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The Sub Master Equation

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Three postulates are proposed concerning the probabilistic dynamics of chemically reactive systems: the occurrence of the elementary event is a random variable characterized by a Poisson process; the state of the chemical system is a multivariate random variable characterized by a Markov process; the identity of any chemical species in the system is an independent random variable. These postulates when applied to chemically reactive systems in a uniform manner lead to a hierarchy of equations describing in detail how each k subpopulation varies with time. By summing over all permutations of the equation for $f_n^{(n)}(e_1, \ldots, e_n; t)$ we obtain the usual master equation. This paper focuses on the simple isomerization reaction $X \underset{\mu}{\overset{\lambda}{\rightleftharpoons}} Y$.

KEY WORDS: Sub master equation; evolution operator.

1. INTRODUCTION

The purpose of this initial paper is to set the foundation for an alternative approach to the stochastic treatment of simple chemical systems. The treatment is based on three postulates describing the probabilistic dynamic nature of three ubiquitous random variables: (1) the occurrence of an elementary event; (2) the state of the chemical system; and (3) the identity of a chemical species.

The focus here is on the simple isomerization reaction as the elementary event, $X \underset{\mu}{\overset{\lambda}{\rightleftharpoons}} Y$. A sub master equation is developed which describes the probabilistic time rate of change of the complete n-particle system in terms of the identity of each particle. This equation in component form represents 2^n coupled linear differential equations where $n \sim 10^{23}$. It is shown how a solution to this system can be analytically expressed in terms of the 2×2 evolution matrix $E_{(1)}(t)$.

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The analysis also shows that the system satisfies a factorization theorem (propagation of chaos) analogous to the result of Kac[10] and McKean[16] for the Boltzmann equation.

The master equation probability function, $P_2(x; t \mid x^0; 0)$, is shown to be the convolution of the probability distribution functions for the random variables k, $x^0 - k$, $x - k$, and $y^0 - (x - k)$, which are, respectively, the number of x^0 that become x, the number of x^0 that become y, the number of y^0 that become x, and the number of y^0 that become y. It is shown that k and $x - k$ are independent normally distributed random variables and that their sum is then also a normally distributed random variable.

Finally, the random force of the corresponding Langevin equation is derived as a function of the four fundamental sub master 2 state transition density functions.

There are three fundamental postulates in the sub master equation theory:

(I) The number of *occurrences* of an elementary event is a Poisson process.
(II) The *state* of the system is a Markov process.
(III) The *identity* of any particle in the system is an independent random variable.

The point being made by the three postulates is that there are three characteristics of kinetically changing systems that are common to all systems: (1) occurrence of the process of change; (2) the state of the whole group of particles as an entity in itself; and (3) the identity of any and each particle as an entity in itself.

The occurrence of the elementary event can safely be said to be a random process. The number of occurrences in any time interval should not depend on the past history of the number of occurrences; that is, the system can be seen to be like a radioactive nuclide with respect to its ability to produce a number of elementary events. Furthermore, the probability of a number of occurrences of the elementary event happening in any interval of time depends only on the length of the time interval and not on when in the history of the kinetically changing system the time interval was studied. Finally, we would also wish to guarantee that the probability of two occurrences happening at the same time is nil.

These characteristics transcend whatever elementary mechanism is proposed and therefore apply to all. Hence the number of occurrences of an elementary event for an irreversible unimolecular process will be probabilistically similar to the number of occurrences of an elementary event for a reversible bimolecular process or of any process governing the production of events. The nature of the random process governing the number of occurrences of the elementary event is independent of the specific type of

chemistry involved. But this just describes a Poisson counting process (Parzen,[1] Gnedenko[2]).

For the isomerization reaction $X \underset{\mu}{\overset{\lambda}{\rightleftharpoons}} Y$ then, the probability of the number of occurrences of the forward process (reverse process) will be

$$P_n(t) = \begin{cases} \dfrac{(\lambda t)^n}{n!} e^{-\lambda t} & \text{forward process} \\ \dfrac{(\mu t)^n}{n!} e^{-\mu t} & \text{reverse process} \end{cases} \tag{1}$$

The meaning of the constants λ and μ are more fundamental than the rate constants usually associated with the law of mass action $X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y$. Here λ and μ take their meaning from the probabilistic nature of the number of occurrences of the isomerization.

The state of the system is a specification of the identity of each object in the system. For large systems undergoing incredibly large numbers of occurrences of elementary events it is not unreasonable to expect that the system taken as a whole loses sight of its past history.

That the identity of any object in the system be an independent random variable is a reflection of the great number of objects in the system. Hence what one moiety should be at any time should be uncorrelated with any other identity.

We emphasize that the objective in the stosszahlansatz is to formulate the nature of the probabilistic dynamics of kinetically changing systems in terms of laws that apply to all systems undergoing change regardless of the specifics of the set of elementary events involved.

2. THE SUB MASTER EQUATION FOR $X \underset{\mu}{\overset{\lambda}{\rightleftharpoons}} Y$

We start by defining our notation for the state of the system and the probability of the state of the system having an isomerization as the elementary event and changing due to large numbers of occurrences of this elementary process:

$$\begin{aligned} e(t) &= (e_1, e_2, \ldots, e_n; t) = \text{the state of the system at time } t \\ &= \text{the specification of each identity, } e_i, \text{ of the objects in the system} \end{aligned} \tag{2}$$

$$f_n^{(n)}(e_1, \ldots, e_n; t) = \text{the joint probability that object 1 has identity } e_1, \ldots, \text{ object } n \text{ has identity } e_n \text{ at time } t. \tag{3}$$

By Postulate II, the probability of state e occurring at time $t + \tau$ is related

to the occurrence of a particular subset of all possible states at time t and not to any prior states.

