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Physical applications of multiplicative stochastic processes. II. Derivation of the Bloch equations for magnetic relaxation

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The multiplicative stochastic process treatment of the time development of the density matrix for a subsystem in contact with a heat reservoir is applied to the specific problem of the relaxation of a nuclear magnetic moment which is interacting with a fluctuating magnetic environment. A model for the fluctuating interaction Hamiltonian, appropriate for the magnetic moment case, is presented, and the Bloch equations for nuclear magnetic relaxation are constructed as a consequence. Agreement with empirical observations is noted.

I. INTRODUCTION

Consider a subsystem in contact with a heat reservoir. The Hamiltonians for the subsystem and for the reservoir will be denoted by $\mathbf{H}_S$ and $\mathbf{H}_R$, respectively. It will be assumed that the state of the reservoir is given, on the average, by its equilibrium state throughout all time. Therefore, the interaction between the subsystem and the reservoir will be represented by a stationary, purely random, Gaussian interaction Hamiltonian, $\tilde{\mathbf{H}}(t)$.[1-4]

Latin indices will be used to denote eigenstates of the subsystem Hamiltonian:

$$\mathbf{H}_S|i\rangle = E_i|i\rangle. \tag{1}$$

Greek indices will be used to denote reservoir eigenstates:

$$\mathbf{H}_R|\alpha\rangle = E_\alpha|\alpha\rangle. \tag{2}$$

The identity matrices for the subsystem eigenstate manifold and for the reservoir eigenstate manifold are denoted by $\mathbf{1}_S$ and $\mathbf{1}_R$, respectively. The total Hamiltonian which acts in the direct product manifold of the subsystem manifold and the reservoir manifold is given by

$$\mathbf{H}_{\text{total}} = \mathbf{H}_S \otimes \mathbf{1}_R + \mathbf{1}_S \otimes \mathbf{H}_R + \tilde{\mathbf{H}}(t). \tag{3}$$

Clearly, $\tilde{\mathbf{H}}(t)$ acts in the direct product manifold since it provides the interaction coupling. It has a matrix representation in the direct product manifold given by

$$\tilde{H}_{i\alpha j\beta}(t) \equiv \langle\alpha|\langle i|\tilde{\mathbf{H}}(t)|j\rangle\beta\rangle. \tag{4}$$

The Schrödinger wavefunction $\Psi(t)$ may be expanded in terms of direct product basis states giving

$$\Psi(t) = \sum_i \sum_\alpha C_{i\alpha}(t)|i\rangle|\alpha\rangle. \tag{5}$$

The density matrix for the complete system is defined by

$$\rho_{i\alpha j\beta}(t) \equiv C^*_{i\alpha}(t)C_{j\beta}(t). \tag{6}$$

Two physically motivated assumptions are imposed in order to arrive at a dynamical equation for the density matrix for the subsystem only. The assumptions are: (a) the interaction is energy conserving which means

$$\tilde{H}_{i\alpha j\beta}(t) = 0 \quad \text{unless } E_i + E_\alpha = E_j + E_\beta \tag{7}$$

and (2) the averaged total density matrix factors for all times into a product of a time-dependent averaged subsystem density matrix and a time-independent averaged reservoir density matrix[3]:

$$\langle\rho_{i\alpha j\beta}(t)\rangle \to \langle\rho_{ij}(t)\rangle\langle\rho_{\alpha\beta}\rangle, \tag{8}$$

where

$$\langle\rho_{\alpha\beta}\rangle = (1/Q_R)\exp(-E_\alpha/K_BT)\delta_{\alpha\beta}, \tag{9}$$

with

$$Q_R = \sum_\alpha \exp(-E_\alpha/K_BT), \tag{10}$$

where K_B is Boltzmann's constant and T is the temperature.

The resulting dynamical equation for the averaged subsystem density matrix is[3]

$$\frac{d}{dt}\langle\rho_{ij}(t)\rangle = -i(E_i - E_j)\langle\rho_{ij}(t)\rangle - T_{iji'j'}\langle\rho_{i'j'}(t)\rangle, \tag{11}$$

where $T_{iji'j'}$ is defined by[3]

$$T_{iji'j'} \equiv \sum_\alpha \sum_{\alpha'} R_{i\alpha j\alpha i'\alpha'j'\alpha'}(1/Q_R)\exp(-E_{\alpha'}/K_BT) \tag{12}$$

in which $R_{i\alpha j\beta i'\alpha'j'\beta'}$ is defined by[3]

$$\begin{aligned} R_{i\alpha j\beta i'\alpha'j'\beta'} \equiv{}& \delta_{ii'}\delta_{\alpha\alpha'}\sum_\theta\sum_{\theta'} Q_{j\beta\theta\theta'\theta\theta'j'\beta'} \\ &+ \delta_{jj'}\delta_{\beta\beta'}\sum_\theta\sum_{\theta'} Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'} - 2Q_{j\beta j'\beta'i'\alpha'i\alpha}, \end{aligned} \tag{13}$$

wherein $Q_{i\alpha j\beta i'\alpha'j'\beta'}$ is determined by the second moments of $\tilde{\mathbf{H}}(t)$ through the definition[3]

$$\langle\tilde{H}_{i\alpha j\beta}(t)\tilde{H}_{i'\alpha'j'\beta'}(s)\rangle = 2Q_{i\alpha j\beta i'\alpha'j'\beta'}\delta(t-s). \tag{14}$$

The assumption of energy conservation may be used to show

$$T_{iji'j'} = T^*_{i'j'ij}\exp[-(E_j + E_i - E_{j'} - E_{i'})/2K_BT] \tag{15}$$

which is a generalization of the detailed balancing condition for a thermally buffered system.

These formal considerations provide a context in which to present the stochastic description of the relaxation of a magnetic moment in an environment which produces a fluctuating magnetic field. In the next section a specific model for the interaction piece of the Hamiltonian will be introduced, and the Bloch equations will be constructed from the interaction.

II. DERIVATION OF BLOCH'S EQUATIONS

Denoting the x, y, and z components of the averaged magnetic moment by M_x, M_y, and M_z, the Bloch equations are given by

$$\frac{d}{dt}M_z(t) = -\frac{1}{T_1}(M_z(t) - M_z(\infty)), \tag{16}$$

$$\frac{d}{dt}M_x(t) = -\frac{1}{T_2}M_x(t) - (E_\uparrow - E_\downarrow)M_y(t), \tag{17}$$

$$\frac{d}{dt}M_y(t) = -\frac{1}{T_2}M_y(t) + (E_\uparrow - E_\downarrow)M_x(t), \tag{18}$$

in which T_1 is the longitudinal relaxation time and T_2 is the transverse relaxation time. $M_z(\infty)$ is the asymptotic equilibrium value of $M_z(t)$, and is nonzero if the whole system is at temperature T, and in the presence of a constant external magnetic field along the z axis. Under these conditions, $M_z(\infty)$ for a spin $\frac{1}{2}$ magnetic moment will be given by

$$M_z(\infty) = \frac{\exp(-E_\uparrow/K_BT) - \exp(-E_\downarrow/K_BT)}{\exp(-E_\uparrow/K_BT) + \exp(-E_\downarrow/K_BT)}, \tag{19}$$

where $E_\uparrow$ and $E_\downarrow$ are the energies for the magnetic moment when it is parallel and antiparallel to the external field.

Redfield has reviewed the problem of deriving the Bloch equations from a density matrix equation, which equation is often referred to as Redfield's equation.[5] The derivation of Redfield's equation utilizes 2nd-order perturbation theory for short time intervals, and makes minimal use of the stochastic properties of the interaction.[5] The derivation of the equation (11)[3] used in this paper makes no perturbation series approximations and depends critically upon the stochastic nature of the interaction. Kubo has emphasized the difficulty in obtaining the Boltzmann factors in $M_z(\infty)$ when a stochastic approach to this problem is attempted.[6] In this present paper it is seen how the Boltzmann factors appear naturally through the factorization of the total density matrix for a subsystem and a reservoir.[3]

The structure of the interaction Hamiltonian to be used here depends upon the following considerations:

(1) The magnetic moment will correspond to a spin $\frac{1}{2}$ object.
(2) The effect of the reservoir will be manifested by an effective spin $\frac{1}{2}$ reservoir magnetic moment.
(3) The interaction will have the same form as in the Heisenberg ferromagnetic interaction, but with fluctuating coupling constants.
(4) Energy will be conserved by the interaction.

Both the subsystem and the reservoir correspond with two state manifolds, and consequently Pauli spin matrices may be used to represent both the magnetic moment and the effective reservoir magnetic moment. The interaction Hamiltonian is, then

$$\tilde{H}_{i\alpha j\beta}(t) = [\sigma^x_{ij}\sigma^x_{\alpha\beta}\tilde{h}^x(t) + \sigma^y_{ij}\sigma^y_{\alpha\beta}\tilde{h}^y(t)]\delta_{i\beta}\delta_{j\alpha} + \sigma^z_{ij}\sigma^z_{\alpha\beta}\tilde{h}^z_{i\alpha}(t), \tag{20}$$

wherein the Pauli spin matrices are

$$\sigma^x_{ij}, \sigma^x_{\alpha\beta} \to \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^y_{ij}, \sigma^y_{\alpha\beta} \to \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^z_{ij}, \sigma^z_{\alpha\beta} \to \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{21}$$

The factor $\delta_{i\beta}\delta_{j\alpha}$ in (20) provides for energy conservation during the transition, and it appears with the x and y components only because the z component terms automatically conserve energy. Both $\tilde{h}^x(t)$ and $\tilde{h}^y(t)$ represent fluctuating coupling coefficients. They factor completely in the x and y terms because the interaction Hamiltonian is Hermitian. The z component, however, contains different coupling coefficients for each possible choice of indices and is, therefore, given with appropriate indices. The Hermiticity of the z component terms is guaranteed by its form. It is assumed that all six coupling coefficients are purely random, stationary, Gaussian stochastic processes with average values of zero. Furthermore, no cross correlations are assumed to exist, and the x and y fluctuations have identical second moments. These conditions are expressed by

$$\langle\tilde{h}^x(t)\rangle = \langle\tilde{h}^y(t)\rangle = \langle\tilde{h}^z_{i\alpha}(t)\rangle = 0 \quad \text{for } i = 1, 2 \text{ and } \alpha = 1, 2, \tag{22}$$

$$\langle\tilde{h}^x(t)\tilde{h}^y(S)\rangle = \langle\tilde{h}^x(t)\tilde{h}^z_{i\alpha}(S)\rangle = \langle\tilde{h}^y(t)\tilde{h}^z_{i\alpha}(S)\rangle = \langle\tilde{h}^z_{i\alpha}(t)\tilde{h}^z_{j\beta}(S)\rangle = 0, \tag{23}$$

for $i = 1, 2$ $j = 1, 2$ $\alpha = 1, 2$ and $\beta = 1, 2$ but not both $i = j$ and $\alpha = \beta$,

$$\langle\tilde{h}^x(t)\tilde{h}^x(S)\rangle = \langle\tilde{h}^y(t)\tilde{h}^y(S)\rangle = 2Q^{x,y}\delta(t-S)$$
and
$$\langle\tilde{h}^z_{i\alpha}(t)\tilde{h}^z_{i\alpha}(S)\rangle = 2Q^z\delta(t-S). \tag{24}$$

In a constant external magnetic field directed along the z axis, the magnetic moment takes on two energy values for its spin parallel or antiparallel with the external field. These energies are given by

$$E_\uparrow = +g\beta H \quad \text{and } E_\downarrow = -g\beta H, \tag{25}$$

where g is the nuclear g factor, β is the nuclear magneton, and H is the external field strength, for the case of a nuclear magnetic moment such as a proton. Equations (25) and (20) lead to a special instance of (11) with the requirement that $T_{iji'j'}$ be determined from (20) using (22), (23), and (24).

In order to get an expression for $T_{iji'j'}$ Eqs. (12), (13), and (14) will be used, in reverse order. An outline of this computation follows.

Equations (14), (20), (23), and (24) lead to

$$Q_{i\alpha j\beta i'\alpha' j'\beta'} = (\sigma^x_{ij}\sigma^x_{\alpha\beta}\sigma^x_{i'j'}\sigma^x_{\alpha'\beta'} + \sigma^y_{ij}\sigma^y_{\alpha\beta}\sigma^y_{i'j'}\sigma^y_{\alpha'\beta'}) \times Q^{x,y}\delta_{i\beta}\delta_{j\alpha}\delta_{i'\beta'}\delta_{j'\alpha'} + \sigma^z_{ij}\sigma^z_{\alpha\beta}\sigma^z_{i'j'}\sigma^z_{\alpha'\beta'}Q^z\delta_{ii'}\delta_{\alpha\alpha'}. \tag{26}$$

In order to calculate $R_{i\alpha j\beta i'\alpha' j'\beta'}$ according to (13), some special cases of (26) are needed.

$$\sum_\theta\sum_{\theta'} Q_{j\beta\theta\theta'\theta\theta' j'\beta'} = \sum_\theta\sum_{\theta'}(\sigma^x_{j\theta}\sigma^x_{\beta\theta'}\sigma^x_{\theta j'}\sigma^x_{\theta'\beta'} + \sigma^y_{j\theta}\sigma^y_{\beta\theta'}\sigma^y_{\theta j'}\sigma^y_{\theta'\beta'}) \times Q^{x,y}\delta_{j\theta}\delta_{\theta\beta}\delta_{\beta\theta'}\delta_{j'\theta'} + \sigma^z_{j\theta}\sigma^z_{\beta\theta'}\sigma^x_{\theta j'}\sigma^z_{\theta'\beta'}Q^z\delta_{j\theta}\delta_{\beta\theta'}$$
$$= \delta_{jj'}\delta_{\beta\beta'}(\sigma^x_{j\beta}\sigma^x_{\beta j}\sigma^x_{\beta j}\sigma^x_{j\beta} + \sigma^y_{j\beta}\sigma^y_{\beta j}\sigma^y_{\beta j}\sigma^y_{j\beta})Q^{x,y} + \sigma^z_{jj}\sigma^z_{\beta\beta}\sigma^z_{jj'}\sigma^z_{\beta\beta'}Q^z, \tag{27}$$

$$\sum_\theta\sum_{\theta'} Q_{\theta\theta' i\alpha i'\alpha'\theta\theta'} = \delta_{ii'}\delta_{\alpha\alpha'}(\sigma^x_{\alpha i}\sigma^x_{i\alpha}\sigma^x_{i\alpha}\sigma^x_{\alpha i} + \sigma^y_{\alpha i}\sigma^y_{i\alpha}\sigma^y_{i\alpha}\sigma^y_{\alpha i})Q^{x,y} + \sigma^z_{i'i}\sigma^z_{\alpha'\alpha}\sigma^z_{i'i}\sigma^z_{\alpha'\alpha}Q^z. \tag{28}$$

Therefore, it follows that

$$R_{i\alpha j\beta i'\alpha' j'\beta'} = \delta_{ii'}\delta_{\alpha\alpha'}\delta_{jj'}\delta_{\beta\beta'}(\sigma^x_{j\beta}\sigma^x_{bj}\sigma^x_{\beta j}\sigma^x_{j\beta} + \sigma^y_{j\beta}\sigma^y_{\beta j}\sigma^y_{\beta j}\sigma^y_{j\beta} + \sigma^x_{\alpha i}\sigma^x_{i\alpha}\sigma^x_{i\alpha}\sigma^x_{\alpha i} + \sigma^y_{\alpha i}\sigma^y_{i\alpha}\sigma^y_{i\alpha}\sigma^y_{\alpha i})Q^{x,y} + (\delta_{ii'}\delta_{\alpha\alpha}\sigma^z_{jj}\sigma^z_{\beta\beta}\sigma^z_{jj}\sigma^z_{\beta\beta'} + \delta_{jj'}\delta_{\beta\beta'}\sigma^z_{i'i}\sigma^z_{\alpha'\alpha}\sigma^z_{i'i'}\sigma^z_{\alpha'\alpha'})Q^z - 2(\sigma^x_{jj'}\sigma^x_{\beta\beta'}\sigma^x_{i'i}\sigma^x_{\alpha'\alpha} + \sigma^y_{jj'}\sigma^y_{\beta\beta'}\sigma^y_{i'i}\sigma^y_{\alpha'\alpha}) \times Q^{x,y}\delta_{j\beta'}\delta_{\beta j'}\delta_{i'\alpha}\delta_{\alpha' i} - 2\sigma^z_{jj'}\sigma^z_{\beta\beta'}\sigma^z_{i'i}\sigma^z_{\alpha'\alpha}Q^z\delta_{ji'}\delta_{\beta\alpha'}. \tag{29}$$

To get $T_{iji'j'}$ according to (12) requires

$$\sum_\alpha R_{i\alpha j\alpha i'\alpha' j'\beta'} = \delta_{ii'}\delta_{jj'}\delta_{\alpha'\beta}(\sigma^x_{j\alpha}\sigma^x_{\alpha' j}\sigma^x_{\alpha' j}\sigma^x_{j\alpha'} + \sigma^y_{j\alpha'}\sigma^y_{\alpha' j}\sigma^y_{\alpha' j}\sigma^y_{j\alpha'} + \sigma^x_{\alpha' i}\sigma^x_{i\alpha'}\sigma^x_{i\alpha'}\sigma^x_{\alpha' i} + \sigma^y_{\alpha' i}\sigma^y_{i\alpha'}\sigma^y_{i\alpha'}\sigma^y_{\alpha' i})Q^{x,y} + (\delta_{ii'}\sigma^z_{jj}\sigma^z_{\alpha'\alpha'}\sigma^z_{jj'}\sigma^z_{\alpha'\beta'} + \delta_{jj'}\sigma^z_{i'i}\sigma^z_{\alpha'\beta'}\sigma^z_{i'i'}\sigma^z_{\alpha'\alpha'})Q^z - 2(\sigma^x_{jj'}\sigma^x_{i'\beta'}\sigma^x_{i'i}\sigma^x_{\alpha' i'} + \sigma^y_{jj'}\sigma^y_{i'\beta'}\sigma^y_{i'i}\sigma^y_{\alpha' i'})Q^{x,y}\delta_{ij'}\delta_{i\alpha'}\delta_{j\beta'} - 2\sigma^z_{jj'}\sigma^z_{\alpha'\beta'}\sigma^z_{i'i}\sigma^z_{\alpha'\alpha}Q^z\delta_{ij}. \tag{30}$$

Therefore,

$$T_{ij i'j'} = \sum_{\alpha}\sum_{\alpha'} R_{i\alpha j\alpha i'\alpha' j'\alpha'} \frac{1}{Q_R}\exp\left(-\frac{E_{\alpha'}}{K_B T}\right)$$
$$= \delta_{ii'}\delta_{jj'}\left\{2\left[1-\frac{1}{Q_R}\exp\left(-\frac{E_j}{K_B T}\right)\right]\right.$$
$$\left. + 2\left[1-\frac{1}{Q_R}\exp\left(-\frac{E_i}{K_B T}\right)\right]\right\} Q^{x,y}$$
$$+ \delta_{ii'}\delta_{jj'} 2Q^z - 2\delta_{i'j'}\delta_{ij} 2(1-\delta_{jj'})Q^{x,y}\frac{1}{Q_R}$$
$$\times \exp\left(-\frac{E_i}{K_B T}\right) - 2\delta_{ij}\delta_{i'j'}\delta_{ii'}Q^z, \tag{31}$$

wherein (21) was used as well as $(1/Q_R)\exp(-E_1/K_B T) + (1/Q_R)\exp(-E_2/K_B T) = 1$. Several special cases of (31) will be used and are given by

$$T_{ijij} = 2Q^{x,y} + 2Q^z \quad \text{for } i \neq j, \tag{32}$$

$$T_{iiii} = 4Q^{x,y}[1 - (1/Q_R)\exp(-E_i/K_B T)], \tag{33}$$

$$T_{iii'i'} = -4Q^{x,y}(1/Q_R)\exp(-E_i/K_B T) \quad \text{for } i \neq i', \tag{34}$$

$$T_{ijji} = 0. \tag{35}$$

All other choices of indices for $T_{ij i'j'}$ lead to zero values as with (35). This situation greatly simplifies Eq. (11).

The x, y, and z components of the magnetic moment are given, on the average, in terms of the averaged density matrix, $\langle \rho_{ij}(t)\rangle$, by

$$M_x(t) = g\beta \sum_{ij} \sigma^x_{ij}\langle \rho_{ij}(t)\rangle, \tag{36}$$

$$M_y(t) = g\beta \sum_{ij} \sigma^y_{ij}\langle \rho_{ij}(t)\rangle, \tag{37}$$

$$M_z(t) = g\beta \sum_{ij} \sigma^z_{ij}\langle \rho_{ij}(t)\rangle. \tag{38}$$

Using (21) gives

$$M_x(t) = g\beta(\langle \rho_{12}(t)\rangle + \langle \rho_{21}(t)\rangle), \tag{39}$$

$$M_y(t) = g\beta i(\langle \rho_{21}(t)\rangle - \langle \rho_{12}(t)\rangle), \tag{40}$$

$$M_z(t) = g\beta(\langle \rho_{11}(t)\rangle - \langle \rho_{22}(t)\rangle). \tag{41}$$

From (11) and (32)–(35) it follows that

$$\frac{d}{dt}\langle \rho_{12}(t)\rangle = -i(E_\downarrow - E_\uparrow)\langle \rho_{12}(t)\rangle - T_{1212}\langle \rho_{12}(t)\rangle, \tag{42}$$

$$\frac{d}{dt}\langle \rho_{21}(t)\rangle = -i(E_\uparrow - E_\downarrow)\langle \rho_{21}(t)\rangle - T_{2121}\langle \rho_{21}(t)\rangle, \tag{43}$$

$$\frac{d}{dt}\langle \rho_{11}(t)\rangle = -T_{1111}\langle \rho_{11}(t)\rangle - T_{1122}\langle \rho_{22}(t)\rangle, \tag{44}$$

$$\frac{d}{dt}\langle \rho_{22}(t)\rangle = -T_{2211}\langle \rho_{11}(t)\rangle - T_{2222}\langle \rho_{22}(t)\rangle. \tag{45}$$

The combination of (32)–(35), (39)–(41), and (42)–(45) gives

$$\frac{d}{dt}M_x(t) = (E_\downarrow - E_\uparrow)M_y(t) - 2(Q^{x,y} + Q^z)M_x(t), \tag{46}$$

$$\frac{d}{dt}M_y(t) = -(E_\downarrow - E_\uparrow)M_x(t) - 2(Q^{x,y} + Q^z)M_y(t), \tag{47}$$

$$\frac{d}{dt}M_z(t) = -4Q^{x,y}(M_z(t) - M_z(\infty)), \tag{48}$$

where

$$M_z(\infty) \equiv \frac{1}{Q_R}\left[\exp\left(-\frac{E_\uparrow}{K_B T}\right) - \exp\left(-\frac{E_\downarrow}{K_B T}\right)\right]. \tag{49}$$

Equations (46)–(49) are clearly equivalent with Eqs. (16)–(19) when the identifications

$$1/T_1 \equiv 4Q^{x,y} \quad \text{and} \quad 1/T_2 \equiv 2(Q^{x,y} + Q^z) \tag{50}$$

are made.

It should be noted that when there is no external, constant magnetic field present, then $E_\uparrow = E_\downarrow$, and it would be expected in isotropic media that the second moments of the fluctuating magnetic field produced by the reservoir would be isotropic, which means

$$Q^z = Q^{x,y}. \tag{51}$$

Therefore, (50) shows that $T_1 = T_2$ and the relaxation is isotropic. In the presence of an external, constant field, or in the case of anisotropic media Q^z and $Q^{x,y}$ will not necessarily remain equal, and both $Q^z > Q^{x,y}$ and $Q^{x,y} > Q^z$ lead to the special cases $T_1 > T_2$ and $T_1 \approx \frac{1}{2}T_2$, respectively. These special cases are observed experimentally.[7]

III. CONCLUSION

The theory of multiplicative stochastic processes has been used to arrive at a density matrix description of a subsystem in contact with a thermal reservoir. In this paper an application to the problem of the relaxation of a magnetic moment interacting with the fluctuating magnetic environment of a reservoir has been made. Kubo's dilemma concerning how to properly include the Boltzmann factors has been resolved. Moreover, the derivation of Bloch's equations did not require the approximation of 2nd-order perturbation theory for short time intervals because the stochastic properties of the fluctuating quantities were fully utilized.

The quantitative determination of Q^z and $Q^{x,y}$ in terms of the exact microscopic interactions involved remains as a problem. This problem may be raised in the more general setting of Sec. I with respect to quantitatively computing $Q_{i\alpha j\beta i'\alpha' j'\beta'}$ in Eq. (14) from a microscopic theory of the exact interactions. This problem will be treated elsewhere.

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Multiplicative stochastic processes, Fokker–Planck equations, and a possible dynamical mechanism for critical behavior

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A derivation of the Fokker-Planck equations for additive stochastic processes is given which involves treating the continuity equation in the configuration space representation of the additive stochastic process as a multiplicative stochastic process. The average of the continuity equation becomes the Fokker–Planck equation. A presentation of the "multiplicative stochastic, Markov approximation" follows. This approximation is applied to the analysis of the dynamics of a heavy particle in a molecular fluid as described by Hamilton's equations. The nonperturbative approximation technique leads to the Fokker–Planck equation for simple Brownian motion. As part of the analysis, "intrinsic diffusion" is discovered and used to show ergodicity for the autocorrelation formula which appears during the Brownian motion calculation. An account of how these methods might be used to study the dynamical origins of critical behavior is given.

INTRODUCTION

The purpose of this paper is to illustrate connections between additive and multiplicative stochastic processes. The distinction between additive and multiplicative stochastic processes was explained in an earlier paper.[1] In several subsequent papers,[2–5] application was made of multiplicative stochastic processes to the description of quantum mechanical phenomena. Such applications may be thought of as the generalization for quantum mechanical processes of Brownian motion, an additive stochastic process, and Kubo[6] has referred to such applications as quantum mechanical Brownian motion. A general theory for additive stochastic processes has been presented[7,8] within the framework of stationary, Gaussian, Markov processes. The domain of applicability for additive stochastic processes includes Brownian motion,[9–11] irreversible thermodynamics,[12] fluctuating hydrodynamics,[13] and light scattering from simple fluids and fluid mixtures,[14–16] as well as other topics. It would appear that additive stochastic processes are of relevance for classical physics rather than for quantum physics. This separation of applicability of additive or multiplicative stochastic processes to classical or quantal physics, respectively, is not of a fundamental nature: For most purposes it is a natural separation. However, Haken[17] has reviewed the use of additive stochastic processes in quantum mechanical contexts, and this paper will exhibit the utility of multiplicative stochastic processes in classical physics.

The primary connection to be described involves a technique for the derivation of the Fokker–Planck equation for an additive stochastic process. The technique, however, uses a multiplicative stochastic process which is generated by the original additive stochastic process. In this way, the relationship between the Markov nature of the process and the properties of the second moments of the fluctuating forces is highlighted.

The technique just referred to suggests a method for the derivation of the Fokker–Planck equation for Brownian motion which connects the dissipative, friction constant of Brownian motion with interparticle potentials, in a model of Brownian motion in which the fluid is treated as N interacting fluid molecules obeying conservative classical mechanics. This problem is worked out in detail and involves an unusual type of diffusive behavior characterized by a Green's function

$$\left(2\pi\frac{K_BT}{m}t^2\right)^{-1/2}\exp\left[-\frac{(q-q')^2}{2(K_BT/m)t^2}\right]$$

in one dimension. This peculiar diffusion provides for a proof that the autocorrelation formula, for the dissipative, friction constant which is derived, is ergodic.

The conclusion of this paper considers certain infinite series which arise in the Brownian motion problem. The possibility of summing the series is raised. In addition, it is suggested that the series provides the possibility for understanding the origin of critical behavior in terms of a dynamical mechanism.

