-3}$$

This method, when contrasted with the more common method of determining the constants from transient (non-steady state) data, would appear to be advantageous since data collection under transient conditions is more demanding, and must be repeated many times to obtain meaningful results. Measurement of the correlation function, however, is done at steady-state conditions, and thus can be performed in a single run of sufficient duration to ensure that the correlation function can be accurately determined.

5.3 MONTE CARLO SIMULATION OF PROCESS

For large lattices, or conditions where migration of entire groups of entities is important, exact calculations using the expressions derived in

the proceeding section can be unwieldy or inaccurate, in which case direct simulation of the process is a valuable alternative. Handa and Matthews (1983) have used a Monte Carlo approach to investigate sintering and redispersion of supported metal catalysts for the case of migration of single atoms for both diffusion and coalescense as the limiting rate. Simulation of the present model using the Monte Carlo approach requires the generation of uniformly distributed random numbers from which decisions are made as to which of the processes will occur, and over what time interval. By definition of the rates of transition function, the probability that a particular event occurs during a small time interval, say with rate of transition equal to λ_1, given that an event has occurred is given by

$$P(\text{Event } 1 \,|\, \text{Event has occurred}) = \frac{\lambda_1}{\Sigma\lambda_i} \tag{5-42}$$

where the summation is over all possible events. Note that the event with the largest transition rate is the one most likely to occur.

One important property of processes which have the Markov property is that the waiting time between events is exponentially distributed with the parameter equal to the rate of transition. It is this property, along with Eq. 5-42 which allow for the simulation of the process by generation of uniform random numbers.

For the 2-dimensional lattice, let

ε = maximum value of the index j

η = maximum value of the index i,

i.e., the lattice is a ε x η rectangular lattice. The total number of lattice points is then $\eta\varepsilon$. For lattice points on the interior of the lattice there are a total of sixteen transition rate functions (for each of the eight neighboring lattice points, there is one transition rate for individual entities, and one for the entire group). For

lattice points on the edge, excluding corner points, there are ten transition functions; for corner points, six. There are, thus, a total of $4(4\varepsilon\eta - 3\varepsilon - 3\eta + 2)$ transition functions for the entire lattice. Note that some of these may very well be equal to zero, e.g., when there are no entities at the lattice point in question. For the purpose of the simulation, each of the $4(4\varepsilon\eta - 3\varepsilon - 3\eta + 2)$ transition functions is assigned an index running from 1 to $4(4\varepsilon\eta - 3\varepsilon - 3\eta + 2)$. The generic symbol λ_i is used to denote the transition function with index i.

Assuming that the transition rate functionals are known, the simulation itself begins by stipulating initial conditions for the state variables, and the number of entities at each of the $\varepsilon\eta$ lattice points. The simulation clock should also be set at its starting value. With this information, the transition rates, λ_i, can be calculated for each i. The simulation can then proceed as follows:

0) Set an index equal to zero, i.e.,

$$j = 0$$

i) Calculate rate functions λ_i for all i

ii) Calculate $\lambda^* = \sum_i \lambda_i$

iii) Generate a uniform (0,1) random variable X_1

iv) Calculate

$$Y_1 = X_1 \lambda^*$$

v) Add one to index, i.e.,

$$j \rightarrow j+1$$

vi) Return to step v) with $Y_{j+1} = Y_j - \lambda_j$, if $Y_j > \lambda_j$

Proceed to the next step if $Y_j \leq \lambda_j$

vii) Adjust the number of entities at lattice points according to event j

viii) Generate a uniform (0,1) random variable, X_2

ix) Calculate waiting time

$$W = -\ell n(X_2)\lambda^{*-1}$$

x) Adjust simulation clock

$$t \rightarrow t+W$$

xi) Print current time and lattice distribution

xii) Return to step 0)

The means, covariances, and correlation functions for each lattice point can be found from the results of the simulation. Model parameters can then be correlated with these statistics in order to determine the effects of parameter changes on the dynamic behavior of the group distribution. The large amounts of data generated from such a simulation will require efficient computational algorithms for handling and processing. Treating the output in step xi) as the signal from a real experimental observation, it would be possible to use online techniques for the direct calculation of the means and correlation function using available computer software. In this way, storage of all the data generated during the simulation would not be necessary, representing a large savings in computer memory space.

NOTATION

A_h = first jump moment.

$\tilde{A}_h$ = A_h/Ω

$\tilde{A}_{hn}$ = coefficient matrix from expansion of $\tilde{A}_h$.

B_{hn} = second jump moment.

$\tilde{B}_{hn}$ = B_{hn}/Ω

C_1, C_2 = constants

$Cov[N_{ij}N_{p\ell}]$ = $\langle N_{ij}N_{p\ell}\rangle - \langle N_{ij}\rangle\langle N_{p\ell}\rangle$

$Cov[Z_{ij}Z_{p\ell}]$ = $\langle Z_{ij}Z_{p\ell}\rangle - \langle Z_{ij}\rangle\langle Z_{p\ell}\rangle$

$H(x)$ = Heaviside step function.

$K_{ijp\ell}(\tau)$ = $\langle N_{ij}(0)N_{ij}(\tau)\rangle - \langle N_{ij}(0)\rangle\langle N_{ij}(\tau)\rangle$

N_{ij} = number of entities in the group located at the point $\{i,j\}$ on the 2-dimensional lattice.

$\langle N_{ij}\rangle$ = expected value of N_{ij}.

W = waiting time.

$W_t(\cdot,\cdot)$ = intensity of transition function.

X_1, X_2 = uniform (0,1) random variables.

$\langle Z_{ij}\rangle$ = expected value of fluctuation part of N_{ij}.

Greek Letters

$\alpha(n_{pk}, n_{ij})$ = rate at which individual entities at the point $\{p,k\}$ migrate to the point $\{i,j\}$.

$\beta(n_{pk}, n_{ij})$ = rate at which the entire group of entities at the point $\{p,k\}$ migrates to the point $\{i,j\}$.

$\delta^k(\cdot)$ = Kronecker delta where $\delta^k(0)=1$ and $\delta^k(x)=0$ for $x\neq 0$.

$\Delta(ijp\ell)$ = 1 for neighboring lattice points, and 0 otherwise.

ε = maximum value of index j.

η = maximum value of index i.

θ_1, θ_2 = constants appearing in correlation functions.

λ_i = rate of transtion of event i.

ϕ_{ij} = $\langle N_{ij} \rangle / \Omega$

Ω = system size.

CHAPTER 6

APPLICATION OF GENERALIZED MASTER EQUATION TO COMBUSTION OF PARTICLES IN A FLUIDIZED-BED REACTOR

In a fluidized-bed reactor operating under conditions where the solid particles introduced and combusted in the reactor have a non-negligible residence time, the external gas concentration variations in different parts of the reactor coupled with the random motion of the particles will influence the time needed for total conversion. The random motion of the solid particles suggests the utilization of a stochastic compartmental model where the random variables are the number of solid particles of a given size in a given compartment. Since the rate processes responsible for the reduction in size of the particles are on a molecular scale, these processes can be assumed to obey deterministic rate equations. Assuming stochastic rate equations would yield equivalent results, with additional effort, and would indicate that the resulting distribution is a sharp spike (variance approximately zero) about the deterministic results. In contrast, the random motion of a finite population of particles about the interior of the bed could result in a significant distribution in the concentration of reactant gas. The magnitude of variance of this distribution will depend on the magnitude of the reactant gas inter-compartmental exchange rate. If the rate is very large, then the variance of the concentration distribution will be negligible. If the rate is small, then the random accumulation of particles in regions of high or low concentration should result in a significant spread in the concentration distribution. Note, however, that the rate is dependent upon the rates

of coalescense and movement of the bubbles in a compartment. These processes and the resulting bubble population distribution were modeled in an earlier chapter where it was seen that fluctuations in the population distribution can be quite significant. Such fluctuations would lead to a stochastic description for the inter-phase gas exchange rate, and thus to a description of the concentration in each phase of each compartment as a random variable.