Hence we have

$$
\begin{aligned}
&f_n^{(n)}(e_1, \ldots, e_n; t+\tau) \\
&\quad = (\lambda\tau e^{-\lambda\tau})\left[\sum_{i=1}^{n} f_n^{(n)}(e_1, \ldots, X_i, \ldots, e_n; t)\delta_{e_i Y}\right] \\
&\qquad + (\mu\tau e^{-\mu\tau})\left[\sum_{i=1}^{n} f_n^{(n)}(e_1, \ldots, Y_i, \ldots, e_n; t)\delta_{e_i X}\right] \\
&\qquad + \left[1 - \sum_{i=1}^{n}\left(\lambda\tau e^{-\lambda\tau}\delta_{e_i X} + \mu\tau e^{-\mu\tau}\delta_{e_i Y}\right)\right] f_n^{(n)}(e_1, \ldots, e_n; t) \\
&\qquad + O(\tau)
\end{aligned} \tag{4}
$$

where $\delta_{ee'}$ is the Kronecker delta.

This equation simply relates the probability of being in state $e = (e_1, \ldots, e_n)$ at time $t + \tau$ to the probability of being in the appropriate prior state $e' = (e_1, \ldots, X_i, \ldots, e_n)$ or $e'' = (e_1, \ldots, Y_i, \ldots, e_n)$ times the probability of a single occurrence of a λ-event, $X \xrightarrow{\lambda} Y$, or of a μ-event, $X \xleftarrow[\mu]{} Y$, respectively. Of course, there is a multiplicity of different prior states other than those related to state e at time $t + \tau$ by a single occurrence. The prior state could be one such that k λ-events and j μ-events must occur in time τ to obtain state e at time $t + \tau$.

These higher-order terms having the form

$$
\left(\frac{(\lambda\tau)^k}{k!} e^{-\lambda\tau}\right)\left(\frac{(\mu\tau)^j}{j!} e^{-\mu\tau}\right)\Sigma \tag{5}
$$

where Σ is a sum over the probabilities of the appropriate prior states, are seen to be proportional to τ^{k+j}, $k + j > 1$. These terms are all lumped into the term represented by $O(\tau)$ since upon dividing by τ it is easily seen that all these terms are zero in the limit as $\tau \to 0$. Hence taking $f_n^{(n)}(e_1, \ldots, e_n; t)$ to the left-hand side in (4), dividing both sides by τ, and taking the limit $\tau \to 0$ we find what we call the sub master equation for the reversible unimolecular isomerization reaction

$$
\begin{aligned}
&\frac{\partial}{\partial t} f_n^{(n)}(e_1, \ldots, e_n; t) \\
&\quad = \lambda \sum_{i=1}^{n} f_n^{(n)}(e_1, \ldots, X_i, \ldots, e_n; t)(\delta_{e_i Y} - \delta_{e_i X}) \\
&\qquad + \mu \sum_{i=1}^{n} f_n^{(n)}(e_1, \ldots, Y_i, \ldots, e_n; t)(\delta_{e_i X} - \delta_{e_i Y})
\end{aligned} \tag{6}
$$

The details can be found in Conlan.[3]

This equation governs the probabilistic emergence of the state of the system from $f_n^{(n)}(e_1, \ldots, e_n; 0)$ to $f_n^{(n)}(e_1, \ldots, e_n; t)$ and will lead to both the master equation and deterministic equation for the isomerization process. What is important to realize at this point is that the constants λ and μ are related to the Poisson nature of the occurrences of the elementary event and that the theory is essentially determined by single events. All multiple events dropped out of expression (6) since in the short time τ only single occurrences of the λ or μ events can affect the time rate of change of $f_n^{(n)}(e_1, \ldots, e_n; t)$.

3. THE MASTER EQUATION

The master equation for the reversible unimolecular isomerization is a statement about the emergence of the probability of the number of X or Y species. Since this type of probability function is order independent, we see that the relationship between $f_n^{(n)}(e_1, \ldots, e_n; t)$ and $P(x; t)$ is

$$\sum_{\forall P} f_n^{(n)}(e_1, \ldots, e_n; t) = x!\, y!\, P(x; t) \tag{7}$$

where by summing over all permutations of n objects composed of x X particles and y Y particles ($x + y = n$) any dependence upon the order is eliminated. Performing this operation on Eq. (6) leads directly to the master equation for the isomerization reaction[4,5]

$$\frac{\partial}{\partial t} P(x; t) = \lambda(x + 1)P(x + 1; t) + \mu\big(n - (x + 1)\big)P(x - 1; t) - \big[\lambda x + \mu(n - x)\big]P(x; t) \tag{8}$$

The remarkable observation to make is that the coefficients are derived and not assumed *ad hoc* as heretofore has been the case. For example, $\lambda(x + 1)$ is seen to be

$$\lambda(x + 1) = \lambda\left[\frac{(x + 1)!\,(y - 1)!}{x!\, y!} \cdot y\right] \tag{9}$$

and is the ratio of the number of identical permutations of $x + 1$ X particles and $y - 1$ Y particles to the number of identical permutations of x X particles and y Y particles times the number of Y particles (y) in $e = (e_1, \ldots, e_n; t)$.

4. THE REDUCED SUB MASTER EQUATIONS AND THE SUB MASTER HIERARCHY

The new feature introduced by the sub master formalism is obtained by summing over all possible identities of $(e_{k+1}, \ldots, e_n)$ in $f_n^{(n)}(e_1, \ldots, e_n; t)$. This system of reduced equations describes the rate of change of the

probability of a subset of k identities. Hence we are led to a whole hierarchy of relationships reminiscent of the analogous BBGKY hierarchy that occurs in the Boltzmann equation theory.[6] As expected for a unimolecular mechanism the rate of change of $f_n^{(k)}(e_1, \ldots, e_k; t)$ is not related to $f_n^{(k+1)}(e_1, \ldots, e_{k+1}; t)$. It takes at least a bimolecular mechanism to achieve this type of relationship.