FOKKER-PLANCK EQUATIONS

The complete stochastic description of an additive stochastic process is given by the solution to its associated Fokker–Planck equation. For the case of Brownian motion, in one dimension, the additive stochastic process is given by Langevin's equation

$$M\frac{d}{dt}u(t) = -\alpha u(t) + \tilde{F}(t) \tag{1}$$

where $\alpha > 0$, and $\tilde{F}(t)$ is a purely random, stationary, Gaussian force satisfying

$$\langle\tilde{F}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{F}(t)\tilde{F}(s)\rangle = 2\lambda\delta(t-s) \tag{2}$$

where $\langle\cdots\rangle$ denotes stochastic averaging.[7,10,11] The delta function in (2) implies the Markov property for the stochastic process $u(t)$,[11] as must be proved using the definition of a Markov process, which definition involves specific behavior by the higher than second-order correlation distributions for $u(t)$.[11] The Markov property is then used to imply the validity of the Smoluchowski equation, which for Eq. (1) is written as[11]

$$P(u(0)\,|\,u, t+\Delta t) = \int P(u(0)\,|\,u', t)P(u'\,|\,u, \Delta t)\,du' \tag{3}$$

where $P(u(0)\,|\,u, t)\,du$ is the conditional probability that the value of $u(t)$ and time t will be between u and $u+du$ given that at time $t=0$, $u(t)$ had the value $u(0)$. The Smoluchowski equation is used to derive the Fokker–Planck equation which in this example becomes

$$\frac{\partial}{\partial t}P(u(0)\,|\,u,t) = -\frac{\partial}{\partial u}\left(-\frac{\alpha}{M}uP(u(0)\,|\,u,t)\right) + \frac{\lambda}{M^2}\frac{\partial^2}{\partial u^2}P(u(0)\,|\,u,t) \tag{4}$$

The solution to Eq. (4) is subject to the initial condition at $t=0$ that $P(u(0)\,|\,u,0)=\delta(u-u(0))$. The solution to the Fokker–Planck equation provides the conditional probability distribution which for a Markov process contains all possible information about the time evolution of the process. The solution to (4) is

$$P(u(0)\,|\,u,t) = \left(2\pi\frac{K_BT}{M}(1-\rho^2(t))\right)^{-1/2}\exp\left(-\frac{(M(u-\rho(t)u(0))^2}{2K_BT(1-\rho^2(t))}\right) \tag{5}$$

where $\rho(t)\equiv\exp[-(\alpha/M)t]$, and we have used the relation

$$\lambda = K_BT\alpha \tag{6}$$

which is Einstein's relation within the context of Langevin's equation. Relation (6) follows from the requirement that the solution to (4) satisfy the asymptotic limit

$$\lim_{t\to\infty}P(u(0)\,|\,u,t) = \left(2\pi\frac{K_BT}{M}\right)^{-1/2}\exp\left(-\frac{Mu^2}{2K_BT}\right) \tag{7}$$

where the right-hand side of (7) is the Maxwell distribution. In Einstein's treatment of Brownian motion,[18] the analog of (6) is derived

$$D = K_BT/\alpha \tag{8}$$

where D is the diffusion constant. Both relations (6) and (8) are referred to as Einstein's relation in the literature. Relation (8) is the original relation which follows from the diffusion equation, whereas relation (6) is the prototype for fluctuation–dissipation theorems.[7]

Multicomponent generalizations of Langevin's equation lead to the general theory of stationary, Gaussian, Markov processes[7,19] which are described by the equations

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + S_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{F}_\alpha(t) \tag{9}$$

where $\alpha=1,2,\ldots,N$, $A_{\alpha\alpha'}$ is an antisymmetric matrix, $S_{\alpha\alpha'}$ is a symmetric matrix with nonpositive eigenvalues, and $\tilde{F}_\alpha(t)$ is an n-component, purely random, Gaussian fluctuating force satisfying

$$\langle\tilde{F}_\alpha(t)\rangle = 0 \quad \text{for each } \alpha, \tag{10}$$

$$\langle\tilde{F}_\alpha(t)\tilde{F}_\beta(s)\rangle = 2Q_{\alpha\beta}\delta(t-s), \tag{11}$$

where $Q_{\alpha\beta}$ is a symmetric matrix with nonnegative eigenvalues. The corresponding Fokker–Planck equation is given by

$$\frac{\partial}{\partial t}P(\mathbf{a}(0)\,|\,\mathbf{a},t) = -\frac{\partial}{\partial a_\alpha}[(A_{\alpha\alpha'}a_{\alpha'}+S_{\alpha\alpha'}a_{\alpha'})P(\mathbf{a}(0)\,|\,\mathbf{a},t)] + \frac{\partial^2}{\partial a_\alpha\,\partial a_\beta}[Q_{\alpha\beta}P(\mathbf{a}(0)\,|\,\mathbf{a},t)] \tag{12}$$

with the initial condition $P(\mathbf{a}(0)\,|\,\mathbf{a},0)=\delta(\mathbf{a}-\mathbf{a}(0))$. The solution to (12) is given by[7,19]

$$P(\mathbf{a}(0)\,|\,\mathbf{a},t) = \left[\frac{\|\mathbf{C}(t)\|}{(2\pi)^n}\right]^{1/2}\exp[-\tfrac{1}{2}(a_\alpha - D_{\alpha\alpha'}(t)a_{\alpha'}(0))C_{\alpha\beta}(t) \times (a_\beta - D_{\beta\beta'}(t)a_{\beta'}(0))] \tag{13}$$

where $\|\mathbf{C}(t)\|$ denotes the determinant of $\mathbf{C}(t)$, and $D_{\alpha\alpha'}(t)$ is defined by

$$\mathbf{D}(t) \equiv \exp[(\mathbf{A}+\mathbf{S})t] \tag{14}$$

and $C_{\alpha\beta}(t)$ is defined by

$$\mathbf{C}^{-1}(t) \equiv \mathbf{E}^{-1} - \mathbf{D}(t)\mathbf{E}^{-1}\mathbf{D}^{+}(t) \tag{15}$$

in which the matrix $\mathbf{E}$ is determined by the entropy $S(t)$, given by

$$S(t) = S_0 - \tfrac{1}{2}K_Ba_\alpha(t)E_{\alpha\beta}a_\beta(t), \tag{16}$$

so that $\mathbf{E}$ is symmetric with positive eigenvalues. To get (13) from (12) we have used the generalized fluctuation–dissipation theorem[7,19]

$$2Q_{\alpha\beta} = -(A_{\alpha\theta}+S_{\alpha\theta})E^{-1}_{\theta\beta} + E^{-1}_{\alpha\theta}(A_{\theta\beta}-S_{\theta\beta}) \tag{17}$$

which follows from the requirement that

$$\lim_{t\to\infty}P(\mathbf{a}(0)\,|\,\mathbf{a}t) = W_0\exp(-\tfrac{1}{2}a_\alpha E_{\alpha\beta}a_\beta) \tag{18}$$

where $W_0 = [\|\mathbf{E}\|/(2\pi)^n]^{1/2}$, and the right-hand side of (18) is seen to be the Boltzmann–Planck formula because the entropy is given by (16). The derivation of (12) requires proving that (9) with (11) describes a Markov process. Then a generalization to n components of Smoluchowski's equation leads to (12).[11]

A further generalization is possible in which one deals with continuous, variable indices. Analogs to (9), (11), and (17) result in

$$\frac{\partial}{\partial t}a_i(\mathbf{r},t) = -\int A_{ij}(\mathbf{r},\mathbf{r}')a_j(\mathbf{r}',t)\,d\mathbf{r}' - \int S_{ij}(\mathbf{r},\mathbf{r}')a_j(\mathbf{r}',t)\,d\mathbf{r}' + \tilde{F}_i(\mathbf{r},t), \tag{19}$$

$$\langle\tilde{F}_i(\mathbf{r},t)\tilde{F}_j(\mathbf{r}',s)\rangle = 2Q_{ij}(\mathbf{r},\mathbf{r}')\delta(t-s), \tag{20}$$

$$2Q_{ij}(\mathbf{r},\mathbf{r}') = \int[(A_{il}(\mathbf{r},\mathbf{r}'')+S_{il}(\mathbf{r},\mathbf{r}''))E^{-1}_{lj}(\mathbf{r}'',\mathbf{r}') + E^{-1}_{il}(\mathbf{r},\mathbf{r}'')(-A_{lj}(\mathbf{r}'',\mathbf{r}')+S_{lj}(\mathbf{r}'',\mathbf{r}'))]\,d\mathbf{r}'' \tag{21}$$

where $E_{IK}(\mathbf{r},\mathbf{r}')$ is the entropy matrix analog of (16)

$$S(t) = S_0 - \tfrac{1}{2}K_B\int\int a_i(\mathbf{r},t)E_{ij}(\mathbf{r},\mathbf{r}')a_j(\mathbf{r}'t)\,d\mathbf{r}\,d\mathbf{r}'. \tag{22}$$

This form of the general theory of stationary, Gaussian, Markov processes leads to hydrodynamical applications,[7,14–16] as well as to applications in other field dependent problems.[8,20] There is also in this case a corresponding Fokker–Planck equation which will involve utilization of the techniques of functional differentiation. We shall not write down this equation.

At this point a partial review of the structure and significance of the Fokker–Planck equation for additive stochastic processes has been presented. It is necessary, before proceeding further with Fokker–Planck equations, to review the basic theorem in the theory of multiplicative stochastic processes.

Consider an equation of the form

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{23}$$

where $\alpha=1,2,\ldots,N$, $A_{\alpha\alpha'}=-A_{\alpha'\alpha}$, $\tilde{A}_{\alpha\alpha'}(t)=-\tilde{A}_{\alpha'\alpha}(t)$, and the matrix $\tilde{A}_{\alpha\alpha'}(t)$ is a purely random, Gaussian

matrix with mean value zero, which implies that[1]

$$\langle \tilde{A}_{\alpha\alpha'}(t)\rangle = 0 \quad \text{and} \quad \langle \tilde{A}_{\alpha\alpha'}(t)\tilde{A}_{\beta\beta'}(s)\rangle = 2Q_{\alpha\alpha'\beta\beta'}\delta(t-s) \tag{24}$$

and that the higher-order averaged moments are given by

$$\langle \tilde{A}_{\alpha_1\alpha_1'}(t_1)\cdots A_{\alpha_{2n-1}\alpha_{2n-1}'}(t_{2n-1})\rangle = 0, \tag{25}$$

$$\langle A_{\alpha_1\alpha_1'}(t_1)\cdots A_{\alpha_{2n}\alpha_{2n}'}(t_{2n})\rangle = \frac{1}{2^n n!}\sum_{p\in S_{2n}}\prod_{j=1}^{n}\langle A_{\alpha_{p(2j-1)}\alpha_{p(2j-1)}'}(t_{p(2j-1)}A_{\alpha_{p(2j)}\alpha_{p(2j)}'}(t_{p(2j)})\rangle \tag{26}$$

where $\sum_{p\in S_{2n}}$ denotes the sum over all permutations of the symmetric group of order $(2n)!$. Equations (25) and (26) are consequences of the Gaussian property of $\tilde{A}(t)$. It has been proved that these properties of $\tilde{A}(t)$ lead to the averaged equation[1]

$$\frac{d}{dt}\langle a_\alpha(t)\rangle = A_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + Q_{\alpha\theta\theta\alpha'}\langle a_{\alpha'}(t)\rangle \tag{27}$$

in which the matrix $Q_{\alpha\theta\theta\alpha'}$ is determined by (24) which implies that it is symmetric with nonpositive eigenvalues. Whereas (23) describes fluctuating oscillations, (27) describes damped oscillations.

The proof of (27) from (23) using the properties of (24), (25), and (26) goes through unchanged if the $A_{\alpha\alpha'}$ in (23) is augmented by the addition of a symmetric matrix $S_{\alpha\alpha'}$ which has nonpositive eigenvalues. That is,

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + S_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{28}$$

leads to

$$\frac{d}{dt}\langle a_\alpha(t)\rangle = A_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + S_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + Q_{\alpha\theta\theta\alpha'}\langle a_{\alpha'}(t)\rangle \tag{29}$$

upon performing the average of (28).

In addition, this result can be generalized to infinite matrices and to continuous indices. Therefore, we shall also use the theorem in the form

$$\frac{\partial}{\partial t}f(q,t) = L(q)f(q,t) + \tilde{L}(q,t)f(q,t) \tag{30}$$

leads to

$$\frac{\partial}{\partial t}\langle f(q,t)\rangle = L(q)\langle f(q,t)\rangle + D(q)\langle f(q,t)\rangle \tag{31}$$

where $L(q)$ is a linear differential or integral operator, $\tilde{L}(q,t)$ is a purely random, Gaussian, fluctuating linear differential or integral operator with mean value zero, and $D(q)$ is a linear differential or integral operator given by

$$\langle \tilde{L}(q,t)\tilde{L}(q,t')\rangle = 2D(q)\delta(t-t'). \tag{32}$$

In (30), it will be assumed that $\tilde{L}(q,t)$ is an antisymmetric operator, which means that if $\{\varphi_i(q)\}$ is a complete set of real orthonormal functions of the coordinates q, then

$$[\tilde{L}(t)]_{iK} = -[\tilde{L}(t)]_{Ki} \tag{33}$$

where $[\tilde{L}(t)]_{iK} \equiv \int \varphi_i(q)\tilde{L}(q,t)\varphi_K(q)\,dq$. Consequently, $D(q)$ is a symmetric operator, which means that

$$[D]_{iK} = [D]_{Ki} \tag{34}$$

where $[D]_{iK} \equiv \int \varphi_i(q)D(q)\varphi_K(q)\,dq$ because

$$[D]_{iK} = \int_0^t \langle [L(t)]_{ij}[L(s)]_{jk}\rangle\,ds. \tag{35}$$

From (35) it is also seen that the eigenspectrum of $D(q)$ is entirely nonpositive. The operator $L(q)$ in (30) may be either antisymmetric or of mixed symmetry in analogy with (23) and (28), respectively. Specific examples of these formal expressions will occur in the following paragraphs.

The q in (30) and (31) may represent a single variable, or it may represent a set of variables. Suppose we explicitly have N q's: $q_1, q_2, \ldots, q_N$. Consider the configuration space corresponding with these q_j's and let $f(q_1q_2\cdots q_Nt)$ be the distribution function in configuration space. If $N=2m$ and m of the q_j's are coordinates and m of the q_j's are momenta, then the associated configuration space becomes phase space and f becomes the phase space distribution. However, in several contexts it is not phase space which will interest us and, therefore, we use the notation q_j's for a generalized configuration space of N variables.

It is always the case that the continuity equation is true in configuration space. In our notation this becomes

$$\frac{\partial}{\partial t}f(q_1\cdots q_Nt) = -\frac{\partial}{\partial q_j}(\dot{q}_j f(q_1\cdots q_Nt)) \tag{36}$$

where $\dot{q}_j \equiv d/dt\,q_j(t)$. If we are actually dealing with phase space and a conservative system for which Hamilton's equations are valid, then (36) leads to Liouville's equation.[21] However, in general we will not necessarily be in phase space or be dealing with a conservative system, so that Liouville's theorem is not generally valid although (36) is. In the general case, some relationship between the $\dot{q}_j$'s and the q_j's must hold if (36) is to lead to anything useful.

Returning to (9), we will take for the q_j's the a_α's. Therefore, (36) is seen to be given by

$$\frac{\partial}{\partial t}f(a_1\cdots a_Nt) = -\frac{\partial}{\partial a_\alpha}(\dot{a}_\alpha f(a_1\cdots a_Nt)) \tag{37}$$

For the a_α's we use (9) which converts (37) into

$$\frac{\partial}{\partial t}f(a_1\cdots a_Nt) = -\frac{\partial}{\partial a_\alpha}[(A_{\alpha\alpha'}a_{\alpha'} + S_{\alpha\alpha'}a_{\alpha'} + \tilde{F}_\alpha(t))f(a_1\cdots a_Nt)] \tag{38}$$

which is clearly a multiplicative stochastic process in the form of (30) if we identify

$$L(q) \to -\frac{\partial}{\partial a_\alpha}(A_{\alpha\alpha'}a_{\alpha'} + S_{\alpha\alpha'}a_{\alpha'})x$$

and

$$\tilde{L}(q,t) \to -\frac{\partial}{\partial a_\alpha}\tilde{F}_\alpha(t)x = -\tilde{F}_\alpha(t)\frac{\partial}{\partial a_\alpha}. \tag{39}$$

The analog of (31) is then

$$\frac{\partial}{\partial t}\langle f(a_1\cdots a_Nt)\rangle = -\frac{\partial}{\partial a_\alpha}[A_{\alpha\alpha'}a_{\alpha'} + S_{\alpha\alpha'}a_{\alpha'})\langle f(a_1\cdots a_Nt)\rangle]$$

$$+\frac{\partial^2}{\partial a_\alpha \partial a_\beta}[Q_{\alpha\beta}\langle f(a_1 \cdots a_N t)\rangle]. \tag{40}$$

This is precisely the Fokker–Planck equation (12) if we identify

$$P(\mathbf{a}(0)\,|\,\mathbf{a}, t) \to \langle f(a_1 \cdots a_N t)\rangle. \tag{41}$$

Consequently, given an additive stochastic process, we can write out its associated continuity equation in its configuration space and we arrive at a multiplicative stochastic process, the average of which is the Fokker–Planck equation of the original additive stochastic process.

Because the connection between (38) and (40) requires that $\tilde{F}_\alpha(t)$ is purely random, we see the Markov property and its connection with the Fokker–Planck equation without having to proceed via the Smoluchowski equation. As a special case of (38) and (40), we momentarily return to (1) from which the analogs of (37) and (38) follow:

$$\frac{\partial}{\partial t} f(u, t) = -\frac{\partial}{\partial u}(\dot{u} f(u, t)), \tag{42}$$

$$\frac{\partial}{\partial t} f(u, t) = -\frac{\partial}{\partial u}\left[\left(-\frac{\alpha}{M}u + \frac{\tilde{F}(t)}{M}\right) f(u, t)\right].$$

The average of (42) is

$$\frac{\partial}{\partial t}\langle f(u, t)\rangle = \frac{\partial}{\partial u}\left(\frac{\alpha}{M} u\langle f(u, t)\rangle\right) + \frac{\lambda}{M^2}\frac{\partial^2}{\partial u^2}\langle f(u, t)\rangle \tag{43}$$

which is identical with the Fokker–Planck equation (4).

THE MULTIPLICATIVE STOCHASTIC, MARKOV APPROXIMATION

In this section we will discuss an approximation procedure which will be referred to as the multiplicative stochastic, Markov approximation. Its connection with the preceeding section will be illustrated, and it will provide the background necessary for the analysis of Brownian motion which follows in the next section. The approximation procedure introduced here is nonperturbative.

Suppose we have a particle in a fluid. It is, on the average, at rest, although it does execute a fluctuating motion. We could describe this motion of the particle phenomenologically by the equation

$$M\frac{dx}{dt} = \tilde{p}(t) \tag{44}$$

in which the fluctuating momentum $\tilde{p}(t)$ is assumed to be a purely random, Gaussian stochastic process with average value zero and a second moment given by

$$\langle \tilde{p}(t)\tilde{p}(s)\rangle = 2M^2 D\delta(t - s) \tag{45}$$

in which M is the mass, as in (44), and D is a constant. The continuity equation in the configuration space description of (44) is

$$\frac{\partial}{\partial t} f(x, t) = -\frac{\partial}{\partial x}(\dot{x} f(x, t))$$

$$= -\frac{\partial}{\partial x}\frac{\tilde{p}(t)}{M} f(x, t)$$

$$= -\frac{\tilde{p}(t)}{M}\frac{\partial}{\partial x} f(x, t). \tag{46}$$

This is again a multiplicative stochastic process with a purely random, Gaussian stochastic operator. The average equation is, therefore,

$$\frac{\partial}{\partial t}\langle f(x, t)\rangle = D\frac{\partial^2}{\partial x^2}\langle f(x, t)\rangle \tag{47}$$

which is recognized as the diffusion equation with diffusion constant D. Equations (46) and (47) are special cases of (37), (38), and (40).

It may be objected that from Brownian motion we know that (45) is not so, but that instead

$$(\!\langle \tilde{p}(t)\tilde{p}(s)\rangle\!) = MK_B T \exp\left(-\frac{\alpha}{M}|t - s|\right) \tag{48}$$

which follows from (5), and in which the rounded $(\cdots)$ denote an average over the initial value distribution in addition to the stochastic average denote by $\langle \cdots \rangle$. The second average makes (48) a stationary expression depending upon $|t - s|$.[10] Using (48) in (46) leads again to

$$\frac{\partial}{\partial t} f(x, t) = -\frac{\tilde{p}(t)}{M}\frac{\partial}{\partial x} f(x, t) \tag{49}$$

which is still a multiplicative stochastic process, but the stochastic operator is now no longer purely random, so that we cannot use our theorem for averaged multiplicative stochastic processes. However, the $\tilde{p}(t)$ in (48) and (49) is still a Gaussian process because the $u(t)$ in (1) inherits the Gaussian property from the $\tilde{F}(t)$ in (1) since (1) is a linear equation. In the Appendix it is shown that the Gaussianness of $\tilde{p}(t)$ leads to the exact result

$$\frac{\partial}{\partial t}(\!\langle f(xt)\rangle\!) = \int_0^t \frac{1}{M^2}(\!\langle \tilde{p}(t)\tilde{p}(s)\rangle\!)\, ds \frac{\partial^2}{\partial x^2}(\!\langle f(xt)\rangle\!). \tag{50}$$

Using (48) in (50) permits performance of the integration giving

$$\frac{\partial}{\partial t}(\!\langle f(xt)\rangle\!) = \frac{K_B T}{\alpha}\left[1 - \exp\left(-\frac{\alpha}{M}t\right)\right]\frac{\partial^2}{\partial x^2}(\!\langle f(xt)\rangle\!) \tag{51}$$

which differs from (47) by the presence of a time dependent diffusion constant: $(K_B T/\alpha)\{1 - \exp[-(\alpha/M)t]\}$. For times long compared with M/α we can neglect the exponential term, and this constitutes the multiplicative stochastic, Markov approximation. The integral in (50) can be used to define a diffusion constant when we neglect the exponential part in (51). We get

$$D' = \lim_{t\to\infty}\frac{1}{M^2}\int_0^t (\!\langle \tilde{p}(t)\tilde{p}(s)\rangle\!)\, ds \tag{52}$$

where D' will be used in an expression like (45). Because of the infinite decay tail in (48), we have taken the limit $t \to \infty$ in (52), although the greatest part of the integral comes early. Using (48) in (52) gives

$$D' = K_B T/\alpha. \tag{53}$$

Note that (52) also gives the strength of the second moment for $M^{-1}\tilde{p}(t)$ as expressed by (45) since

$$D = \lim_{t\to\infty}\frac{1}{M^2}\int_0^t \langle \tilde{p}(t)\tilde{p}(s)\rangle\, ds. \tag{54}$$

Therefore, if $D \equiv D'$ we have the multiplicative stochastic, Markov approximation for (48) and (49) given by (45) and (46). The average equation (47) or (51) is the

diffusion equation, and the connection between diffusion and Brownian motion given by

$$D = K_B T/\alpha \tag{55}$$

is Einstein's original formula (8).[18] The self-consistency of the multiplicative stochastic, Markov approximation requires that the D' we get from (52) not be too large so that diffusion is slow compared with the relaxation of (48) which is governed by the magnitude of α. Indeed, (48) decays faster for larger α which via (53) results in a smaller D' which implies a slower diffusion. Therefore, in this example, the multiplicative stochastic, Markov approximation is seen to be intrinsically self-consistent. The reciprocal relation between D' and α generalizes to the more general case of multicomponent processes.

In the next section, analogs of (52) will arise in which a stochastic quantity has a non-purely-random second moment correlation formula from which we are calculating its strength. A formula like (52) will be used to calculate the strength to be used in the replacement correlation formula which is purely random. This will be analogous to the replacement of (48) by (45) where the D in (45) satisfies (55). The presence of the infinite time limit is formal, and it will be shown that the correlation integrand actually decays significantly in a very short time interval, as was the case with (52) with (48) in the integrand.

Before proceeding further, it is worth remarking that while we can actually solve (49), given (48), by writing (50), because of the Gaussian property, it is not a generally valid procedure for situations in which the stochastic operator does not commute with itself at different times.[22] Here, commutivity is guaranteed by the simple form of (49). When there is noncommutivity, then the Gaussian property alone is not sufficient for the reduction of the averaged equation to a workable form, and the multiplicative stochastic, Markov approximation becomes essential.[22]

MICROSCOPIC MODEL OF BROWNIAN MOTION

In this section we shall bring to bear the techniques of the preceeding sections as we attempt a derivation of the Fokker–Planck equation (4), for a Brownian particle, starting from a description involving a heavy particle interacting with N fluid molecules according to Hamilton's equations of motion. This is not a new program as far as its objective is concerned. Others, using other contexts and techniques, have also made this objective their goal.[23–27] Our present context and techniques were suggested by Kubo[26] in his remarkable pioneering work on multiplicative stochastic processes. The results in this paper differ somewhat with Kubo's results because he used some simplifying assumptions which we have found unnecessary. It will be seen that the analysis presented here goes beyond that of any of the other references cited in terms of the detailed account of what is happening dynamically. Two main consequences accrue: (1) A new kind of "intrinsic diffusion" is discovered which enables us to show ergodicity for the correlation formulae which appear, and (2) a connection with the dynamical origins of critical phenomena is seen. The first point will be emphasized as it comes up later in this section, while the second point will be discussed in the section following the next section.

Our starting point is the Hamiltonian

$$H = \frac{|\mathbf{P}|^2}{2M} + \sum_{j=1}^{N} \frac{|\mathbf{p}_j|^2}{2m} + \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) + \frac{1}{2}\sum_{j\neq k}^{N} U(\mathbf{r}_j, \mathbf{r}_k) \tag{56}$$

where the heavy particle has mass M, position $\mathbf{R}$, and momentum $\mathbf{P}$, and the fluid molecules have mass m, position $\mathbf{r}_j$, and momenta $\mathbf{p}_j$ where $j = 1, 2, \ldots, N$. $\varphi(\mathbf{R}, \mathbf{r}_j)$ is the interaction potential between fluid molecule j and the heavy particle, and $U(\mathbf{r}_j, \mathbf{r}_k)$ is the interaction potential for the fluid molecules. Because our description is that of a conservative system we may use Liouville's theorem to express the continuity equation corresponding with the phase space picture for the system:

$$\frac{\partial}{\partial t} f = -i\mathbf{L} f \tag{57}$$

where $f \equiv f(\mathbf{R}\mathbf{P}\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N t)$ and $-i\mathbf{L}$ is defined by

$$-i\mathbf{L} \equiv -\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}} - \sum_{j=1}^{N}\frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j} + \sum_{j=1}^{N}\nabla_{\mathbf{R}}\varphi(\mathbf{R}, \mathbf{r}_j)\cdot(\nabla_{\mathbf{P}} - \nabla_{\mathbf{p}_j}) + \sum_{j\neq k}\nabla_{\mathbf{r}_j}U(\mathbf{r}_j, \mathbf{r}_k)\cdot\nabla_{\mathbf{p}_j}. \tag{58}$$

The Liouville operator defined by (58) will be separated into two parts:

$$-i\mathbf{L}_B \equiv -\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}} + \sum_{j=1}^{N}\nabla_{\mathbf{R}}\varphi(\mathbf{R}, \mathbf{r}_j)\cdot\nabla_{\mathbf{P}}, \tag{59}$$

$$-i\mathbf{L}_R \equiv -\sum_{j=1}^{N}\frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j} + \sum_{j=1}^{N}\nabla_{\mathbf{r}_j}\varphi(\mathbf{R}, \mathbf{r}_j)\cdot\nabla_{\mathbf{p}_j} + \sum_{j\neq k}^{N}\nabla_{\mathbf{r}_j}U(\mathbf{r}_i, \mathbf{r}_k)\cdot\nabla_{\mathbf{p}_j}. \tag{60}$$

Now, define $\hat{f}$ by

$$f \equiv \exp(-it\mathbf{L}_R)\hat{f} \tag{61}$$

where $\hat{f} \equiv \hat{f}(\mathbf{R}\mathbf{P}\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N t)$. Using (57) through (61) leads to

$$\frac{\partial}{\partial t}\hat{f} = -i\tilde{\mathbf{L}}_B(t)\hat{f} \tag{62}$$

where $\tilde{\mathbf{L}}_B(t)$ is defined by

$$-i\tilde{\mathbf{L}}_B(t) \equiv \exp(it\mathbf{L}_R)(-i\mathbf{L}_B)\exp(-it\mathbf{L}_R). \tag{63}$$

Our notation suggests that $\tilde{\mathbf{L}}_B(t)$ is a stochastic operator. Of course, it is clearly not a stochastic operator as is explicitly evident if (59) and (60) are inserted into (63). However, it acts like a stochastic operator because the noncommutivity of $\mathbf{L}_B$ and $\mathbf{L}_R$ results in extremely rapid variations in $\tilde{\mathbf{L}}_B(t)$ if N is sufficiently large. Moreover, (59) and (60) may be used to exhibit $\mathbf{L}_B(t)$ as a sum of N similar terms. This suggests that to treat $\tilde{\mathbf{L}}_B(t)$ as Gaussian for large N is not unreasonable. Therefore, we shall invoke the nonperturbative, multiplicative stochastic, Markov approximation while we treat $\tilde{\mathbf{L}}_B(t)$ as stochastic.

It shall be assumed that the average of $\hat{f}$, $\langle\hat{f}\rangle$, factors for all time as follows:

$$\langle\hat{f}\rangle = g_B(Pt)W_R^{eq}(\mathbf{R}\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N) \tag{64}$$

where $W_R^{eq}(\mathbf{R}_1\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N)$ is the canonical equilibrium

distribution for the fluid molecules in the presence of the heavy particle at $\mathbf{R}$, and is given by

$$W_R^{eq}(\mathbf{R}\mathbf{r}_1\mathbf{p}_1\cdots\mathbf{r}_N\mathbf{p}_N) \equiv \frac{1}{Q_N}\exp\left[-\beta\left(\sum_{j=1}^{N}\frac{|\mathbf{p}_j|^2}{2m}+\sum_{j=1}^{N}\varphi(\mathbf{R},\mathbf{r}_j)+\frac{1}{2}\sum_{j\neq k}^{N}U(\mathbf{r}_j,\mathbf{r}_k)\right)\right] \tag{65}$$

where Q_N the normalization constant which satisfies

$$\int\cdots\int W_R^{eq}(\mathbf{R}\mathbf{r}_1\mathbf{p}_1\cdots\mathbf{r}_N\mathbf{p}_N)\,d\mathbf{R}\,d\mathbf{r}_1\cdots d\mathbf{r}_N\,d\mathbf{p}_1\cdots d\mathbf{p}_N = 1. \tag{66}$$

The heavy particle coordinates $\mathbf{R}$ appear in (65) because the inertia of the heavy particle is so large that the fluid molecules achieve thermal equilibrium relative to the instantaneous position $\mathbf{R}$ of the heavy particle very rapidly compared with the rate of change of the position $\mathbf{R}$. This situation is analogous to the technique used to derive the Langevin equation starting with a heavy particle in a fluctuating fluid, in which case the fluid fluctuations must be computed subject to boundary conditions representing the presence of the heavy particle.[7,28,29] The response of the fluid to the presence of the heavy particle must appear in the computation if sensible results are desired.

Returning to (62) and using (64) we get, on the average,

$$\frac{\partial}{\partial t}g_B(\mathbf{P}t) = -\int_0^\infty\int\cdots N\cdots\int\int\cdots N+1\cdots\int\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)\times W_R^{eq}(\mathbf{R}\mathbf{r}^N\mathbf{p}^N)\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}\,ds\,g_B(\mathbf{P}t), \tag{67}$$

where we have integrated over the fluid variables and $\mathbf{R}$, and the quantity

$$-\int_0^\infty\int\cdots N\cdots\int\int\cdots N+1\cdots\int\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)\,W_R^{eq}(\mathbf{R}\mathbf{r}^N\mathbf{p}^N)\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}\,ds \tag{68}$$

is almost the analog of the correlation strength given in (52). The minus sign comes from $(i)^2$ and $\mathbf{r}^N$ denotes $\mathbf{r}_1\cdots\mathbf{r}_N$ whereas $d^N\mathbf{r}$ denotes $d\mathbf{r}_1\cdots d\mathbf{r}_N$, etc. The integration over the variables in W_R^{eq} corresponds with the round brackets average in (48) and provides the analog of stationarity. Note that (68) is not exactly the analog of (52) because it is still an operator. Equation (67) is what would result if $\tilde{\mathbf{L}}_B(t)$ were really a stochastic, Gaussian process for which the Markov property holds. We have implicitly assumed that the average of $\tilde{\mathbf{L}}_B(t)$ is zero in writing (67). We shall digress for a moment and explicitly demonstrate that $\tilde{\mathbf{L}}_B(t)$ has a zero average, and that (68) is stationary. The average of $\tilde{\mathbf{L}}_B(t)$ is given by

$$\langle\langle\tilde{\mathbf{L}}_B(t)\rangle\rangle \equiv \int\cdots\int\tilde{\mathbf{L}}_B(t)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} = \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B\exp(-it\mathbf{L}_R)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}. \tag{69}$$

The operator given by (69) acts upon functions of $\mathbf{P}$. Using (60) and (65) it follows that

$$\exp(-it\mathbf{L}_R)(W_R^{eq}\psi(\mathbf{P})) = W_R^{eq}\exp(-it\mathbf{L}_R)(\psi(\mathbf{P})) = W_R^{eq}\psi(\mathbf{P}) \tag{70}$$

where $\psi(\mathbf{P})$ is an arbitrary function of $\mathbf{P}$, because $\mathbf{L}_R(W_R^{eq}) = 0$ and $\mathbf{L}_R(W_R^{eq}\psi(\mathbf{P})) = \mathbf{L}_R(W_R^{eq})\psi(\mathbf{P}) + W_R^{eq}\mathbf{L}_R(\psi(\mathbf{P}))$, and $\mathbf{L}_R(\psi(\mathbf{P})) = 0$ since $\mathbf{L}_R$ does not involve $\mathbf{P}$. Therefore, we have

$$\langle\langle\mathbf{L}_B(t)\rangle\rangle = \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}. \tag{71}$$

Expanding $\exp(it\mathbf{L}_R)$ in a power series and integrating each term by parts leads to

$$\langle\langle\tilde{\mathbf{L}}_B(t)\rangle\rangle = \int\cdots\int\mathbf{L}_B W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} \tag{72}$$

since all but the first term in the power series give zero because W_R^{eq} vanishes at the boundaries of integration. Using (59) and (65) gives

$$i\langle\langle\tilde{\mathbf{L}}_B(t)\rangle\rangle = \int\cdots\int\left[\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}}(W_R^{eq})+\nabla_{\mathbf{R}}(W_R^{eq})\cdot\frac{1}{\beta}\nabla_{\mathbf{P}}\right]d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} = 0 \tag{73}$$

where the second equality follows from integration by parts with respect to the coordinates $\mathbf{R}$. The stationarity relation follows from similar arguments beginning with

$$\langle\langle\tilde{\mathbf{L}}_B(t)\tilde{\mathbf{L}}_B(s)\rangle\rangle \equiv \int\cdots\int\tilde{\mathbf{L}}_B(t)\tilde{\mathbf{L}}_B(s)\,W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} = \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B\exp(-it\mathbf{L}_R)\times\exp(is\mathbf{L}_R)\mathbf{L}_B\exp(-is\mathbf{L}_R)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}. \tag{74}$$

Using an argument which is like that used in going from (70) to (71), we can go in the reverse direction and get

$$\begin{aligned}\langle\langle\mathbf{L}_B(t)\mathbf{L}_B(s)\rangle\rangle &= \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B\exp(-it\mathbf{L}_R)\times\exp(is\mathbf{L}_R)\mathbf{L}_B\exp(-is\mathbf{L}_R)\exp(it\mathbf{L}_R)\\ &\quad\times W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}\\ &= \int\cdots\int\mathbf{L}_B\exp[i(s-t)\mathbf{L}_R]\mathbf{L}_B\\ &\quad\times\exp[-i(s-t)\mathbf{L}_R]W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}\end{aligned} \tag{75}$$

where the second equality follows from an argument identical with that used to get from (71) to (72). Therefore, the quantity given by (68) is in general

$$\int_t^\infty\langle\langle\tilde{\mathbf{L}}_B(t)\tilde{\mathbf{L}}_B(s)\rangle\rangle\,ds = \int_t^\infty\langle\langle\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s-t)\rangle\rangle\,ds = \int_0^\infty\langle\langle L_B(0)L_B(s')\rangle\rangle\,ds' \tag{76}$$

where the first equality follows from (75) and the second equality follows from the change of variables $s' = s - t$. This ends our digression. The expression in (67) is an approximation to the exact behavior described by (62), and we shall analyze the detailed behavior of (68) regorously from here on, to the end of this section.