6.1 TWO PHASE MODEL BALANCE EQUATIONS

It will be assumed that the fluidized bed can be modeled using the two-phase model presented by Peters et al. (1982) wherein the material balance equations for the reacting gas in both phases of compartment p of the m compartments are written as;

Bubble phase

$$V_{b_p} \frac{dC_{b_p}}{dt} = U_{bs_{p-1}} AC_{b_{p-1}} - U_{bs_p} AC_{b_p} + G_{be_p} AC_{e_p} + F_{be_p} V_{b_p} (C_{e_p} - C_{b_p}) \qquad (6\text{-}1)$$

for compartment p where

$$1 \leq p \leq m$$

Emulsion phase

$$\varepsilon_{mf} V_{e_p} \frac{dC_{e_p}}{dt} = U_{es_{p-1}} AC_{e_{p-1}} - U_{es_p} AC_{e_p} - G_{be_p} AC_{e_p} - F_{be_p} V_{b_p} (C_{e_p} - C_{b_p}) + V_{e_p} \eta_{e_p} \qquad (6\text{-}2)$$

for compartment p where

$$U_{es_{p-1}} \geq 0$$

$$U_{es_p} \geq 0,$$

$$\epsilon_{mf} V_{e_p} \frac{dC_{e_p}}{dt} = |U_{es_p}| AC_{e_{p+1}} + U_{es_{p-1}} AC_{e_{p-1}} - G_{be_p} AC_{e_p}$$

$$- F_{be_p} V_{b_p} (C_{e_p} - C_{b_p}) + V_{e_p} \eta_{e_p} \qquad (6\text{-}3)$$

for compartment p where

$$U_{es_{p-1}} \leq 0$$

$$U_{es_p} \leq 0,$$

$$\epsilon_{mf} V_{e_p} \frac{dC_{e_p}}{dt} = U_{es_{p-1}} AC_{e_p} - U_{es_p} AC_{e_{p+1}} - G_{be_p} AC_{e_p}$$

$$- F_{be_p} V_{b_p} (C_{e_p} - C_{b_p}) + V_{e_p} \eta_{e_p} \qquad (6\text{-}4)$$

for compartment p where

$$U_{es_p} \leq 0$$

$$U_{es_{p-1}} \leq 0,$$

and

$$\varepsilon_{mf} V_{e_p} \frac{dC_{e_p}}{dt} = U_{es_{p-1}} AC_{e_p} - U_{es_p} AC_{e_p}$$

$$- G_{be_p} AC_{e_p}$$

$$- F_{be_p} V_{b_p} (C_{e_p} - C_{b_p}) + V_{e_p} \eta_{e_p}$$

for compartment p where

$$U_{es_p} \geq 0$$

$$U_{es_{p-1}} \leq 0$$

where

A = cross-sectional area of the bed

C_{b_p} = gas concentration in the bubble phase in compartment p

C_{e_p} = gas concentration in the emulsion phase in compartment p

F_{be_p} = gas interchange coefficient from the bubble phase to the emulsion phase in compartment p per unit volume of the bubble phase

G_{be_p} = crossflow from the bubble to the emulsion phase

U_{bs_p} = superficial gas velocity in the bubble phase in compartment p

U_{es_p} = superficial gas velocity in the emulsion phase in compartment p

V_{b_p} = volume of the bubble phase in compartment p

V_{e_p} = volume of the emulsion phase in compartment p

ε_{mf} = void fraction of the bed at U_{mf}

η_{e_p} = reaction rate in compartment p

Note, following the discussion in an earlier chapter on the stochastic nature of the bubble population in a fluidized-bed, several of the quantities which appear in Eqs. 6-1 through 6-5 should be considered as random. These include V_{b_p}, V_{e_p}, C_{b_p}, C_{e_p}, U_{bs_p}, U_{es_p}, G_{be_p}, F_{be_p}; all of which depend on the characteristics of the bubbles in the compartment. η_{e_p} is also a random quantity depending on the random motion of the solid particles throughout the bed. In this light, Eq. 6-1 through 6-5 should be considered as Stochastic Differential Equations with non-white noise terms. The actual nature of the noise term can be found from the correlation functions derived in the chapter on modeling the bubble population mentioned earlier. However, since the noise is non-white noise, it is more difficult to deal with, and may require a simulation procedure such as that employed by Ligon and Amundson (1981) in their study of correlated noise models. The focus of this chapter will, however, be the effect of the random motion of solid particles on the reaction term, $\eta_{e_p}^{\ell}$.

6.2 STOCHASTIC MODEL FOR SOLID PARTICLES

In the following it is assumed that the solid phase in the fluidized-bed reactor is made-up of inert fluidized solids plus a small fraction of solid particles which are involved in reaction. In this way it can be safely concluded that the reaction does not significantly change the nature of the emulsion phase, e.g., the voidage is the same as in the absence of reaction. It is visualized that reacting particles enter the reactor at some point (compartment) and circulate between compartments until they are completely consumed. The solid phase is thus attributed a circulation rate, which may or may not be compartment specific, which determines the extent of solid mixing in the bed. In

this context perfect mixing would correspond to an infinite circulation rate. It will be assumed that such solid mixing rates are available or can be found from experimental studies.

Focusing attention, then, on a single solid particle in a compartment of the reactor, it can be seen that at any instant this particle has a certain probability to change compartments (a probability which is proportional to the circulation rate between the two compartments in question) or to remain in the compartment of origin, in which case it will continue to degrade at a reaction rate dependent on the reactant gas concentration in the compartment. There are, therefore, two important characteristics attributable to a particle: its size, and its location.

Turning attention to the population of particles as a whole, a stochastic model based on the master equation can be developed to model the distribution of particles of differing sizes in specific compartments in the bed. In the following, the random variables of interest are

$$\{N_p(r): p \in \{1,2,\ldots,m\},\ r \in [0,R]\}$$

where

$N_p(r)dr$ = number of particles in compartment p with a size between r and r+dr

m = number of compartments

R = maximum particle size

As discussed earlier, the size variable, r, obeys a differential equation dependent on the reactant gas concentration in the compartment.

Assuming that chemical reaction controls, and that the particles are shrinking spheres, results in the following expression for first-order kinetics;

$$\frac{dr}{dt} = -\frac{bk_s}{\rho_B} C_{e_p} \tag{6-6}$$

where

r = radius of particle

b = mols of solid per mol of gas consumed

k_s = reaction rate based on surface reaction

ρ_B = molar density of solid

C_{e_p} = gas concentration in emulsion phase of compartment p

Note that through C_{e_p}, Eq. 6-6 is compartment specific. In the discussion following Eq. 6-5, it was noted that C_{e_p} is a random quantity due to fluctuating nature of the bubble population. In this case, Eq. 6-6 should be written as a stochastic differential equation with a noise term corresponding to the concentration fluctuations; from which it follows that r is also a random quantity.