Defining the sum over all possible states of e_{k+1} (i.e., X and Y) as

$$\sum_{e_{k+1}=X,\,Y} f_n^{(k+1)}(e_1, \ldots, e_{k+1}; t) = f_n^{(k)}(e_1, \ldots, e_k; t) \tag{10}$$

it is straightforward to show that

$$\begin{aligned}\frac{\partial}{\partial t} f_n^{(k)}(e_1, \ldots, e_k; t) &= \lambda \sum_{i=1}^{k} f_n^{(k)}(e_1, \ldots, X_i, \ldots, e_k; t)(\delta_{e_i Y} - \delta_{e_i X}) \\ &\quad + \mu \sum_{i=1}^{k} f_n^{(k)}(e_1, \ldots, Y_i, \ldots, e_k; t)(\delta_{e_i X} - \delta_{e_i Y})\end{aligned} \tag{11}$$

(See Conlan[3] for details.) Specializing the equation to $f_n^{(1)}(e; t)$ we find

$$\frac{\partial}{\partial t} f_n^{(1)}(e; t) = \lambda f_n^{(1)}(X; t)(\delta_{eY} - \delta_{eX}) + \mu f_n^{(1)}(Y; t)(\delta_{eX} - \delta_{eY}) \tag{12}$$

which in vector notation can be written as

$$\frac{\partial}{\partial t} \mathbf{f}_n^{(1)}(t) = \begin{bmatrix} -\lambda & \mu \\ \lambda & -\mu \end{bmatrix} \mathbf{f}_n^{(1)}(t) \tag{13}$$

The solution to (13) will play an important role in solving the complete equation (6). Introducing our notation for the differential operator in (13)

$$\text{(def.)} \quad \Delta_{(1)} \equiv \begin{bmatrix} -\lambda & \mu \\ \lambda & -\mu \end{bmatrix} \tag{14}$$

we see at once that $\Delta_{(1)}$ is the operator in the $\mathbf{f}$ vector space that affects the time differential of objects. We also define the vector $\mathbf{f}_n^{(1)}(t)$ as

$$\text{(def.)} \quad \mathbf{f}_n^{(1)}(t) \equiv \begin{Bmatrix} f_n^{(1)}(X; t) \\ f_n^{(1)}(Y; t) \end{Bmatrix} \tag{15}$$

5. SOLUTION OF THE SUB MASTER EQUATION FOR $f_n^{(1)}(e; t)$

It is obvious from Eq. (6) that what is involved here is a set of 2^n coupled linear first-order differential equations where n is of the order of

10^{24}. Clearly this is an impossible situation. However, owing to a rather remarkable product rule for matrices, the Kronecker product, and to an assumed ordering principle, the build-up principle, we can obtain the solution of (6) by studying the solution of the reduced equation for $f_n^{(1)}(e;t)$ derived in the previous section.

Starting with Eq. (13) and using standard techniques[7] the solution is found to be

$$\mathbf{f}_n^{(1)}(t) = \begin{bmatrix} \frac{\mu}{\mu+\lambda} + \frac{\lambda}{\mu+\lambda} e^{-(\mu+\lambda)t} & \frac{\mu}{\mu+\lambda} - \frac{\mu}{\mu+\lambda} e^{-(\mu+\lambda)t} \\ \frac{\lambda}{\mu+\lambda} - \frac{\lambda}{\mu+\lambda} e^{-(\mu+\lambda)t} & \frac{\lambda}{\mu+\lambda} + \frac{\mu}{\mu+\lambda} e^{-(\mu+\lambda)t} \end{bmatrix} \mathbf{f}_n^{(1)}(0) \tag{16}$$

We define the matrix in (16) to be the evolution matrix, $E_{(1)}(t)$, and write (16) in the condensed form

$$\mathbf{f}_n^{(1)}(t) = E_{(1)}(t)\mathbf{f}_n^{(1)}(0) \tag{17}$$

$E_{(1)}(t)$ is a rather useful matrix as it contains information about the time evolution of the probability of being X or Y in a system of n species undergoing isomerization.

We first note that the fundamental objects $(E_{(1)}(t))_{ij}$ are the single-particle conditional sub master equation probability functions:

$$\begin{aligned} &f_n^{(1)}(X;t\,|\,X;0) \equiv \frac{\mu}{\mu+\lambda} + \frac{\lambda}{\mu+\lambda} e^{-(\mu+\lambda)t} \\ &f_n^{(1)}(X;t\,|\,Y;0) \equiv \frac{\mu}{\mu+\lambda} - \frac{\mu}{\mu+\lambda} e^{-(\mu+\lambda)t} \\ (\text{def.}) \qquad &f_n^{(1)}(Y;t\,|\,X;0) \equiv \frac{\lambda}{\mu+\lambda} - \frac{\lambda}{\mu+\lambda} e^{-(\mu+\lambda)t} \\ &f_n^{(1)}(Y;t\,|\,Y;0) \equiv \frac{\lambda}{\mu+\lambda} + \frac{\mu}{\mu+\lambda} e^{-(\mu+\lambda)t} \end{aligned} \tag{18}$$

Hence we obtain immediately two nice properties of $E_{(1)}(t)$

$$E_{(1)}(0) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{19}$$

$$E_{(1)}(\infty) = E^e = \begin{bmatrix} \frac{\mu}{\mu+\lambda} & \frac{\mu}{\mu+\lambda} \\ \frac{\lambda}{\mu+\lambda} & \frac{\lambda}{\mu+\lambda} \end{bmatrix} \tag{20}$$

the $\det(E_{(1)}(t))$ furthermore has the value

$$|E_{(1)}(t)| = e^{-(\mu+\lambda)t} \tag{21}$$

which indicates that the evolution of an isomerizing system of particles proceeds relentlessly toward the singular state (which in this system is at equilibrium) characterized by an evolution operator that possesses no inverse. Furthermore, at equilibrium the system is described in probabilistic terms independently of the initial single-particle probability distribution, $\mathbf{f}^{(1)}(0)$:

$$\mathbf{f}_n^{(1)}(\infty) = \mathbf{f}_n^{(1)e} = \begin{Bmatrix} \dfrac{\mu}{\mu + \lambda} \\ \dfrac{\lambda}{\mu + \lambda} \end{Bmatrix} \tag{22}$$

It is easy to generalize (18) to an arbitrary initial time, τ, wherein we obtain

$$E_{(1)}(t - \tau) = E_{(1)}(t) \cdot E_{(1)}(-\tau) = E_{(1)}(t) \cdot \left[E_{(1)}(\tau)\right]^{-1} \tag{23}$$

where we use the property of $E_{(1)}(t)$

$$E_{(1)}(\tau) = E_{(1)}(\tau - t) \cdot E_{(1)}(t) \tag{24}$$

and that

$$\left[E_{(1)}(t)\right]^n = E_{(1)}(nt), \qquad t < +\infty \tag{25}$$

As Eq. (17) shows, all the time variation of $\mathbf{f}_n^{(1)}(t)$ is contained in $E_{(1)}(t)$. Moreover, it is easily shown from Eq. (13) that

$$\frac{\partial}{\partial t} E_{(1)}(t) = \Delta_{(1)} \cdot E_{(1)}(t) \tag{26}$$

This equation is fundamental in what follows.