It is very convenient to get the W_R^{eq} term in (68) as far to the left as possible before attempting to perform integrations. This requires letting $\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)$ act on W_R^{eq} as is appropriate. Using (63) gives

$$-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)W_R^{eq}g_B = -\mathbf{L}_B\exp(is\mathbf{L}_R)\mathbf{L}_B\exp(-is\mathbf{L}_R)W_R^{eq}g_B. \tag{77}$$

As is indicated in (67) there will be an integration over $\mathbf{R}$. Using (59) for $\mathbf{L}_B$ and integrating over $\mathbf{R}$ by parts shows that

$$\int\cdots\int\left(-\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}}+\sum_{j=1}^{N}\nabla_{\mathbf{R}}\varphi(\mathbf{R},\mathbf{r}_j)\cdot\nabla_{\mathbf{P}}\right)\exp(is\mathbf{L}_R)\mathbf{L}_B\times\exp(-is\mathbf{L}_R)W_R^{eq}g_B\,d\mathbf{R}$$

$$= \int \cdots \int \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} (\exp(is\mathbf{L}_R)\mathbf{L}_B \times \exp(-is\mathbf{L}_R) W_R^{eq} g_B)\, d\mathbf{R} \tag{78}$$

where the integrated term at the boundaries vanishes because W_R^{eq} vanishes there. Equation (78) shows that the $\mathbf{L}_B$ on the left in (77) acts only through the potential term

$$-i\mathbf{L}_B' = \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}}. \tag{79}$$

Therefore, in effect (77) reduces to

$$-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \to -\mathbf{L}_B' \exp(is\mathbf{L}_R)\mathbf{L}_B \exp(-is\mathbf{L}_R) W_R^{eq} g_B, \tag{80}$$

at least after the $\mathbf{R}$ integration is performed. Returning to the justification of (70), we see that

$$\exp(-is\mathbf{L}_R) W_R^{eq} g_B = W_R^{eq} g_B. \tag{81}$$

Using (59) and (65), it is seen that

$$-i\mathbf{L}_B W_R^{eq} g_B = W_R^{eq} \left(-\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) \right) g_B. \tag{82}$$

Furthermore, we have

$$\exp(is\mathbf{L}_R) W_R^{eq} h = W_R^{eq} \exp(is\mathbf{L}_R) h, \tag{83}$$

where h is any function of the variables $\mathbf{P}$, $\mathbf{R}$, $\mathbf{r}_j$, and $\mathbf{p}_j$ for $j = 1, 2, \ldots, N$. This relation follows from the reasons given in justification of (70). Therefore, (80)—(83) give

$$\begin{aligned} &-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \\ &\to -\mathbf{L}_B' W_R^{eq} \exp(is\mathbf{L}_R) \left(-\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) \right) g_B \\ &= W_R^{eq} \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} \exp(is\mathbf{L}_R) \\ &\quad \times \left(-\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) \right) g_B \end{aligned} \tag{84}$$

where the last equality follows from a result analogous to (82) which depends upon (79):

$$-i\mathbf{L}_B' W_R^{eq} h = W_R^{eq} (-i\mathbf{L}_B') h. \tag{85}$$

The expression in (84) becomes an equality when the $\mathbf{R}$ integration is performed. Note also that the $\mathbf{P}/M \cdot \nabla_{\mathbf{R}}$ operator in (84) acts on g_B only, and because g_B depends upon $\mathbf{P}$ only the effect is zero. Therefore, (84) becomes

$$\begin{aligned} &-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \\ &\to W_R^{eq} \left(\sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_k) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{k=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_k) \right) g_B. \end{aligned} \tag{86}$$

Finally, since $\mathbf{L}_R$ does not contain $\mathbf{P}$, we may combine terms as follows:

$$\begin{aligned} &-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \\ &\to W_R^{eq} \left(\sum_{j=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j) \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k) \right) \frac{\partial}{\partial P_\mu} \left(\beta \frac{P_\nu}{M} + \frac{\partial}{\partial P_\nu} \right) g_B. \end{aligned} \tag{87}$$

Returning to (68), we have found that

$$\begin{aligned} &-\int_0^\infty \int \cdots N \cdots \int \int \cdots N+1 \cdots \int \tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} \\ &\quad \times d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, g_B \\ &\quad = \int \int \cdots N \cdots \int \int \cdots N+1 \cdots \int W_R^{eq} \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j) \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k) \right) \frac{\partial}{\partial P_\mu} \left(\beta \frac{P_\nu}{M} + \frac{\partial}{\partial P_\nu} \right) \\ &\quad \times d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, ds\, g_B. \end{aligned} \tag{88}$$

If for a moment we specialize the above results to one dimension, and use the fact that $P = Mu$, then we have

$$\frac{\partial}{\partial P_\mu} \left(\beta \frac{P_\nu}{M} + \frac{\partial}{\partial P_\nu} \right) \to \frac{\partial}{\partial u} \left(\beta \frac{u}{M} + \frac{1}{M^2} \frac{\partial}{\partial u} \right) \tag{89}$$

and

$$\begin{aligned} &\int_0^\infty \int \cdots \int W_R^{eq} \left(\sum_{j=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j) \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k) \right) d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, ds \\ &\quad \to \int_0^\infty \int \cdots \int W_R^{eq} \left(\sum_{j=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_j) \right) \exp(isL_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_k) \right) d^N r\, dR\, d^N p\, ds, \end{aligned} \tag{90}$$

where W_R^{eq} and L_R are one-dimensional expressions in the last expression above. Comparing these results with (4), we see that we have the Fokker—Planck equation for a Brownian particle in (67), if we use the one-dimensional analogs given by (89) and (90). Using (6), it is seen that we have the identity

$$\begin{aligned} \lambda = &\int_0^\infty \int \cdots \int W_R^{eq} \sum_{j=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_j) \exp(isL_R) \\ &\times \sum_{k=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_k)\, d^N r\, dR\, d^N p\, ds. \end{aligned} \tag{91}$$

This is all reasonable since we can readily associate

$$\sum_{j=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_j) \to -\tilde{F}(0)$$

and (92)

$$\exp(isL_R) \sum_{k=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_k) \to -\tilde{F}(s).$$

This second association is perhaps even clearer if we reinsert $\exp(-isL_R)$ on the right of the integrand of (91), which changes nothing as was seen in going from (69) to (71). The strength of the stationary correlation, $\langle\langle \tilde{F}(0)\tilde{F}(s) \rangle\rangle$, follows from (2) and a formula like (52)

which reads

$$\lambda = \int_0^\infty (\langle F(0)F(s)\rangle)\, ds. \tag{93}$$

In Eq. (88), we actually have the three-dimensional generalization of (4) which gives

$$\lambda_{\mu\nu} \equiv \int_0 \int \cdots \int W_R^{\mathrm{eq}} \left(\sum_{j=1}^N \frac{\partial}{\partial R_\mu}\varphi(\mathbf{R}, \mathbf{r}_j)\right) \exp(isL_R) \times \left(\sum_{k=1}^N \frac{\partial}{\partial R_\nu}\varphi(\mathbf{R}, \mathbf{r}_k)\right) d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, ds \tag{94}$$

where $\lambda_{\mu\nu}$ is the friction tensor,[7] and it is useful in describing rotational Brownian motion if the potential φ is not spherically symmetric.[29]

It is to be especially noted that $\exp(is\mathbf{L}_R)$ appears in (94) and not the full Liouville evolution operator $\exp(is\mathbf{L})$. This point has been emphasized by Mori,[30,31] who also gets this type of result from a different approach. Other treatments involve $\exp(is\mathbf{L})$ in analogous expressions, and lead to certain technical difficulties, sometimes referred to as the "plateau value problem."[23,24,27] The relationship of (94) to Kubo's transport coefficient formula may be found in the references just cited.

ERGODICITY

A phase space function $f(q_1 \cdots q_N p_1 \cdots p_N t)$ is said to be ergodic if

$$\lim_{s\to\infty} (f(q_1 \cdots q_N p_1 \cdots p_N 0) f(q_1 \cdots q_N p_1 \cdots p_N s)) = 0 \tag{95}$$

where $(\cdots)$ denotes the canonical, initial value average.[32] We would like to show that the force on the Brownian particle $\sum_{j=1}^N \partial/\partial R_\nu\, \varphi(R, r_j)$ in Eq. (94) is ergodic in the sense of (95). Furthermore, if the vanishing of the correlation function in (94) is fast enough, then the integral over s will be finite. To show ergodicity it is necessary to analyze the detailed structure of $\exp(is\mathbf{L}_R)$. In doing so, we will discover a phenomenon which we shall call "intrinsic diffusion." This intrinsic diffusion has interest in its own right, independently of our particular context here.[33]

The time ordered exponential for a time dependent operator which does not commute with itself at different times is defined by

$$\underset{\leftarrow}{T} \exp\left(\int_0^s \mathbf{O}(s')\, ds'\right) \equiv \sum_{n=1}^\infty \int_0^s \int_0^{s_1} \int_0^{s_2} \cdots \int_0^{s_{n-2}} \int_0^{s_{n-1}} \mathbf{O}(s_1)\mathbf{O}(s_2)\cdots\mathbf{O}(s_{n-1})\mathbf{O}(s_n) \times ds_n\, ds_{n-1} \cdots ds_2\, ds_1. \tag{96}$$

Given an operator of the form $\exp[is(\mathbf{A}+\mathbf{B})]$ where $\mathbf{A}$ and $\mathbf{B}$ are noncommuting differential operators, we have the following disentanglement theorem:

$$\exp[is(\mathbf{A}+\mathbf{B})] = \exp(is\mathbf{A}) \underset{\leftarrow}{T} \exp\left[i\int_0^s \exp(-is'\mathbf{A})\mathbf{B} \times \exp(is'\mathbf{A})\, ds'\right]. \tag{97}$$

Both sides of (97) are clearly equal for $s=0$, and differentiation of both sides for $s\neq 0$ gives identical results, proving the validity of (97).

When (97) is applied to $\exp(is\mathbf{L}_R)$, where we use (60), we get

$$\exp(is\mathbf{L}_R) = \exp\left(s\sum_{j=1}^N \frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right) \underset{\leftarrow}{T} \exp\left[-\int_0^s \exp\left(-s\sum_{k=1}^N \frac{\mathbf{p}_k}{m}\cdot\nabla_{\mathbf{r}_k}\right) \times\left(\sum_{l=1}^N \nabla_{\mathbf{r}_l}\varphi(\mathbf{R}, \mathbf{r}_l)\cdot\nabla_{\mathbf{p}_l} + \sum_{l\neq i}^N \nabla_{\mathbf{r}_l} U(\mathbf{r}_l, \mathbf{r}_i)\cdot\nabla_{\mathbf{p}_l}\right) \times \exp\left(s'\sum_{k'=1}^N \frac{\mathbf{p}_{k'}}{m}\cdot\nabla_{\mathbf{r}_{k'}}\right) ds'\right]. \tag{98}$$

The expression in (98) will be studied in detail in this paper with respect to the leading term only. This term is

$$\exp\left(s\sum_{j=1}^N \frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right). \tag{99}$$

The detailed analysis of this term will indicate how the analysis goes for higher-order terms, although in this paper no explicit expressions for the higher-order terms will be offered.

Returning to (94), we see that we need to calculate the canonical average of expression (99). We shall perform the momenta integrations first. The leading term in (99) gives

$$(2\pi m K_B T)^{-3N/2} \int \cdots \int \exp\left(-\beta\sum_{k=1}^N \frac{|\mathbf{p}_j|^2}{2m}\right) \times \exp\left(s\sum_{j=1}^N \frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right) d^N\mathbf{p} = (2\pi m K_B T)^{-3N/2} \prod_{j=1}^N \int\int\int \exp\left(-\beta\frac{|\mathbf{p}_j|^2}{2m}\right) \exp\left(s\frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right) d\mathbf{p}_j. \tag{100}$$

For a fixed j, we shall now consider the integral over the x component of $\mathbf{p}_j$ because the other components and the other momenta integrals all work out similarly. We have, therefore, as a typical integral

$$(2\pi m K_B T)^{-1/2} \int_{-\infty}^{\infty} \exp\left(-\beta\frac{p_{jx}^2}{2m}\right) \exp\left(s\frac{p_{jx}}{\partial x}\frac{\partial}{\partial x}\right) dp_{jx} = \sum_{n=0}^\infty \frac{[(s/m)(\partial/\partial x)]^n}{n!}\langle p_{jx}^n\rangle \tag{101}$$

where

$$\langle p_{jx}^n\rangle \equiv (2\pi m B K_B T)^{-1/2} \int_{-\infty}^{\infty} p_{jx}^n \exp\left(-\beta\frac{p_{jx}^2}{2m}\right) dp_{jx}.$$

These Gaussian integrals are well known and are given by

$$\langle p_{jx}^n\rangle = 0 \qquad \text{for } n = 2m+1 \text{ where } m = 0, 1, 2, \cdots$$

and (102)

$$\langle p_{jx}^n\rangle = \frac{(2m)!}{2^m m!}\langle p_{jx}^2\rangle^m \quad \text{for } n = 2m \text{ where } m = 0, 1, 2, \cdots.$$

Inserting these averages into (101) gives

$$(2\pi m K_B T)^{-1/2} \int_{-\infty}^{\infty} \exp\left(-\beta\frac{p_{jx}^2}{2m}\right) \exp\left(s\frac{p_{jx}}{m}\frac{\partial}{\partial x}\right) dp_{jx} = \exp\left(s^2\frac{K_B T}{2m}\frac{\partial^2}{\partial x^2}\right) \tag{103}$$

because $\langle p_{jx}^2\rangle = m K_B T$. Returning to (100), we get

$$(2\pi m K_B T)^{-3N/2} \prod_{j=1}^{N} \iiint \exp\left(-\beta \frac{|\mathbf{p}_j|^2}{2m}\right) \exp\left(s \frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j}\right) d\mathbf{p}_j = \prod_{j=1}^{N} \exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_j}\right). \tag{104}$$

If only the leading term in (99) is used in expression (94), then the canonical momenta averages give

$$\lambda^0_{\mu\nu} = \int_0^\infty \cdots \int W^{eq}_*(\mathbf{R}, \mathbf{r}_1 \cdots \mathbf{r}_N) \left(\sum_{j=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j)\right) \times \prod_{l=1}^{N} \exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_l}\right) \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k)\right) d^N\mathbf{r}\, d\mathbf{R}\, ds \tag{105}$$

where $W^{eq}_*(\mathbf{R}, \mathbf{r}_1 \cdots \mathbf{r}_N)$ is the coordinate dependent factor in W^{eq}_R, and the superscript on $\lambda^0_{\mu\nu}$ indicates the lowest order truncation of the series implicit in (98) by virtue of (96). A typical term in (105) has an integrand factor such as

$$\exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_l}\right) \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_l)\right). \tag{106}$$

We shall express (106) in a different form which is suggested by an analogy with diffusion. It is worthwhile to digress for a moment in order to make the analogy clear.

The diffusion equation in three dimensions is

$$\frac{\partial}{\partial t} D(\mathbf{r}, t) = D \nabla^2_{\mathbf{r}} D(\mathbf{r}, t) \tag{107}$$

where D is the diffusion constant. A formal solution to (107) may be written as

$$D(\mathbf{r}, t) = \exp(tD\nabla^2_{\mathbf{r}}) D(\mathbf{r}, 0) \tag{108}$$

as is readily verified by differentiation. In addition, the solution to (107) in an infinite volume, with the initial condition $D(\mathbf{r}, 0) = \delta(\mathbf{r} - \mathbf{r}^0)$, is given by

$$D_G(\mathbf{r}, t) = (4\pi D t)^{-3/2} \exp - \frac{|\mathbf{r} - \mathbf{r}^0|^2}{4Dt} \tag{109}$$

where the subscript G indicates that this solution can be used as a Green's function, which enables us to conclude from (108) and (109) that

$$\exp(tD\nabla^2_{\mathbf{r}}) D(\mathbf{r}, 0) = (4\pi D t)^{-3/2} \iiint \exp - \frac{|\mathbf{r} - \mathbf{r}^0|^2}{4Dt} D(\mathbf{r}^0, 0)\, d\mathbf{r}^0 \tag{110}$$

for arbitrary initial distrubutions $D(\mathbf{r}^0, 0)$.

The analogy between these results for diffusion and expression (106) should be clear. The important differences are $K_B T/2m$ in (106) where D is in (108), and s^2 in (106) where t is in (108). However, remarkably enough, there is a Green's function which goes with (106) given by

$$\exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_l}\right) \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_l)\right) = \left(4\pi \frac{K_B T}{2m} s^2\right)^{-3/2} \iiint \exp\left(-\frac{|\mathbf{r}_l - \mathbf{r}'_l|^2}{4(K_B T/2m)s^2}\right) \times \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}'_l)\right) d\mathbf{r}'_l. \tag{111}$$

The corresponding differential equation follows from (106) and is

$$\frac{\partial}{\partial s} D(\mathbf{r}, s) = 2s \frac{K_B T}{2m} \nabla^2_{\mathbf{r}}(\mathbf{r}, s) \tag{112}$$

which is analogous with (107). One may check all this by showing that the Green's function in (111) satisfies (112) with initial condition $D(\mathbf{r}, 0) = \delta(\mathbf{r} - \mathbf{r}^0)$, in an infinite volume. We shall refer to the behavior exhibited by (111) as "intrinsic diffusion" to distinguish it from true diffusion as exhibited by (110) while suggesting the marked similarities. Notice in particular, that "intrinsic diffusion" acts like true diffusion with a diffusion coefficient which grows linearly with time: $D \to (K_B T/2m)s$. Therefore, "intrinsic diffusion" smooths out coordinate dependent functions increasingly rapidly compared with true diffusion. Moreover, it increases the rate of smoothing proportionately with temperature and inverse fluid molecule mass.

Returning to (105), and using (111), we get

$$\lambda^0_{\mu\nu} = \sum_{j=1}^{N} \sum_{k=1}^{N} \int_0^\infty \cdots \int W^{eq}_*\left(\frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j)\right) \left(4\pi \frac{K_B T}{2m} s^2\right)^{-3/2} \times \exp\left(-\frac{|\mathbf{r}_k - \mathbf{r}'_k|^2}{4(K_B T/2m)s^2}\right) \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}'_k)\right) d^N\mathbf{r}'\, d^N\mathbf{r}\, d\mathbf{R}\, ds. \tag{113}$$

It is convenient to use a Fourier transformation representation of the potentials in evaluating further expression (113). Define $\hat{\varphi}(\rho)$ by

$$\varphi(\mathbf{R}, \mathbf{r}_k) \equiv \frac{1}{2\pi}^3 \iiint \exp[i\rho \cdot (\mathbf{R} - \mathbf{r}_k)] \hat{\varphi}(\rho)\, d\rho \tag{114}$$

using (111) in (113) with (114) gives

$$\lambda^0_{\mu\nu} = \sum_{j=1}^{N} \sum_{k=1}^{N} \int_0^\infty \cdots \int W^{eq}_*\left(\frac{1}{2\pi}\right)^6 (i\rho_\mu) \exp[i\rho \cdot (\mathbf{R} - \mathbf{r}_j)] \hat{\varphi}(\rho) \times \exp\left(-s^2 \frac{K_B T}{2m} |\rho'|^2\right) \exp[i\rho' \cdot (\mathbf{R} - \mathbf{r}_k)] \hat{\varphi}(\rho') \times d\rho'\, d\rho\, d^N\mathbf{r}\, d\mathbf{R}\, ds. \tag{115}$$

Equation (115) also follows directly from (105) using (114). In getting (115) we have used $\exp[s^2(K_B T/2m)\nabla^2_{\mathbf{r}}] \times \exp(i\rho' \cdot \mathbf{r}) = \exp[-s^2(K_B T/2m)|\rho'|^2]$. Either (113) or (115) shows that to this lowest order of truncation we have ergodic behavior. Note that in (115) the $\rho' = 0$ term, which does not decay, is multiplied by $i\rho'_\nu$, which is zero. In (113) we see that qualitatively, "intrinsic diffusion" smoothes out the force at time s, for large s, so that we are left with the canonical coordinate average of the initial force times essentially a constant:

$$\lim_{s \to \infty} (\text{time integrand of } \lambda^0_{\mu\nu}) \approx \sum_{j=1}^{N} \sum_{k=1}^{N} \int \cdots \int W^{eq}_*\left(\frac{\partial}{\partial R_\mu} \varphi(R, r_j)\right) C\, d^N\mathbf{r}\, d\mathbf{R} = 0 \tag{116}$$

where C is the constant corresponding with the smoothed force at time s, and the second equality follows from a result similar to (73). In addition, (115) may be integrated over s explicitly giving

$$\lambda^0_{\mu\nu} = \sum_{j=1}^{N}\sum_{k=1}^{N}\int\cdots\int W^{eq}_{*}\left(\frac{1}{2\pi}\right)^6 (i\rho_\mu)\exp[i\rho\cdot(\mathbf{R}-\mathbf{r}_j)]\hat{\varphi}(\rho)$$
$$\times\left(\frac{\pi m}{2K_BT|\rho'|^2}\right)^{1/2}(i\rho'_\nu)\exp[i\rho'\cdot(\mathbf{R}-\mathbf{r}_k)]\,\hat{\varphi}(\rho')$$
$$\times d\rho'\,d\rho\,d^N\mathbf{r}\,d\mathbf{R}. \qquad (117)$$

As long as $\hat{\varphi}(0)$ is finite, the $(|\rho'|^2)^{1/2}$ denominator in (117) does not create a divergence because of the factor $(i\rho'_\nu)$. If $\varphi(\mathbf{R},\mathbf{r}_k)$ is spherically symmetric, (114) may be inverted to show that $\hat{\varphi}(0) = 4\pi\int_0^\infty r^2\varphi(r)\,dr$, which is finite for a large class of physically reasonable potentials, which do not possess too terribly singular hard cores, and which tail off rapidly with increased separation of the interacting particles. The presence of W^{eq}_{*} in (117) makes it effectively impossible to perform the coordinate integrals in general. We will end our present discussion of $\lambda^0_{\mu\nu}$ by approximating the coordinate integrals for high temperatures.

At sufficiently high temperatures we shall approximate W^{eq}_{*} by $V^{-(N+1)}$, where V is the volume of our system, which volume we have been taking to be essentially infinite during much of the preceeding analysis. Although (113) is valid only for an infinite V, since the Green's function in its integrand obtains only for an infinite V, (117) is valid for finite V since it follows from (105) and (114) without any restriction on V. The approximation for W^{eq}_{*} by $V^{-(N+1)}$ requires that the potential have a hard core repulsion which, while very large, is finite. The limit $V\to\infty$ is accompanied by $N\to\infty$ while N/V remains equal to a constant $\hat{n}$. This is the thermodynamic limit. With the thermodynamic limit the coordinate integrals in (117) can be performed, and we get

$$\lambda^0_{\mu\nu} \approx \lim_{\text{thermo}} V^{-(N+1)}\sum_{j=1}^{N}\sum_{k=1}^{N}\int\cdots\int\left(\frac{1}{2\pi}\right)^6(i\rho_\mu)$$
$$\times\exp[i\rho\cdot(\mathbf{R}-\mathbf{r}_j)]\hat{\varphi}(\rho)\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho'|}(i\rho'_\nu)$$
$$\times\exp[i\rho'\cdot(\mathbf{R}-\mathbf{r}_k)]\hat{\varphi}(\rho')\,d\rho'\,d\rho\,d^N\mathbf{r}\,d\mathbf{R}$$
$$= \hat{n}\iiint\frac{1}{2\pi}^3(\rho_\mu\rho_\nu)|\hat{\varphi}(\rho)|^2\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho|}\,d\rho$$
$$+\hat{n}^2\iiint\delta(\rho)(\rho_\mu\rho_\nu)|\hat{\varphi}(\rho)|^2\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho|}\,d\rho$$
$$= \hat{n}\iiint\frac{1}{2\pi}^3(\rho_\mu\rho_\nu)|\hat{\varphi}(\rho)|^2\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho|}\,d\rho. \qquad (118)$$

The expression given by the second equality has a term proportional to $\hat{n}$ which comes from the double sum $\sum_j\sum_k$ when $j=k$, and a term proportional to $\hat{n}^2$ which comes when $j\neq k$. The $\mathbf{R}$ integration produced a factor $\delta(\rho+\rho')$ which converted $\hat{\varphi}(\rho)\hat{\varphi}(\rho')$ into $\hat{\varphi}(\rho)\hat{\varphi}(-\rho)$ $=\hat{\varphi}(\rho)\hat{\varphi}^*(\rho)\equiv|\hat{\varphi}(\rho)|^2$ as is seen using (114). The $|\rho|$ denominator in each term causes no trouble because of compensating numerator factors in $\rho_\mu\rho_\nu$, which also explain how the $\hat{n}^2$ term vanishes. If $|\hat{\varphi}(\rho)|^2$ vanishes for large $|\rho|$ sufficiently rapidly, then the remaining integral is finite. In general, when W^{eq}_{*} is present and no approximation is used the value of $\lambda^0_{\mu\nu}$ does not have such simple $\hat{n}$ or T dependence.

These techniques need to be extended for the analysis of higher order terms in (94) using (98).

CRITICAL BEHAVIOR

That something can be said about critical behavior within the context of this paper follows from the observation that a Brownian particle can be used as a probe which manifests the state of a fluid. If the fluid passes through a phase transition, the Brownian particle should exhibit noticeably altered behavior. In particular, for high enough temperatures the fluid will be a liquid or gas, and the Brownian motion should be normal with a finite value for $\lambda_{\mu\nu}$. However, if we freeze the fluid, we should expect that $\lambda_{\mu\nu}\to\infty$. Using (6) and (8), we see that this implies a vanishing diffusion constant D.[34]

If a complete analysis of (94) using (98) were possible, we would end up with the infinite series: $\lambda_{\mu\nu}=\lambda^0_{\mu\nu}+\lambda^1_{\mu\nu}+\lambda^2_{\mu\nu}+\cdots$ in which the superscripts indicate the number of times a potential appears in the corresponding term. We suspect that intrinsic diffusion will result in each term being finite, as was seen for $\lambda^0_{\mu\nu}$. When $T=0$, however, we have a special case in which each term is in fact infinite. For $\lambda^0_{\mu\nu}$, this is seen in (115) because the exponential can no longer damp out the integrand when $T=0$. Consequently, $\lambda_{\mu\nu}$ diverges for $T=0$; a fact consistent with intuitive expectations. For $T\neq0$ each term in $\lambda_{\mu\nu}=\lambda^0_{\mu\nu}+\lambda^1_{\mu\nu}+\lambda^2_{\mu\nu}+\cdots$ will be finite, or at least this is plausible following our analysis of $\lambda^0_{\mu\nu}$, and if the temperature is sufficiently large, we expect the series to be summable. This expectation is based upon qualitative analysis of (94) using (98) which suggests that the $\lambda_{\mu\nu}$ series goes like a series in powers of the ratio of potential energy and thermal energy. For large temperatures this ratio gets small and the series converges. The possibility exists that each term in $\lambda_{\mu\nu}=\lambda^0_{\mu\nu}+\lambda^1_{\mu\nu}+\lambda^2_{\mu\nu}+\cdots$ is finite while the sum diverges, if the temperature is small, but nonzero. This suggests that there exists a temperature T_c such that for $T>T_c$ the series sums while for $T\leq T_c$ the series diverges, even though it is comprised of finite terms. If T_c exists, we identify it as the critical temperature for the fluid. It is desirable to try to achieve a rigorous basis for the analysis of (94) using (98) so that these conjectures may be tested.

CONCLUDING REMARKS

The theory of multiplicative stochastic processes has provided a method for nonperturbative approximate solution of complicated dynamical equations. It has been shown how to interpret an exact dynamical quantity as a stochastic quantity. By such an interpretation an averaged equation is written which serves as a nonperturbative approximation for the original dynamics. In this manner we have derived the Fokker–Planck equation for Brownian motion, starting from the exact dynamics for a heavy particle moving in a molecular fluid.

The discovery of "intrinsic diffusion" has permitted an analysis of the ergodicity of the force autocorrelation function which was derived. Because Brownian motion leads to ordinary diffusion, "intrinsic diffusion" and ordinary diffusion are connected by our analysis. "Intrinsic diffusion" will also arise in other contexts.[33]

The analysis of Brownian motion in this paper leads to a calculation of λ, the dissipative constant, in terms of the interparticle potentials. The calculation involves the time integral of a force autocorrelation function which connects λ with the dynamics of the system. A conjectured relationship between λ and critical phenomena is presented, which if eventually justified rigorously, would provide a dynamical basis for the understanding of some aspects of critical behavior.

In our other work on the quantum mechanical density matrix,[3,5] the problem of calculating the matrices, $Q_{\alpha\beta\mu\nu}$, which are the analogs of λ, has been raised. We shall pursue this problem in another paper.

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APPENDIX: DERIVATION OF (50) FROM (48) AND (49).

The correlation formula in (48) follows directly from the solution to Eqs. (1) and (2). In addition, the Gaussian property of $\tilde{F}(t)$ in (1) is inherited by $\tilde{p}(t)$ in (48).[11] This implies

$$\langle\langle \tilde{p}(t_1)\cdots\tilde{p}(t_{2m-1})\rangle\rangle = 0 \quad \text{for } m = 1, 2, \cdots \tag{A1}$$

and

$$\begin{aligned}\langle\langle \tilde{p}(t_1)\cdots\tilde{p}(t_{2m})\rangle\rangle &= \frac{1}{2^m m!}\sum_{p\in S_{2m}}\prod_{j=1}^{m}\langle\langle \tilde{p}(t_{p(2j-1)})\tilde{p}(t_{p(2j)})\rangle\rangle \\ &= \frac{(MK_BT)^m}{2^m m!}\sum_{p\in S_{2m}}\prod_{j=1}^{m}\times\exp\left[-\frac{\alpha}{M}\left|t_{p(2j)}-t_{(2j-1)}\right|\right] \\ &\qquad \text{for } m = 1, 2, \cdots\end{aligned} \tag{A2}$$

The formal solution to (49) is

$$f(x,t) = \exp\left(-\int_0^t \frac{\tilde{p}(s)}{M}\,ds\frac{\partial}{\partial x}\right)f(x,0), \tag{A3}$$

as is verified by substitution and differentiation. Expanding the exponential and averaging gives

$$\langle\langle f(x,t)\rangle\rangle = \left[\left\langle\sum_{n=0}^{\infty}\left(-\frac{1}{M}\right)^n\frac{1}{n!}\left(\int_0^t\tilde{p}(s)\,ds\right)^n\frac{\partial^n}{\partial x^n}\right\rangle\right]f(x,0). \tag{A4}$$

Using (A1) and (A2) in (A4) gives

$$\begin{aligned}\langle\langle f(x,t)\rangle\rangle &= \sum_{m=0}^{\infty}\left(-\frac{1}{M}\right)^{2m}\frac{1}{(2m)!}\frac{(MK_BT)^m}{2^m m!}\sum_{p\in S_{2m}}\prod_{j=1}^{m}\int_0^t\int_0^t \\ &\quad\times\exp\left(-\frac{\alpha}{M}\left|t_{p(2j)}-t_{p(2j-1)}\right|\right)dt_{p(2j)}\,dt_{p(2j-1)} \\ &\quad\times\frac{\partial^{2m}}{\partial x^{2m}}f(x,0) \\ &= \sum_{m=0}^{\infty}\left(\frac{K_BT}{M}\right)^{2m}\frac{1}{2^m m!}\left(\int_0^t\int_0^t\exp\left[-\frac{\alpha}{m}\left|s-s'\right|\right]ds\,ds'\right)^m \\ &\quad\times\left(\frac{\partial^2}{\partial x^2}\right)^m f(x,0) \\ &= \sum_{m=0}^{\infty}\frac{1}{2^m m!}\frac{1}{M^{2m}}\left(\int_0^t\int_0^t\langle\langle\tilde{p}(s)\tilde{p}(s')\rangle\rangle\,ds\,ds'\right)^m \\ &\quad\times\left(\frac{\partial^2}{\partial x^2}\right)^m f(x,0).\end{aligned} \tag{A5}$$

Therefore,

$$\frac{\partial}{\partial t}\langle\langle f(x,t)\rangle\rangle = \int_0^t\frac{1}{M^2}\langle\langle\tilde{p}(t)\tilde{p}(s)\rangle\rangle\,ds\frac{\partial^2}{\partial x^2}\langle\langle f(xt)\rangle\rangle \tag{A6}$$

which is (50), and which follows from (A5) by differentiation, followed by rearrangement of terms.