The fluctuating part of the random variables, $N_p(r)$, should contain terms due to both the random motion between compartments, and to the random nature of the size variable. The rates of transition functions for these processes can be written as follows:

Movement between compartments

$$W_t(\{n_p(r),n_j(r)\},\{n_p(r)-1,n_j(r)+1\}) = \gamma_{pj} n_p(r) \tag{6-7}$$
$$\text{for } j \in \{p-1,p+1\}$$

where

γ_{pj} = rate at which particles in compartment p move to compartment j

Change due to reaction

$$W_t(\{n_p(r), n_p(r-dr)\}, \{n_p(r)-1, n_p(r-dr)+1\}) = \nu_p \dot{n}_p(r) \qquad \text{for all } p \tag{6-8}$$

where

$$\nu_p = -\left(\frac{dr}{dt}\right) \text{ in compartment } p$$

Note that particles are restricted to movement to either the next highest or next lowest compartment. Equations 6-7 and 6-8 can be written in terms of $\{n\}$ and $\{\xi\}$ as follows;

$$W_t(\{n_p(r), n_j(r)\}, \{-1, 1\}) = \gamma_{pj} n_p(r) \qquad \text{for } j \in \{p-1, p+1\} \tag{6-9}$$

$$W_t(\{n_p(r), n_p(r-dr)\}, \{-1, 1\}) = \nu_p n_p(r) \qquad \text{for all } p \tag{6-10}$$

where, as in previous chapters, all null elements in the set $\{\xi\}$ are omitted, and the remaining elements correspond to those in $\{n\}$.

To continue in the same manner as was done in previous chapters the continuous variable, r, must first be partitioned into a discrete set with index i and characteristic size ε, i.e.,

$$r \to i\varepsilon$$

With this transformation, Eqs. 6-9 and 6-10 can be written as

$$W_t(\{n_p(i),n_j(i)\},\{-1,1\}) = \gamma_{pj} n_p(i) \qquad (6\text{-}11)$$

for all i, and j ε {p-1,p+1}

$$W_t(\{n_p(i),n_p(i-1)\},\{-1,1\}) = \nu'_p n_p(i) \qquad (6\text{-}12)$$

for all p and i

where

ν'_p = equivalent of ν_p for discrete r

Finally, to include the addition of particles to the bed, the following transition rate is needed,

$$W_t(\{n_p(i)\},\{1\}) = \Omega f_p(i) \qquad (6\text{-}13)$$

for all p and i

where

$\Omega f_p(i)$ = rate at which particles of size iε are added to compartment p

The jump moments can now be calculated after the change to a single index denoted by the subscript h; for convenience it is defined as

$$h = p+m(i-1) \qquad (6\text{-}14)$$

where

p = subscript denoting the compartment number

i = index denoting particle size

m = number assigned to last compartment

The variable $n_p(i)$ now appears as

$$n_{p+m(i-1)}$$

The jump monents, A_h and B_{hn}, can now be found as follows;

$$\begin{aligned} A_h = \sum_p \sum_i \{ & \sum_j [-\delta^k(h-p-mi+m) + \delta^k(h-j-mi+m)] \\ & [\delta^k(j-p+1)(1-\delta^k(j)) \\ & + \delta^k(j-p-1)(1-\delta^k(p-m))]\gamma_{pj} n_{p+m(i-1)} \\ & + [-\delta^k(h-p-mi+m) + \delta^k(h-p-mi+2m)] \\ & \cdot \nu'_p n_{p+m(i-1)} \\ & + \delta^k(h-p-mi+m)\Omega f_p(i) \} \end{aligned} \qquad (6\text{-}15)$$

$$\begin{aligned} B_{hn} = \sum_p \sum_i \{ & \sum_j [-\delta^k(h-p-mi+m) + \delta^k(h-j-mi+m)] \\ & \cdot [-\delta^k(n-p-mi+m) + \delta^k(n-j-mi+m)] \\ & \cdot [\delta^k(j-p+1)(1-\delta^k(j)) + \delta^k(j-p-1)(1-\delta^k(p-m))] \\ & \cdot \gamma_{pj} n_{p+m(i-1)} \\ & + [-\delta^k(h-p-mi+m) + \delta^k(h-p-mi+2m)] \end{aligned}$$

$$\cdot[-\delta^k(n-p-mi+m) + \delta^k(n-p-mi+2m)]$$

$$\cdot\nu'_p n_{p+m(i-1)}$$

$$+ \delta^k(h-n)\delta^k(h-p-mi+m)\Omega f_p(i)\ \} \qquad (6\text{-}16)$$

The first of these expressions together with Eq. 2-18 gives

$$\frac{d\langle N_p(i)\rangle}{dt} = -\{\gamma_{pp+1}[1-\delta^k(p-m)] + \gamma_{pp-1}[1-\delta^k(p-1)]\}\ \langle N_p(i)\rangle$$

$$+[1-\delta^k(p-m)]\gamma_{p+1p}\langle N_{p+1}(i)\rangle + [1-\delta^k(p-1)]\gamma_{p-1p}\langle N_{p-1}(i)\rangle$$

$$+ \nu'_p(\langle N_p(i+1)\rangle - \langle N_p(i)\rangle)$$

$$+ \Omega f_p(i) \qquad (6\text{-}17)$$

or, in terms of the continuous variable r,

$$\frac{\partial\langle N_p(r)\rangle}{dt} = -\{[1 - \delta^k(p-m)]\gamma_{pp+1} + [1 - \delta^k(p-1)]\gamma_{pp-1}\}\langle N_p(r)\rangle$$

$$+[1-\delta^k(p-m)]\gamma_{p+1p}\langle N_{p+1}(r)\rangle + [1-\delta^k(p-1)]\gamma_{p-1p}\langle N_{p-1}(r)\rangle$$

$$+ \nu_p\frac{\partial\langle N_p(r)\rangle}{dr} + \Omega f_p(r) \qquad (6\text{-}18)$$

where

$$\nu_p = -\left\langle\frac{dr}{dt}\right\rangle_p$$

= expected value of $\left(-\frac{dr}{dt}\right)$ in compartment p

The moments of the fluctuating component can be found from the following expression for $\tilde{A}_{hn}$;

$$\tilde{A}_{hn} = \sum_p \sum_i \{ \sum_j [-\delta^k(h-p-mi+m) + \delta^k(h-j-mi+m)] \cdot [\delta^k(j-p+1)(1-\delta^k(j)) + \delta^k(j-p-1)(1-\delta^k(p-m))] \cdot \gamma_{pj}\delta^k(n-p-mi+m) + [-\delta^k(h-p-mi+m) + \delta^k(h-p-mi+2m)] \cdot \nu'_p\delta^k(n-p-mi+m) \} \quad (6\text{-}19)$$

Transforming into a continuous size variable, this expression in conjunction with Eq. 2-20 yields

$$\frac{d\langle Z_p(r)\rangle}{dt} = -\{[1-\delta^k(p+m)]\gamma_{pp+1} + [1-\delta^k(p-1)]\gamma_{pp-1}\}\langle Z_p(r)\rangle + [1-\delta^k(p-m)]\gamma_{p+1p}\langle Z_{p+1}(r)\rangle + [1-\delta^k(p-1)]\gamma_{p-1p}\langle Z_{p-1}(r)\rangle + \nu_p \frac{\partial\langle Z_p(r)\rangle}{dr} \quad (6\text{-}20)$$

Note that, except for the term due to addition of particles, $\langle N_p(r)\rangle$ and $\langle Z_p(r)\rangle$ obey the same equations. This is due to the fact that the rates of transition are linear functions of $n_p(r)$.