6. THE REDUCED SUB MASTER EQUATION FOR THE k-PARTICLE DISTRIBUTION FUNCTION

We recall that $\Delta_{(1)}$ was the 2×2 operator in Eq. (13) obtained in the matrix formulation of the sub master equation for $\mathbf{f}_n^{(1)}(t)$. In examining the k-particle distribution function for $1 < k \leqslant n$, we introduce a more complete vector formulation. Thus, for example, we use the Kronecker tensor product, $\otimes$, to define the 2^k-dimensional column vector

$$\mathbf{f}_n^{(k)}(t) = \sum_e f_n^{(k)}(e_1, \ldots, e_k; t) \otimes \begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_k X} \\ \delta_{e_k Y} \end{Bmatrix} \tag{27}$$

where the sum is over all states $e_1, \ldots, e_k$ for $1 \leqslant k \leqslant n$. Rewriting (11) we

have

$$\frac{\partial}{\partial t} f_n^{(k)}(e_1, \ldots, e_k; t) = \sum_{i=1}^{n} \Big[-\lambda f_n^{(k)}(e_1, \ldots, X_i, \ldots, e_k; t) + \mu f_n^{(k)}(e_1, \ldots, Y_i, \ldots, e_k; t) \Big] \delta_{e_i X} + \Big[\lambda f_n^{(k)}(e_1, \ldots, X_i, \ldots, e_k; t) - \mu f_n^{(k)}(e_1, \ldots, Y_i, \ldots, e_k; t) \Big] \delta_{e_i Y} \quad (28)$$

We recognize that the ith member of the sum represents an application of $\Delta_{(1)}$ to the ith $X-Y$ pair in $f_n^{(k)}(e_1, \ldots, e_n; t)$ in the ordered vector $\mathbf{f}_n^{(k)}(t)$ defined by Eq. (27). Since $f_n^{(k)}(e_1, \ldots, e_k; t)$ is a scalar in Eq. (27) we can place it anywhere within

$$\begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_k X} \\ \delta_{e_k Y} \end{Bmatrix}$$

Hence to transform (28) to vector form, we multiply both sides of the equation by

$$\begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_k X} \\ \delta_{e_k Y} \end{Bmatrix}$$

and sum over all states of $e_i (e_i = X \text{ or } Y;\ i = 1, \ldots, k)$:

$$\frac{\partial}{\partial t} \mathbf{f}_n^{(k)}(t) = \sum_{i=1}^{k} \Bigg[\sum_{e_1, \ldots, e_k} \begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{bmatrix} -\lambda & \mu \\ \lambda & -\mu \end{bmatrix}_i \times \begin{Bmatrix} f_n^{(k)}(e_1, \ldots, X_i, \ldots, e_k; t) \\ f_n^{(k)}(e_1, \ldots, Y_i, \ldots, e_k; t) \end{Bmatrix} \otimes \begin{Bmatrix} \delta_{e_{i+1} X} \\ \delta_{e_{i+1} Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_k X} \\ \delta_{e_k Y} \end{Bmatrix} \Bigg] \quad (29)$$

Recalling the Kronecker product property, $(A \otimes B) \cdot (C \otimes D) = (A \cdot C) \otimes (B \cdot D)$, we can write (29) as

$$\frac{\partial}{\partial t} \mathbf{f}_n^{(k)}(t) = \left(\sum_{i=1}^{k} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \cdots \otimes (\Delta_{(1)})_i \otimes \cdots \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right) \cdot \mathbf{f}_n^{(k)}(t) \quad (30)$$

Hence we have the following result that

$$\frac{\partial}{\partial t} \mathbf{f}_n^{(k)}(t) = \Delta_{(k)} \mathbf{f}_{(n)}^{(k)}(t)$$

where

$$\Delta_{(k)} = \sum_{i=1}^{k} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \cdots \otimes \Delta_{(1)} \otimes \cdots \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

We call this the Leibnitz rule because of its relationship to the differential formula for a product of functions.

7. THE GENERAL SOLUTION

The general solution to (6) follows after some preliminary observations about $E_{(1)}(t)$. We recall from Eq. (17) that $E_{(1)}(t)$ evolves $\mathbf{f}_n^{(1)}(0)$ into $\mathbf{f}_n^{(1)}(t)$. $E_{(1)}(t)$ can also operate upon the "delta vector" $\begin{Bmatrix} \delta_{eX} \\ \delta_{eY} \end{Bmatrix}$ to give

$$\boldsymbol{\delta}(e;t) \equiv E_{(1)}(t) \begin{Bmatrix} \delta_{eX} \\ \delta_{eY} \end{Bmatrix} = \begin{Bmatrix} \dfrac{\mu}{\mu+\lambda} + \left(\delta_{eX} - \dfrac{\mu}{\mu+\lambda}\right) e^{-(\mu+\lambda)t} \\ \dfrac{\lambda}{\mu+\lambda} + \left(\delta_{eY} - \dfrac{\lambda}{\mu+\lambda}\right) e^{-(\mu+\lambda)t} \end{Bmatrix} \tag{31}$$

Thus

$$\begin{aligned} \boldsymbol{\delta}(X;t) &= \begin{Bmatrix} f_n^{(1)}(X;t \mid X;0) \\ f_n^{(1)}(Y;t \mid X;0) \end{Bmatrix} \\ \boldsymbol{\delta}(Y;t) &= \begin{Bmatrix} f_n^{(1)}(X;t \mid Y;0) \\ f_n^{(1)}(Y;t \mid Y;0) \end{Bmatrix} \end{aligned} \tag{32}$$

Then Eq. (17) can be rewritten as

$$\begin{aligned} E_{(1)}(t) \cdot \mathbf{f}_n^{(1)}(0) &= \sum_e E_{(1)}(t) \cdot \begin{Bmatrix} \delta_{eX} \\ \delta_{eY} \end{Bmatrix} \otimes f_n^{(1)}(e;0) \\ &= \sum_e \boldsymbol{\delta}(e;t) \otimes f_n^{(1)}(e;0) \end{aligned} \tag{33}$$