Equation (A6) can be integrated to give (51) of the text. The solution to (51) is given by

$$\begin{aligned}\langle\langle f(xt)\rangle\rangle &= \left\{4\pi\frac{K_BT}{\alpha}\left[t-\frac{M}{\alpha}+\frac{M}{\alpha}\exp\left(-\frac{\alpha}{M}t\right)\right]\right\}^{-1/2} \\ &\quad\times\exp\left(-\frac{\alpha}{4K_BT}\frac{(x-x_0)^2}{\{t-(M/\alpha)+(M/\alpha)\exp[-(\alpha/M)t]\}}\right)\end{aligned} \tag{A7}$$

if $\langle\langle f(x,0)\rangle\rangle = \delta(x-x_0)$. This expression can be checked by substitution. It leads to the Orstein—Fürth formula[35]

$$\langle\langle x(t)-x_0)^2\rangle\rangle = \frac{2MK_BT}{\alpha^2}\left[\frac{\alpha}{M}t-1+\exp\left(-\frac{\alpha}{M}t\right)\right]. \tag{A8}$$

Note also that for the short times, $t < M/\alpha$, that (A7) reduces to

$$\left(4\pi\frac{K_BT}{2M}t^2\right)^{-1/2}\exp\left(-\frac{(x-x_0)^2}{4(K_BT/2M)t^2}\right) \tag{A9}$$

which is the Green's function for intrinsic diffusion in the text. However, for long time, $t > M/\alpha$, (A7) becomes the one-dimensional analog of (109) in the text which is valid for ordinary diffusion. The intrinsic diffusion Green's function has the form (A9) for all times!

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Application of cumulant techniques to multiplicative stochastic processes

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The use of cumulant techniques for analyzing time dependent, stochastic matrix expressions of the form $\langle \underline{T} \exp[\int_0^t \tilde{\mathbf{B}}(S)dS] \rangle$ is explained. Because cumulants are complicated expressions when $\tilde{\mathbf{B}}(t)$ does not commute with itself at unequal times, we explicitly work out cumulant expressions up to fourth order. The fourth order terms can be used to demonstrate that noncommutivity prevents the generalization, to time-dependent, stochastic matrices which do not commute with themselves at unequal times, of the result which applies to commuting stochastic processes that states: If the stochastic process is Gaussian, then its cumulant expansion truncates after the second cumulant. Furthermore, it is argued that if the stochastic matrix process is both Gaussian *and* purely random then the cumulant expansion does truncate after the second cumulant, after all. The significance of this result with respect to the application of approximation involving cumulants is mentioned.

INTRODUCTION

It is the purpose of this paper to apply cumulant techniques to the analysis of multiplicative stochastic processes.[1] When the stochastic matrices, which appear in the differential equations defining a particular multiplicative stochastic process, have special properties, the use of cumulants can lead to significant simplifications in the analysis of solutions to the differential equations. In general, when no special conditions are imposed on the properties of the stochastic matrices, cumulant expressions contain all of the information of the original problem, but without any particular advantages for further analysis. Kubo[2] has introduced cumulant techniques for the study of multiplicative stochastic processes, and he has attempted to approach the problem in as general a setting as possible. Fox[1] has studied multiplicative stochastic processes without using cumulant techniques, and has restricted his approach to the problem to the use of stochastic matrices which are purely random and Gaussian. It will be demonstrated in this paper that the restriction to purely random, Gaussian, stochastic matrices corresponds with the special conditions alluded to earlier for which cumulant techniques are most useful.

In the course of this paper we will show how the utility of cumulant techniques is related to the Gaussian property of the stochastic matrices. When the stochastic matrices are time independent, the Gaussian property alone guarantees major simplifications in analysis if cumulants are used. When the stochastic matrices are time dependent and do not commute for unequal times, then the Gaussian property alone is insufficient, and must be augmented by the purely random property if efficacy is to be achieved using cumulant methods. It is this last point that requires emphasis when one is using approximation methods which rely upon cumulants expansions.

TIME ORDERING AND CUMULANTS

Consider a multiplicative stochastic process described by[1]

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{1}$$

in which $A_{\alpha\alpha'} = -A_{\alpha'\alpha}$, $\tilde{A}_{\alpha\alpha'}(t) = -\tilde{A}_{\alpha'\alpha}(t)$, $\tilde{A}_{\alpha\alpha'}(t)$ is a stochastic matrix with averaged value zero, $\alpha = 1, 2, \ldots, N$, and repeated indices are summed. If $\tilde{A}_{\alpha\alpha'}(t)$ had a nonzero averaged value, we could include its averaged value in the term $A_{\alpha\alpha'}$ and start over again with $\tilde{A}_{\alpha\alpha'}(t) - \langle \tilde{A}_{\alpha\alpha'}(t) \rangle$ as the stochastic matrix, where $\langle \cdots \rangle$ denotes stochastic averaging. We would then have a process such as described by (1) with the average value of $\tilde{A}_{\alpha\alpha'}(t)$ equal to zero. A useful manner for obtaining the solution to (1) is to use the transformation

$$a_\alpha(t) = [\exp(t\mathbf{A})]_{\alpha\alpha'}b_{\alpha'}(t). \tag{2}$$

Consequently, the b_α's satisfy

$$\begin{aligned}\frac{d}{dt}b_\alpha(t) &= [\exp(-t\mathbf{A})]_{\alpha\beta}\tilde{A}_{\beta\beta'}(t)[\exp(t\mathbf{A})]_{\beta'\alpha'}b_{\alpha'}(t) \\ &\equiv \tilde{B}_{\alpha\alpha'}(t)b_{\alpha'}(t)\end{aligned} \tag{3}$$

where the second equality defines $\tilde{\mathbf{B}}(t)$. Note that the averaged value of $\tilde{\mathbf{B}}(t)$ is zero since it is linear in the matrix elements of $\tilde{\mathbf{A}}(t)$. In general, $\mathbf{A}$ and $\tilde{\mathbf{A}}(t)$ will not commute, neither will $\tilde{\mathbf{A}}(t)$ and $\tilde{\mathbf{A}}(s)$ nor $\tilde{\mathbf{B}}(t)$ and $\tilde{\mathbf{B}}(s)$ for $t \neq s$.

The formal solution to (3) must be written with a time ordered exponential[3] defined by

$$\begin{aligned}b_\alpha(t) &= [\underline{T}\exp(\textstyle\int_0^t \tilde{\mathbf{B}}(s)\,ds)]_{\alpha\alpha'}b_{\alpha'}(0) \\ &\equiv \sum_{n=0}^{\infty}\int_0^t\int_0^{t_1}\int_0^{t_2}\cdots\int_0^{t_{n-2}}\int_0^{t_{n-1}}[\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\cdots \\ &\quad \tilde{B}_{\mu_{n-2}\mu_{n-1}}(t_{n-1})\tilde{B}_{\mu_{n-1}\alpha'}(t_n)]\,dt_n\,dt_{n-1}\cdots dt_2\,dt_1 b_{\alpha'}(0)\end{aligned} \tag{4}$$

where the $n=0$ term is defined to be 1. If $\tilde{\mathbf{B}}(t)$ and $\tilde{\mathbf{B}}(s)$ commuted for $t \neq s$, then (4) would reduce to an ordinary exponential

$$\sum_{n=0}^{\infty}\frac{1}{n!}\int_0^t\cdots n\cdots\int_0^t[\tilde{B}_{\alpha\mu_1}(S_1)\cdots\tilde{B}_{\mu_{n-1}\alpha'}(S_n)]dS_n\cdots dS_1 b_{\alpha'}(0).$$

If $\tilde{\mathbf{B}}(t)$ is in fact time independent, then all time integrations are easily performed giving the ordinary exponential

$$\sum_{n=0}^{\infty}\frac{1}{n!}t^n[(\tilde{B})^n]_{\alpha\alpha'}b_{\alpha'}(0).$$

Cumulants arise when one wishes to perform the stochastic average of an expression like (4) or its more simple forms given above, at the end of the preceeding

paragraph. Historically speaking, cumulants arose in statistics and were known as Thiele semi-invariants.[4]

Suppose that we have a time independent stochastic variable $\tilde{X}$ and we are interested in calculating $\langle \exp(\tilde{X}) \rangle$, where $\tilde{X}$ may be either a scalar or a matrix stochastic quantity determined by the distribution function for its values. The cumulants for $\tilde{X}$ are defined by

$$\langle \exp(\tilde{X}) \rangle = \left\langle \sum_{n=0}^{\infty} \frac{1}{n!} (\tilde{X})^n \right\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \langle (\tilde{X})^n \rangle$$
$$\equiv \exp\left(\sum_{n=1}^{\infty} \frac{1}{n!} \langle (\tilde{X})^n \rangle_c \right) \tag{5}$$

where $\langle \cdots \rangle_c$ denotes the cumulant average. Cumulant averaging is by definition a homogeneous process with respect to multiplication of $\tilde{X}$ by a constant, just as is the case with ordinary averaging. Therefore, $\langle (\lambda \tilde{X})^n \rangle_c = \lambda^n \langle (\tilde{X})^n \rangle_c$, and

$$\langle \exp(\lambda \tilde{X}) \rangle = \exp\left(\sum_{n=1}^{\infty} \frac{\lambda^n}{n!} \langle (\tilde{X})^n \rangle_c \right). \tag{6}$$

Differentiating (6) n times with respect to λ, followed by setting $\lambda = 0$, gives for $n = 1, 2, 3, 4, \cdots$

$$\begin{aligned}
&\langle \tilde{X} \rangle = \langle \tilde{X} \rangle_c, \\
&\langle (\tilde{X})^2 \rangle = \langle (\tilde{X})^2 \rangle_c + \langle \tilde{X} \rangle_c^2, \\
&\langle (\tilde{X})^3 \rangle = \langle (\tilde{X})^3 \rangle_c + 3\langle (\tilde{X})^2 \rangle_c \langle \tilde{X} \rangle_c + \langle \tilde{X} \rangle_c^3, \\
&\langle (\tilde{X})^4 \rangle = \langle (\tilde{X})^4 \rangle_c + 4\langle (\tilde{X})^3 \rangle_c \langle \tilde{X} \rangle_c + 3\langle (\tilde{X})^2 \rangle_c^2 + 6\langle (\tilde{X})^2 \rangle_c \langle \tilde{X} \rangle_c^2 + \langle \tilde{X} \rangle_c^4 \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot
\end{aligned} \tag{7}$$

Starting with the first line, these equations may be successively inverted to give expressions for cumulant averages in terms of ordinary stochastic averages:

$$\begin{aligned}
&\langle \tilde{X} \rangle_c = \langle \tilde{X} \rangle, \\
&\langle (\tilde{X})^2 \rangle_c = \langle (\tilde{X})^2 \rangle - \langle \tilde{X} \rangle^2, \\
&\langle (\tilde{X})^3 \rangle_c = \langle (\tilde{X})^3 \rangle - 3\langle (\tilde{X})^2 \rangle \langle \tilde{X} \rangle + 2\langle \tilde{X} \rangle^3, \\
&\langle (\tilde{X})^4 \rangle_c = \langle (\tilde{X})^4 \rangle - 4\langle (\tilde{X})^3 \rangle \langle \tilde{X} \rangle - 3\langle (\tilde{X})^2 \rangle^2 + 12\langle (\tilde{X})^2 \rangle \langle \tilde{X} \rangle^2 - 6\langle \tilde{X} \rangle^4 \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot
\end{aligned} \tag{8}$$

It is possible to define cumulants even when we are dealing with time-dependent stochastic matrices which do not commute at unequal times.[2] One gets time-ordered cumulants defined by

$$\left\langle \underset{\leftarrow}{T} \exp\left(\int_0^t \tilde{\mathbf{B}}(S)\, dS \right) \right\rangle \equiv \underset{\leftarrow}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \int_0^{t_1} \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} \times \langle \tilde{\mathbf{B}}(t_1) \tilde{\mathbf{B}}(t_2) \cdots \tilde{\mathbf{B}}(t_{n-1}) \tilde{\mathbf{B}}(t_n) \rangle_c \times dt_n\, dt_{n-1} \cdots dt_2\, dt_1 \right). \tag{9}$$

Because it is so easy to misinterpret the precise meaning of (9), we introduce here the following notational scheme which permits unambiguous rendering of (9). Define $g_{\alpha\beta}^{(n)}(t_1)$ by

$$g_{\alpha\beta}^{(n)}(t_1) \equiv \int_0^{t_1} \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \cdots \tilde{B}_{\mu_{n-2}\mu_{n-1}}(t_{n-1}) \tilde{B}_{\mu_{n-1}\beta}(t_n) \rangle_c\, dt_n\, dt_{n-1} \cdots dt_3\, dt_2. \tag{10}$$

Therefore,

$$\left\langle \underset{\leftarrow}{T} \exp\left(\int_0^t \tilde{\mathbf{B}}(S)\, dS \right) \right\rangle = \underset{\leftarrow}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \mathbf{g}^{(n)}(t_1)\, dt_1 \right). \tag{11}$$

As before, we can introduce a parameter λ, and using (10) leads to

$$\left\langle \underset{\leftarrow}{T} \exp\left(\int_0^t \lambda \tilde{\mathbf{B}}(S)\, dS \right) \right\rangle = \underset{\leftarrow}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \lambda^n \mathbf{g}^{(n)}(t_1)\, dt_1 \right). \tag{12}$$

Differentiating (12) with respect to λ, n times, followed by setting $\lambda = 0$, gives for $n = 1, 2, 3, 4, \cdots$

$$\int_0^t \langle \tilde{B}_{\alpha\beta}(t_1) \rangle\, dt_1 = \int_0^t g_{\alpha\beta}^{(1)}(t_1)\, dt_1 = \int_0^t \langle \tilde{B}_{\alpha\beta}(t_1) \rangle_c\, dt_1,$$

$$\begin{aligned}
\int_0^t \int_0^{t_1} \langle \tilde{B}_{\alpha\mu}(t_1) \tilde{B}_{\mu\beta}(t_2) \rangle\, dt_2\, dt_1 &= \int_0^t g_{\alpha\beta}^{(2)}(t_1)\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(1)}(t_1) g_{\mu\beta}^{(1)}(t_2)\, dt_2\, dt_1 \\
&= \int_0^t \int_0^{t_1} \langle \tilde{B}_{\alpha\mu}(t_1) \tilde{B}_{\mu\beta}(t_2) \rangle_c\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \langle \tilde{B}_{\alpha\mu}(t_1) \rangle_c \langle \tilde{B}_{\mu\beta}(t_2) \rangle_c\, dt_2\, dt_1,
\end{aligned}$$

$$\begin{aligned}
\int_0^t \int_0^{t_1} \int_0^{t_2} &\langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\beta}(t_3) \rangle\, dt_3\, dt_2\, dt_1 \\
&= \int_0^t g_{\alpha\mu}^{(3)}(t_1)\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(2)}(t_1) g_{\mu\beta}^{(1)}(t_2) + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(1)}(t_1) g_{\mu\beta}^{(2)}(t_2)\, dt_2\, dt_1 \\
&\quad + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\beta}^{(1)}(t_3)\, dt_3\, dt_2\, dt_1 \\
&= \int_0^t \int_0^{t_1} \int_0^{t_2} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\beta}(t_3) \rangle_c\, dt_3\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \int_0^{t_1} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(S_2) \rangle_c \langle \tilde{B}_{\mu_2\beta}(t_2) \rangle_c\, dt_2\, dS_2\, dt_1 \\
&\quad + \int_0^t \int_0^{t_1} \int_0^{t_2} \langle B_{\alpha\mu_1}(t_1) \rangle_c \langle B_{\mu_1\mu_2}(t_2) B_{\mu_2\beta}(t_3) \rangle_c\, dt_3\, dt_2\, dt_1 + \int^t \int^{t_1} \int^{t_2} \langle B_{\alpha\mu_1}(t_1) \rangle_c \langle B_{\mu_1\mu_2}(t_2) \rangle_c \langle B_{\mu_2\beta}(t_3) \rangle_c\, dt_3\, dt_2\, dt_1,
\end{aligned}$$

$$\begin{aligned}
\int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} &\langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\mu_3}(t_3) \tilde{B}_{\mu_3\beta}(t_4) \rangle\, dt_4\, dt_3\, dt_2\, dt_1 \\
&= \int_0^t g_{\alpha\beta}^{(4)}(t_1)\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(3)}(t_1) g_{\mu\beta}^{(1)}(t_2)\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(1)}(t_1) g_{\mu\beta}^{(3)}(t_2)\, dt_2\, dt_1 \\
&\quad + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(2)}(t_1) g_{\mu\beta}^{(2)}(t_2)\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(2)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\beta}^{(1)}(t_3)\, dt_3\, dt_2\, dt_1 \\
&\quad + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(2)}(t_2) g_{\mu_2\beta}^{(1)}(t_3)\, dt_3\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\beta}^{(2)}(t_3)\, dt_3\, dt_2\, dt_1 \\
&\quad + \int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\mu_3}^{(1)}(t_3) g_{\mu_3\beta}^{(1)}(t_4)\, dt_4\, dt_3\, dt_2\, dt_1 \\
&= \int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\mu_3}(t_3) \tilde{B}_{\mu_3\beta}(t_4) \rangle_c\, dt_4\, dt_3\, dt_2\, dt_1
\end{aligned}$$

$$
\begin{aligned}
&+\int_0^t\int_0^{t_1}\int_0^{S_2}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle_c\,dt_2\,dS_3\,dS_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle_c\,dS_3\,dt_2\,dS_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_2)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_3)\rangle_c\,dt_3\,dt_2\,dS_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_3)\rangle_c\,dt_3\,dS_3\,dt_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_3)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1. \qquad (13)
\end{aligned}
$$

Especially notice the limits of integration in several of the terms which contribute to the third and fourth order expressions. By successively inverting these equations we get expressions for the cumulants in terms of the ordinary stochastic averages:

$$\int_0^t\langle\tilde{B}_{\alpha\beta}(t_1)_c\,dt_1=\int_0^t\langle\tilde{B}_{\alpha\beta}(t_1)\rangle\,dt_1,$$

$$\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle_c\,dt_2\,dt_1=\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle\,dt_2\,dt_1-\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\rangle\langle\tilde{B}_{\mu\beta}(t_2)\rangle\,dt_2\,at_1,$$

$$
\begin{aligned}
&\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle_c\,dt_3\,dt_2\,dt_1\\
&\quad=\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle\,dt_3\,dt_2\,dt_1-\int_0^t\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\beta}(t_2)\rangle\,dt_2\,dS_2\,dt_1\\
&\quad\quad-\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t)\rangle\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle\,dt_3\,dt_2\,dt_1+\int_0^t\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(t_2)\rangle\langle\tilde{B}_{\mu_2\beta}(t_3)\rangle\,dt_3\,dt_2\,dt_1,
\end{aligned}
$$

$$
\begin{aligned}
&\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1\\
&\quad=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle\,dt_4\,dt_3\,dt_2\,dt_1\\
&\quad\quad-\int_0^t\int_0^{t_1}\int_0^{S_2}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\quad\quad+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\quad\quad+\int_0^t\int_0^{t_1}\int_0^{S_2}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(S_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\quad\quad-\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\quad\quad-\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle\,dt_4\,dt_3\,dt_2\,dt_1\\
&\quad\quad-\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle\,dS_3\,dt_2\,dS_2\,dt_1\\
&\quad\quad+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle\,dS_3\,dt_2\,dS_2\,dt_1. \qquad (14)
\end{aligned}
$$

Again, especially notice the limits of integration in several of the terms which contribute to the third and fourth order expressions. By studying the special cases in which either $\tilde{\mathbf{B}}(t)$ commutes for unequal times, or $\tilde{\mathbf{B}}$ is time independent, it may be shown that (14) reduces to (8), and (13) reduces to (7). It should by now be clear how to obtain the higher order cumulants for $\tilde{\mathbf{B}}(t)$ when it does not commute with itself for unequal times, even though the expressions become quite complicated.

THE GAUSSIAN PROPERTY

Throughout this discussion of the Gaussian property, it is convenient to invoke the condition that the averaged value of $\tilde{\mathbf{B}}(t)$ is zero. This simplifies considerations without loss of generality, as was explained at the beginning of the last section. The analogous condition for $\tilde{X}$ is that $\langle\tilde{X}\rangle=0$.

Suppose that $\tilde{X}$ is Gaussian with averaged value zero. Then it is known that the moments of $\tilde{X}$ satisfy[5]

$$\langle(\tilde{X})^{2m+1}\rangle=0 \quad \text{for } m=0,1,2,\cdots, \qquad (15)$$

$$\langle(\tilde{X})^{2m}\rangle=1\times3\times5\times\cdots\times(2m-1)\langle(\tilde{X})^2\rangle^m \quad \text{for } m=1,2,\cdots.$$

If we return to (8) we see that

$$\langle\tilde{X}\rangle_c=0, \quad \langle(\tilde{X})^2\rangle_c=\langle(\tilde{X})^2\rangle, \qquad (16)$$

$$\langle(\tilde{X})^3\rangle_c=0, \quad \langle(\tilde{X})^4\rangle_c=0.$$

The last result follows from the cancellation of the two nonvanishing terms: $\langle(\tilde{X})^4\rangle$ and $-3\langle(\tilde{X})^2\rangle^2$, as may be seen using the second equation in (15). It may be proved generally that all cumulants of order higher than four also vanish. The proof may be performed by the method of induction. We assume it is true that except for the nonvanishing, second order cumulant, all cumulants up to and including order $2m$ for $m>2$ vanish. We shall now show that cumulants of order $2m+1$ and $2m+2$ also vanish.

The cumulant of order $2m+1$ will be expressible as an expansion in terms of the moments of $\tilde{X}$ up to order $2m+1$ as is indicated by (8). The leading term will be $\langle(\tilde{X})^{2m+1}\rangle$ which is zero according to (15). All other terms in the expansion will involve products of lower order moments in which at least one factor is an odd order, lower than $2m+1$ order moment. By (15), such moments vanish and we conclude that $\langle(\tilde{X})^{2m+1}\rangle_c=0$.

The consideration of the cumulant of order $2m+2$ is best pursued using the relationships given by (7). These relationships show that $\langle(\tilde{X})^{2m+2}\rangle$ may be expressed in terms of cumulants of order less than or equal to $2m+2$. The Gaussian properties given by (15) show that $\langle(\tilde{X})^{2m+2}\rangle$ is nonvanishing. Its expansion, according to

(7), in terms of cumulants begins with $\langle(\tilde{X})^{2m+2}\rangle_c$, which we wish to compute, and involves other terms, each of which is a product of lower order cumulants. By hypothesis, all lower order cumulant, except the second order and $2m+1$ order cumulants, vanish, and we have already seen that the cumulant of order $2m+1$ also vanishes. Therefore, all products vanish except the single term which is the product of $m+1$ second order cumulants. Therefore, it follows that $\langle(\tilde{X})^{2m+2}\rangle = \langle(\tilde{X})^{2m+2}\rangle_c + C\langle(\tilde{X})^2\rangle_c^{m+1}$ where C is a coefficient which has to be determined. Looking at (6), it may be seen that the $\langle(\tilde{X})^2\rangle_c^{m+1}$ term comes from the $m+1$ term in the expansion of the exponential on the right-hand side of (6). Such a term has a factor of $1/(m+1)!$ associated with it. Each factor of $\langle(\tilde{X})^2\rangle_c$ has associated with it a factor $1/2!$ as is directly evident in (6). Therefore, $\langle(\tilde{X})^2\rangle_c^{m+1}$ will have a factor, overall, of $[1/(m+1)!](1/2!)^{m+1}$. This must be multiplied by $(2m+2)!$ to get C as a result of the $2m+2$ fold differentiation of λ^{2m+2}. Consequently, $C=(2m+2)!/(m+1)!\,2^{m+1}$. Using (15), it is seen that $\langle(\tilde{X})^{2m+2}\rangle = 1\times3\times5\times\cdots\times(2m+1)\langle(\tilde{X})^2\rangle^{m+1}$. Therefore,

$$\begin{aligned}\langle(\tilde{X})^{2m+2}\rangle_c &= 1\times3\times5\times\cdots\times(2m+1)\langle(\tilde{X})^2\rangle^{m+1} \\ &\quad - \frac{(2m+2)!}{(m+1)!\,2^{m+1}}\langle(\tilde{X})^2\rangle_c^{m+1} \\ &= 0 \end{aligned} \tag{17}$$

since $\langle(\tilde{X})^2\rangle = \langle(\tilde{X})^2\rangle_c$. This completes the proof.

The conclusion is that if $\tilde{X}$ is Gaussian, with averaged value zero, then

$$\langle\exp[\tilde{X}]\rangle = \exp[\tfrac{1}{2}\langle(\tilde{X})^2\rangle] \tag{18}$$

which is especially simple. The cumulant expansion reduces to a single term!

Before attempting to generalize this result for consideration of stochastic matrices which do not commute for unequal times, it is worthwhile to observe that if $\tilde{X}$ is replaced by a scalar, time dependent stochastic quantity, $\tilde{F}(t)$, then the Gaussian property again leads to great simplifications. We make this digression in order to point out that time dependence, *per se*, does not lead to complications. The complications which will arise in our discussion of stochastic matrices, which depend upon time but which do not commute for unequal times, come from the noncommutivity.

Suppose $\tilde{F}(t)$ has averaged value zero, and is Gaussian. It can then be shown that[6]

$$\langle\exp[\textstyle\int_0^t \tilde{F}(S)\,dS]\rangle = \exp[\tfrac{1}{2}\int_0^t\int_0^t\langle\tilde{F}(S_1)\tilde{F}(S_2)\rangle\,dS_1\,dS_2]. \tag{19}$$

Equation (19) is the time dependent generalization of (18) for a time-dependent, scalar, stochastic process. Again, the cumulant expansion reduces to a single term.

The generalization of this result to time-dependent stochastic matrices which do not commute at unequal times cannot be made. The Gaussian property for $\tilde{\mathbf{B}}(t)$ is expressed by[1]

$$\langle\tilde{B}_{\mu_1\nu_1}(t_1)\cdots\tilde{B}_{\mu_{2m+1}\nu_{2m+1}}(t_{2m+1})\rangle = 0 \quad \text{for } m=0,1,2,\cdots, \tag{20}$$

$$\langle\tilde{B}_{\mu_1\nu_1}(t_1)\cdots\tilde{B}_{\mu_{2m}\nu_{2m}}(t_{2m})\rangle = \frac{1}{2^m m!} \times\sum_{p\in S_{2m}}\prod_{j=1}^{m}\langle\tilde{B}_{\mu_{p(2j-1)}\nu_{p(2j-1)}}(t_{p(2j-1)})\tilde{B}_{\mu_{p(2j)}\nu_{p(2j)}}(t_{p(2j)})\rangle \quad \text{for } m=1,2,\cdots,$$

where $\sum_{p\in S_{2m}}$ is the sum over all permutations p in the symmetric group of order $(2m)!$, S_{2m}. Even though we can think of a Gaussian $\tilde{\mathbf{B}}(t)$ in the sense of (20), the Gaussian property alone will prove insufficient for the reduction of (9) to a form analogous with (18) or (19). It is necessary that $\tilde{\mathbf{B}}(t)$ be Gaussian *and* purely random in order to write

$$\langle\underset{\leftarrow}{T}\exp[\textstyle\int_0^t\tilde{\mathbf{B}}(S)\,dS]\rangle = \underset{\leftarrow}{T}\exp[\int_0^t\int_0^{t_1}\langle\tilde{\mathbf{B}}(t_1)\tilde{\mathbf{B}}(t_2)\rangle\,dt_2\,dt_1]. \tag{21}$$

The purely random property is defined by[1]

$$\langle\tilde{B}_{\alpha\beta}(t)\tilde{B}_{\mu\nu}(S)\rangle = 2Q_{\alpha\beta\mu\nu}\delta(t-S) \tag{22}$$

in which the time delta function characterizes the purely random property. Defining $R_{\alpha\beta}$ by $R_{\alpha\beta}\equiv Q_{\alpha\theta\theta\beta}$, wherein summation over θ is implicit, Eq. (21) becomes

$$\langle\underset{\leftarrow}{T}\exp[\textstyle\int_0^t\tilde{\mathbf{B}}(S)\,dS]\rangle_{\alpha\beta} = [\exp(\mathbf{R}t)]_{\alpha\beta} \tag{23}$$

which is especially simple. We shall now proceed to demonstrate why Gaussianness alone is insufficient for the justification of (23) or (21).

That Gaussianness alone does not result in the vanishing of all but the second order cumulants of $\tilde{\mathbf{B}}(t)$ may be seen by studying (13) and (14). First of all, because $\langle\tilde{\mathbf{B}}(t)\rangle = 0$ is assumed, the expressions in (13) and (14) simplify greatly. We get immediately

$$\begin{aligned}&\int_0^t\langle\tilde{B}_{\alpha\beta}(t_1)\rangle_c\,dt_1 = 0, \\ &\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle_c\,dt_2\,dt_1 \\ &= \int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle\,dt_2\,dt_1, \\ &\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle_c\,dt_3\,dt_2\,dt_1 = 0.\end{aligned} \tag{24}$$

Differentiation of these equations with respect to time leads to equations for the integrands. Difficulty arises with the fourth order term. From (14) we get

$$\begin{aligned}&\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c \\ &\quad\times dt_4\,dt_3\,dt_2\,dt_1 \\ &= \int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle \\ &\quad\times dt_4\,dt_3\,dt_2\,dt_1 \\ &\quad - \int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle \\ &\quad\times\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle\,dS_3\,dt_2\,dS_2\,dt_1.\end{aligned} \tag{25}$$

It can be seen that this is nonvanishing if $\tilde{\mathbf{B}}(t)$ is not purely random by considering the special case in which

$$\langle\tilde{B}_{\alpha\beta}(t)\tilde{B}_{\mu\nu}(S)\rangle = 2Q_{\alpha\beta\mu\nu}\varphi(t-S), \tag{26}$$

wherein $\varphi(t-S)$ is not a delta function, but instead is nonvanishing for nonzero values of $|t-S|$. For example, $\varphi(t-S)$ may be proportional to $\exp(-\alpha|t-S|)$. Using the two symmetries $Q_{\alpha\beta\mu\nu}=Q_{\mu\nu\alpha\beta}$ and $\varphi(t-S)=\varphi(S-t)$, the Gaussian property, as expressed by (20), leads to the following expression for (25):

$$\begin{aligned}&\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c \\ &\quad\times dt_4\,dt_3\,dt_2\,dt_1\end{aligned}$$

$$= 4\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\{Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta}\varphi(t_1-t_2)\varphi(t_3-t_4)$$
$$+ Q_{\alpha\mu_1\mu_2\mu_3}Q_{\mu_1\mu_2\mu_3\beta}\varphi(t_1-t_3)\varphi(t_2-t_4)$$
$$+ Q_{\alpha\mu_1\mu_3\beta}Q_{\mu_1\mu_2\mu_2\mu_3}\varphi(t_1-t_4)\varphi(t_2-t_3)\}\,dt_4\,dt_3\,dt_2\,dt_1$$
$$- 4\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta}\varphi(t_1-S_2)\varphi(t_2-S_3)$$
$$\times\, dS_3\,dt_2\,dS_2\,dt_1. \qquad (27)$$

The factors of 4 come from 2^2 as indicated by (26). The negative term is the negative term in (25) replaced by (26). The three preceeding positive terms are the $m=2$ case of the second equation in (20). There are 24 permutations to sum over, but only three distinct terms occur as a result of the two symmetries mentioned above. Only the first positive term in the right-hand side of (27) contains a matrix expression which matches the matrix expression of the negative term. The other two positive terms cannot be cancelled out at all! However, if $\varphi(t-S)\equiv\delta(t-S)$ then study of these extra two terms will show that their integrals vanish as a result of the time-ordered upper limits of integration,[7] and the remaining positive and negative two terms will exactly cancel! When $\varphi(t-S)\neq\delta(t-S)$, the above vanishing of integrals and cancellation of nonvanishing integrals fails to occur.