To calculate $\mathrm{Cov}[Z_p(r)Z_j(s)]$ from Eq. 2-21, it is first necessary to find $\tilde{B}_{pj}(r,s)$ from B_{hn} in Eq. 6-16; this yields

$$\tilde{B}_{pj}(r,s) = \Omega^{-1}\delta^k(r-s)\{\delta^k(p-j)\gamma_{pp-1}[1-\delta^k(p-1)]<N_p(r)>$$

$$+ \delta^k(p-j)\gamma_{pp+1}[1-\delta^k(p-m)]<N_p(r)>$$

$$- \delta^k(p-j-1)\gamma_{pj}[1-\delta^k(j)]<N_p(r)>$$

$$- \delta^k(p-j+1)\gamma_{pj}[1-\delta^k(p-m)]<N_p(r)>$$

$$- \delta^k(p-j+1)\gamma_{jp}[1-\delta^k(p)]<N_j(r)>$$

$$- \delta^k(p-j-1)\gamma_{jp}[1-\delta^k(j-m)]<N_j(r)>$$

$$+ \delta^k(p-j)\gamma_{j+1j}[1-\delta^k(p)]<N_{p+1}(r)>$$

$$+ \delta^k(p-j)\gamma_{p+1p}[1-\delta^k(p-1-m)]<N_{p-1}(r)>$$

$$+ \delta^k(p-j)\Omega f_p(i)\} \qquad (6\text{-}21)$$

With Eq. 6-19 and this expression, the following expression for $\mathrm{Cov}[N_p(r)N_j(s)]$ is found;

$$\frac{\partial}{\partial t}\mathrm{Cov}[N_p(r)N_j(s)] = -\{[1-\delta^k(p-m)] + [1-\delta^k(p-1)]\gamma_{pp-1}\}\mathrm{Cov}[N_p(r)N_j(s)]$$

$$+[1-\delta^k(p-m)]\gamma_{p+1p}\mathrm{Cov}[N_{p+1}(r)N_j(s)]$$

$$+[1-\delta^k(p-1)]\gamma_{p-1p}\mathrm{Cov}[N_{p-1}(r)N_j(s)]$$

$$+ \nu_p \frac{\partial}{\partial r}\mathrm{Cov}[N_p(r)N_j(s)]$$

$$-\{[1-\delta^k(j-m)]\gamma_{jj+1} + [1-\delta^k(j-1)]\gamma_{jj-1}\}\mathrm{Cov}[N_p(r)N_j(s)]$$

$$+[1-\delta^k(j-m)]\gamma_{j+1j}\mathrm{Cov}[N_p(r)N_{j+1}(s)]$$

$$+[1-\delta^k(j-1)]\gamma_{j-1j}\mathrm{Cov}[N_p(r)N_{j-1}(s)]$$

$$+ \nu_j \frac{\partial}{\partial s} \mathrm{Cov}[N_p(r)N_j(s)]$$

$$+ \delta^k(r-s)\{(\delta^k(p-j)\gamma_{pp-1}[1-\delta^k(p-1)]$$

$$+\delta^k(p-j)\gamma_{pp+1}[1-\delta^k(p-m)]$$

$$-\delta^k(p-j-1)\gamma_{pj}$$

$$-\delta^k(p-j+1)\gamma_{pj}[1-\delta^k(p-m)]\}\langle N_p(r)\rangle$$

$$-(\delta^k(p-j+1)\gamma_{jp}$$

$$+\delta^k(p-j-1)\gamma_{jp}[1-\delta^k(j-m))]\langle N_j(r)\rangle$$

$$+\delta^k(p-j)\gamma_{p+1p}\langle N_{p+1}(r)\rangle$$

$$+\delta^k(p-j)\gamma_{p+1p}[1-\delta^k(p-1-m)]\langle N_{p-1}(r)\rangle$$

$$+\delta^k(p-j)\Omega f_p(r)\} \qquad (6\text{-}22)$$

Note that this expression follows by ignoring the fluctuating component in Eq. 6-6. To include this component, it is necessary to add two additional terms to Eq. 6-22. These terms are

$$\langle N_j(s)\nu_{op}\rangle \frac{\partial\langle N_p(r)\rangle}{\partial r} \qquad (6\text{-}23)$$

$$\langle N_p(r)\nu_{oj}\rangle \frac{\partial\langle N_j(s)\rangle}{\partial s} \qquad (6\text{-}24)$$

where

$$\langle \nu_{op} \rangle = 0$$

$$\langle \nu_{op}(0)\nu_{op}(\tau) \rangle = \frac{b^2 k_s^2}{\rho_B^2} \langle [C_{e_p}(0) - \langle C_{e_p}(0) \rangle][C_{e_p}(\tau) - \langle C_{e_p}(\tau) \rangle] \rangle$$

$\langle [C_{e_p}(0) - \langle C_{e_p}(0) \rangle][C_{e_p}(\tau) - \langle C_{e_p}(\tau) \rangle] \rangle$ = Correlation function of concentration fluctuations in compartment p

Writing Eq. 6-18 as a stochastic differential equation yields,

$$\frac{\partial n_p(r)}{\partial t} = - \{[1-\delta^k(p-m)]\gamma_{pp+1} + [1-\delta^k(p-1)]\gamma_{pp-1}\} n_p(r)$$
$$+ [1-\delta^k(p-m)]\gamma_{p+1p} n_{p+1}(r) + [1-\delta^k(p-1)]\gamma_{p-1p} n_{p-1}(r)$$
$$+ \nu_p \frac{\partial n_p(r)}{\partial r} + \nu_{o_p} \frac{\partial n_p(r)}{\partial r}$$
$$+ \Omega f_p(r) + W(t) \qquad (6\text{-}25)$$

where

W(t) = noise term yielding Eq. 6-21

i.e.,

$$\langle W(t)\,[n_p(r) + n_j(s)] \rangle = \overset{\gamma}{B}_{pj}(r,s) \qquad (6\text{-}26)$$

Starting with the random variable in discrete form, n_h, and using Eq. 6-15 and 6-16, this stochastic differential equation can also be written as

$$dn_h = A'_h dt + C_{hi} dW_i(t) \tag{6-27}$$

where

$$\Sigma_i \; C_{hi} C_{in} = B_{hn}$$

$dW_i(t)$ = multivariable Wiener Process

A'_h = A_h with ν'_p replaced by $(\nu'_p + \nu'_{op}(t))$, where $\nu'_{op}(t)$ is the discrete form of ν_{op} defined after Eq. 6-24

This expression can transformed to the same form as Eq. 6-25, or worked with directly. In either case, the non-white nature of the noise term, ν_{op}, leads to difficulties. Gardiner (1983) presents a solution for the case when the noise is uncorrelated, and Van Kampen (1981) has an apporoximation procedure for almost white noise. In this system, depending on the rates of coalescence and movement of the bubbles, the correlation time for the concentration fluctuations may be significant, thus neither method would be valid. In this case dynamic simulation of the process may be a valuable alternative (Ligon and Amundson, 1981).