In the solution for $f_n^{(1)}(t)$ we found that the evolution matrix contained all the time variation so that $E_{(1)}(t)$ satisfied the operator equation

$$\frac{\partial}{\partial t} E_{(1)}(t) = \Delta_{(1)} \cdot E_{(1)}(t) \tag{34}$$

where $(\partial/\partial t)E_{(1)}(t)$ indicates the matrix

$$\dot{E}_{(1)}(t) = \begin{bmatrix} \dot{E}_{11} & \dot{E}_{12} \\ \dot{E}_{21} & \dot{E}_{22} \end{bmatrix}$$

It is shown in Conlan[3] by a tedious calculation that $E_{(2)} = E_{(1)} \otimes$

$E_{(1)}(t)$ satisfied the following equation:

$$\begin{aligned}\frac{\partial}{\partial t} E_{(2)}(t) &= \Delta_{(2)} \cdot E_{(1)}(t) \otimes E_{(1)}(t) \\ &= \sum_{i=1}^{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \begin{bmatrix} -\lambda & \mu \\ \lambda & -\mu \end{bmatrix}_i \cdot E_{(1)}(t) \otimes E_{(1)}(t) \\ &= E_{(1)}(t) \otimes \dot{E}_{(1)}(t) + \dot{E}_{(1)}(t) \otimes E_{(1)}(t) \end{aligned} \tag{35}$$

Furthermore, it is also shown that

$$\mathbf{f}_n^{(2)}(t) = E_{(1)}(t) \otimes E_{(1)}(t) \cdot \mathbf{f}_n^{(2)}(0) \tag{36}$$

and that this is the precise $\mathbf{f}_n^{(2)}(t)$ that satisfies the sub master equation

$$\frac{\partial}{\partial t} \mathbf{f}_n^{(2)}(t) = \Delta_{(2)} \cdot \mathbf{f}_n^{(2)}(t) \tag{37}$$

All that is needed to find the general solution is to show that $E_{(n)}(t)$ satisfies

$$\frac{\partial}{\partial t} E_{(n)}(t) = \Delta_{(n)} \cdot E_{(n)}(t) \tag{38}$$

where $E_{(n)}(t)$ is defined by

$$E_{(n)}(t) \equiv \underbrace{E_{(1)}(t) \otimes \cdots \otimes E_{(1)}}_{n}(t) \tag{39}$$

Then defining $\alpha_n^{(n)}(t) = E_{(n)}(t) \cdot \alpha_n^{(n)}(0)$, we find that $\alpha_n^{(n)}(t)$ satisfies

$$\frac{\partial}{\partial t} \alpha_n^{(n)}(t) = \Delta_{(n)} \cdot \alpha_n^{(n)}(t) \tag{40}$$

the sub master equation derived in (30) for $k = n$.

Theorem. For $E_{(n)}(t)$ defined as in Eq. (39)

$$\frac{\partial}{\partial t} E_{(n)}(t) = \Delta_{(n)} \cdot E_{(n)}(t)$$

Proof. By Eqs. (29) and (39), the proof follows immediately. ■

Hence the solution to the sub master equation (6) is

$$\mathbf{f}_n^{(n)}(t) = E_{(n)}(t) \cdot \mathbf{f}_n^{(n)}(0) \tag{41}$$

8. PROPAGATION OF CHAOS

Kac[9,10] developed a factorization theorem for the Boltzmann equation which showed that individual molecules behave independently when a system of molecules is large. Keizer[11] in a recent article extends Kac's theorem and uses it to provide a more elementary proof of a theorem of

Kurtz dealing with the types of differential equations satisfied by the averages in certain birth and death processes in large systems. Due to the remarkable simplicity of the solution to the sub master equation for the reversible unimolecular reaction, we present here a factorization theorem for $\mathbf{f}_n^{(n)}(t)$.

Theorem (Propagation of Chaos). The exact type of factorization of the initial state probability function propagates in time.

Proof. From (41) we found that

$$\mathbf{f}_n^{(n)}(t) = E_{(n)}(t) \cdot \mathbf{f}_n^{(n)}(0)$$

is the solution to the sub master equation (6). Then let $\mathbf{f}_n^{(n)}(0)$ be factored accordingly:

$$\mathbf{f}_n^{(n)}(0) = \sum_{e_1} \cdots \sum_{e_n} \begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_n X} \\ \delta_{e_n Y} \end{Bmatrix} \cdot f_n^{(k)}(e_1, \ldots, e_k; 0)$$
$$\times f_n^{(1)}(e_{k+1}; 0) \cdots f_n^{(1)}(e_n; 0) \tag{42}$$

Then

$$\mathbf{f}_n^{(n)}(t) = \sum_{e_1} \cdots \sum_{e_n} E_{(1)}(t) \otimes \cdots \otimes E_{(1)}(t) \cdot \begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_n X} \\ \delta_{e_n Y} \end{Bmatrix}$$
$$\times f_n^{(k)}(e_1, \ldots, e_k; 0) f_n^{(1)}(e_{k+1}; 0) \cdots f_n^{(1)}(e_n; 0)$$
$$= \sum_{e_1} \cdots \sum_{e_n} \Bigg[E_{(1)}(t) \otimes \cdots \otimes E_{(1)}(t) \cdot \begin{Bmatrix} \delta_{e_1 X} \\ \delta_{e_1 Y} \end{Bmatrix} \otimes \cdots \otimes \begin{Bmatrix} \delta_{e_k X} \\ \delta_{e_k Y} \end{Bmatrix}$$
$$\times f_n^{(k)}(e_1, \ldots, e_k; 0) \Bigg] \otimes E_{(1)}(t)$$
$$\cdot \begin{Bmatrix} \delta_{e_{k+1} X} \\ \delta_{e_{k+1} Y} \end{Bmatrix} f_n^{(1)}(e_{k+1}; 0) \otimes \cdots \otimes E_{(1)}(t) \cdot \begin{Bmatrix} \delta_{e_n X} \\ \delta_{e_n Y} \end{Bmatrix} f_n^{(1)}(e_n; 0) \tag{43}$$

by application of the Kronecker product property.