That the purely random property ultimately leads to (23) will not be proved here since it has been proved in another paper.[1] However, here it has been shown that without the purely random property, already the fourth order cumulant will not vanish for time dependent stochastic matrices which do not commute at unequal times. Consequently, the cumulant expansion will not truncate to a single term, but will involve all even order cumulants. Thus, no real simplification is achieved using cumulants.

APPROXIMATION PROCEDURES

Various physical problems involve computation of a quantity of the form

$$\langle \underset{\leftarrow}{T} \exp[\textstyle\int_0^t \mathbf{O}(S)\,dS]\rangle, \qquad (28)$$

wherein $\mathbf{O}(S)$ is an operator parameterized by S, which may or may not be the time variable, and $\langle\cdots\rangle$ denotes some kind of averaging such as a canonical average over some or all of the variables $\mathbf{O}(S)$ depends upon, or a ground state expectation value, or some other "averaging." Many times one sees in the literature the introduction of cumulant techniques in order to handle the computation of (28). Often it is argued that to good approximation $\mathbf{O}(S)$ behaves as if it were Gaussian, and then the cumulant expansion is truncated after the second cumulant. However, the validity of such approximations also requires that it be demonstrated that to good approximation $\mathbf{O}(S)$ behaves as if it were also purely random. Then, and only then, the truncation of the cumulant expansion is a good approximation.

One application of this kind of approximation procedure in which both Gaussianness and pure randomness were considered has been presented by the author in another paper.[6]

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Physical applications of multiplicative stochastic processes. III. Nonequilibrium entropy

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It is argued that the expression $-K_B$ Trace $[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle]$, which appears in a stochastic treatment of the dynamics of the density matrix is indeed the nonequilibrium entropy. The reasoning involves consideration of the time evolution of the free energy for a relaxing magnetic moment in a fluctuating magnetic environment. It is shown that the H theorem, and the monotonic decrease of the free energy, as described by Pauli's master equation can be generalized to the full density matrix, at least for the case of magnetic relaxation, which requires the presence of off-diagonal density matrix elements.

INTRODUCTION

In this paper, we shall argue that the expression

$$-K_B \,\mathrm{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle] \tag{1}$$

is indeed the entropy for nonequilibrium behavior in quantum mechanical systems. Previously, it has been shown that $H(t)$, which is defined by the above expression without the $-K_B$, is a monotonically decreasing function of time.[1] However, it was not argued that $H(t)$ leads directly to the entropy. Such a connection requires a consideration of the physical quantity heat and its relation with the above expression. In this paper, it will be shown, in the special case of magnetic relaxation, how experimental verification of such a connection could be achieved.

The contention that thermodynamics quantities can have meaning in nonequilibrium situations requires support. Here, we will explicitly write out expressions for internal energy, entropy, and free energy which are assumed to be valid for nonequilibrium situations. We shall proceed by establishing the close relationship between these expressions and expressions found in the earlier literature on this subject. It will be seen that such expressions can be reasonably interpreted as nonequilibrium thermodynamical quantities.

The mathematical context for these ideas is given by the stochastic Schrödinger equation[2]

$$i\frac{d}{dt}C_\alpha(t) = M_{\alpha\alpha'}C_{\alpha'}(t) + \tilde{M}_{\alpha\alpha'}(t)C_{\alpha'}(t) \tag{2}$$

in which $M_{\alpha\alpha'} = M^*_{\alpha'\alpha}$ and $\tilde{M}_{\alpha\alpha'}(t) = \tilde{M}^*_{\alpha'\alpha}(t)$ and $\tilde{M}_{\alpha\alpha'}(t)$ is a purely random Gaussian stochastic Hamiltonian.

The corresponding density matrix equation is

$$\frac{d}{dt}\rho_{\alpha\beta}(t) = -iL_{\alpha\beta\alpha'\beta'}\rho_{\alpha'\beta'}(t) - i\tilde{L}_{\alpha\beta\alpha'\beta'}(t)\rho_{\alpha'\beta'}(t), \tag{3}$$

in which $\rho_{\alpha\beta}(t) \equiv C^*_\alpha(t)C_\beta(t)$, $L_{\alpha\beta\alpha'\beta'} \equiv \delta_{\alpha\alpha'}M_{\beta\beta'} - \delta_{\beta\beta'}M^*_{\alpha\alpha'}$, and $\tilde{L}_{\alpha\beta\alpha'\beta'}(t) = \delta_{\alpha\alpha'}\tilde{M}_{\beta\beta'}(t) - \delta_{\beta\beta'}\tilde{M}^*_{\alpha\alpha'}(t)$. The stochastic average of (3) is

$$\frac{d}{dt}\langle\rho_{\alpha\beta}(t)\rangle = -iL_{\alpha\beta\alpha'\beta'}\langle\rho_{\alpha'\beta'}(t)\rangle - R_{\alpha\beta\alpha'\beta'}\langle\rho_{\alpha'\beta'}(t)\rangle, \tag{4}$$

in which $R_{\alpha\beta\alpha'\beta'}$ is given by

$$R_{\alpha\beta\alpha'\beta'} = \delta_{\alpha\alpha'}Q_{\beta\theta\theta\beta'} + \delta_{\beta\beta'}Q_{\theta\alpha\alpha'\theta} - 2Q_{\beta\beta'\alpha'\alpha}, \tag{5}$$

wherein $Q_{\alpha\beta\alpha'\beta'}$ is determined by the second moments of $\tilde{M}_{\alpha\alpha'}(t)$,

$$\langle\tilde{M}_{\alpha\beta}(t)\tilde{M}_{\alpha'\beta'}(s)\rangle = 2Q_{\alpha\beta\alpha'\beta'}\delta(t-s). \tag{6}$$

The $\langle\rho_{\alpha\beta}(t)\rangle$ in (4) has been used in

$$H(t) \equiv \mathrm{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle] \tag{7}$$

to prove that

$$\frac{d}{dt}H(t) \leq 0, \tag{8}$$

which is an H theorem for quantum mechanical systems.[1] This H theorem differs from previously published H theorems for quantum mechanical systems which instead show that if, at $t=0$, $\langle\rho_{\alpha\beta}(0)\rangle$ has no off-diagonal matrix elements, then $H(t) < H(0)$ for $t > 0$.[3] However, for $s > 0$ as well, it can not be decided whether or not $H(s) > H(t)$ when $t > s$. Therefore, the H theorem given by (8) is much stronger, and closely related in form to Boltzmann's original H theorem for classical gases.[4]

If we now shift attention to consideration of a subsystem in contact with a heat reservoir, we can get an equation for the time evolution of the subsystem alone, which is[5]

$$\frac{d}{dt}\langle\rho_{ij}(t)\rangle = -i(E_i - E_j)\langle\rho_{ij}(t)\rangle - T_{iji'j'}\langle\rho_{i'j'}(t)\rangle, \tag{9}$$

wherein $T_{iji'j'}$ satisfies a detailed balancing condition given by

$$T_{iji'j'} = T^\dagger_{i'j'ij}\exp[-(1/2K_BT)(E_i + E_j - E_{i'} - E_{j'})]. \tag{10}$$

In (10), T is the temperature of the heat reservoir. The interaction between the sybsystem and the reservoir has been assumed to be an energy conserving, stochastic interaction which leaves the reservoir always in equilibrium while the subsystem relaxes. The $T_{iji'j'}$ comes from the average over the stochastic interaction followed by a trace over all reservoir states. Equation (9) has been used to show, for the case of magnetic relaxation by a spin $\frac{1}{2}$ magnetic moment in a fluctuating magnetic environment, how the Block equations are rigorously constructed.[6] In general, Eq. (9) with (10) leads to the canonical equilibrium density matrix asymptotically in time.

EARLIER THEORIES

The Pauli master equation

$$\frac{d}{dt}P_\alpha(t)=\sum_\beta[W_{\alpha\beta}P_\beta(t)-W_{\beta\alpha}P_\alpha(t)], \tag{11}$$

in which $W_{\alpha\beta}=W_{\beta\alpha}$ and $W_{\alpha\beta}>0$ for $\alpha\neq\beta$ has been used as a model for nonequilibrium thermodynamics.[7] The $P_\alpha(t)$'s correspond with the diagonal density matrix elements: $P_\alpha(t)=\langle\rho_{\alpha\alpha}(t)\rangle$. Pauli's equation does not include off-diagonal density matrix elements. Its original appeal stems from the fact that

$$H(t)\equiv\sum_\alpha P_\alpha(t)\ln P_\alpha(t) \tag{12}$$

is montonically decreasing, as is readily seen from (11) by

$$\begin{aligned}\frac{d}{dt}H(t)&=\sum_\alpha\frac{d}{dt}P_\alpha(t)\ln P_\alpha(t)\\&=\sum_\alpha\sum_\beta[W_{\alpha\beta}P_\beta(t)-W_{\beta\alpha}P_\alpha(t)]\ln P_\alpha(t)\\&=\sum_\alpha\sum_\beta W_{\alpha\beta}[P_\beta(t)-P_\alpha(t)]\ln P_\alpha(t)\\&=\tfrac{1}{2}\sum_\alpha\sum_\beta W_{\alpha\beta}[P_\beta(t)-P_\alpha(t)]\ln\frac{P_\alpha(t)}{P_\beta(t)}\\&\leq 0.\end{aligned} \tag{13}$$

To prove (13), we used $W_{\alpha\beta}=W_{\beta\alpha}$ and $\sum_\alpha P_\alpha(t)=1$ for all t. The identification of $-K_BH(t)$ in this case with the entropy is very natural because the microcanonical equilibrium distribution for the probabilities, P_α^{eq}, as determined by equilibrium statistical mechanics, is

$$P_\alpha^{eq}=1/N \quad \text{when } \alpha=1,2,\ldots,N. \tag{14}$$

Consequently,

$$-K_B\sum_\alpha P_\alpha^{eq}\ln P_\alpha^{eq}=K_B\sum_{\alpha=1}^{N}\frac{1}{N}\ln N \tag{15}$$

or

$$S-S_0=K_B\ln N. \tag{16}$$

This is the Boltzmann–Planck formula for the entropy, $S-S_0$, when there are N states, each equally probable. Thus, Pauli's formula for $-K_BH(t)$ surely gives the correct nonequilibrium expression for the entropy.

There is more appeal to Pauli's equation then this. If we again consider a subsystem interacting with a heat reservoir, Pauli's equation becomes

$$\frac{d}{dt}P_\alpha(t)=\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)] \tag{17}$$

in which $T_{\alpha\beta}=T_{\beta\alpha}\exp[-(1/K_BT)(E_\alpha-E_\beta)]$ is the detailed balancing condition.[8] It is therefore natural to take for the free energy the expression

$$F(t)=\sum_\alpha P_\alpha(t)E_\alpha+TK_B\sum_\alpha P_\alpha(t)\ln P_\alpha(t) \tag{18}$$

since the first sum is surely the internal energy, even in nonequilibrium situations, and the second sum is the negative of T, the temperature, times the nonequilibrium entropy. Using (17) with the detailed balancing condition, we get

$$\begin{aligned}\frac{d}{dt}F(t)&=\sum_\alpha\frac{d}{dt}P_\alpha(t)E_\alpha+TK_B\sum_\alpha\frac{d}{dt}P_\alpha(t)\ln P_\alpha(t)\\&=\sum_\alpha\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)]E_\alpha\\&\quad+TK_B\sum_\alpha\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)]\ln P_\alpha(t)\\&=\tfrac{1}{2}\sum_\alpha\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)](E_\alpha-E_\beta)\\&\quad+TK_B\tfrac{1}{2}\sum_\alpha\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)]\ln\frac{P_\alpha(t)}{P_\beta(t)}\\&=\frac{TK_B}{2}\sum_\alpha\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)]\ln\frac{T_{\beta\alpha}}{T_{\alpha\beta}}+\ln\frac{P_\alpha(t)}{P_\beta(t)}\\&=\frac{TK_B}{2}\sum_\alpha\sum_\beta[T_{\alpha\beta}P_\beta(t)-T_{\beta\alpha}P_\alpha(t)]\ln\frac{T_{\beta\alpha}P_\alpha(t)}{T_{\alpha\beta}P_\beta(t)}\\&\leq 0.\end{aligned} \tag{19}$$

Thus, the free energy monotonically decreases to equilibrium, as it should.

The identification of $-K_BH(t)$, in this case, with the entropy is again very natural because the canonical equilibrium distribution for the probabilities, P_α^{eq}, as determined by equilibrium statistical mechanics, is

$$P_\alpha^{eq}=(1/Q)\exp(-E_\alpha/K_BT) \tag{20}$$

where $Q=\sum_\alpha\exp(-E_\alpha/K_BT)$. Now, note that $\ln P_\alpha^{eq}=-\ln Q-(1/K_BT)E_\alpha$. Consequently,

$$\begin{aligned}-K_B\sum_\alpha P_\alpha^{eq}\ln P_\alpha^{eq}&=K_B\sum_\alpha P_\alpha^{eq}\ln Q+(1/T)\sum_\alpha P_\alpha^{eq}E_\alpha\\&=K_B\ln Q+(1/T)U,\end{aligned} \tag{21}$$

where U is the internal energy. In addition $K_B\ln Q$ is $-(1/T)F$, where F is the Helmholtz free energy. So we have

$$-K_B\sum_\alpha P_\alpha^{eq}\ln P_\alpha^{eq}=-(1/T)F+(1/T)U \tag{22}$$

or

$$S=-K_B\sum_\alpha P_\alpha^{eq}\ln P_\alpha^{eq},$$

where S is the entropy. Thus, Pauli's formula for $-K_BH(t)$ surely gives the correct nonequilibrium for the entropy.

The shortcoming of this approach is that restriction to diagonal density matrix elements only is physically unrealistic. In the case of magnetic relaxation for the spin $\frac{1}{2}$ magnetic moment, we need the full density matrix because the off-diagonal density matrix elements give rise to the transverse relaxation of the magnetization.[6] The diagonal density matrix elements only contribute to the longitudinal relaxation. In general, even though the equilibrium density matrix will be diagonal only, the nonequilibrium density matrix will possess off-diagonal density matrix elements. Equations (9) and (10) are the generalization of Pauli's equation (17).

FULL DENSITY MATRIX TREATMENT

We argue that the natural analog of Pauli's $H(t)$ is

$$\text{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle], \tag{23}$$

wherein the logarithm of a Hamiltonian matrix is defined through its diagonal representation.[1] Equation (23) reduces to (22) when $\langle\rho(t)\rangle$ takes on its equilibrium value

$$\langle\rho_{ij}(t)\rangle \underset{t\to\infty}{\longrightarrow} (1/Q)\delta_{ij}\exp(-E_i/K_BT) \tag{24}$$

in the case of a subsystem in contact with a heat reservoir. It has already been proved that $H(t)$ as given by (23) for an isolated system is monotone.[1] We shall now show, for the case of magnetic relaxation, that

$$F(t) \equiv \sum_i \langle\rho_{ii}(t)\rangle E_i + TK_B\,\text{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle] \tag{25}$$

is also monotone when $\langle\rho_{ij}(t)\rangle$ satisfies (9) with (10). This theorem appears to be difficult in general, so we shall give a proof for the magnetic relaxation case only. Equation (25) is clearly the natural generalization (18).

MAGNETIC RELAXATION AND MONOTONICITY

For a spin $\frac{1}{2}$ magnetic moment, i and j in $\langle\rho_{ij}(t)\rangle$ take on only two values. Therefore, $\langle\rho_{ij}(t)\rangle$ is a 2×2 Hermitian positive definite matrix. The values for $T_{iji'j'}$ can be worked out and are[6]

$$\begin{aligned}
&T_{ijij} = 2Q^{x,y} + 2Q^z, \quad i\neq j,\\
&T_{ijji} = 0, \quad i\neq j,\\
&T_{iiii} = 4Q^{x,y}[1-(1/Q_R)\exp(-E_i/K_BT)],\\
&T_{iijj} = -4Q^{x,y}(1/Q_R)\exp(-E_i/K_BT), \quad i\neq j
\end{aligned} \tag{26}$$

where $Q_R = \exp(-E_1/K_BT) + \exp(-E_2/K_BT)$ and $Q^{x,y}$ and Q^z are the second moment correlation strengths for transverse and longitudinal magnetic fluctuations in the magnetic environment. To get the time derivative of $F(t)$ in (25), we proceed in the following way.

$\langle\rho(t)\rangle$ has two eigenvalues given by

$$\lambda_\pm = \tfrac{1}{2} \pm \tfrac{1}{2}\sqrt{1-4\det\langle\rho(t)\rangle}. \tag{27}$$

The positive definiteness of $\langle\rho(t)\rangle$ restricts the determinant so that $\frac{1}{4} \geq \det\langle\rho(t)\rangle$. Equivalently, $\lambda_\pm$ are both positive eigenvalues, and it is clear that $\lambda_+ + \lambda_- = 1$ as should be the case for the eigenvalues of a density matrix. The entropy term in (25) can be written as

$$TK_B\,\text{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle] = TK_B(\lambda_+\ln\lambda_+ + \lambda_-\ln\lambda_-) \tag{28}$$

since the trace is invariant under a unitary similarity transformation. Moreover, $\lambda_+ + \lambda_- = 1$ for all t implies that $(d/dt)\lambda_+ = -(d/dt)\lambda_-$. Therefore,

$$\frac{d}{dt}F(t) = E_1\frac{d}{dt}\langle\rho_{11}(t)\rangle + E_2\frac{d}{dt}\langle\rho_{22}(t)\rangle + TK_B\left(\frac{d}{dt}\lambda_+\right)\ln\frac{\lambda_+}{\lambda_-}. \tag{29}$$

Similarly, $\langle\rho_{11}(t)\rangle + \langle\rho_{22}(t)\rangle = 1$ for all t so that $(d/dt)\langle\rho_{11}(t)\rangle = -(d/dt)\langle\rho_{22}(t)\rangle$. Therefore,

$$\frac{d}{dt}F(t) = (E_1-E_2)\frac{d}{dt}\langle\rho_{11}(t)\rangle + K_BT\left(\frac{d}{dt}\lambda_+(t)\right)\ln\frac{\lambda_+(t)}{\lambda_-(t)}. \tag{30}$$

To get $(d/dt)\lambda_+(t)$, we find

$$\frac{d}{dt}\lambda_+(t) = \tfrac{1}{4}[1-4\det\langle\rho(t)\rangle]^{-1/2}\left[-4\frac{d}{dt}\det\langle\rho(t)\rangle\right]. \tag{31}$$

Using (9) and (26), one gets

$$\begin{aligned}
&\frac{d}{dt}\det\langle\rho(t)\rangle\\
&= \langle\dot\rho_{11}\rangle\langle\rho_{22}\rangle + \langle\rho_{11}\rangle\langle\dot\rho_{22}\rangle - \langle\dot\rho_{12}\rangle\langle\rho_{21}\rangle - \langle\rho_{12}\rangle\langle\dot\rho_{21}\rangle \qquad (32)\\
&= -4Q^{x,y}(1/Q_R)\exp(-E_2/K_BT)\langle\rho_{11}\rangle\langle\rho_{22}\rangle\\
&\quad + 4Q^{x,y}(1/Q_R)\exp(-E_1/K_BT)\langle\rho_{22}\rangle^2\\
&\quad - 4Q^{x,y}(1/Q_R)\exp(-E_1/K_BT)\langle\rho_{11}\rangle\langle\rho_{22}\rangle\\
&\quad + 4Q^{x,y}(1/Q_R)\exp(-E_2/K_BT)\langle\rho_{11}\rangle^2\\
&\quad + (2Q^{x,y}+2Q^z)(\langle\rho_{12}\rangle\langle\rho_{21}\rangle + \langle\rho_{12}\rangle\langle\rho_{21}\rangle)\\
&= 4(Q^{x,y}+Q^z)\langle\rho_{12}\rangle\langle\rho_{21}\rangle - 4Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle\\
&\quad + 4Q^{x,y}[(1/Q_R)\exp(-E_1/K_BT)\langle\rho_{22}\rangle^2\\
&\quad + (1/Q_R)\exp(-E_2/K_BT)\langle\rho_{11}\rangle^2]\\
&= 4(Q^{x,y}+Q^z)\langle\rho_{12}\rangle\langle\rho_{21}\rangle - 8Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle + 4Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle\\
&\quad + 4Q^{x,y}[(1/Q_R)\exp(-E_1/K_BT)\langle\rho_{22}\rangle^2\\
&\quad + (1/Q_R)\exp(-E_2/K_BT)\langle\rho_{11}\rangle^2]\\
&= 4(Q^{x,y}+Q^z)\langle\rho_{12}\rangle\langle\rho_{21}\rangle - 8Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle\\
&\quad + 4Q^{x,y}(1/Q_R)\exp(-E_1/K_BT)\langle\rho_{22}\rangle\\
&\quad + 4Q^{x,y}(1/Q_R)\exp(-E_2/K_BT)\langle\rho_{11}\rangle
\end{aligned}$$

since $(1/Q_R)\exp(-E_1/K_BT) + (1/Q_R)\exp(-E_2/K_BT) = 1$ and $\langle\rho_{11}\rangle + \langle\rho_{22}\rangle = 1$.

Again using (9) and (26), we get

$$\begin{aligned}
&(E_1-E_2)\frac{d}{dt}\langle\rho_{11}(t)\rangle\\
&= (E_1-E_2)4Q^{x,y}\frac{1}{Q_R}\left[\exp\left(-\frac{E_1}{K_BT}\right)\langle\rho_{22}\rangle - \exp\left(-\frac{E_2}{K_BT}\right)\langle\rho_{11}\rangle\right].
\end{aligned} \tag{33}$$

Therefore,

$$\begin{aligned}
\frac{d}{dt}F(t) &= (E_1-E_2)4Q^{x,y}\frac{1}{Q_R}\left[\exp\left(-\frac{E_1}{K_BT}\right)\langle\rho_{22}\rangle - \exp\left(-\frac{E_2}{K_BT}\right)\langle\rho_{11}\rangle\right]\\
&\quad - K_BT\frac{\{4(Q^{x,y}+Q^z)\langle\rho_{12}\rangle\langle\rho_{21}\rangle - 8Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle + 4Q^{x,y}(1/Q_R)[\exp(-E_1/K_BT)\langle\rho_{22}\rangle + \exp(-E_2/K_BT)\langle\rho_{11}\rangle]\}}{\sqrt{1-4\det\langle\rho(t)\rangle}}\ln\frac{\lambda_+}{\lambda_-}.
\end{aligned} \tag{34}$$

To see monotonicity in (34) we must express various of the terms in different form, using $\beta = 1/K_BT$:

$$\frac{1}{Q_R}[\exp(-\beta E_2)\langle\rho_{11}\rangle - \exp(-\beta E_1)\langle\rho_{22}\rangle] = \frac{(1/Q_R)[\exp(-\beta E_2)\langle\rho_{11}\rangle - \exp(-\beta E_1)\langle\rho_{22}\rangle](\langle\rho_{11}\rangle - \langle\rho_{22}\rangle)}{(\langle\rho_{11}\rangle - \langle\rho_{22}\rangle)}$$

$$=\frac{(1/Q_R)[\exp(-\beta E_2)\langle\rho_{11}\rangle^2+\exp(-\beta E_1)\langle\rho_{22}\rangle^2]-\langle\rho_{11}\rangle\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}$$

$$=\frac{(1/Q_R)[\exp(-\beta E_2)(\langle\rho_{11}\rangle^2+\langle\rho_{11}\rangle\langle\rho_{22}\rangle)+\exp(-\beta E_1)(\langle\rho_{22}\rangle^2+\langle\rho_{22}\rangle\langle\rho_{11}\rangle)]-2\langle\rho_{11}\rangle\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}$$

$$=\frac{(1/Q_R)[\exp(-\beta E_2)\langle\rho_{11}\rangle+\exp(-\beta E_1)\langle\rho_{22}\rangle]-2\langle\rho_{11}\rangle\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}. \tag{35}$$

Therefore,

$$(E_1-E_2)4Q^{x,y}(1/Q_R)[\exp(-\beta E_1)\langle\rho_{22}\rangle-\exp(-\beta E_2)\langle\rho_{11}\rangle]$$
$$=K_BT\frac{[4Q^{x,y}(1/Q_R)(\exp(-\beta E_2)\langle\rho_{11}\rangle+\exp(-\beta E_1)\langle\rho_{22}\rangle)-8Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle]}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}\ln\exp[-\beta(E_1-E_2)]. \tag{36}$$

Consequently,

$$\frac{d}{dt}F(t)=K_BT\Bigg(4Q^{x,y}\frac{1}{Q_R}[\exp(-\beta E_2)\langle\rho_{11}\rangle+\exp(-\beta E_1)\langle\rho_{22}\rangle)$$
$$-8Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle\Bigg)\left(\frac{1}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}\ln\left(\frac{\exp(-\beta E_1)}{\exp(-\beta E_2)}\right)\right.$$
$$\left.+\frac{1}{\sqrt{1-4\det\langle\rho(t)\rangle}}\ln\frac{\lambda_-}{\lambda_+}\right)$$
$$+K_BT4(Q^{x,y}+Q^z)\langle\rho_{12}\rangle\langle\rho_{21}\rangle\frac{1}{\sqrt{1-4\det\langle\rho(t)\rangle}}\ln\frac{\lambda_-}{\lambda_+}. \tag{37}$$

From (27) it is seen that

$$\sqrt{1-4\det\langle\rho(t)\rangle}=\lambda_+-\lambda_-. \tag{38}$$

The second summand in (37) is, therefore,

$$K_BT4(Q^{x,y}+Q^z)\langle\rho_{12}\rangle\langle\rho_{21}\rangle[1/(\lambda_+-\lambda_-)]\ln(\lambda_-/\lambda_+)\leq 0. \tag{39}$$

If the first summand in (37) is also nonpositive, then we will have monotonicity. To see that this is so, we first note that

$$\frac{1}{\lambda_+-\lambda_-}\ln\frac{\lambda_-}{\lambda_+}\leq\frac{1}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}\ln\frac{\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle}. \tag{40}$$

The proof of (40) requires writing $\langle\rho_{11}\rangle$ and $\langle\rho_{22}\rangle$ as

$$\langle\rho_{11}\rangle=\tfrac{1}{2}+r \quad\text{and}\quad \langle\rho_{22}\rangle=\tfrac{1}{2}-r, \tag{41}$$

where r is positive. This means, of course, that $\langle\rho_{11}\rangle\geq\langle\rho_{22}\rangle$. This does not limit the generality of our proof because the situation $\langle\rho_{22}\rangle>\langle\rho_{11}\rangle$ can be treated in a similar manner, using on the right-hand side of (40) the expression $[1/(\langle\rho_{22}\rangle-\langle\rho_{11}\rangle)]\ln(\langle\rho_{11}\rangle/\langle\rho_{22}\rangle)$, which is in fact equal to the right-hand side of (40). Therefore, we proceed with (41) with $\frac{1}{2}\geq r\geq 0$. Now, from (27) we see that

$$\lambda_\pm=\tfrac{1}{2}\pm\tfrac{1}{2}\sqrt{1-4(\langle\rho_{11}\rangle\langle\rho_{22}\rangle-\langle\rho_{12}\rangle\langle\rho_{21}\rangle)}$$
$$=\tfrac{1}{2}\pm\tfrac{1}{2}[1-4(\tfrac{1}{4}-r^2-\langle\rho_{12}\rangle\langle\rho_{21}\rangle)]^{1/2}$$
$$=\tfrac{1}{2}\pm r(1+\langle\rho_{12}\rangle\langle\rho_{21}\rangle/r^2)^{1/2}. \tag{42}$$

Consequently,

$$\lambda_+-\lambda_-=2r(1+\langle\rho_{12}\rangle\langle\rho_{21}\rangle/r^2)^{1/2}\geq 2r=\langle\rho_{11}\rangle-\langle\rho_{22}\rangle. \tag{43}$$

Equivalently,

$$1/(\lambda_+-\lambda_-)\leq 1/(\langle\rho_{11}\rangle-\langle\rho_{22}\rangle) \tag{44}$$

Additionally,

$$\frac{\lambda_-}{\lambda_+}=\frac{\frac{1}{2}-r(1+\langle\rho_{12}\rangle\langle\rho_{21}\rangle/r^2)^{1/2}}{\frac{1}{2}+r(1+\langle\rho_{12}\rangle\langle\rho_{21}\rangle/r^2)^{1/2}}\leq\frac{\frac{1}{2}-r}{\frac{1}{2}+r}=\frac{\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle} \tag{45}$$

since the numerators satisfy $\frac{1}{2}-r(1+\langle\rho_{12}\rangle\langle\rho_{21}\rangle/r^2)^{1/2}\leq\frac{1}{2}-r$ while the denominators satisfy $\frac{1}{2}+r(1+\langle\rho_{12}\rangle\langle\rho_{21}\rangle/r^2)^{1/2}\geq\frac{1}{2}+r$. Consequently, we get

$$\ln\frac{\lambda_-}{\lambda_+}\leq\ln\frac{\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle} \tag{46}$$

since the logarithm is a monotone function. Together, (44) and (46) prove (40).

In (37) the first factor of the first summand can be written as

$$K_BT\{4Q^{x,y}(1/Q_R)[\exp(-\beta E_2)\langle\rho_{11}\rangle+\exp(-\beta E_1)\langle\rho_{22}\rangle]$$
$$-8Q^{x,y}\langle\rho_{11}\rangle\langle\rho_{22}\rangle\}$$
$$=K_BT4Q^{x,y}(1/Q_R)[\exp(-\beta E_2)\langle\rho_{11}\rangle$$
$$-\exp(-\beta E_1)\langle\rho_{22}\rangle](\langle\rho_{11}\rangle-\langle\rho_{22}\rangle). \tag{47}$$

as is seen from (35). Therefore, for the first summand in (37) we get

$$K_BT4Q^{x,y}\frac{1}{Q_R}[\exp(-\beta E_2)\langle\rho_{11}\rangle-\exp(-\beta E_1)\langle\rho_{22}\rangle](\langle\rho_{11}\rangle-\langle\rho_{22}\rangle)$$
$$\times\left[\frac{1}{\langle\rho_{11}\rangle-\langle\rho_{22}\rangle}\ln\left(\frac{\exp(-\beta E_1)}{\exp(-\beta E_2)}\right)+\frac{1}{\lambda_+-\lambda_-}\ln\frac{\lambda_-}{\lambda_+}\right]$$
$$\leq K_BT4Q^{x,y}\frac{1}{Q_R}[\exp(-\beta E_2)\langle\rho_{11}\rangle-\exp(-\beta E_1)\langle\rho_{22}\rangle]$$
$$\times\left[\ln\left(\frac{\exp(-\beta E_1)}{\exp(-\beta E_2)}\right)+\ln\frac{\langle\rho_{22}\rangle}{\langle\rho_{11}\rangle}\right]$$
$$=K_BT4Q^{x,y}\frac{1}{Q_R}[\exp(-\beta E_2)\langle\rho_{11}\rangle-\exp(-\beta E_1)\langle\rho_{22}\rangle]$$
$$\times\left(\ln\left[\frac{\exp(-\beta E_1)\langle\rho_{22}\rangle}{\exp(-\beta E_2)\langle\rho_{11}\rangle}\right]\right)\leq 0. \tag{48}$$

The first inequality in (48) follows from (40) while the second follows from its form, as was the case in (39). Together, (39) and (48) prove

$$\frac{d}{dt}F(t)\leq 0. \tag{49}$$

With the full density matrix for this magnetic relaxation problem we have been able to parallel the Pauli master equation picture described by (19). One can then begin to believe that $F(t)$ as given by (25) is indeed the nonequilibrium free energy.