By assuming that the fluctuating terms arising from the concentration fluctuations (Eqs. 6-23 and 6-24) are negligible, it is possible to continue the calculation, and to derive the following expression for the correlation function;

$$\frac{\partial}{\partial\tau} K_{jp}(s,r,\tau) = -\{[-\delta^k(p-m)]\gamma_{pp+1} + [1-\delta^k(p-1)]\gamma_{pp-1}\}K_{jp}(s,r,\tau)$$

$$+[1-\delta^k(p-m)]\gamma_{p+1p}K_{jp+1}(s,r,\tau) + [1-\delta^k(p-1)]$$

$$\cdot\gamma_{p-1p}K_{jp-1}(s,r,\tau)$$

$$+ \nu_p \frac{\partial}{\partial r} K_{jp}(s,r,\tau) \qquad (6\text{-}28)$$

where

$$K_{jp}(s,r,0) = \mathrm{Cov}[N_j(s)N_p(r)] \quad \text{at steady-state}$$

Including the noise term in this expression would require the addition of the term

$$\frac{\partial}{\partial r} K(n_j(s), n_p(r)\nu_{op}) \qquad (6\text{-}29)$$

, i.e., the cross-correlation between $n_j(s)$ at time zero and $n_p(r)\nu_{op}$ at time τ.

At steady-state, Eq. 6-18 with Eq. 6-6, reduces to

$$\frac{bk_s}{\rho_B} C_{e_p} \frac{d\langle N_p(r)\rangle}{dr} = \{[1-\delta^k(p-m)]\gamma_{pp+1} + [1-\delta^k(p-1)]\gamma_{pp-1}\}\langle N_p(r)\rangle$$

$$-[1-\delta^k(p-m)]\gamma_{p+1p}\langle N_{p+1}(r)\rangle$$

$$-[1-\delta^k(p-1)]\gamma_{p-1p}\langle N_{p-1}(r)\rangle - \Omega f_p(r) \qquad (6\text{-}30)$$

If the feed particles are all of size R, then this expression can be written as

$$\frac{bk_s}{\rho_B} C_{e_p} \frac{d\langle N_p(r)\rangle}{dr} = \{[\,1-\delta^k(p-m)\,]\gamma_{pp+1} + [1-\delta^k(p-1)\,]\gamma_{pp-1}\}\langle N_p(r)\rangle$$

$$- [1-\delta^k(p-m)\,]\gamma_{p+1p}\langle N_{p+1}(r)\rangle$$

$$- [1-\delta^k(p-1)]\,\gamma_{p-1p}\langle N_{p-1}(r)\rangle \qquad (6\text{-}31)$$

with

$$\langle N_p(R)\rangle = \frac{\rho_B F_p}{bk_s C_{e_p}}$$

where

F_p = number of feed particles per unit time fed into compartment p

Under the same conditions, Eq. 6-22 for the covariances can be written as

$$\frac{bk_s}{\rho_B}\left(C_{e_p}\frac{\partial}{\partial r} + C_{e_j}\frac{\partial}{\partial s}\right)\mathrm{Cov}[N_p(r)N_j(s)] = \{[1-\delta^k(p-m)]\gamma_{pp+1} + [1-\delta^k(p-1)]\gamma_{pp-1}\}$$

$$\cdot\mathrm{Cov}[N_p(r)N_j(s)]$$

$$-[1-\delta^k(p-m)]\gamma_{p+1p}\mathrm{Cov}[N_{p+1}(r)N_j(s)]$$

$$-[1-\delta^k(p-1)]\gamma_{p-1p}\mathrm{Cov}[N_{p-1}(r)N_j(s)]$$

$$+\{[1-\delta^k(j-m)]\gamma_{jj+1} + [1-\delta^k(j-1)]\}$$

$$\cdot\mathrm{Cov}[N_p(r)N_j(s)]$$

$$-[1-\delta^k(j-m)]\gamma_{j+1j}\mathrm{Cov}[N_p(r)N_{j+1}(s)]$$

$$-[1-\delta^k(j-1)]\gamma_{j-1j}\mathrm{Cov}[N_p(r)N_{j-1}(s)]$$

$$-\delta^k(r-s)\{(\delta^k(p-j)[1-\delta^k(p-1)]\gamma_{pp-1}$$

$$+\delta^k(p-j)[1-\delta^k(p-m)]\gamma_{pp+1}$$

$$-\delta^k(p-j-1)\gamma_{pj}$$

$$-\delta^k(p-j+1)[1-\delta^k(p-m)]\gamma_{pj})\langle N_p(r)\rangle$$

$$-(\delta^k(p-j+1) + \delta^k(p-j-1)[1-\delta^k(j-m)]\gamma_{jp})$$

$$\cdot\langle N_j(r)\rangle$$

$$+\delta^k(p-j)\gamma_{p+1p}(\langle N_{p+1}(r)\rangle$$

$$+[1-\delta^k(p-1-m)]\langle N_{p-1}(n)\rangle)\} \quad (6\text{-}32)$$

with

$$\mathrm{Cov}[N_p(r)N_p(s)] = \mathrm{Cov}[N_p(s)N_p(r)]$$

$$\mathrm{Cov}[N_p(R)N_p(R)] = \mathrm{Var}[N_p(R)] = \frac{\rho_B}{bk_s C_{e_p}}\,\mathrm{Var}[F_p]$$

$$\mathrm{Cov}[N_p(R)N_j(s)] = \mathrm{Cov}[N_p(r)N_j(R)] = 0$$

where

$\mathrm{Var}[F_p]$ = variance in the feed rate to compartment p

Similarily, Eq. 6-28 for the correlation functions reduces to

$$\frac{\partial}{\partial\tau} K_{jp}(s,r,\tau) - \frac{bk_s}{\rho_B} C_{e_p} \frac{\partial}{\partial r} K_{jp}(s,r,\tau)$$

$$= -\{[1-\delta^{k(p-m)}]\gamma_{pp+1} + [1-\delta^{k(p-1)}]\gamma_{pp-1}\}$$

$$\cdot K_{jp}(s,r,\tau)$$

$$+[1-\delta^{k(p-m)}]\gamma_{p+1p} K_{jp+1}(s,r,\tau)$$

$$+[1-\delta^{k(p-1)}]\gamma_{p-1p} K_{jp-1}(s,r,\tau) \qquad (6\text{-}33)$$

with

$$K_{jp}(s,r,0) = \mathrm{Cov}[N_j(s)N_p(r)]$$

The solution to Eqs. 6-31 through 6-33 characterizes the random variable by their means and correlation functions. The relationship between $N_p(r)$ and n_{e_p} in Eqs. 6-2 through 6-5 must be found in order to use information on $N_p(r)$ to calculate the effect of its stochastic nature on the value of C_{e_p}. For a single particle of size r, the rate at which it consumes reactant gas is given by

$$4\pi r^2 k_s C_{e_p} \qquad \text{(mols/sec-particle)}$$

The combined rate for all particles of all sizes in compartment p is thus

$$4\pi k_s C_{e_p} \int_0^R r^2 N_p(r)dr \quad \text{(mols/sec)}$$

$V_{e_p}\eta_{e_p}$ in Eqs. 6-2 through 6-5 is then

$$V_{e_p}\eta_{e_p} = -4\pi k_s C_{e_p} \int_0^R r^2 N_p(r)dr \tag{6-34}$$

Note, as indicated earlier, both C_{e_p} and $N_p(r)$ are random variables, and thus η_{e_p} is also random. With this in mind, Eqs. 6-1 through 6-5 plus Eq. 2-27 could be treated as a system of stochastic differential equations with correlated noise terms.