Then by summing over states $e_{k+1}, \ldots, e_n$ in (41) the form of $f_n^{(k)}(e_1, \ldots, e_k; t)$ is found to be

$$\mathbf{f}_n^{(k)}(t) = E_{(k)} \cdot \mathbf{f}_n^{(k)}(0)$$

Hence Eq. (43) is found to be

$$\mathbf{f}_n^{(n)}(t) = E_{(k)}(t) f_n^{(k)}(0) \otimes \left[E_{(1)}(t) \cdot \mathbf{f}_n^{(1)}(0) \right]_{k+1} \otimes \cdots \otimes \left[E_{(1)}(t) \cdot \mathbf{f}_n^{(1)}(0) \right]_n$$
$$= \mathbf{f}_n^{(k)}(t) \otimes \left[\mathbf{f}_n^{(1)}(t) \right]_{k+1} \otimes \cdots \otimes \left[\mathbf{f}_n^{(1)}(t) \right]_n \tag{44}$$

and the initial state factorization propagates exactly. ■

9. THE MASTER EQUATION PROBABILITY FUNCTION

Using standard techniques (Conlan,[3] McQuarrie,[4] Ishida,[14] Bartholomay[15]) the master equation probability function, $P_2(x;t\,|\,x^0;0)$, can be obtained for a more general initial condition than heretofore considered.

Defining the moment generating function of $P_2(x;t\,|\,x^0;0)$ as

$$F(s,t) = \sum_{x=0}^{n} P_2(x;t\,|\,x^0;0)s^x \tag{45}$$

McQuarrie[4] has shown that the partial differential equation satisfied by $F(s,t)$ is

$$\frac{\partial}{\partial t}F(s,t) = \left[\lambda + (\mu - \lambda)s - \mu s^2\right]\frac{\partial F(s,t)}{\partial t} + \mu n(s-1)F(s,t) \tag{46}$$

Letting the initial condition be $x(0) = x^0$ and $y(0) = y^0$, Conlan[3] finds that $F(s,t)$ has the following form:

$$F(s,t) = \left[\left(\frac{\lambda}{\mu+\lambda} + \frac{\mu}{\mu+\lambda}e^{-(\mu+\lambda)t}\right) + s\left(\frac{\mu}{\mu+\lambda} - \frac{\mu}{\mu+\lambda}e^{-(\mu+\lambda)t}\right)\right]^{y^0}$$
$$\times\left[\left(\frac{\lambda}{\mu+\lambda} - \frac{\lambda}{\mu+\lambda}e^{-(\mu+\lambda)t}\right) + s\left(\frac{\mu}{\mu+\lambda} + \frac{\lambda}{\mu+\lambda}e^{-(\mu+\lambda)t}\right)\right]^{x^0} \tag{47}$$

Hence we see that $F(s,t)$ is composed of all four of the fundamental sub master transition probabilities and can be expressed as

$$F(s,t) = \left[f_n^{(1)}(Y;t\,|\,Y;0) + sf_n^{(1)}(X;t\,|\,Y;0)\right]^{y^0}$$
$$\times\left[f_n^{(1)}(X;t\,|\,Y;0) + sf_n^{(1)}(X;t\,|\,X;0)\right]^{x^0} \tag{48}$$

Using the binomial theorem in Eq. (47) and comparing to Eq. (45) $P_2(x;t\,|\,x^0;0)$ is easily found to be

$$P_2(x;t\,|\,x^0;0) = \sum_{k=0}^{x}\binom{y^0}{x-k}\binom{x^0}{k}a^k b^{x^0-k}c^{x-k}d^{y^0-(x-k)} \tag{49}$$

where

$$\begin{aligned} a &= a(t) = f_n^{(1)}(X;t\,|\,X;0) \\ b &= b(t) = f_n^{(1)}(Y;t\,|\,X;0) \\ c &= c(t) = f_n^{(1)}(X;t\,|\,Y;0) \\ d &= d(t) = f_n^{(1)}(Y;t\,|\,Y;0) \end{aligned} \tag{50}$$

$P_2(x;t\,|\,x^0;0)$ has a rich structure and some interesting properties. By the definitions of a, b, c, d, $P_2(x;t\,|\,x^0;0)$ satisfies the following initial condition:

$$P_2(x;0\,|\,x^0;0) = \begin{cases} 1 & x = x^0 \\ 0 & \text{otherwise} \end{cases} \tag{51}$$

Furthermore, $P_2(x;t\,|\,x^0;0)$ loses all influence of the initial value $x^0 = x(0)$ in the limit $t \to \infty$

$$P_2(x;t\,|\,x^0;0)\big|_{t\to\infty} = \binom{n}{x}\left(\frac{\mu}{\mu+\lambda}\right)^x\left(\frac{\lambda}{\mu+\lambda}\right)^y$$

$$n = x(t) + y(t) = x^0 + y^0 \tag{52}$$

The random variable x whose distribution is given by Eq. (49) is itself the sum of two random variables: $x = k + (x - k)$. The random variable k is the number of particles from the initial X population that remain X at time t. The random variable $x - k$ is the number of particles from the initial Y population that become X at time t. Each of these random variables has a binomial distribution given by

$$\begin{gathered}
k : p(k;t\,|\,x^0;0) = \binom{x^0}{k} a^k b^{x^0-k} \\
a = a(t) = f_n^{(1)}(X;t\,|\,X;0) = \frac{\mu}{\mu+\lambda} + \frac{\lambda}{\mu+\lambda}e^{-(\lambda+\mu)t} \\
b = b(t) = f_n^{(1)}(Y;t\,|\,X;0) = \frac{\lambda}{\lambda+\mu} - \frac{\lambda}{\lambda+\mu}e^{-(\lambda+\mu)t} \\
\langle k\rangle = a(t)x^0 \\
\sigma_k^2 = a(t)b(t)x^0 \\
x-k : p(x-k;t\,|\,y^0;0) = \binom{y^0}{x-k} c^{x-k} d^{y^0-(x-k)} \\
c = c(t) = f_n^{(1)}(X;t\,|\,Y;0) = \frac{\mu}{\lambda+\mu} - \frac{\lambda}{\lambda+\mu}e^{-(\lambda+\mu)t} \\
d = d(t) = f_n^{(1)}(Y;t\,|\,Y;0) = \frac{\lambda}{\lambda+\mu} + \frac{\mu}{\lambda+\mu}e^{-(\lambda+\mu)t} \\
\langle x-k\rangle = c(t)y^0 \\
\sigma_{x-k}^2 = c(t)d(t)y^0
\end{gathered} \tag{53}$$