EXPERIMENTAL CONFIRMATION

The principal question is whether or not

$$-K_B \,\mathrm{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle] \tag{50}$$

is indeed the nonequilibrium entropy. In (25) the term $\sum_i E_i\langle\rho_{ii}(t)\rangle$ is surely the nonequilibrium internal energy, so that only (50) remains to be considered. The advantage in using this picture of a subsystem in contact with a heat reservoir is that the temperature of the reservoir is held constant. Consequently, one can use

$$-TK_B \,\mathrm{Trace}[\langle\rho(t_2)\rangle \ln\langle\rho(t_2)\rangle] + TK_B \,\mathrm{Trace}[\langle\rho(t_1)\rangle \ln\langle\rho(t_1)\rangle] = \Delta Q \tag{51}$$

as the heat exchanged during the time interval from t_1 to t_2. Equation (51) parallels the quasistatic relationship $dQ = Tds$ of thermodynamics, and appears plausible here because the temperature is constant. Experimentally, one must attempt to measure the heat exchanged with the reservoir by the subsystem magnetic moment and see if the time course of heat exchange follows the time course of

$$-TK_B \,\mathrm{Trace}[\langle\rho(t)\rangle \ln\langle\rho(t)\rangle]$$

as determined by (9). Agreement would confirm all of the physical assignments for the mathematical expressions suggested in this paper.

Such an experimental test is perhaps quite difficult in the case of magnetic relaxation as described here. Two considerations must be made to properly test this theory. First of all, we have assumed that fluctuation correlations are very short lived compared with the relaxation times. This is evidenced in Eq. (6). For longer-lived correlations there are reasons for believing that the initial stages of relaxation do not show monotonic free energy changes until times of the order of the correlation time have elapsed, after which times the relaxation would become monotonic.[9] Second of all, we have treated an isolated magnetic moment in a stochastic magnetic environment. In reality this separation of subsystem and reservoir may not be so clean, or easily achieved experimentally. Instead, the magnetic moment may have nearby neighbors with which there is systematic interaction as well as having a stochastic reservoir interaction. These nearby neighbors can introduce some oscillatory behavior in addition to the relaxation and can renormalize transverse frequencies. A more sophisticated calculation along the lines given here for the case of neighboring magnetic moment interactions, and for correlation times of greater length for the reservoir magnetic fluctuations may be required before experimental confirmation is possible.

Within the context described by Eqs. (9) and (10), it is also desired to find general proof that the free energy as defined by (25) is monotonically decreasing, without specializing considerations to the magnetic relaxation case.

ACKNOWLEDGMENT

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This paper is dedicated to Mark Kac on the occasion of his 60th birthday.

[1] R.F. Fox, J. Math. Phys. **13**, 1726 (1972); K_B is Boltzmann's constant, and $\langle\cdots\rangle$ denotes stochastic averaging.
[2] R.F. Fox, J. Math. Phys. **13**, 1196 (1972); $\hbar = 1$ is assumed throughout.
[3] R.C. Tolman, *The Principles of Statistical Mechanics* (Oxford U.P., London, 1968), Sec. 106.
[4] K. Huang, *Statistical Mechanics* (Wiley, New York, 1963), Chap. 4.
[5] R.F. Fox, J. Math. Phys. **14**, 20 (1973).
[6] R.F. Fox, J. Math. Phys. **15**, 217 (1974).
[7] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), Chap. 15, Sec. 1.
[8] See Ref. 7, Chap. 15, Sec. 2.
[9] If the correlation function is not a delta function, the monotonicity of $F(t)$ depends upon monotonicity of the correlation function. An exponentially decaying correlation function can still lead to a monotone $F(t)$, but a correlation function which is nonmonotonically decaying may not.

Research Report 1975

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Research Report Attachment

Ronald F. Fox, Georgia Tech, Grant #GP 39309

Three reprints are enclosed which indicate the progress made using the multiplicative stochastic process approach. Another paper entitled: "Physical Application of Multiplicative Stochastic Processes III: Non-equilibrium Entropy" will appear in the June, 1975 issue of J. Math. Phys. These papers illustrate progress in both classical and quantum mechanical settings. The paper dealing with Fokker-Planck equations can now be set on a more rigorous footing by using the techniques supplied by the two papers on cumulants. Indeed, the second, cumulant, paper has spawned a fresh development of significantly greater generality for the multiplicative stochastic process approach. Submitted for publication is a long paper treating photon fluctuations and relaxation in atoms and molecules, all of which utilized the cumulant methods.

Thesis work by Joel Davis on Maxwell $\xrightarrow[\tau\to\infty]{}$ Boltzmann has finally reached the publication stage. Mr. Davis proved a difficult combinatorial identity which verifies our expectations that an initial Maxwellian momentum distribution leads to an asymptotic Boltzmannian spatial distribution for a classical particle in an external potential. This work may have profound implications for time correlation formulae approaches to transport coefficients and affords an alternative viewpoint.

This work will be continued for one more year on Grant #MPS73-08945 A01.

A generalized theory of multiplicative stochastic processes using cumulant techniques

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The rules for the construction of the nth order cumulant for time-dependent, stochastic, matrices or operators which do not commute with themselves at unequal times are derived. The results are identical with van Kampen's rules. In the Gaussian case, Kubo's concept of a generalized Gaussian process is criticized. Under certain conditions Kubo's idea becomes asymptotically valid, while the same conditions justify use of the author's earlier delta function theory. A generalized density matrix equation is presented and its behavior during the approach to equilibrium is discussed. A finite correlation time, τ_c, does not necessarily invalidate a monotonic approach to equilibrium.

1. INTRODUCTION

In this paper, the author's earlier theory of multiplicative stochastic processes,[1] with its application to the treatment of the time development of the quantum mechanical density matrix,[2,3] is generalized. The earlier theory was restricted to the consideration of purely random, Gaussian, stochastic matrices, whereas the theory presented here applies to any class of stochastic matrices.

Following earlier work by Kubo[4,5] and more recent work by van Kampen,[6,7] cumulant techniques are used to achieve the generalization. General rules for the construction of the nth order cumulant expressions have been published by van Kampen. In this paper a derivation of those rules is presented, and the derivation requires the introduction of the concept of a time-ordered logarithm. The Gaussian property is introduced, but without the added restriction of "purely randomness," and it is shown that, for stochastic matrices which do not commute with themselves at unequal times, the cumulant expansion does not truncate to the first two cumulants only. While this point has been published before,[8] here it is pointed out that this circumstance invalidates Kubo's concept of a "generalized Gaussian" stochastic, matrix process.[4,5] By studying a special case in which the correlation matrices dampen out exponentially, it is demonstrated that the Gaussian property does lead to the desired truncation, asymptotically in time, after all.

The application of these mathematical results to the density matrix is made in the last section. A generalized density matrix equation for the approach to the microcanonical density matrix is presented. With the Gaussian property imposed, the generalized equation asymptotically approaches the Redfield equation presented earlier.[1] Moreover, the H-theorem, proved within context of the earlier, Gaussian, purely random, theory,[2] can be generalized in some situations which are discussed.

Because the asymptotic behavior of the generalized equations is identical with the earlier, more restricted theory, the general theory has as one of its virtues the property that it justifies the earlier theory, rather than replaces it.

2. MATHEMATICAL FOUNDATIONS

It is the purpose of the following calculations to investigate the averaged behavior of the equation:

$$\frac{d}{dt}a_\alpha(t)=\tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{1}$$

when

$$\langle\tilde{A}_{\alpha\alpha'}(t)\rangle=M_{\alpha\alpha'}, \tag{2}$$

$$\langle\tilde{A}_{\alpha\alpha'}(t)\tilde{A}_{\beta\beta'}(s)\rangle=2Q_{\alpha\alpha'\beta\beta'}(t-s)+M_{\alpha\alpha'}M_{\beta\beta'}; \tag{3}$$

and there are nonvanishing higher order moments of $\tilde{\mathbf{A}}(t)$ which will not be explicitly indicated at this point. Both $\tilde{\mathbf{A}}(t)$ and $\mathbf{M}$ are antisymmetric matrices. Repeated indices imply summation, and the variance tetratic, $Q_{\alpha\alpha'\beta\beta'}(t-s)$, is a function of the time interval $t-s$. In the earlier, purely random, theory, the time dependence was always given by a delta function times a time-independent, tetratic variance, $Q_{\alpha\alpha'\beta\beta'}\times\delta(t-s)$[1]. That restriction is now removed.

The study of Eq. (1) is equivalent to the study of the averaged behavior of

$$\frac{d}{dt}a_\alpha(t)=M_{\alpha\alpha'}a_{\alpha'}(t)+\tilde{A}'_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{4}$$

when

$$\langle\tilde{A}'_{\alpha\alpha'}(t)\rangle=0, \tag{5}$$

$$\langle\tilde{A}'_{\alpha\alpha'}(t)\tilde{A}'_{\beta\beta'}(s)\rangle=2Q_{\alpha\alpha'\beta\beta'}(t-s), \tag{6}$$

and again the higher order moments will not yet be explicity indicated.

It is also equivalent, and convenient, to perform a linear transformation and work with the equation

$$\frac{d}{dt}b_\alpha(t)=\tilde{B}_{\alpha\alpha'}(t)b_{\alpha'}(t) \tag{7}$$

wherein $b_\alpha(t)$ and $\tilde{B}_{\alpha\alpha'}(t)$ are defined by

$$a_\alpha(t)\equiv[\exp(t\mathbf{M})]_{\alpha\alpha'}b_{\alpha'}(t), \tag{8}$$

$$\tilde{B}_{\alpha\alpha'}(t)\equiv[\exp(-t\mathbf{M})]_{\alpha\beta}\tilde{A}_{\beta\beta'}(t)[\exp(t\mathbf{M})]_{\beta'\alpha'}. \tag{9}$$

It follows from (5) and (6) that

$$\langle\tilde{B}_{\alpha\alpha'}(t)\rangle=0, \tag{10}$$

$$\langle\tilde{B}_{\alpha\alpha'}(t)\tilde{B}_{\beta\beta'}(s)\rangle = 2Q_{\mu\mu'\nu\nu'}(t-s)[\exp(-t\mathbf{M})]_{\alpha\mu}[\exp(t\mathbf{M})]_{\mu'\alpha'} \times[\exp(-s\mathbf{M})]_{\beta\nu}[\exp(s\mathbf{M})]_{\nu'\beta'}. \tag{11}$$

Note also that the antisymmetry of $\tilde{\mathbf{A}}(t)$ and $\mathbf{M}$ imply through (9) that

$$\tilde{B}_{\alpha'\alpha}(t) = -\tilde{B}_{\alpha\alpha'}(t) \tag{12}$$

The solution to (7) is expressible as a series of time ordered integrals:

$$\begin{aligned} b_\alpha(t) &= \sum_{n=0}^{\infty} \int_0^t \int_0^{t_1} \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} [\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\cdots \\ &\quad \times \tilde{B}_{\mu_{n-2}\mu_{n-1}}(t_{n-1})\tilde{B}_{\mu_{n-1}\alpha'}(t_n)]dt_n \cdots dt_1 b_{\alpha'}(0) \\ &= [\underset{\sim}{T} \exp(\int_0^t \tilde{\mathbf{B}}(s)ds)]_{\alpha\alpha'} b_{\alpha'}(0) \end{aligned} \tag{13}$$

wherein the $n=0$ term of the sum is defined to be $\delta_{\alpha\alpha'} b_{\alpha'}(0) \equiv b_\alpha(0)$, and the last equivalence defines the time ordering symbol, $\underset{\sim}{T}$.

The average of (13) may be expressed using time ordered cumulants[4-8]:

$$\begin{aligned} &\langle \underset{\sim}{T} \exp(\int_0^t \tilde{\mathbf{B}}(s)ds)\rangle \\ &\quad \equiv \underset{\sim}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \int_0^{t_{n-1}} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} \langle \tilde{\mathbf{B}}(t_1)\tilde{\mathbf{B}}(t_2)\cdots \right. \\ &\qquad \left. \times \tilde{\mathbf{B}}(t_{n-1})\tilde{\mathbf{B}}(t_n)\rangle_c dt_n \cdots dt_1\right) \\ &\quad \equiv \underset{\sim}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \mathbf{G}^{(n)}(s)ds\right), \end{aligned} \tag{14}$$

where $\mathbf{G}^{(n)}(s)$ is defined by

$$\begin{aligned} \mathbf{G}^{(n)}(s) \equiv \int_0^s \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} &\langle \tilde{\mathbf{B}}(s)\tilde{\mathbf{B}}(t_2)\cdots \\ &\times \tilde{\mathbf{B}}(t_{n-1})\tilde{\mathbf{B}}(t_n)\rangle_c dt_n \cdots dt_2. \end{aligned} \tag{15}$$

So far, all that has been done is to define the cumulant averages through (14) and (15), and it is necessary to find expressions for $\mathbf{G}^{(n)}(s)$ solely in terms of ordinary averages of products of $\tilde{\mathbf{B}}(t)$'s if (14) is to be useful. This task is the heart of the difficulty with the cumulant method, and the purpose of this section of this paper will be to demonstrate a general method of solution.

The method of solution begins with the replacement of $\tilde{\mathbf{B}}(t)$ by $\lambda\tilde{\mathbf{B}}(t)$ everywhere in (14) and (15). The parameter λ is an ordinary real number, with respect to which derivatives may be performed. Using (13), (14), and (15) gives

$$\begin{aligned} &\langle \underset{\sim}{T} \exp(\int_0^t \lambda\tilde{\mathbf{B}}(s)ds)\rangle \\ &\quad = \sum_{n=0}^{\infty} \int_0^t \int_0^{t_1} \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} \lambda^n \langle \tilde{\mathbf{B}}(t_1)\tilde{\mathbf{B}}(t_2)\cdots \\ &\qquad \times \tilde{\mathbf{B}}(t_{n-1})\tilde{\mathbf{B}}(t_n)\rangle dt_n \cdots dt_1 \\ &\quad \equiv \sum_{n=0}^{\infty} \lambda^n \int_0^t \mathbf{A}^{(n)}(s)ds \\ &\quad = \underset{\sim}{T} \exp\left(\sum_{n=1}^{\infty} \lambda^n \int_0^t \mathbf{G}^{(n)}(s)ds\right), \end{aligned} \tag{16}$$

where $\mathbf{A}^{(n)}(s)$ is defined by

$$\begin{aligned} \mathbf{A}^{(n)}(s) \equiv \int_0^s \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} &\langle \tilde{\mathbf{B}}(s)\tilde{\mathbf{B}}(t_2)\cdots \tilde{\mathbf{B}}(t_{n-1})\tilde{\mathbf{B}}(t_n)\rangle \\ &\times dt_n \cdots dt_2. \end{aligned} \tag{17}$$

Clearly, $\mathbf{A}^{(n)}(s)$ is the analog, in terms of ordinary averages, of $\mathbf{G}^{(n)}(s)$ which is given in (15) by cumulant averages. Now, notice that if (16) is differentiated with respect to λ, n times, and then λ is set equal to 0, the first and third terms in (16) give

$$\frac{d^n}{d\lambda^n} \left\langle \underset{\sim}{T} \exp\left(\int_0^t \lambda\tilde{\mathbf{B}}(s)d\right)\right\rangle \Big|_{\lambda=0} = n! \int_0^t \mathbf{A}^{(n)}(s)ds. \tag{18}$$

The corresponding quantity which comes from the fourth term in (16) is

$$\frac{d^n}{d\lambda^n} \underset{\sim}{T} \exp\left(\sum_{n=1}^{\infty} \lambda^n \int_0^t \mathbf{G}^{(n)}(s)ds\right) \Big|_{\lambda=0} = ?. \tag{19}$$

The right-hand side of (19) is sufficiently complicated that a special method is required to arrive at an explicit formula.

The evaluation of (19) is a special case of the general problem of evaluating the nth derivative of a composite function which is time ordered. The method to be employed here is suggested by Riordan.[9] Let f be a time ordered composite function of the form

$$f(\lambda) = \underset{\sim}{T} y(w(\lambda)). \tag{20}$$

In (19), $y(u)$ is $\exp(u)$ and $w(\lambda)$ is $\sum_{n=1}^{\infty} \lambda^n \int_0^t \mathbf{G}^{(n)}(s)ds$. Denote $(d^n/d\lambda^n)f(\lambda)$ by f_n, $(d^n/d\lambda^n)w(\lambda)$ by w_n, and $(d^n/du^n)/y(u)$ by y_n. From (20) it follows that

$$\begin{aligned} f_1 &= \underset{\sim}{T}(w_1 y_1), \\ f_2 &= \underset{\sim}{T}(w_2 y_1 + w_1^2 y_2), \\ f_3 &= \underset{\sim}{T}(w_3 y_1 + 2w_2 w_1 y_2 + w_1 w_2 y_2 + w_1^3 y_3), \\ f_4 &= \underset{\sim}{T}(w_4 y_1 + 3w_3 w_1 y_2 + 3w_2^2 y_2 + w_1 w_3 y_2 + 3w_2 w_1^2 y_3 \\ &\quad + 2w_1 w_2 w_1 y_3 + w_1^2 w_2 y_3 + w_1^4 y_4) \end{aligned} \tag{21}$$

. . .

So far, careful preservation of the order of terms in these derivatives has been observed because noncommutivity is in general possible. The presence of the time ordering operator, $\underset{\sim}{T}$, however, makes this scrupulous observance of order unnecessary because $\underset{\sim}{T}$ permits treating the noncommutative quantities as if they commuted up until the time ordering is applied.[10] For example, $\underset{\sim}{T}(2w_2 w_1 y_2 + w_1 w_2 y_2) = \underset{\sim}{T}(3w_2 w_1 y_2)$. Therefore, Eqs. (21) may be rewritten as

$$\begin{aligned} f_1 &= \underset{\sim}{T}(w_1 y_1), \\ f_2 &= \underset{\sim}{T}(w_2 y_1 + w_1^2 y_2), \\ f_3 &= \underset{\sim}{T}(w_3 y_1 + 3w_2 w_1 y_2 + w_1^3 y_3), \\ f_4 &= \underset{\sim}{T}(w_4 y_1 + 4w_3 w_1 y_2 + 3w_2^2 y_2 + 6w_2 w_1^2 y_3 + w_1^4 y_4). \end{aligned} \tag{22}$$

These expressions are sufficient to suggest the conjecture that the nth term is

$$f_n = \sum_{\sum_{l=1}^{\infty} l m_l = n} \underset{\sim}{T} \left\{ \prod_{l=1}^{\infty} \frac{n!}{(l!)^{m_l} m_l!} (w_l)^{m_l} y_p \right\}, \quad \text{where } p \equiv \sum_{l=1}^{\infty} m_l, \tag{23}$$

where $\sum_{l=1}^{\infty} l m_l = n$ defines a partition of n, and the summation in (23) is over all such partitions. The values of the multiplicities, m_l, are 0, 1, 2, $\cdots$. Therefore, $p \equiv \sum_{l=1}^{\infty} m_l$ is always finite because all but a finite number of the m_l's are zero. The formula given by (23) is the time ordered generalization of di Brunno's formula.[11] It may be proved by induction as follows.

Clearly, (23) agrees with (22) for $n=1$, 2, 3, and 4. Therefore, assume that (23) is true for n, and it shall be proved that it is true for $n+1$. Then, by induction, (23) is true for all positive n. Using (23), f_{n+1} can be directly obtained and is given by

$$f_{n+1} = \sum_{\sum_{l=1}^{\infty} l m_l = n} \underset{\sim}{T} \left\{ \prod_{l=2}^{\infty} \frac{n!}{(l!)^{m_l} m_l!} \frac{1}{m_1!} (w_l)^{m_l} (w_1)^{m_1+1} y_{p+1} \right\} \tag{24}$$

$$+\sum_{\sum_{l=1}^{\infty} l m_l = n} \sum_{j=1}^{\infty} \underline{T}\left\{\prod_{\substack{l=1 \\ l\neq j \\ l\neq j+1}}^{\infty} \frac{n!}{(l!)^{m_l} m_l!} \frac{m_j}{(j!)^{m_j} m_j!} \times \frac{1}{((j+1)!)^{m_{j+1}} m_{j+1}!} (w_l)^{m_l} (w_j)^{m_j - 1} (w_{j+1})^{m_{j+1}+1} y_p \right\},$$

where $p \equiv \sum_{l=1}^{\infty} m_l$.

The first summation comes from one more derivative of y which generates another factor of w_1, whereas the second summation comes from the derivative of all other factors in (23) other than the y factor. It must be shown that (24) is of the form given by (23) for $n+1$, which is

$$f_{n+1} = \sum_{\sum_{l=1}^{\infty} l\bar{m}_l = n+1} \underline{T}\left\{\prod_{l=1}^{\infty} \frac{(n+1)!}{(l!)^{\bar{m}_l} \bar{m}_l!} (w_l)^{\bar{m}_l} y_{\bar{p}}\right\}, \quad \text{where } \bar{p} \equiv \sum_{l=1}^{\infty} \bar{m}_l. \tag{25}$$

To show the equivalence of (24) and (25) the following replacements are needed:

$$\frac{1}{m_1!} \to \frac{m_1+1}{(m_1+1)!},$$

$$\frac{1}{(j!)^{m_j}} \to \frac{1}{(j!)^{m_j-1} j!}, \tag{26}$$

$$\frac{1}{((j+1)!)^{m_{j+1}} m_{j+1}!} \to \frac{(j+1)!\,(m_{j+1}+1)}{((j+1)!)^{m_{j+1}+1} (m_{j+1}+1)!}.$$

Using (26) in (24) gives

$$f_{n+1} = \sum_{\sum_{l=1}^{\infty} l m_l = n} \underline{T}\left\{\prod_{l=2}^{\infty} \frac{n!\,(m_1+1)}{(l!)^{m_l} m_l!\,(m_1+1)!} (w_l)^{m_l} (w_1)^{m_1+1} y_{p+1}\right\}$$

$$+\sum_{\sum_{l=1}^{\infty} l m_l = n} \sum_{j=1}^{\infty} \underline{T}\left\{\prod_{\substack{l=1 \\ l\neq j \\ l\neq j+1}}^{\infty} \frac{n!\,(j+1)(m_{j+1}+1)}{(l!)^{m_l} m_l!\,(j!)^{m_j-1}(m_j-1)!\,[(j+1)!]^{m_{j+1}+1}(m_{j+1}+1)!} (w_l)^{m_l} (w_j)^{m_j-1} (w_{j+1})^{m_{j+1}+1} y_p\right\} \quad \text{where } p \equiv \sum_{l=1}^{\infty} m_l. \tag{27}$$

In arriving at (27), $m_j/m_j!$ has been replaced by $1/(m_j-1)!$, and this does not lead to difficulty when $m_j = 0$ if it is simply recalled that

$$\frac{1}{(m_j-1)!} \equiv \frac{m_j}{m_j!} = \frac{0}{0!} = \frac{0}{1} = 0.$$

In the first summation in (27) let $\bar{m}_l = m_l$ for $l \geq 2$ and let $\bar{m}_1 = m_1 + 1$. Then it follows that

$$\sum_{l=1}^{\infty} l\bar{m}_l = (m_1+1) + \sum_{l=2}^{\infty} l m_l = 1 + \sum_{l=1}^{\infty} l m_l = 1 + n.$$

Similarly, in the second summation in (27) let $\bar{m}_l = m_l$ for $l = 1, 2, \cdots$, but $l \neq j$ and $l \neq j+1$, and let $\bar{m}_j = m_j - 1$ while letting $\bar{m}_{j+1} = m_{j+1} + 1$. Then it follows that

$$\sum_{l=1}^{\infty} l\bar{m}_l = \sum_{\substack{l=1 \\ l\neq j \\ l\neq j+1}}^{\infty} l m_l + j(m_j - 1) + (j+1)(m_{j+1}+1)$$

$$= \sum_{l=1}^{\infty} l m_l - j + (j+1) = n+1.$$

In addition, in the first summation in (27)

$$p + 1 = \left(\sum_{l=1}^{\infty} m_l\right) + 1 = \sum_{l=1}^{\infty} \bar{m}_l,$$

whereas in the second summation in (27) $p = \sum_{l=1}^{\infty} m_l = \sum_{l=1}^{\infty} \bar{m}_l = \bar{p}$.

These considerations permit rewriting (27) as

$$f_{n+1} = \sum_{\substack{\sum_{l=1}^{\infty} l\bar{m}_l = n+1 \\ m_1 \geq 1}} \underline{T}\left\{\prod_{l=1}^{\infty} \frac{n!\,\bar{m}_1}{(l!)^{\bar{m}_l} \bar{m}_l!} (w_l)^{\bar{m}_l} y_{\bar{p}}\right\}$$

$$+\sum_{\substack{\sum_{l=1}^{\infty} l\bar{m}_l = n+1 \\ \bar{m}_1 \neq n+1}} \sum_{j=1}^{\infty} \underline{T}\left\{\prod_{l=1}^{\infty} \frac{n!\,(j+1)\bar{m}_{j+1}}{(l!)^{\bar{m}_l} \bar{m}_l!} (w_l)^{\bar{m}_l} y_{\bar{p}}\right\}$$

$$\text{where } \bar{p} \equiv \sum_{l=1}^{\infty} \bar{m}_l. \tag{28}$$

Notice that the summations over partitions of $n+1$ are not unrestricted, and that the numerators still require simplification. Reductions of (28) to (25) requires consideration of two cases, $\bar{m}_1 = 0$ and $\bar{m}_1 \neq 0$. In the case in which $\bar{m}_1 = 0$ only the second summation can contribute and the summation over j gives

$$\sum_{j=1}^{\infty} (j+1)(\bar{m}_{j+1}) = \sum_{j=2}^{\infty} j\bar{m}_j = n+1 \quad \text{when } \bar{m}_1 = 0. \tag{29}$$

Therefore, the numerator becomes $n!\,(n+1) = (n+1)!$ and the j summation is gone. In the case in which $\bar{m}_1 \neq 0$, both summations in (28) contribute, and the combination of the first summation with the j summation in the second summation yields

$$n!\left(\bar{m}_1 + \sum_{j=1}^{\infty} (j+1)\bar{m}_{j+1}\right) = n!\left(\bar{m}_1 + \sum_{j=2}^{\infty} j\bar{m}_j\right)$$

$$= n!\left(\sum_{j=1}^{\infty} j\bar{m}_j\right) = n!\,(n+1) = (n+1)!. \tag{30}$$

Consequently, (28) is identical with (25). This completes the proof of (23).

The original objective was to find the right-hand side of (19) and equate it with the right-hand side of (18). Equation (19) may be treated as an example of (23) in which $y(u) \equiv \exp(u)$ and $w(\lambda) \equiv \sum_{n=1}^{\infty} \lambda^n \int_0^t \mathbf{G}^{(n)}(s)\,ds$ as was previously indicated in the discussion of (20). In this case, it follows that

$$y_n\big|_{\lambda=0} = y_n\big|_{u=0} = 1 \quad \text{for all } n$$

and

$$w_n\big|_{\lambda=0} = n! \int_0^t \mathbf{G}^{(n)}(s)\,ds. \tag{31}$$

Therefore, (23) becomes

$$f_n\big|_{\lambda=0} = \sum_{\sum_{l=1}^{\infty} l m_l = n} \underline{T}\left\{\prod_{l=1}^{\infty} \frac{n!}{(l!)^{m_l} m_l!} (l!)^{m_l} \left(\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^{m_l}\right\}$$

$$= \sum_{\sum_{l=1}^{\infty} l m_l = n} \underline{T}\left\{\prod_{l=1}^{\infty} \frac{n!}{m_l!} \left(\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^{m_l}\right\}. \tag{32}$$

However, from (16) and (18) it is also true that

$$f_n\big|_{\lambda=0} = n! \int_0^t \mathbf{A}^{(n)}(s)\,ds. \tag{33}$$

Therefore, it follows that

$$\int_0^t \mathbf{A}^{(n)}(s)\,ds = \sum_{\sum_{l=1}^{\infty} l m_l = n} \underline{T}\left\{\prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^{m_l}\right\}. \tag{34}$$

By explicitly working out (34) through $n = 4$, agreement with previously published expressions, derived by a more laborious method, will be reached.[8]

The problem of inverting (34) in order to obtain expressions for $\int_0^t \mathbf{G}^{(n)}(s)\,ds$ in terms of appropriate pro-

ducts of $\int_0^t \mathbf{A}^{(l)}(s)ds$ is not simple because (34) is nonlinear in $\int_0^t \mathbf{G}^{(l)}(s)ds$. This problem is the original objective and it has so far lead to (34). Its solution is obtained by applying the method used to obtain (34) in a different manner, as was also suggested by Riordan.[9] Use of (23) will again be required, although this time w and y will be different functions than those used to arrive at (34). It is necessary to find the appropriate new functions.

To get (34), use of (16) has been made; particularly

$$\sum_{n=0}^{\infty}\lambda^n \int_0^t \mathbf{A}^{(n)}(s)ds = \underline{\mathcal{T}}\exp\left(\sum_{n=0}^{\infty}\lambda^n \int_0^t \mathbf{G}^{(n)}(s)ds\right) = \left\langle \underline{\mathcal{T}}\exp\left(\lambda \int_0^t \bar{\mathbf{B}}(s)ds\right)\right\rangle. \tag{35}$$

Define $\mathbf{W}(\lambda, t)$ and $\mathbf{R}(\lambda, t)$ by

$$\mathbf{W}(\lambda, t) \equiv \sum_{n=1}^{\infty}\lambda^n \int_0^t \mathbf{G}^{(n)}(s)ds, \qquad \mathbf{R}(\lambda, t) \equiv \sum_{n=1}^{\infty}\lambda^n \int_0^t \mathbf{A}^{(n)}(s)ds. \tag{36}$$

Using (36) in (35) gives

$$\mathbf{1} + \mathbf{R}(\lambda, t) = \mathbf{1} + \sum_{n=1}^{\infty}\frac{1}{n!}\underline{\mathcal{T}}\{(\mathbf{W}(\lambda, t))^n\}. \tag{37}$$

Finally, define $\mathbf{R}'(\lambda, t)$ by

$$\mathbf{R}'(\lambda, t) \equiv \sum_{n=1}^{\infty}\frac{1}{n!}\underline{\mathcal{T}}\{(\mathbf{W}(\lambda, t))^n\}. \tag{38}$$

Consequently, (37) is simply

$$\mathbf{1} + \mathbf{R}(\lambda, t) = \mathbf{1} + \mathbf{R}'(\lambda, t). \tag{39}$$

For sufficiently small λ, both $\mathbf{R}(\lambda, t)$ and $\mathbf{R}'(\lambda, t)$ can be made to approach the zero matrix as closely as is desired. Therefore, it is possible to define a time-ordered logarithm by the formula

$$\underline{\ln}[\mathbf{1} + \mathbf{R}(\lambda, t)] \equiv \sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\underline{\mathcal{T}}\{(\mathbf{R}(\lambda, t))^l\} = \underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)] \equiv \sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\underline{\mathcal{T}}\{(\mathbf{R}(\lambda, t))^l\} \tag{40}$$

If the matrices in (40) are replaced by commuting quantities, then the time ordering operations become unnecessary and the series correspond with the series expansion for the ordinary logarithm, $\ln(1 + \lambda x)$, which is valid for sufficiently small λ. Because the λ derivatives to be performed will be evaluated at $\lambda = 0$, (40) is entirely sufficient, even though it only makes sense for sufficiently small λ. To use (23) in this case, identify f with $\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)] = \underline{\ln}[\mathbf{1} + \mathbf{R}(\lambda, t)]$. For $y(u)$ in this case take: $y(u) \equiv \sum_{l=1}^{\infty}[(-1)^{l-1}/l]u^l$, and for $w(\lambda)$ take: $w(\lambda) \equiv \mathbf{R}(\lambda, t)$.