6.3 EXAMPLE CALCULATION FOR TWO COMPARTMENTS

For the case of two compartments (m=2) Eq. 6-31 reduces to the following two expressions;

$$\frac{bk_s}{\rho_B} C_{e_1} \frac{d\langle N_1(r)\rangle}{dr} = \gamma_{12}\langle N_1(r)\rangle - \gamma_{21}\langle N_2(r)\rangle \tag{6-35}$$

$$\frac{bk_s}{\rho_B} C_{e_2} \frac{d\langle N_2(r)\rangle}{dr} = \gamma_{21}\langle N_{21}(r)\rangle - \gamma_{12}\langle N_1(r)\rangle \tag{6-36}$$

Combining these expressions yields

$$C_{e_1}\langle N_1(r)\rangle + C_{e_2}\langle N_2(r)\rangle = \frac{\rho_B}{bk_s}(F_1 + F_2) \tag{6-37}$$

Either Eq. 6-35 or Eq. 6-36 can then be used with Eq. 6-37 to yield

$$\langle N_1(r)\rangle = \theta\{\gamma_{21}(F_1 + F_2) + (\frac{C_{e_2}}{C_{e_1}}\gamma_{12}F_1 - \gamma_{21}F_2)\exp[\frac{\phi(r-R)}{C_{e_1}C_{e_2}}]\} \tag{6-38}$$

$$\langle N_2(r)\rangle = \theta\{\gamma_{12}(F_1 + F_2) + (\frac{C_{e_1}}{C_{e_2}}\gamma_{21}F_2 - \gamma_{12}F_1)\exp[\frac{\phi(r-R)}{C_{e_1}C_{e_2}}]\} \tag{6-39}$$

where

$$\theta = \frac{\rho_B}{bk_s(C_{e_1}\gamma_{21} + C_{e_2}\gamma_{12})} \quad , \quad \phi = \frac{\rho_B(C_{e_1}\gamma_{21} + C_{e_2}\gamma_{12})}{bk_s}$$

Note that as γ_{12}, $\gamma_{21} \to +\infty$, with $\frac{\gamma_{21}}{\gamma_{12}} = a$

$$\langle N_1(r)\rangle \to \frac{\rho_B a(F_1 + F_2)}{bk_s(aC_{e_1} + C_{e_2}}$$

$$\langle N_2(r)\rangle \to \frac{\rho_B(F_1 + F_2)}{bk_s(aC_{e_1} + C_{e_2})}$$

for all r except r = R.

With a=1, this limit represents perfect mixing with one-half the particles in compartment one, and the other half in compartment two (assuming equi-volume compartments). In this case the average rate of reaction would be uniform throughout the bed if the gas concentration is also uniform.

The covariances can be found by solving Eq. 6-32. For m=2 this expression reduces to

$$\begin{aligned}\frac{bk_s}{\rho_B} C_{e_1}\left(\frac{\partial}{\partial r} + \frac{\partial}{\partial s}\right)\mathrm{Cov}[N_1(r)N_1(s)] = {} & 2\gamma_{12}\mathrm{Cov}[N_1(r)N_1(s)] \\ & - \gamma_{21}\mathrm{Cov}[N_2(r)N_1(s)] \\ & - \gamma_{21}\mathrm{Cov}[N_1(r)N_2(s)] \\ & - \delta^k(r-s)\{\gamma_{12}\langle N_1(r)\rangle \\ & + \gamma_{21}\langle N_2(r)\rangle\} \qquad (6\text{-}40)\end{aligned}$$

$$\frac{bk_s}{\rho_B}\left(C_{e_2}\frac{\partial}{\partial r}+C_{e_1}\frac{\partial}{\partial s}\right)\mathrm{Cov}[N_2(r)N_1(s)] = \gamma_{21}\mathrm{Cov}[N_2(r)N_1(s)]$$
$$-\gamma_{12}\mathrm{Cov}[N_1(r)N_1(s)]$$
$$+\gamma_{12}\mathrm{Cov}[N_2(r)N_1(s)]$$
$$-\gamma_{21}\mathrm{Cov}[N_2(r)N_2(s)]$$
$$+\delta^k(r-s)\{\gamma_{21}\langle N_2(r)\rangle + \gamma_{12}\langle N_1(r)\rangle\} \quad (6\text{-}41)$$

$$\frac{bk_s}{\rho_B}\left(C_{e_1}\frac{\partial}{\partial r}+C_{e_2}\frac{\partial}{\partial s}\right)\mathrm{Cov}[N_1(r)N_2(s)] = \gamma_{12}\mathrm{Cov}[N_1(r)N_2(s)]$$
$$-\gamma_{21}\mathrm{Cov}[N_2(r)N_2(s)]$$
$$+\gamma_{21}\mathrm{Cov}[N_1(r)N_2(s)]$$
$$-\gamma_{12}\mathrm{Cov}[N_1(r)N_1(s)]$$
$$+\delta^k(r-s)\{\gamma_{21}\langle N_2(r)\rangle + \gamma_{12}\langle N_1(r)\rangle\} \quad (6\text{-}42)$$

$$\frac{bk_s}{\rho_B}C_{e_2}\left(\frac{\partial}{\partial r}+\frac{\partial}{\partial s}\right)\mathrm{Cov}[N_2(r)N_2(s)] = 2\gamma_{21}\mathrm{Cov}[N_2(r)N_2(s)]$$
$$-\gamma_{12}\mathrm{Cov}[N_1(r)N_2(s)]$$
$$-\gamma_{12}\mathrm{Cov}[N_2(r)N_1(s)]$$
$$-\delta^k(r-s)\{\gamma_{21}\langle N_2(r)\rangle + \gamma_{12}\langle N_1(r)\rangle\} \quad (6\text{-}43)$$

These equations are discontinuous at r=s, and must be solved for the two cases, r=s, and r≠s, separately. The resulting sets of coupled partial differential equations may impose difficulties since the auxiliary conditions at the boundaries are not entirely evident. These problems can be avoided by working exclusively in the discrete form. If the size variable, r, is partitioned into n parts, the resulting system of m·n(m·n-1) linear equations relating the covariances can be easily solved. The task is facilitated by low degree of inter-dependence amoung the variables, and the fact that the dependence on the size variable only includes the size of the variable in question and that of the one immediately proceeding it.

The correlation functions also involve a set of coupled partial differential equations. In the case of m=2, these are

$$\frac{\partial}{\partial\tau} K_{j1}(s,r,\tau) - \frac{bk_s}{\rho_B} C_{e_1} \frac{\partial}{\partial r} K_{j1}(s,r,\tau)$$

$$= -\gamma_{12} K_{j1}(s,r,\tau) + \gamma_{21} K_{j2}(s,r,\tau) \qquad (6\text{-}44)$$

$$\frac{\partial}{\partial\tau} K_{j2}(s,r,\tau) - \frac{bk_s}{\rho_B} C_{e_2} \frac{\partial}{\partial r} K_{j2}(s,r,\tau)$$

$$= -\gamma_{21} K_{j2}(s,r,\tau) + \gamma_{12} K_{j1}(s,r,\tau) \qquad (6\text{-}45)$$

$$\text{for } j = 1, 2$$

As with the covariances, these equations can be handled in discrete form, however they involve a set of coupled ordinary differential equations which will require the calculation of the eigenvalues and eigenvectors

of the system of equations. As the partition of the size variable becomes smaller and smaller, the discrete formulation will approach the continuous one.