If the random variables k and $x - k$ are independent then a two-

dimensional random variable $(k, x-k)$ will have the following distribution

$$p(k,x-k;t\,|\,x^0,y^0;0)=\binom{y^0}{x-k}\binom{x^0}{k}a^k b^{x^0-k}c^{x-k}d^{y^0-(x-k)} \tag{54}$$

Then we see that Eq. (49) is the discrete case analog for the distribution of the sum of two random variables

$$P_2(x;t\,|\,x^0;0)=\sum_{k=0}^{x}p(k,x-k;t\,|\,x^0,y^0;0) \tag{55}$$

The independence of the two initial populations is further emphasized in the equations for the mean and variance of x

$$\begin{aligned}\langle x\rangle &= a(t)x^0+c(t)y^0=\langle k\rangle+\langle x-k\rangle\\ \sigma_x^2 &= a(t)b(t)x^0+c(t)d(t)y^0\\ &= \sigma_k^2+\sigma_{x-k}^2\end{aligned} \tag{56}$$

Recognizing the binomial nature of the initial X and Y populations it is of interest to derive the distribution for the sum $k+(x-k)$ in the limit $n\to\infty$. Following the treatment of Gnedenko[2] we start by applying the Local DeMoivre Laplace theorem to $p(k,x-k;t\,|\,x^0,y^0;0)$,

$$\begin{aligned}&p(k,x-k;t\,|\,x^0,y^0;0)\\ &\quad\simeq\frac{1}{2\pi\sigma_k\sigma_{x-k}}\exp\left\{-\frac{1}{2}\left[\frac{(k-\langle k\rangle)^2}{\sigma_k^2}+\frac{\left[(x-k)-\langle x-k\rangle\right]^2}{\sigma_{x-k}^2}\right]\right\}\\ &\qquad\qquad(x^0\to\infty,\ y^0\to\infty)\end{aligned} \tag{57}$$

Then $\mathcal{P}_2(x;t\,|\,x^0;0)$ $(n=x^0+y^0\to\infty)$ is given as the integral

$$\begin{aligned}&\mathcal{P}_2(x;t\,|\,x^0;0)\\ &\quad\simeq\frac{1}{2\pi\sigma_k\sigma_{x-k}}\int\exp\left\{-\frac{1}{2}\left[\frac{(k-\langle k\rangle)^2}{\sigma_k^2}+\frac{\left[(x-k)-\langle x-k\rangle\right]^2}{\sigma_{x-k}^2}\right]\right\}dk\\ &\qquad\qquad(n\to\infty)\end{aligned} \tag{58}$$

The integral is straightforward and the result is

$$\mathcal{P}_2(x;t\,|\,x^0;0)=\frac{1}{(2\pi\sigma_x^2)^{1/2}}\exp\left[-\frac{1}{2}(x-\langle x\rangle)^2/2\sigma_x^2\right] \tag{59}$$

in which the mean $\langle x\rangle$ and variance σ_x^2 are identical to the corresponding mean and variance for the finite case as expressed in Eq. (56). We draw attention to the fact that the time variation in $\mathcal{P}_2(x;t\,|\,x^0;0)$ is in both $\langle x\rangle$ and σ_x. Furthermore, the σ_x^2 structure can now be expressed in terms of the

four transition probabilities and the initial single-particle probabilities as

$$\sigma_x^2 = n\big[f_n^{(1)}(X;t\,|\,X;0)f_n^{(1)}(Y;t\,|\,X;0)f_n^{(1)}(X;0) + f_n^{(1)}(X;t\,|\,Y;0)f_n^{(1)}(Y;t\,|\,Y;0)f_n^{(1)}(Y;0)\big] \tag{60}$$

The variance is strictly less than $\sqrt{n}$ for all time and must exist in a population of single particles undergoing a unimolecular isomerization not only due to the initial state uncertainties but also due to the probabilistic nature of its dynamics; that is, a single particle's identity is governed only by transition probabilities not by any deterministic knowledge.

10. THE LANGEVIN EQUATION AND FLUCTUATING FORCE

From the form of the sub master equation for $f_n^{(1)}(X;t)$

$$\frac{\partial}{\partial t} f_n^{(1)}(X;t) = -\lambda f_n^{(1)}(X;t) + \mu f_n^{(1)}(Y;t) \tag{61}$$

the equation for the macrovariable follows immediately

$$\frac{\partial}{\partial t}\langle x(t)\rangle = -\lambda\langle x(t)\rangle + \mu\langle y(t)\rangle \tag{62}$$

which is consistent with the law of mass action and with Keizer's[12,13] first postulate in his theory of spontaneous fluctuations in macroscopic systems.

The main difference here is the relationship between the phenomenological rate equation and the six probability densities which the sub master theory generates.

$$\frac{\partial}{\partial t}\langle x(t)\rangle = n\big[-\lambda f_n^{(1)}(X;t\,|\,X;0)f_n^{(1)}(X;0) - \lambda f_n^{(1)}(X;t\,|\,Y;0)f_n^{(1)}(Y;0) + \mu f_n^{(1)}(Y;t\,|\,X;0)f_n^{(1)}(X;0) + \mu f_n^{(1)}(Y;t\,|\,Y;0)f_n^{(1)}(Y;0)\big] \tag{63}$$

From the relationship between the differential $\partial/\partial t$ and the differential operator $\Delta_{(1)} = \left[\begin{smallmatrix} -\lambda & \mu \\ \lambda & -\mu \end{smallmatrix}\right]$ Eq. (13) can be rewritten in a form consistent with the Chapman–Kolmogorov treatment

$$\begin{aligned}\frac{\partial}{\partial t} f_n^{(1)}(X;t) &= \big[-\lambda f_n^{(1)}(X;t\,|\,X;0) + \mu f_n^{(1)}(Y;t\,|\,X;0)\big] f_n^{(1)}(X;0) \\ &\quad + \big[-\lambda f_n^{(1)}(X;t\,|\,Y;0) + \mu f_n^{(1)}(Y;t\,|\,Y;0)\big] f_n^{(1)}(Y;0) \\ &= \left[\frac{\partial}{\partial t} f_n^{(1)}(X;t\,|\,X;0)\right] f_n^{(1)}(X;0) \\ &\quad + \left[\frac{\partial}{\partial t} f_n^{(1)}(X;t\,|\,Y;0)\right] f_n^{(1)}(Y;0)\end{aligned} \tag{64}$$

That is, the time variation in $f_n^{(1)}(X;t)$ is due to the time variation in the transition probabilities of the two paths a particle follows in becoming an X particle at time t.