Observe that

$$\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)] = \mathbf{W}(\lambda, t) \tag{41}$$

This remarkable result can be written as

$$\underline{\ln}\{\underline{\mathcal{T}}\exp[\mathbf{W}(\lambda, t)]\} = \mathbf{W}(\lambda, t), \tag{42}$$

where use of (35) and (36) has been made. The proof of (41) and (42) goes as follows:

$$\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)] = \sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\underline{\mathcal{T}}\{(\mathbf{R}'(\lambda, t))^l\} = \sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\underline{\mathcal{T}}\left\{\left(\sum_{n=1}^{\infty}\frac{1}{n!}\underline{\mathcal{T}}\{(\mathbf{W}(\lambda, t))^n\}\right)^l\right\} = \sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\underline{\mathcal{T}}\left\{\left(\sum_{n=1}^{\infty}\frac{1}{n!}(\mathbf{W}(\lambda, t))^n\right)^l\right\}. \tag{43}$$

The last equality follows from the definition of the time ordering operator.[10] It may be expressed by: the time-ordered product of factors which are themselves time-ordered is equal to the time-ordered product of those same factors without internal time ordering.[12] The easiest way to see this point is to use the definition of $\underline{\mathcal{T}}$ which involves θ factions.[10] The last line of (43) is most easily evaluated after taking the time-ordering operator $\underline{\mathcal{T}}$ out in front of the sum over l. The result is

$$\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)] = \underline{\mathcal{T}}\left\{\sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\left(\sum_{n=1}^{\infty}\frac{1}{n!}(\mathbf{W}(\lambda, t))^n\right)^l\right\}. \tag{44}$$

Now, consider e^x for x positive but less than ln2. Then it is so that

$$e^x = 1 + \sum_{n=1}^{\infty}\frac{1}{n!}X^n \quad \text{and} \quad \sum_{n=1}^{\infty}\frac{1}{n!}X^n < 1. \tag{45}$$

Consequently,

$$\ln\left(1 + \sum_{n=1}^{\infty}\frac{1}{n!}X^n\right) = \sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}\left(\sum_{n=1}^{\infty}\frac{1}{n!}X^n\right)^l. \tag{46}$$

The form of (46) is precisely the same as the form of (44) provided λ is small enough. Consequently, because $\ln[1 + \sum_{n=1}^{\infty}(1/n!)X^n] = \ln(e^X) = X$, it follows from (44) that

$$\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)] = \mathbf{W}(\lambda, t). \tag{47}$$

The time-ordering operator in front of the right-hand side of (44) is not present explicitly in (47) because $\mathbf{W}(\lambda, t)$ is already fully time-ordered according to (36) and (15). This completes the proof of (41) and (42), but it must be remembered that the attendant analysis is only valid for sufficiently small λ, and (41) and (42) have not been proved for arbitrary λ.

Returning to the discussion between Eqs. (40) and (41), it follows that

$$f_n\big|_{\lambda=0} = \frac{d^n}{d\lambda^n}\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)]\big|_{\lambda=0} = \frac{d^n}{d\lambda^n}\mathbf{W}(\lambda, t)\Big|_{\lambda=0} = n!\int_0^t \mathbf{G}^{(n)}(s)ds. \tag{48}$$

On the other hand, the equivalence of $\underline{\ln}[\mathbf{1} + \mathbf{R}'(\lambda, t)]$ and $\underline{\ln}[\mathbf{1} + \mathbf{R}(\lambda, t)]$, along with the choices for $y(u)$ and $w(\lambda)$ given in the discussion between Eqs. (40) and (41), imply through (23) that

$$f_n\big|_{\lambda=0} = \sum_{\sum_{l=1}^{\infty} l m_l = n}\underline{\mathcal{T}}\left\{\prod_{l=1}^{\infty}\frac{n!}{(l!)^{m_l} m_l!}(w_l)^{m_l} y_p\Big|_{\lambda=0}\right\} = \sum_{\sum_{l=1}^{\infty} l m_l = n}\underline{\mathcal{T}}\left\{\prod_{l=1}^{\infty}\frac{n!}{(l!)^{m_l} m_l!}\left(l!\int_0^t \mathbf{A}^{(l)}(s)ds\right)^{m_l}(-1)^{p-1}(p-1)!\right\}, \tag{49}$$

where $p \equiv \sum_{l=1}^{\infty} m_l$. To get (49), the following two identities were used:

$$w_l\big|_{\lambda=0} = \frac{d^l}{d\lambda^l}\left(\sum_{n=1}^{\infty}\lambda^n\int_0^t \mathbf{A}^{(n)}(s)ds\right)\Big|_{\lambda=0} = l!\int_0^t A^{(n)}(s)ds \tag{50}$$

and

$$y_p\Big|_{\lambda=0} = \frac{d^p}{du^p}\left(\sum_{l=1}^{\infty}(-1)^{l-1}\frac{1}{l}u^l\right)_{u=0}$$
$$= (-1)^{p-1}(p-1)!, \tag{51}$$

wherein $u=0$ corresponds with $\lambda=0$.

Combining (48) and (49) provides the desired inversion formula:

$$\int_0^t \mathbf{G}^{(n)}(s)ds = \sum_{\sum_{l=1}^{\infty} l m_l = n} (-1)^{p-1}(p-1)!\,\underline{T}\left\{\prod_{l=1}^{n}\frac{1}{m_l!}\left(\int_0^t \mathbf{A}^{(l)}(s)ds\right)^{m_l}\right\}, \tag{52}$$

where $p=\sum_{l=1}^{\infty} m_l$ in each summand of the partition summation. Formula (52) is identical with the results obtained from van Kampen's rules.[6,7] Together, (19), (17), and (52) provide a general expression for the nth order, time-ordered cumulant averages in terms of ordinary, time-ordered averages.

The averaged solution to (7) can be written using (13) and (14) as

$$\langle b_\alpha(t)\rangle = \left[\underline{T}\exp\left(\sum_{n=1}^{\infty}\int_0^t \mathbf{G}^{(n)}(s)ds\right)\right]_{\alpha\alpha'} b_{\alpha'}(0). \tag{53}$$

The corresponding differential equation is

$$\frac{d}{dt}\langle b_\alpha(t)\rangle = \sum_{n=1}^{\infty}[\mathbf{G}^{(n)}(t)]_{\alpha\alpha'}\langle b_{\alpha'}(t)\rangle. \tag{54}$$

By using (8), this corresponds with

$$\frac{d}{dt}\langle a_\alpha(t)\rangle = M_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + [\exp(t\mathbf{M})]_{\alpha\beta}\sum_{n=1}^{\infty}[\mathbf{G}^{(n)}(t)]_{\beta\beta'} \times [\exp(-t\mathbf{M})]_{\beta'\alpha'}\langle a_{\alpha'}(t)\rangle. \tag{55}$$

Because only the first two moments of $\tilde{\mathbf{B}}(t)$ have been explicitly indicated in (10) and (11), only for $n=1$ and $n=2$ in (55) will explicit expressions be given at this point. From (52) it follows that

$$\mathbf{G}^{(1)}(t) = \mathbf{A}^{(1)}(t) = \langle\tilde{\mathbf{B}}(t)\rangle = 0. \tag{56}$$

The second and third equalities follow from (17) and (10) respectively. Again from (52), it follows that

$$\mathbf{G}^{(2)}(t) = \mathbf{A}^{(2)}(t) = \int_0^t \langle\tilde{\mathbf{B}}(t)\tilde{\mathbf{B}}(s)\rangle ds, \tag{57}$$

where the second equality follows from (17). Therefore, the $n=2$ term in (55) becomes

$$[\exp(t\mathbf{M})]_{\alpha\beta}\mathbf{G}^{(2)}_{\beta\beta'}(t)[\exp(-t\mathbf{M})]_{\beta'\alpha'} = \int_0^t \langle\tilde{A}'_{\alpha\mu}(t)[\exp((t-s)\mathbf{M}]_{\mu\nu}\tilde{A}'_{\nu\theta}(s)[\exp((s-t)\mathbf{M})]_{\theta\alpha'}\rangle ds = 2\int_0^t Q_{\alpha\mu\nu\theta}(t-s)[\exp((s-t)\mathbf{M}]_{\mu\nu}[\exp((s-t)\mathbf{M})]_{\theta\alpha'}ds, \tag{58}$$

where (9) and (6) have been used to get the last two lines. lines. Without explicit expressions for the higher order moments of $\tilde{\mathbf{A}}'(t)$, the higher order terms in (55) can be rewritten part way only, giving

$$\exp(t_1\mathbf{M})\mathbf{G}^{(n)}(t_1)\exp(-t_1\mathbf{M}) = \int_0^{t_1}\int_0^{t_2}\cdots\int_0^{t_{n-2}}\int_0^{t_{n-1}}\langle\tilde{\mathbf{A}}'(t_1)\prod_{l=2}^{n}\exp[(t_{l-1}-t_l)\mathbf{M}]\tilde{\mathbf{A}}'(t_l) \times\exp[(t_l-t_1)\mathbf{M}]\rangle_c dt_n\,dt_{n-1}\cdots dt_2. \tag{59}$$

This expression contains cumulant averaging in the integrand, and (52) must be used to get an expression in terms of ordinary averaging. The explicit, very complicated expression will not be written down here.

3. THE GAUSSIAN PROPERTY

When dealing with stochastic processes which do not involve the difficulties of noncommutivity, the stipulation that the stochastic process is Gaussian leads to great simplifications in the cumulant expression.[8] All cumulants of order higher than two vanish for Gaussian, commutative, stochastic processes.[8] However, the presence of noncommutivity leads to nonvanishing higher than second order cumulants.[8] It is for this reason that Kubo's concept of a generalized Gaussian process in the noncommutative case is invalid.[4,5] To further clarify this situation, the following brief review of the principal points of relevance are presented.

For convenience assume that $\mathbf{M}=0$ in the preceding section. It then follows that $\tilde{\mathbf{A}}(t)\equiv\tilde{\mathbf{A}}'(t)\equiv\tilde{\mathbf{B}}(t)$, and

$$\langle\tilde{\mathbf{A}}(t)\rangle = 0, \tag{60}$$

$$\langle\tilde{A}_{\alpha\beta}(t)\tilde{A}_{\alpha'\beta'}(s)\rangle = 2Q_{\alpha\beta\alpha'\beta'}(t-s). \tag{61}$$

The Gaussian property leads to explicit expressions for all higher order moments:

$$\langle\tilde{A}_{\alpha_1\beta_1}(t_1)\cdots A_{\alpha_{2n-1}\beta_{2n-1}}(t_{2n-1})\rangle = 0, \tag{62}$$

$$\langle\tilde{A}_{\alpha_1\beta_1}(t_1)\cdots\tilde{A}_{\alpha_{2n}\beta_{2n}}(t_{2n})\rangle = \frac{1}{2^n n!}\sum_{p\in S_{2n}}\prod_{j=1}^{n}\langle\tilde{A}_{\alpha_{p(2j-1)}\beta_{p(2j-1)}}(t_{p(2j-1)})\tilde{A}_{\alpha_{p(2j)}\beta_{p(2j)}}(t_{p(2j)})\rangle, \tag{63}$$

where p is a permutation in the symmetric group of order $(2n)!$, S_{2n}. The easiest way to understand the origin of these formulas is to use the method of S. O. Rice.[13,14] $\tilde{A}(t)$ is represented by a Fourier series:

$$\tilde{A}(t) = \left(\frac{2}{T}\right)^{1/2}\sum_{n=1}^{N}\left(\tilde{\mathbf{A}}_n\cos\frac{2\pi nt}{T} + \tilde{\mathbf{B}}_n\sin\frac{2\pi nt}{T}\right), \tag{64}$$

in which both N and T ultimately are allowed to go to infinity and the coefficients $\tilde{\mathbf{A}}_n$ and $\tilde{\mathbf{B}}_n$ are time-independent, statistically independent, stochastic matrices with Gaussian distributions. In particular, the distribution for $\tilde{A}_n$ is of the form

$$D(\mathbf{A}_n) = \left(\frac{\|\mathbf{G}_n\|}{(2\pi)^n}\right)^{1/2}\exp(-\tfrac{1}{2}\mathbf{A}_n\circ\mathbf{G}_n\circ\mathbf{A}_n), \tag{65}$$

where $\mathbf{G}_n$ is a positive definite tetratic correlation with determinant $\|\mathbf{G}_n\|$. Using (64) in the left-hand side of (63) leads to all the different products of pairs on the right-hand side. In the special case in which all the correlation tetratics for all the $\mathbf{A}_n$'s and $\mathbf{B}_n$'s are identical, the time dependence in (61) will be $\delta(t-s)$, and $2\mathbf{Q}\equiv\mathbf{G}^{-1}$. This is seen by using (64) in (61) which gives

$$\langle A_{\alpha\beta}(t)A_{\alpha'\beta'}(s)\rangle = \frac{2}{T}\sum_{n=1}^{N}\left(\langle\tilde{A}_{n\alpha\beta}\tilde{A}_{n\alpha'\beta'}\rangle\cos\frac{2\pi nt}{T}\cos\frac{2\pi ns}{T} + \langle\tilde{B}_{n\alpha\beta}\tilde{B}_{n\alpha'\beta'}\rangle\sin\frac{2\pi nt}{T}\sin\frac{2\pi ns}{T}\right) \tag{66}$$

$$= \frac{2}{T}\sum_{n=1}^{N}\left(G^{-1}_{(\alpha\beta)(\alpha'\beta')}\cos\frac{2\pi nt}{T}\cos\frac{2\pi ns}{T}\right.$$

$$+G^{-1}_{(\alpha\beta)(\alpha'\beta')}\sin\frac{2\pi nt}{T}\sin\frac{2\pi ns}{T}\Big)$$

$$=\frac{2}{T}G^{-1}_{(\alpha\beta)(\alpha'\beta')}\sum_{n=1}^{N}\cos\frac{2\pi n(t-s)}{T}$$

$$\to G^{-1}_{(\alpha\beta)(\alpha'\beta')}\delta(t-s)\quad\text{as } T\to\infty \text{ and } N\to\infty.$$

The first equality follows from the postulated statistical independence of all the stochastic, matrix coefficients in (64). The second equality follows from the assumption for this special case that all correlation tetratics are the same, and the fact that

$$\langle\tilde{A}_{n_{\mu\nu}}\tilde{A}_{n_{\mu'\nu'}}\rangle=\int\cdots\int\left(\frac{\|\mathbf{G}\|}{(2\pi)^n}\right)^{1/2}\exp[-\tfrac{1}{2}A_{n_{\alpha\beta}}G_{(\alpha\beta)(\alpha'\beta')}A_{n_{\alpha'\beta'}}]$$

$$\times A_{n_{\mu\nu}}A_{n_{\mu'\nu'}}d\mathbf{A}_n=G^{-1}_{(\mu\nu)(\mu'\nu')}. \tag{67}$$

The validity of (67) is perhaps best seen in a more familiar matrix notation in the case of a vector process, $\tilde{X}_i$, where $i=1, 2, \cdots, N$ with a Gaussian distribution given by

$$D(X)=[\|\mathbf{E}\|/(2\pi)^n]^{1/2}\exp(-\tfrac{1}{2}X_iE_{ij}X_j), \tag{68}$$

where $\|\mathbf{E}\|$ is the determinant of E_{ij} which is positive definite and symmetric. Therefore,

$$\langle X_lX_k\rangle=\int\cdots\int\left(\frac{\|\mathbf{E}\|}{(2\pi)^n}\right)^{1/2}\exp(-\tfrac{1}{2}X_iE_{ij}X_j)X_lX_k d\mathbf{X}$$

$$=E^{-1}_{ij}. \tag{69}$$

Equation (67) is the natural generalization of (69) when vectors become matrices, and matrices become tetratics. Other special cases will involve G_n's which are not all equal, and as a consequence the time dependence in (61) will not be simply $\delta(t-s)$ as in (66). Of particular interest is the special case in which G_n^{-1} has the form

$$\mathbf{G}_n^{-1}=2\mathbf{Q}\frac{\tau_c}{1+(2\pi n/T)^2\tau_c^2}[1-\exp(-T/\tau_c)]. \tag{70}$$

Following the procedure used in (66) leads to

$$\langle\tilde{A}_{\alpha\beta}(t)\tilde{A}_{\alpha'\beta'}(s)\rangle=2Q_{(\alpha\beta)(\alpha'\beta')}\frac{2}{T}\sum_{n=1}^{N}\cos\frac{2\pi n}{T}(t-s)$$

$$\times\frac{\tau_c}{1+(2\pi n/T)^2\tau_c^2}[1-\exp(-T/\tau_c)]$$

$$\to 2Q_{(\alpha\beta)(\alpha'\beta')}\exp(-|t-s|/\tau_c)$$

$$\text{as } N\to\infty \text{ and } T\to\infty \tag{71}$$

This special case will be of interest when Kubo's concept of a generalized Gaussian process is considered.

With the stipulation $\mathbf{M}\equiv 0$, introduced at the beginning of this section, the fourth-order cumulant, according to (52), (17), (15), and (9), is

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{\mathbf{A}}(t_1)\tilde{\mathbf{A}}(t_2)\tilde{\mathbf{A}}(t_3)\tilde{\mathbf{A}}(t_4)\rangle_c dt_4dt_3dt_2dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{\mathbf{A}}(t_1)\tilde{\mathbf{A}}(t_2)\tilde{\mathbf{A}}(t_3)\tilde{\mathbf{A}}(t_4)\rangle dt_4dt_3dt_2dt_1$$

$$-\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_3}\langle\tilde{\mathbf{A}}(t_1)\tilde{\mathbf{A}}(t_2)\rangle\langle\tilde{\mathbf{A}}(t_3)\tilde{\mathbf{A}}(t_4)\rangle dt_4dt_3dt_2dt_1. \tag{72}$$

Notice the upper limits on the second multiple integral of the right-hand side of (72). These upper limits follow from the time ordering in (52). Using (63) yields for the first multiple integral of the right-hand side of (72) the identity

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_2\mu_3}(t_3)\tilde{A}_{\mu_3\beta}(t_4)\rangle dt_4dt_3dt_2dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}[\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_2)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_3)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$+\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_2\mu_3}(t_3)\rangle\langle\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$+\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_3\beta}(t_4)\rangle\langle\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_2\mu_3}(t_3)\rangle]dt_4dt_3dt_2dt_1. \tag{73}$$

The second multiple integral of the right-hand side of (72) may be simplified also by noting the identity

$$\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_3dt_2dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_3dt_2dt_1$$

$$+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_3dt_2dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_3dt_2dt_1$$

$$+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_2dt_3dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_3dt_2dt_1$$

$$+\int_0^t\int_0^{t_1}\int_0^{t_3}\int_0^{t_2}g(t_1t_2t_3t_4)dt_4dt_2dt_3dt_1$$

$$+\int_0^t\int_0^{t_1}\int_0^{t_3}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_2dt_3dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}g(t_1t_2t_3t_4)dt_4dt_3dt_2dt_1$$

$$+\int_0^t\int_0^{t_1}\int_0^{t_3}\int_0^{t_2}g(t_1t_2t_3t_4)dt_4dt_2dt_3dt_1$$

$$+\int_0^t\int_0^{t_1}\int_0^{t_3}\int_0^{t_4}g(t_1t_2t_3t_4)dt_2dt_4dt_3dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}[g(t_1t_2t_3t_4)+g(t_1t_3t_2t_4)$$

$$+g(t_1t_4t_2t_3)]dt_4dt_3dt_2dt_1. \tag{74}$$

The first and third equalities follow from: $\int_0^x=\int_0^y+\int_y^x$. The second and fourth equalities follow from interchange of the order of integration: $\int_0^t\int_s^t dt'ds=\int_0^t\int_0^{t'}dsdt'$. The last equality follows from a renaming of time variable indices. The arbitrary function $g(t_1t_2t_3t_4)$ respects the order of the occurrence of the different indices on the time variables which are its arguments. Applying (74) to the case at hand gives

$$-\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_3}\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_2)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_3)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$\times dt_4dt_3dt_2dt_1$$

$$=-\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}[\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_2)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_3)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$+\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_3)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_2)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$+\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_4)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_2)\tilde{A}_{\mu_3\beta}(t_3)\rangle]dt_4dt_3dt_2dt_1. \tag{75}$$

Putting (73) and (75) into (72) gives

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_2\mu_3}(t_3)\tilde{A}_{\mu_3\beta}(t_4)\rangle_c dt_4dt_3dt_2dt_1$$

$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}[\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_2\mu_3}(t_3)\rangle\langle\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$-\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_3)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_2)\tilde{A}_{\mu_3\beta}(t_4)\rangle$$

$$+\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_3\beta}(t_4)\rangle\langle\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_2\mu_3}(t_3)\rangle$$
$$-\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_4)\rangle\langle\tilde{A}_{\mu_2\mu_3}(t_2)\tilde{A}_{\mu_3\beta}(t_3)\rangle\}dt_4dt_3dt_2dt_1. \tag{76}$$

Only the leading terms in each of (73) and (75) cancel out in general. Therefore, Kubo's specification that the fourth order cumulant vanish for a "generalized" Gaussian, stochastic, matrix process cannot, in general, occur. However, the situation is not too bad, after all, for the following reasons.

If the time dependence for the second moments of $\tilde{\mathbf{A}}(t)$ is the delta function $\delta(t-s)$, then (76) does indeed vanish, as do all higher order cumulants.[8,15] This is seen for (76) because the time integrals become

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\delta(t_1-t_3)\delta(t_2-t_4)dt_4dt_3dt_2dt_1=0$$

and

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\delta(t_1-t_4)\delta(t_2-t_3)dt_4dt_3dt_2dt_1=0. \tag{77}$$

If instead the time dependence is as in (71), the integrals become

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\exp\left(-\frac{t_1-t_3}{\tau_c}\right)\exp\left(-\frac{t_2-t_4}{\tau_c}\right)dt_4dt_3dt_2dt_1$$
$$=t\left[\frac{\tau_c^3}{2}+\tau_c^3\exp\left(-\frac{t}{\tau_c}\right)\right]+2\frac{\tau_c^4}{2}\left[\exp\left(-\frac{t}{\tau_c}\right)-1\right]$$
$$+\frac{\tau_c^4}{4}\left[\exp\left(-\frac{2t}{\tau_c}\right)-1\right]$$
$$=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\exp\left(-\frac{t_1-t_4}{\tau_c}\right)\exp\left(-\frac{t_2-t_3}{\tau_c}\right)$$
$$\times dt_4dt_3dt_2dt_1. \tag{78}$$

Indeed, (78) can be used to prove (77) if it is noticed that

$$\lim_{\tau_c\to 0}(1/\tau_c)\exp(-|\tau|/\tau_c)=\tfrac{1}{2}\delta(\tau). \tag{79}$$

For $t\gg\tau_c$, (78) becomes $\frac{1}{2}t\tau_c^3$. By using all of (71) the entire fourth cumulant becomes in this case

$$\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\mu_2}(t_2)\tilde{A}_{\mu_2\mu_3}(t_3)\tilde{A}_{\mu_3\beta}(t_4)\rangle_c dt_4dt_3dt_2dt_1$$
$$\xrightarrow[t\gg\tau_c]{}4(Q_{\alpha\mu_1\mu_2\mu_3}Q_{\mu_1\mu_2\mu_3\beta}-Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta}$$
$$+Q_{\alpha\mu_1\mu_3\beta}Q_{\mu_1\mu_2\mu_2\mu_3}-Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta})\tfrac{1}{2}t\tau_c^3. \tag{80}$$

Clearly, for a nonmatrix process there would be no indices and there would be a cancellation. The second cumulant in the case of (71) is

$$\int_0^t\int_0^{t_1}\langle\tilde{A}_{\alpha\mu_1}(t_1)\tilde{A}_{\mu_1\beta}(t_2)\rangle_c dt_2dt_1\xrightarrow[t\gg\tau_c]{}2Q_{\alpha\mu_1\mu_1\beta}t\tau_c \tag{81}$$

Both (80) and (81) are linear in t. However, suppose Q is proportional to a relaxation time τ_R, taken to the minus two power:

$$\mathbf{Q}^N\approx\tau_R^{-2}. \tag{82}$$

This is dimensionally correct, and it suggests that (80) and (81) have the forms

$$2Q_{\alpha\mu_1\mu_1\beta}t\tau_c\to 2Nt\tau_c/\tau_R^2$$

and

$$4(Q_{\alpha\mu_1\mu_2\mu_3}Q_{\mu_1\mu_2\mu_3\beta}+Q_{\alpha\mu_1\mu_3\beta}Q_{\mu_1\mu_2\mu_2\mu_3}$$
$$-2Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta})\tfrac{1}{2}t\tau_c^3\to 2N^3t\tau_c^3/\tau_R^4, \tag{83}$$

where N is the approximate number of terms in the sum $Q_{\alpha\mu\mu\beta}$ which are large and of order τ_R^{-2}. This means that the ratio of the fourth order cumulant and the second order cumulant is $N^2\tau_c^2/\tau_R^2$. Now, suppose there are N' states labeled by the indices α, β, μ, ν, etc. If N is comparable to N' then the effective relaxation time is τ_R/N', which for large enough N' will surely be less than τ_c. Moreover, $N^2\tau_c^2/\tau_R^2$ will then be greater than 1, and the fourth cumulant becomes more important than the second. On the other hand, if $N\gg N'$ because not all pairs of states are coupled by equally strong stochastic matrix elements, then the effective relaxation time τ_R/N can still be longer than τ_c. In this situation the fourth order cumulant becomes unimportant compared with the second cumulant when $t>\tau_c$. This situation would imply that the $\langle a_\alpha(t)\rangle$'s relax more slowly than do the fluctuation correlations. In physical applications, it is this situation which is of most interest, and for it the second cumulant provides the dominant effects when $t>\tau_c$. Thus, two conditions are required:

$$t>\tau_c \text{ and } N\tau_c/\tau_R<1 \tag{84}$$

if the dynamics is to be dominated by the second cumulant only. This is, of course, essentially equivalent to the delta function theory[1], as was indicated by (79).

In summary, it may be claimed that Kubo's "generalized" Gaussian, stochastic, matrix process only obtains for a delta function correlation, for otherwise a truly Gaussian process will involve fourth and higher order cumulants. If, however, condition (84) holds, then the asymptotic behavior is dominated by the second cumulant after all. The fully rigorous justification of these remarks requires analysis of the higher order cumulants in special cases such as the ones studied here. It is perhaps ironic that the general theory presented here using cumulants, actually justifies the earlier, more simple, delta function theory[1], rather than superseding it, if (84) is satisfied. It should also be noted that dominance by the second cumulant in this situation requires $t>\tau_c$ but t need not be very very much greater than τ_c since $t\approx 10-100\tau_c$ already reduces the higher order corrections to very small effects.

4. THE DENSITY MATRIX

The mathematical results developed in the preceding sections will be applied now to the treatment of the stochastic Schrödinger equation[2,3]

$$i\frac{d}{dt}C_\alpha(t)=M_{\alpha\alpha'}C_{\alpha'}(t)+\tilde{M}_{\alpha\alpha'}(t)C_{\alpha'}(t), \tag{85}$$

in which $M_{\alpha\alpha'}=M^*_{\alpha'\alpha}$ and $\tilde{M}_{\alpha\alpha'}(t)=\tilde{M}^*_{\alpha'\alpha}(t)$. $\tilde{M}_{\alpha\alpha'}(t)$ corresponds to a stochastic Hamiltonian which is Hermitian. Suppose that a change of basis states is made so that $M_{\alpha\alpha'}$ becomes diagonal. Suppose further that there are N states corresponding with the degenerate eigenvalue λ. If consideration is restricted to these N degenerate eigenstates of $\mathbf{M}$, then (85) becomes

$$i\frac{d}{dt}C'_\alpha(t)=\lambda C'_\alpha(t)+\tilde{M}'_{\alpha\alpha'}(t)C'_{\alpha'}(t), \tag{86}$$

where α and α' range over 1, 2, $\cdots$, N. The stochastic Hamiltonian $\tilde{M}_{\alpha\alpha'}(t)$ will not couple eigenstates of $\mathbf{M}$

which belong to different degeneracy classes. This requirement is imposed in order to insure that the description given by (86) leads to a microcanonical equilibrium density matrix and not to the uniform density matrix. The reader is especially urged to see Ref. 3 for more details concerning this point. For convenience, the primes in (86) will be dropped in the following, and confusion with (85) should be avoided.

The moments for $\tilde{M}_{\alpha\alpha'}(t)$ are given by

$$\langle \tilde{M}_{\alpha\alpha'}(t)\rangle = 0, \tag{87}$$

$$\langle \tilde{M}_{\alpha\alpha'}(t)\tilde{M}_{\beta\beta'}(s)\rangle = 2Q_{\alpha\alpha'\beta\beta'}(t-s). \tag{88}$$

In (88), the time dependence of $Q_{\alpha\alpha'\beta\beta'}(t-s)$ can change as the values of the indices change, in general. The specific case in which the time dependence for all values of the indices is a delta function has been extensively treated in earlier publications.[1-3,16,17]

Although, in general it is unnecessary to do so, the imposition that $\tilde{M}_{\alpha\alpha'}(t)$ be also Gaussian can be made and leads to

$$\langle \tilde{M}_{\mu_1\nu_1}(t_1)\cdots\tilde{M}_{\mu_{2n-1}\nu_{2n-1}}(t_{2n-1})\rangle = 0, \tag{89}$$

$$\begin{aligned}&\langle \tilde{M}_{\mu_1\nu_1}(t_1)\cdots\tilde{M}_{\mu_{2n}\nu_{2n}}(t_{2n})\rangle\\ &= \frac{1}{2^n n!}\sum_{p\in S_{2n}}\prod_{j=1}^{n}\langle \tilde{M}_{\mu_{p(2j-1)}\nu_{p(2j-1)}}(t_{p(2j-1)})\\ &\quad\times\tilde{M}_{\mu_{p(2j)}\nu_{p(2j)}}(t_{p(2j)})\rangle\\ &= \frac{1}{n!}\sum_{p\in S_{2n}}\prod_{j=1}^{n}Q_{\mu_{p(2j-1)}\nu_{p(2j-1)}\mu_{p(2j)}\nu_{p(2j)}}(t_{p(2j-1)}-t_{p(2j)}).\end{aligned} \tag{90}$$

The density matrix $\rho_{\alpha\beta}(t)$ will be defined by[18]

$$\rho_{\alpha\beta}(t) \equiv C_\alpha^*(t)C_\beta(t), \tag{91}$$

and it satisfies the equation

$$\frac{d}{dt}\rho_{\alpha\beta}(t) = -i\tilde{L}_{\alpha\beta\alpha'\beta'}(t)\rho_{\alpha'\beta'}(t), \tag{92}$$

where $\tilde{L}_{\alpha\beta\alpha'\beta'}(t)$ is defined by

$$\tilde{L}_{\alpha\beta\alpha'\beta'}(t) \equiv \delta_{\alpha\alpha'}\tilde{M}_{\beta\beta'}(t) - \delta_{\beta\beta'}\tilde{M}^*_{\alpha\alpha'}(t). \tag{93}$$

Equation (92) is a special case of (4) when the $\mathbf{M}$ in (4) is zero. Of course, one must think of $\rho_{\alpha\beta}(t)$ as a doubly indexed vector, and $\tilde{L}_{\alpha\beta\alpha'\beta'}(t)$ as a quadruply indexed matrix to see the connection between (4) and (92). Therefore, the average of (92) is a special case of (55) in which the $\tilde{\mathbf{M}}$ in (55) is zero. This gives

$$\frac{d}{dt}\langle\rho_{\alpha\beta}(t)\rangle = \sum_{n=1}^{\infty}R^{(n)}_{\alpha\beta\alpha'\beta'}(t)\langle\rho_{\alpha'\beta'}(t)\rangle \tag{94}$$

wherein $R^{(n)}_{\alpha\beta\alpha'\beta'}(t)$ is defined by

$$\int_0^t \mathbf{R}^{(n)}(s)ds = \sum_{\sum_{I=1}^{\infty} I m_I = n}(-1)^{p-1}(p-1)!\,T\left\{\prod_{I=1}^{\infty}\frac{1}{m_I!}\left(\int_0^t \mathbf{D}^{(I)}(s)ds\right)^{m_I}\right\}, \tag{95}$$

where $p \equiv \sum_{I=1}^{\infty} m_I$ and $n \geq 2$. For $n=1$, $R^{(1)}=0$. The $\mathbf{D}^{(I)}(s)$ in (95) is defined by

$$\begin{aligned}\mathbf{D}^{(n)}(s) \equiv (i)^n\int_0^s\int_0^{t_2}\cdots\int_0^{t_{n-2}}\int_0^{t_{n-1}}&\langle\tilde{\mathbf{L}}(s)\tilde{\mathbf{L}}(t_2)\cdots\\ &\times\tilde{\mathbf{L}}(t_{n-1})\tilde{\mathbf{L}}(t_n)\rangle dt_n\cdots dt_2.\end{aligned} \tag{96}$$

Equations (95) and (96) are special cases of (52) and (15) respectively, when $\mathbf{M}$ is zero in (52) and (15). The condition, $\mathbf{R}^{(1)}=0$, follows from (87) and (67).