To calculate the concentration of reactant gas in each compartment it is necessary to solve the balance equation introduced earlier. The parameters which enter these equations depend on the bubble size distribution in the bed. A complete model of the bed can thus be developed if information about the rates of reaction, bubble coalescence and movement, and particle migration are known. The resulting set of coupled stochastic differential equations, with the noise terms uniquely specified by the underlying processes, could be studied to determine the effects of the fluctuating nature of the fluidized bed on the reactant gas concentration profile. Such a project would involve a simulation procedure where the coupled stochastic differential equation are solved with the random noise terms being generated according to expressions found for the correlation functions of the underlying processes. It is also possible to write the entire set of equations in the form of Eq. 6-27. The resulting vector stochastic differential equation could then be solved. Note that the noise terms are uniquely determined in Eq. 6-27 through the relationship between the second jump moment, B_{hm}, and C_{hi} in Eq. 6-27, i.e., (Ryter and Deker, 1980)

$$\sum_i C_{hi} C_{in} = B_{hn} \tag{6-46}$$

B_{hn} is explictly determined by the underlying processes, e.g. rates of coalescence and migration, and thus C_{hi} can be found from Eq. 6-46.

NOTATION

A = cross-sectional area of the bed.

A_h = first jump moment.

A'_h = A_h with fluctuating reaction rate.

$\tilde{A}_h$ = A_h/Ω

$\tilde{A}_{hn}$ = coefficient matrix from the expansion of $\tilde{A}_h$.

b = mols of solid per mol of gas consumed.

B_{hn} = second jump moment.

$\tilde{B}_{hn}$ = B_{hn}/Ω

C_{b_p} = gas concentration in the bubble phase in compartment p.

C_{e_p} = gas concentration in the emulsion phase in compartment p.

C_{hi} = coefficient matrix on noise term in the Stochastic Differentical Equation.

$\mathrm{Cov}[N_p(r)N_j(s)]$ = $\langle N_p(r)N_j(s)\rangle - \langle N_p(r)\rangle\langle N_j(s)\rangle$

$\mathrm{Cov}[Z_p(r)Z_j(s)]$ = $\langle Z_p(r)Z_j(s)\rangle - \langle Z_p(r)\rangle\langle Z_j(s)\rangle$

F_p = number of feed particles fed into compartment p.

F_{be_p} = gas interchange coefficient from the bubble phase to the emulsion phase in compartment p per unit volume of the bubble phase.

G_{be_p} = crossflow from the bubble to the emulsion phase.

k_s = reaction rate based on surface reaction.

$K_{jp}(s,r,\tau)$ = $\langle N_j(s,0)N_p(r,\tau)\rangle - \langle N_j(s,0)\rangle\langle N_p(r,\tau)\rangle$

m = number of compartments.

$N_p(r)dr$ = number of particles in compartment p with a size between r and r+dr.

$\langle N_p(r)\rangle$ = expexted value of $\langle N_p(r)\rangle$.

r = radius of particle.

R = maximum particle size.

U_{bs_p} = superficial gas velocity in the bubble phase in compartment p.

U_{es_p} = superficial gas velocity in the emulsion phase in compartment p.

V_{b_p} = volume of the bubble phase in compartment p.

V_{e_p} = volume of the emulsion phase in compartment p.

$Var[F_p]$ = variance in the feed rate to compartment p.

$W_t(\cdot,\cdot)$ = intensity of transition function.

$\langle Z_p(p) \rangle$ = expected value of fluctuating component of $N_p(r)$.

Greek Letters

γ_{pj} = rate at which particles in compartment p move to compartment j.

$\delta^k(\cdot)$ = Kronecker delta where $\delta^k(0)=1$ and $\delta^k(x)=0$ for $x \neq 0$.

ε = characteristic unit of size.

ε_{mf} = void fraction of the bed at U_{mf}.

η_{e_p} = reaction rate in compartment p.

θ = constant.

ν_p = rate of size reduction of particles in compartment p.

ν_{op} = fluctating component of ν_p.

ρ_B = molar density of solid.

ϕ = constant.

Ω = system size.

$\Omega f_p(i)$ = rate at which particles of size $i\varepsilon$ are added to compartment p.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

This study has yielded the following conclusions:

1. A generalized master equation for discrete or continuous variable systems evolving through changes in the number of entities in the population has been derived and approximate solutions have been found using the System Size Expansion. It is thus possible to characterize the population by solving differential equations for the mean and covariances of the number of entities in the population. The dynamic behavior of the population is expressed in the form of the correlation functions which can be determined uniquely from the expressions resulting from the System Size Expansion. This formulation thus offers a viable alternative to the traditional deterministic population balance equations.

2. Given the rates of coalescence and the rise velocity of bubbles in a fluidized-bed, it is possible to model the fluctuations as well as the average of the number of bubbles of varying size in a bubbling fluidized-bed.

3. The compartment height in the present model for a bubbling fluidized-bed can be used to control the number of bubbles sizes which must be considered in each compartment. This in turn makes it possible to solve the bubble coalescence model to determine the mean and variance of the number of bubbles in a compartment.

4. For the parameters considered, it is shown that fluctuations in the total surface area of the bubble phase in the first compartment of a bubbling fluidized-bed have a standard deviation of more than 19 percent. These fluctuations would effect the inter-phase mass transfer and thus reaction rates in the emulsion phase. The magnitude of the effects can be studied using the correlation function and a suitable stochastic differential equation.

5. It is demonstrated that a generalized master equation derivation of the population balance equation for coalescence and dispersion phenomena involving binary breakage and coalescence leads to a result which parallels that used in the literature for the mean number of particles of a given size.

6. In addition to an expression for the mean number of particles of a given size, the more general stochastic derivation gives rise to expressions for the covariances and correlation functions. These expressions can in turn be used with time series analysis to determine rate constants from steady-state population data, thus freeing the experimental study of the system from the necessity to correlate transient data in the effort to extract the rate constants.

7. By introducing a new variable representing the "distance" of a particle from formation, it has been shown that the assumption of binary breakage is still logically tenable. The determination of binary breakage rates as s function of the new varible is however an important, unaddressed obstacle to the implementation of such a strategy, which can only be resolved by further study.

8. The transformation of a discrete size variable to the continuous one which is usually found in the literature has been successfully performed. However, it has been shown that due to certain point discontinuities in the discrete equation, the limiting process, as the size interval tended to zero, results in the absence of several terms in the continuous counterpart. These point discontinuities, which exist most notably at points where two particles of equal size are formed from a parent particle, cannot be recovered, without a priori knowledge of their form, when transforming the continuous equation back to the discrete form. Therefore, for systems which are truely discrete in nature, the proper route for their modelling would begin with the discrete equation containing all the necessary terms.

9. The probability of forming a daughter particle of a certain size given the size of the parent particle was derived from the probability of the possible ordered sets (those sets with non-zero probability). For breakage other than binary, it is noted that this probability will be unsymmetrical about the point corresponding to one-half of the parent particle. This, in turn, implies that the breakage function for systems exhibiting breakage of higher order than binary breakage cannot be rationally modeled by using the breakage probability for binary breakage multiplied by the order of breakage as is common practice in the literature. Such a distribution does normalize properly, but is necessarily symmetrical and thus is in contridication with the rigorous derivation.

10. A rigorous approach to the derivation of the daughter particle size distribution was presented by consideration of the excess surface energy per unit volume among the daughter particles. Heuristic arguements assigning the variance of the excess surface energy distribuion as a direct measure of the probability of an ordered set led to reasonable expressions for the daughter particle size distribution.

11. An example calculation for a coalescence and dispersion system led to an expression for the average total surface area of dispersed phase as well as expressions for the covariance and correlation function. In this example the standard deviation of the total surface area of dispersed phase was more than 10 percent, indicating that fluctuations may effect the inter-phase mass transfer processes.

12. A generalized master equation for coalescence and redispersion on a two dimensional lattice has been studied; it is found that when migration and coalence of entire groups of particles are included, and the rate of constants are significant, the System Size Expansion fails.