From the work in the previous section we found the measure of fluctuations to have the form

$$\sigma_x^2 = f_n^{(1)}(X;t \mid X;0) f_n^{(1)}(Y;t \mid X;0) x^0 + f_n^{(1)}(X;t \mid Y;0) f_n^{(1)}(Y;t \mid Y;0) y^0 \tag{65}$$

It is straightforward to show that the differential equation satisfied by σ_x^2 is

$$\frac{\partial}{\partial t}\sigma_x^2 = -2(\lambda + \mu)\sigma_x^2 + \Gamma(t) \tag{66}$$

$$\Gamma(t) = n\big[\lambda f_n^{(1)}(X;t \mid X;0) f_n^{(1)}(X;0) + \lambda f_n^{(1)}(X;t \mid Y;0) f_n^{(1)}(Y;0) + \mu f_n^{(1)}(Y;t \mid X;0) f_n^{(1)}(X;0) + \mu f_n^{(1)}(Y;t \mid Y;0) f_n^{(1)}(Y;0)\big] \tag{67}$$

$\Gamma(t)$ is then recognized as the time-dependent covariance matrix of the random force postulated in Keizer's[12] theory.

A Langevin equation for the dynamic fluctuations can then be formulated to reproduce the equation for σ_x^2

$$\frac{\partial}{\partial t}\delta x(t) = -(\lambda + \mu)\delta x(t) + \hat{f}(t) \tag{68}$$

$$\langle \hat{f}(t)\hat{f}(s)\rangle = n\Gamma(t)\delta(t-s) \tag{69}$$

which are identical to those postulated by Keizer.[12]

11. CONCLUSION

The theory outlined above gives a dynamical analysis of the sub master probability function, $\mathbf{f}_n^{(n)}(t)$. At the nth level, the master equation for the probability density $P_2(x;t \mid x^0;0)$ is generated showing immediately that the random variable $\delta x(t) = x(t) - \langle x(t)\rangle$ is Gaussian with variance $\sigma_x^2 = \sigma_k^2 + \sigma_{x-k}^2$ in the limit as $x^0 \to \infty$, $y^0 \to \infty$. At the lowest level the sub master probability function, $\mathbf{f}_n^{(1)}(t)$, is shown to satisfy a very simple operator equation which generates the four fundamental sub master transition probability densities. These four transition densities along with the initial state densities then generate by simple multiplication the equations for the macroscopic variables $\langle x(t)\rangle$, $\sigma_x^2(t)$, and $\langle \hat{f}(t)\hat{f}(s)\rangle$.

The incorporation of the Kronecker product into the formulation produced an analytical expression for $\mathbf{f}_n^{(n)}(t)$ in terms of $E_{(1)}(t)$, which is tantamount to solving a set of 2^n ($n \sim 10^{23}$) coupled linear differential equations.

The Kronecker product also led to the remarkable observation that the set of 2^n equations when expressed in vector operator form is nothing other than the mathematical expression of the Leibnitz rule for the operator $\Delta_{(n)}$.

The development of a factorization theorem for the probability densities indicated that the character of the correlation remains with the system forever only "blinking out" at equilibrium.

The set of hierarchical equations describing the time rate of change of subgroups of k molecules or particles in the n-body system indicates that these k subgroups have the same type of dynamics and time evolution as the complete n-body system. It is important to note that it requires at least a bimolecular process to produce a hierarchical set of differential equations relating the time rate of change of $\mathbf{f}_n^{(k)}(t)$ to a linear combination of $\mathbf{f}_n^{(k+1)}(t)$. The unimolecular process only connects the time rate of change of $\mathbf{f}_n^{(k)}(t)$ to a linear combination of $\mathbf{f}_n^{(k)}(t)$.

The sub master theory also produces the probabilistic dynamic structure for $\langle x(t)\rangle$, $\sigma_x^2(t)$, and $\langle \hat{f}(t)\hat{f}(s)\rangle$ summarized as follows:

$$\begin{bmatrix} \langle x(t)\rangle \\ \langle y(t)\rangle \end{bmatrix} = n \begin{bmatrix} f_n^{(1)}(X;t\,|\,X;0) & f_n^{(1)}(X;t\,|\,Y;0) \\ f_n^{(1)}(Y;t\,|\,X;0) & f_n^{(1)}(Y;t\,|\,Y;0) \end{bmatrix} \begin{bmatrix} f_n^{(1)}(X;0) \\ f_n^{(1)}(Y;0) \end{bmatrix}$$

$$\sigma_x^2 = n\big[f_n^{(1)}(X;t\,|\,X;0) f_n^{(1)}(Y;t\,|\,X;0) f_n^{(1)}(X;0) + f_n^{(1)}(X;t\,|\,Y;0) f_n^{(1)}(Y;0)\big] \tag{70}$$

$$\langle \hat{f}(t)\hat{f}(s)\rangle = n\big[\lambda f_n^{(1)}(X;t\,|\,X;0) f_n^{(1)}(X;0) + \lambda f_n^{(1)}(X;t\,|\,Y;0) f_n^{(1)}(Y;0) + \mu f_n^{(1)}(Y;t\,|\,X;0) f_n^{(1)}(X;0) + \mu f_n^{(1)}(Y;t\,|\,Y;0) f_n^{(1)}(Y;0)\big]$$

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