13. A Monte Carlo procedure is presented; it is used to simulate the coalescence and redispersion process on a two dimensional lattice. Such a simulation procedure is necessary when the System Size Expansion fails to be valid.

14. Due to the fluctuations in the bubble population in a fluidized-bed reactor, the quantities which appear in the two-phase model equations for the reactor will be stochastic. This implies that these equations can be treated as stochastic differential equations to determine the influence of the fluctuations on the concentration at the outlet and inside each phase of each compartment.

15. The random motion of solid particles undergoing combustion in the emulsion phase of a fluidized-bed can be modeled using a generalized master equation given the inter-compartmental migration rates. The fluctuations in the particle number can be incorporated into the two-phaae model equation yielding a vector atochastic differential equation where the noise terms are uniquely determined by the underlying procesaes of bubble coalescence and bubble/particle migration.

16. An example calculation involving a continuoua particle aize resulted in expressions for the correlation functions and covariances which involved partial differential equations for which no solution is given. It is however to be noted that discretization leads to a unique solution from which, in the limit of decreasing step size, the limiting solution to the continuous case can be found.

17. The vector stochastic differential equation governing the atochastic evolution of the variablea describing a fluidized-bed reactor can, in principal, be uniquely determined from a model for the coaleacence and migration of bubblea and a model of the particle migration between compartments. However, the solution of

this equation will require a simulation procedure, possibly involving non-white noise, to produce any tangible results concerning the effects of the fluctuations on the operating conditions in the reactor.

Recommendations for future work are listed below.

1. Determination of coalescence rate expression for bubbles in a bubbling fluidized-bed. In the present study a simple form for the rate expression was assumed to allow for an example calculation. For future study, an expression based on bubble hydrodynamics would be necessary. The resulting expression should, however, still possess the properties outlined in the section on determination of rate-of-coalescence function in Chapter 2.

2. Relate time constants in correlation functions to model parameters. In the example calculations presented, all time constants in the correlation functions have a unique numerical value since numerical values were assumed for the original rate constants. It would be highly desirable to determine these time constants as functions of the assumed rate constants. This would allow for comparison between experimental data and the theoretical correlation functions from which the rate constants could be determined.

3. Determination of breakage rates as a function of the "distance" from formatation, and determination of the rate of change of the "distance" variable. A new variable describing the "distance" from formation has been introduced to describe coalescence and dispersion phenomena. However, no physical basis has been proposed

for measurement and correlation of such a variable. Thus, further use of such an approach will require information about the rates of breakage as a function of this variable, as well as information about the mechaniams by which a particle becomes more and more diatant from its formation.

4. Calculation of the daughter size distribution and the probabilities of forming ordered sets from fundamental knowledge about particle energy levels and particle-fluid interactions. A method has been presented for determining the daughtersize distribution from the probabilities of forming the possible ordered sets. These probabilities, however, must be found from fundamental knowledge about the system under study. For dispersed fluid phase droplets, it has been proposed that the excess surface energy may be related to these probabilities. However, experimental investigation as well as deeper theoretical study should be combined to further puraue the question.

5. Simulation and comparison of generalized master equation for coalescence and redispersion on a two dimensional lattice. It has been shown that in some cases the System Size Expansion is not valid necessitating the use of a Monte Carlo simulation procedure. It would, therefore, be of interest to apply both methods to a system where the rate constants are known (e.g., sintering and redispersion in supported metal catalysis) to determine the relative error of the System Size Expanaion approximation as compared to the exact simulation results. Furthermore, the aimulation reaults can be uaed to determine the rate constants

through the use of the auto-correlation function. The relative sensitivity of the model to changes in parameters could then be determined.

6. Solution of the vector stochastic differential equation governing the evaluation of a fluidized-bed reactor. The random motion of a fluidized-bed reactor induced by the coalescence and migration of bubbles and the random motion of the solid particles in the emulsion phase results in a vector stochastic differential equation whose noise terms are uniquely determined by the above processes. The solution of this non-linear, multiplicative noise, vector differential equation is non-trivial even when reduced, through addition of variables, to a process involving only white noise. Its solution is, however, necessary in order to ascertain the true, non-stationary behavior of the fluidized-bed reactor.

LITERATURE CITED

1. Coulaloglou, C.A. and L.L. Tavlarides, "Description of Interaction Process in Agitated Liquid-Liquid Dispersion," Chem. Eng. Sci., 32, 1289 (1977).

2. Darton, R.C., R.D. LaNauze, J.F. Davidson, D. Harrison, "Bubble Growth Due to Coalescence in Fluidized Beds," Trans. IChem E., 55, 274 (1977).

3. Gardiner, C.W., Handbook of Stochastic Methods, Springer-Verlag, New York, 1983.

4. Handa, P.K. and J.C. Matthews, "Modeling of Sintering and Redispersion of Supported Metal Catalysts," AIChE J., 29, 717 (1983).

5. Howarth, W.J., "Coalescence of Drops in a Turbulent Flow Field," Chem Eng. Sci., 19, 33 (1964).

6. Ligon, J.R. and N.R. Amundson, "Modeling of Fluidized Bed Reactors. VI(a). An Isothermal Bed with Stochastic Bubbles," Chem Eng. Sci., 36, 653 (1981a).

7. Peters, M.H., L.S. Fan, and T.L. Sweeny, "Reactant Dynamics in Catalytic Fluidized Bed Reactors with Flow Reversal of Gas in the Emulsion Phase," Chem. Eng. Sci., 37 553 (1982).

8. Ruckenstein, E. and D.B. Dadyburjor, "Sintering and Redispersion in Supported Metal Catalysts," Reviews in Chem. Eng., 1, 251 (1983).

9. Ryter, D. and U. Deker, "Properties of the noise-induced spurious drift." J. Math Phys., 21, 2662 (1980).

10. Sovova, H., "Breakage and Coalescense of Drops in a Batch Stirred Vessel-II," Chem. Eng. Sci., 36, 1567 (1981).

11. Tavlavides, L.L. and P.M. Bapat, "Models for Scale-up of Dispersed Phase Liquid-Liquid Reactors," AIChE Symposium Series, 80, 12 (1983).

12. Van Kampen, N.G., Stochastic Processes in Physics and Chemistry, North-Holland, Netherlands, 1981.

DERIVATION AND APPLICATIONS OF THE GENERALIZED MASTER EQUATION

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ABSTRACT

A stochastic population balance based on the conditional probability of a transition between two particular states of the population which is assumed to possess the Markov property is derived. In the literature the resulting expression is known as the master equation as it offers a general formulation with which many physical processes can be modeled. An analytical solution to the master equation is however not guaranteed, and thus a rational approximation technique, known as the System Size Expansion, is used to obtain expressions for the means and the correlation functions of the random variables which characterize the population. The correlation functions are particular to the stochastic treatment, and allow for a quantification of the dynamic behavior and magnitude of the fluctuations in the population.

The generalized master equation is applied to model four systems of interest to chemical engineering. These systems are: (i) the bubble population in a bubbling fluidized bed, (ii) coalescence and dispersion in dispersed phases, (iii) coalescence and redispersion on a two dimensional lattice, and (iv) combustion of particles in a fluidized bed reactor. All the populations modeled in these systems sre characterized by their complex behavior depending on difficult to quantify variables, and by the relatively small number of members in the population. These characteristics are hallmarks of populations for which the master equation, and stochastic formulations in general, can offer an important modeling alternative.