The explicit expression for $R^{(2)}_{\alpha\beta\alpha'\beta'}(t)$ is

$$\begin{aligned}R^{(2)}_{\alpha\beta\alpha'\beta'}(t) &= -\int_0^t\langle\tilde{L}_{\alpha\beta\mu\nu}(t)\tilde{L}_{\mu\nu\alpha'\beta'}(s)\rangle ds\\ &= -\int_0^t\{\delta_{\alpha\alpha'}Q_{\beta\nu\nu\beta'}(t-s)+\delta_{\beta\beta'}Q_{\mu\alpha\alpha'\mu}(t-s)\\ &\quad -Q_{\beta\beta'\alpha'\alpha}(t-s)-Q_{\alpha'\alpha\beta\beta'}(t-s)\}ds.\end{aligned} \tag{97}$$

If it is further assumed that the stochastic Hamiltonian is stationary, then $Q_{\alpha\beta\alpha'\beta'}(t-s)=Q_{\alpha'\beta'\alpha\beta}(s-t)=Q_{\alpha'\beta'\alpha\beta}(t-s)$. This is equivalent with microscopic reversibility.[19] Using (89) and (90) in (96) and (95) provides explicit expressions for $\mathbf{R}^{(n)}(t)$ for $n>2$ in the Gaussian case.

In general, the microcanonical density matrix

$$\rho^{\text{microcanonical}}_{\alpha\beta} \equiv (1/N)\delta_{\alpha\beta} \tag{98}$$

is a solution to Eq. (94) regardless of any special assumptions about $\tilde{\mathbf{M}}(t)$, such as Gaussianness. This is seen from (95) and (96) as follows. It is necessary to show that

$$R_{\alpha\beta(n)\alpha'\beta'}(t)(1/N)\delta\alpha'\beta' = 0 \tag{99}$$

for each n. By using (97), this is clearly true for $n=2$. The second equality in (97) leads to

$$\begin{aligned}&-\int_0^t\{\delta_{\alpha\alpha'}Q_{\beta\nu\nu\beta'}(t-s)+\delta_{\beta\beta'}Q_{\mu\alpha\alpha'\mu}(t-s)-Q_{\beta\beta'\alpha'\alpha}(t-s)\\ &\quad -Q_{\alpha'\alpha\beta\beta'}(t-s)\}ds(1/N)\delta_{\alpha'\beta'}\\ &= -\int_0^t\{Q_{\beta\nu\nu\alpha}(t-s)+Q_{\mu\alpha\beta\mu}(t-s)-Q_{\beta\theta\theta\alpha}(t-s)\\ &\quad -Q_{\theta\alpha\beta\theta}(t-s)\}(1/N)ds \equiv 0.\end{aligned} \tag{100}$$

Alternatively, the first equality in (97) may be used to obtain the same result:

$$\begin{aligned}&-\int_0^t\langle L_{\alpha\beta\mu\nu}(t)\tilde{L}_{\mu\nu\alpha'\beta'}(t)\rangle ds(1/N)\delta_{\alpha'\beta'}\\ &\quad = -\int_0^t\langle\tilde{L}_{\alpha\beta\mu\nu}(t)\tilde{L}_{\mu\nu\alpha'\beta'}(t)(1/N)\delta_{\alpha'\beta'}\rangle ds \equiv 0\end{aligned} \tag{101}$$

because $\tilde{L}_{\mu\nu\theta\theta}(t)=0$ as follows from (93) and the hermiticity of $\tilde{\mathbf{M}}(t)$. It is the proof of (99) for $n=2$ given by (101) which readily generalizes to arbitrary n. Equation (95) shows that the computation of $R^{(n)}_{\alpha\beta\alpha'\beta'}(t)(1/N)\delta_{\alpha'\beta'}$ involves a sum over partitions of n in which each summand involves a sum of time ordered products of $\int_0^t\mathbf{D}^{(I)}(s)ds$'s. Each such time ordered product, according to (96), ends with some $\mathbf{D}^{(I)}(s)$ which ends with $\tilde{L}_{\mu\nu\alpha'\beta'}(t_{I'})$ in its integrand. Consequently, as in (101), $R^{(n)}_{\alpha\beta\alpha'\beta'}(t)(1/N)\delta_{\alpha'\beta'}$ ultimately reduces to an expression containing $\tilde{L}_{\mu\nu\alpha'\beta'}(t_{I'})(1/N)\delta_{\alpha'\beta'}\equiv 0$. This completes the proof of (99).

It is also the case in general that the time dependent solution to (94) satisfies

$$\langle\rho_{\alpha\alpha}(t)\rangle = 1. \tag{102}$$

To see this, it is sufficient to note that

$$R^{(n)}_{\alpha\alpha\alpha'\beta'}(t) = 0 \tag{103}$$

for each n. The proof of (103) is very similar to the proof of (99) and depends upon $\tilde{L}_{\alpha\alpha\alpha'\beta'}(t)\equiv 0$ as follows from (93) and the hermiticity of $\tilde{\mathbf{M}}(t)$.

Whether or not the microcanonical density matrix is approached asymptotically in time starting from an arbitrary initial density matrix depends upon the struc-

ture of $\sum_{n=1}^{\infty} R^{(n)}_{\alpha\beta\alpha'\beta'}(t)$. In the special case previously considered by the author in which the correlation in (88) is a delta function in time and $\tilde{\mathbf{M}}(t)$ is also Gaussian, it was shown that the approach to the microcanonical density matrix was in fact monotone because an H theorem was provable.[2] In the present, more general setting, a greater variety of behaviors is possible, including nonmonotonic approach to the microcanonical density matrix.

In the special case in which

$$Q_{\alpha\alpha'\beta\beta'}(t-s) = Q_{\alpha\alpha'\beta\beta'} \exp(-|t-s|/\tau_c), \tag{104}$$

the presence of a finite correlation time τ_c does not necessarily destroy monotonicity. To see this, note that (104) implies

$$\langle \tilde{M}_{\alpha\alpha'}(t)\tilde{M}_{\beta\beta'}(s)\rangle = \langle \tilde{M}_{\alpha\alpha'}(t)\tilde{M}_{\beta\beta'}(t)\rangle \exp(-|t-s|/\tau_c). \tag{105}$$

Therefore, if $X_{\alpha\beta}$ is an arbitrary hermitian matrix, then

$$\begin{aligned} X^*_{\alpha\beta} R^{(2)}_{\alpha\beta\alpha'\beta'} X_{\alpha'\beta'} &= -\int_0^t \langle X^*_{\alpha\beta} \tilde{L}_{\alpha\beta\mu\nu}(t) \tilde{L}_{\mu\nu\alpha'\beta'}(s) X_{\alpha'\beta'}\rangle ds \\ &= -\int_0^t \langle (\tilde{L}_{\mu\nu\alpha\beta}(t)X_{\alpha\beta})^* (\tilde{L}_{\mu\nu\alpha'\beta'}(t)X_{\alpha'\beta'})\rangle \exp(-|t-s|/\tau_c) ds \\ &= -\langle (\tilde{L}_{\mu\nu\alpha\beta}(t)X_{\alpha\beta})^* (\tilde{L}_{\mu\nu\alpha'\beta'}(t)X_{\alpha'\beta'})\rangle \tau_c [1-\exp(-t/\tau_c)] \\ &\leq 0. \end{aligned} \tag{106}$$

The first equality in (106) follows from (97), the second follows from (105) and $L_{\alpha\beta\mu\nu}(t) = L^*_{\mu\nu\alpha\beta}(t)$ which follows from (93), and the inequality follows from the form of the third equality. Therefore, the tetratic $R^{(2)}_{\alpha\beta\alpha'\beta'}(t)$, has nonpositive eigenvalues for its "eigenmatrices." As shown in (99), it also has a zero eigenvalue for the "eigenmatrix" $(1/N)\delta_{\alpha'\beta'}$. If it has no other zero eigenvalues, and this depends upon the details of $Q_{\alpha\alpha'\beta\beta'}$ in (104), then $R^{(2)}_{\alpha\beta\alpha'\beta'}(t)$ already shows an approach to equilibrium. It is also of interest to analyze the higher order terms in $\sum_{n=1}^{\infty} R^{(n)}_{\alpha\beta\alpha'\beta'}(t)$, but it has already been argued that that $R^{(2)}_{\alpha\beta\alpha'\beta'}(t)$ will dominate the asymptotic behavior of (94) provided that $\tilde{\mathbf{M}}(t)$ is Gaussian and that conditions analogous to (84) are satisfied. These results should be compared with the delta function theory.[1,2]

5. CONCLUDING REMARKS

The paper has addressed the following points:

(1) The rules for the construction of the nth order cumulant in the case of time dependent, stochastic, matrices or operators, as given by van Kampen have been derived. The derivation generalizes di Bruno's formula to the noncommutative situation, and makes use of the time ordered logarithm.

(2) Kubo's concept of a generalized Gaussian, stochastic, matrix or operator is criticized and shown to be valid only asymptotically, if certain conditions are met.

(3) The conditions which lead to asymptotic validity of Kubo's concept of a generalized Gaussian process also justify the delta function theory presented earlier by the author.

(4) A generalized density matrix equation is given. A discussion of the monotonicity of approach to the microcanonical density matrix follows the equation.

Remaining is the problem of discussing the details of how to describe the approach to canonical equilibrium of a subsystem in contact with a thermal reservoir. This is a special case of the microcanonical problem discussed here, and its presentation will be deferred.[3]

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Multiplicative stochastic processes, Fokker–Planck equations, and a possible dynamical mechanism for critical behavior

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A derivation of the Fokker-Planck equations for additive stochastic processes is given which involves treating the continuity equation in the configuration space representation of the additive stochastic process as a multiplicative stochastic process. The average of the continuity equation becomes the Fokker–Planck equation. A presentation of the "multiplicative stochastic, Markov approximation" follows. This approximation is applied to the analysis of the dynamics of a heavy particle in a molecular fluid as described by Hamilton's equations. The nonperturbative approximation technique leads to the Fokker–Planck equation for simple Brownian motion. As part of the analysis, "intrinsic diffusion" is discovered and used to show ergodicity for the autocorrelation formula which appears during the Brownian motion calculation. An account of how these methods might be used to study the dynamical origins of critical behavior is given.

INTRODUCTION

The purpose of this paper is to illustrate connections between additive and multiplicative stochastic processes. The distinction between additive and multiplicative stochastic processes was explained in an earlier paper.[1] In several subsequent papers,[2–5] application was made of multiplicative stochastic processes to the description of quantum mechanical phenomena. Such applications may be thought of as the generalization for quantum mechanical processes of Brownian motion, an additive stochastic process, and Kubo[6] has referred to such applications as quantum mechanical Brownian motion. A general theory for additive stochastic processes has been presented[7,8] within the framework of stationary, Gaussian, Markov processes. The domain of applicability for additive stochastic processes includes Brownian motion,[9–11] irreversible thermodynamics,[12] fluctuating hydrodynamics,[13] and light scattering from simple fluids and fluid mixtures,[14–16] as well as other topics. It would appear that additive stochastic processes are of relevance for classical physics rather than for quantum physics. This separation of applicability of additive or multiplicative stochastic processes to classical or quantal physics, respectively, is not of a fundamental nature: For most purposes it is a natural separation. However, Haken[17] has reviewed the use of additive stochastic processes in quantum mechanical contexts, and this paper will exhibit the utility of multiplicative stochastic processes in classical physics.

The primary connection to be described involves a technique for the derivation of the Fokker–Planck equation for an additive stochastic process. The technique, however, uses a multiplicative stochastic process which is generated by the original additive stochastic process. In this way, the relationship between the Markov nature of the process and the properties of the second moments of the fluctuating forces is highlighted.

The technique just referred to suggests a method for the derivation of the Fokker–Planck equation for Brownian motion which connects the dissipative, friction constant of Brownian motion with interparticle potentials, in a model of Brownian motion in which the fluid is treated as N interacting fluid molecules obeying conservative classical mechanics. This problem is worked out in detail and involves an unusual type of diffusive behavior characterized by a Green's function

$$\left(2\pi\frac{K_BT}{m}t^2\right)^{-1/2}\exp\left[-\frac{(q-q')^2}{2(K_BT/m)t^2}\right]$$

in one dimension. This peculiar diffusion provides for a proof that the autocorrelation formula, for the dissipative, friction constant which is derived, is ergodic.

The conclusion of this paper considers certain infinite series which arise in the Brownian motion problem. The possibility of summing the series is raised. In addition, it is suggested that the series provides the possibility for understanding the origin of critical behavior in terms of a dynamical mechanism.

FOKKER-PLANCK EQUATIONS

The complete stochastic description of an additive stochastic process is given by the solution to its associated Fokker–Planck equation. For the case of Brownian motion, in one dimension, the additive stochastic process is given by Langevin's equation

$$M\frac{d}{dt}u(t) = -\alpha u(t) + \tilde{F}(t) \tag{1}$$

where $\alpha > 0$, and $\tilde{F}(t)$ is a purely random, stationary, Gaussian force satisfying

$$\langle\tilde{F}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{F}(t)\tilde{F}(s)\rangle = 2\lambda\delta(t-s) \tag{2}$$

where $\langle\cdots\rangle$ denotes stochastic averaging.[7,10,11] The delta function in (2) implies the Markov property for the stochastic process $u(t)$,[11] as must be proved using the definition of a Markov process, which definition involves specific behavior by the higher than second-order correlation distributions for $u(t)$.[11] The Markov property is then used to imply the validity of the Smoluchowski equation, which for Eq. (1) is written as[11]

$$P(u(0)\,|\,u, t+\Delta t) = \int P(u(0)\,|\,u', t)P(u'\,|\,u, \Delta t)\,du' \tag{3}$$

where $P(u(0)\,|\,u, t)\,du$ is the conditional probability that the value of $u(t)$ and time t will be between u and $u+du$ given that at time $t=0$, $u(t)$ had the value $u(0)$. The Smoluchowski equation is used to derive the Fokker–Planck equation which in this example becomes

$$\frac{\partial}{\partial t}P(u(0)\,|\,u,t) = -\frac{\partial}{\partial u}\left(-\frac{\alpha}{M}uP(u(0)\,|\,u,t)\right) + \frac{\lambda}{M^2}\frac{\partial^2}{\partial u^2}P(u(0)\,|\,u,t) \tag{4}$$

The solution to Eq. (4) is subject to the initial condition at $t=0$ that $P(u(0)\,|\,u,0)=\delta(u-u(0))$. The solution to the Fokker–Planck equation provides the conditional probability distribution which for a Markov process contains all possible information about the time evolution of the process. The solution to (4) is

$$P(u(0)\,|\,u,t) = \left(2\pi\frac{K_BT}{M}(1-\rho^2(t))\right)^{-1/2}\exp\left(-\frac{(M(u-\rho(t)u(0))^2}{2K_BT(1-\rho^2(t))}\right) \tag{5}$$

where $\rho(t)\equiv\exp[-(\alpha/M)t]$, and we have used the relation

$$\lambda = K_BT\alpha \tag{6}$$

which is Einstein's relation within the context of Langevin's equation. Relation (6) follows from the requirement that the solution to (4) satisfy the asymptotic limit

$$\lim_{t\to\infty}P(u(0)\,|\,u,t) = \left(2\pi\frac{K_BT}{M}\right)^{-1/2}\exp\left(-\frac{Mu^2}{2K_BT}\right) \tag{7}$$

where the right-hand side of (7) is the Maxwell distribution. In Einstein's treatment of Brownian motion,[18] the analog of (6) is derived

$$D = K_BT/\alpha \tag{8}$$

where D is the diffusion constant. Both relations (6) and (8) are referred to as Einstein's relation in the literature. Relation (8) is the original relation which follows from the diffusion equation, whereas relation (6) is the prototype for fluctuation–dissipation theorems.[7]

Multicomponent generalizations of Langevin's equation lead to the general theory of stationary, Gaussian, Markov processes[7,19] which are described by the equations

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + S_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{F}_\alpha(t) \tag{9}$$

where $\alpha=1,2,\ldots,N$, $A_{\alpha\alpha'}$ is an antisymmetric matrix, $S_{\alpha\alpha'}$ is a symmetric matrix with nonpositive eigenvalues, and $\tilde{F}_\alpha(t)$ is an n-component, purely random, Gaussian fluctuating force satisfying

$$\langle\tilde{F}_\alpha(t)\rangle = 0 \quad \text{for each } \alpha, \tag{10}$$

$$\langle\tilde{F}_\alpha(t)\tilde{F}_\beta(s)\rangle = 2Q_{\alpha\beta}\delta(t-s), \tag{11}$$

where $Q_{\alpha\beta}$ is a symmetric matrix with nonnegative eigenvalues. The corresponding Fokker–Planck equation is given by

$$\frac{\partial}{\partial t}P(\mathbf{a}(0)\,|\,\mathbf{a},t) = -\frac{\partial}{\partial a_\alpha}[(A_{\alpha\alpha'}a_{\alpha'}+S_{\alpha\alpha'}a_{\alpha'})P(\mathbf{a}(0)\,|\,\mathbf{a},t)] + \frac{\partial^2}{\partial a_\alpha\,\partial a_\beta}[Q_{\alpha\beta}P(\mathbf{a}(0)\,|\,\mathbf{a},t)] \tag{12}$$

with the initial condition $P(\mathbf{a}(0)\,|\,\mathbf{a},0)=\delta(\mathbf{a}-\mathbf{a}(0))$. The solution to (12) is given by[7,19]

$$P(\mathbf{a}(0)\,|\,\mathbf{a},t) = \left[\frac{\|\mathbf{C}(t)\|}{(2\pi)^n}\right]^{1/2}\exp[-\tfrac{1}{2}(a_\alpha - D_{\alpha\alpha'}(t)a_{\alpha'}(0))C_{\alpha\beta}(t) \times (a_\beta - D_{\beta\beta'}(t)a_{\beta'}(0))] \tag{13}$$

where $\|\mathbf{C}(t)\|$ denotes the determinant of $\mathbf{C}(t)$, and $D_{\alpha\alpha'}(t)$ is defined by

$$\mathbf{D}(t)\equiv\exp[(\mathbf{A}+\mathbf{S})t] \tag{14}$$

and $C_{\alpha\beta}(t)$ is defined by

$$\mathbf{C}^{-1}(t)\equiv\mathbf{E}^{-1} - \mathbf{D}(t)\mathbf{E}^{-1}\mathbf{D}^{+}(t) \tag{15}$$

in which the matrix $\mathbf{E}$ is determined by the entropy $S(t)$, given by

$$S(t) = S_0 - \tfrac{1}{2}K_Ba_\alpha(t)E_{\alpha\beta}a_\beta(t), \tag{16}$$

so that $\mathbf{E}$ is symmetric with positive eigenvalues. To get (13) from (12) we have used the generalized fluctuation–dissipation theorem[7,19]

$$2Q_{\alpha\beta} = -(A_{\alpha\theta}+S_{\alpha\theta})E^{-1}_{\theta\beta} + E^{-1}_{\alpha\theta}(A_{\theta\beta}-S_{\theta\beta}) \tag{17}$$

which follows from the requirement that

$$\lim_{t\to\infty}P(\mathbf{a}(0)\,|\,\mathbf{a}t) = W_0\exp(-\tfrac{1}{2}a_\alpha E_{\alpha\beta}a_\beta) \tag{18}$$

where $W_0=[\|\mathbf{E}\|/(2\pi)^n]^{1/2}$, and the right-hand side of (18) is seen to be the Boltzmann–Planck formula because the entropy is given by (16). The derivation of (12) requires proving that (9) with (11) describes a Markov process. Then a generalization to n components of Smoluchowski's equation leads to (12).[11]

A further generalization is possible in which one deals with continuous, variable indices. Analogs to (9), (11), and (17) result in

$$\frac{\partial}{\partial t}a_i(\mathbf{r},t) = -\int A_{ij}(\mathbf{r},\mathbf{r}')a_j(\mathbf{r}',t)\,d\mathbf{r}' - \int S_{ij}(\mathbf{r},\mathbf{r}')a_j(\mathbf{r}',t)\,d\mathbf{r}' + \tilde{F}_i(\mathbf{r},t), \tag{19}$$

$$\langle\tilde{F}_i(\mathbf{r},t)\tilde{F}_j(\mathbf{r}',s)\rangle = 2Q_{ij}(\mathbf{r},\mathbf{r}')\delta(t-s), \tag{20}$$

$$2Q_{ij}(\mathbf{r},\mathbf{r}') = \int[(A_{il}(\mathbf{r},\mathbf{r}'')+S_{il}(\mathbf{r},\mathbf{r}''))E^{-1}_{lj}(\mathbf{r}'',\mathbf{r}') + E^{-1}_{il}(\mathbf{r},\mathbf{r}'')(-A_{lj}(\mathbf{r}'',\mathbf{r}')+S_{lj}(\mathbf{r}'',\mathbf{r}'))]\,d\mathbf{r}'' \tag{21}$$

where $E_{lK}(\mathbf{r},\mathbf{r}')$ is the entropy matrix analog of (16)

$$S(t) = S_0 - \tfrac{1}{2}K_B\int\int a_i(\mathbf{r},t)E_{ij}(\mathbf{r},\mathbf{r}')a_j(\mathbf{r}'t)\,d\mathbf{r}\,d\mathbf{r}'. \tag{22}$$

This form of the general theory of stationary, Gaussian, Markov processes leads to hydrodynamical applications,[7,14–16] as well as to applications in other field dependent problems.[8,20] There is also in this case a corresponding Fokker–Planck equation which will involve utilization of the techniques of functional differentiation. We shall not write down this equation.

At this point a partial review of the structure and significance of the Fokker–Planck equation for additive stochastic processes has been presented. It is necessary, before proceeding further with Fokker–Planck equations, to review the basic theorem in the theory of multiplicative stochastic processes.

Consider an equation of the form

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{23}$$

where $\alpha=1,2,\ldots,N$, $A_{\alpha\alpha'}=-A_{\alpha'\alpha}$, $\tilde{A}_{\alpha\alpha'}(t)=-\tilde{A}_{\alpha'\alpha}(t)$, and the matrix $\tilde{A}_{\alpha\alpha'}(t)$ is a purely random, Gaussian

matrix with mean value zero, which implies that[1]

$$\langle \tilde{A}_{\alpha\alpha'}(t)\rangle = 0 \quad \text{and} \quad \langle \tilde{A}_{\alpha\alpha'}(t)\tilde{A}_{\beta\beta'}(s)\rangle = 2Q_{\alpha\alpha'\beta\beta'}\delta(t-s) \tag{24}$$

and that the higher-order averaged moments are given by

$$\langle \tilde{A}_{\alpha_1\alpha_1'}(t_1)\cdots A_{\alpha_{2n-1}\alpha_{2n-1}'}(t_{2n-1})\rangle = 0, \tag{25}$$

$$\langle A_{\alpha_1\alpha_1'}(t_1)\cdots A_{\alpha_{2n}\alpha_{2n}'}(t_{2n})\rangle = \frac{1}{2^n n!}\sum_{p\in S_{2n}}\prod_{j=1}^{n}\langle A_{\alpha_{p(2j-1)}\alpha_{p(2j-1)}'}(t_{p(2j-1)})A_{\alpha_{p(2j)}\alpha_{p(2j)}'}(t_{p(2j)})\rangle \tag{26}$$

where $\sum_{p\in S_{2n}}$ denotes the sum over all permutations of the symmetric group of order $(2n)!$. Equations (25) and (26) are consequences of the Gaussian property of $\tilde{A}(t)$. It has been proved that these properties of $\tilde{A}(t)$ lead to the averaged equation[1]

$$\frac{d}{dt}\langle a_\alpha(t)\rangle = A_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + Q_{\alpha\theta\theta\alpha'}\langle a_{\alpha'}(t)\rangle \tag{27}$$

in which the matrix $Q_{\alpha\theta\theta\alpha'}$ is determined by (24) which implies that it is symmetric with nonpositive eigenvalues. Whereas (23) describes fluctuating oscillations, (27) describes damped oscillations.

The proof of (27) from (23) using the properties of (24), (25), and (26) goes through unchanged if the $A_{\alpha\alpha'}$ in (23) is augmented by the addition of a symmetric matrix $S_{\alpha\alpha'}$ which has nonpositive eigenvalues. That is,

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + S_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{28}$$

leads to

$$\frac{d}{dt}\langle a_\alpha(t)\rangle = A_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + S_{\alpha\alpha'}\langle a_{\alpha'}(t)\rangle + Q_{\alpha\theta\theta\alpha'}\langle a_{\alpha'}(t)\rangle \tag{29}$$

upon performing the average of (28).

In addition, this result can be generalized to infinite matrices and to continuous indices. Therefore, we shall also use the theorem in the form

$$\frac{\partial}{\partial t}f(q,t) = L(q)f(q,t) + \tilde{L}(q,t)f(q,t) \tag{30}$$

leads to

$$\frac{\partial}{\partial t}\langle f(q,t)\rangle = L(q)\langle f(q,t)\rangle + D(q)\langle f(q,t)\rangle \tag{31}$$

where $L(q)$ is a linear differential or integral operator, $\tilde{L}(q,t)$ is a purely random, Gaussian, fluctuating linear differential or integral operator with mean value zero, and $D(q)$ is a linear differential or integral operator given by

$$\langle \tilde{L}(q,t)\tilde{L}(q,t')\rangle = 2D(q)\delta(t-t'). \tag{32}$$

In (30), it will be assumed that $\tilde{L}(q,t)$ is an antisymmetric operator, which means that if $\{\varphi_l(q)\}$ is a complete set of real orthonormal functions of the coordinates q, then

$$[\tilde{L}(t)]_{lK} = -[\tilde{L}(t)]_{Kl} \tag{33}$$

where $[\tilde{L}(t)]_{lK} \equiv \int \varphi_l(q)\tilde{L}(q,t)\varphi_K(q)\,dq$. Consequently, $D(q)$ is a symmetric operator, which means that

$$[D]_{lK} = [D]_{Kl} \tag{34}$$

where $[D]_{lK} \equiv \int \varphi_l(q)D(q)\varphi_K(q)\,dq$ because

$$[D]_{lK} = \int_0^t \langle [L(t)]_{lj}[L(s)]_{jk}\rangle\,ds. \tag{35}$$

From (35) it is also seen that the eigenspectrum of $D(q)$ is entirely nonpositive. The operator $L(q)$ in (30) may be either antisymmetric or of mixed symmetry in analogy with (23) and (28), respectively. Specific examples of these formal expressions will occur in the following paragraphs.

The q in (30) and (31) may represent a single variable, or it may represent a set of variables. Suppose we explicitly have N q's: $q_1, q_2, \ldots, q_N$. Consider the configuration space corresponding with these q_j's and let $f(q_1q_2\cdots q_Nt)$ be the distribution function in configuration space. If $N=2m$ and m of the q_j's are coordinates and m of the q_j's are momenta, then the associated configuration space becomes phase space and f becomes the phase space distribution. However, in several contexts it is not phase space which will interest us and, therefore, we use the notation q_j's for a generalized configuration space of N variables.

It is always the case that the continuity equation is true in configuration space. In our notation this becomes

$$\frac{\partial}{\partial t}f(q_1\cdots q_Nt) = -\frac{\partial}{\partial q_j}(\dot{q}_j f(q_1\cdots q_Nt)) \tag{36}$$

where $\dot{q}_j \equiv d/dt\,q_j(t)$. If we are actually dealing with phase space and a conservative system for which Hamilton's equations are valid, then (36) leads to Liouville's equation.[21] However, in general we will not necessarily be in phase space or be dealing with a conservative system, so that Liouville's theorem is not generally valid although (36) is. In the general case, some relationship between the $\dot{q}_j$'s and the q_j's must hold if (36) is to lead to anything useful.

Returning to (9), we will take for the q_j's the a_α's. Therefore, (36) is seen to be given by

$$\frac{\partial}{\partial t}f(a_1\cdots a_Nt) = -\frac{\partial}{\partial a_\alpha}(\dot{a}_\alpha f(a_1\cdots a_Nt)) \tag{37}$$

For the a_α's we use (9) which converts (37) into

$$\frac{\partial}{\partial t}f(a_1\cdots a_Nt) = -\frac{\partial}{\partial a_\alpha}[(A_{\alpha\alpha'}a_{\alpha'} + S_{\alpha\alpha'}a_{\alpha'} + \tilde{F}_\alpha(t))f(a_1\cdots a_Nt)] \tag{38}$$

which is clearly a multiplicative stochastic process in the form of (30) if we identify

$$L(q) \to -\frac{\partial}{\partial a_\alpha}(A_{\alpha\alpha'}a_{\alpha'} + S_{\alpha\alpha'}a_{\alpha'})x$$

and

$$\tilde{L}(q,t) \to -\frac{\partial}{\partial a_\alpha}\tilde{F}_\alpha(t)x = -\tilde{F}_\alpha(t)\frac{\partial}{\partial a_\alpha}. \tag{39}$$

The analog of (31) is then

$$\frac{\partial}{\partial t}\langle f(a_1\cdots a_Nt)\rangle = -\frac{\partial}{\partial a_\alpha}[A_{\alpha\alpha'}a_{\alpha'} + S_{\alpha\alpha'}a_{\alpha'})\langle f(a_1\cdots a_Nt)\rangle]$$

$$+\frac{\partial^2}{\partial a_\alpha \partial a_\beta}[Q_{\alpha\beta}\langle f(a_1\cdots a_N t)\rangle]. \tag{40}$$

This is precisely the Fokker–Planck equation (12) if we identify

$$P(\mathbf{a}(0)\,|\,\mathrm{a},t)\to\langle f(a_1\cdots a_N t)\rangle. \tag{41}$$

Consequently, given an additive stochastic process, we can write out its associated continuity equation in its configuration space and we arrive at a multiplicative stochastic process, the average of which is the Fokker–Planck equation of the original additive stochastic process.

Because the connection between (38) and (40) requires that $\tilde{F}_\alpha(t)$ is purely random, we see the Markov property and its connection with the Fokker–Planck equation without having to proceed via the Smoluchowski equation. As a special case of (38) and (40), we momentarily return to (1) from which the analogs of (37) and (38) follow:

$$\frac{\partial}{\partial t}f(u,t)=-\frac{\partial}{\partial u}(\dot{u}f(u,t)), \tag{42}$$

$$\frac{\partial}{\partial t}f(u,t)=-\frac{\partial}{\partial u}\left[\left(-\frac{\alpha}{M}u+\frac{\tilde{F}(t)}{M}\right)f(u,t)\right].$$

The average of (42) is

$$\frac{\partial}{\partial t}\langle f(u,t)\rangle=\frac{\partial}{\partial u}\left(\frac{\alpha}{M}u\langle f(u,t)\rangle\right)+\frac{\lambda}{M^2}\frac{\partial^2}{\partial u^2}\langle f(u,t)\rangle \tag{43}$$

which is identical with the Fokker–Planck equation (4).

THE MULTIPLICATIVE STOCHASTIC, MARKOV APPROXIMATION

In this section we will discuss an approximation procedure which will be referred to as the multiplicative stochastic, Markov approximation. Its connection with the preceeding section will be illustrated, and it will provide the background necessary for the analysis of Brownian motion which follows in the next section. The approximation procedure introduced here is nonperturbative.

Suppose we have a particle in a fluid. It is, on the average, at rest, although it does execute a fluctuating motion. We could describe this motion of the particle phenomenologically by the equation

$$M\frac{dx}{dt}=\tilde{p}(t) \tag{44}$$

in which the fluctuating momentum $\tilde{p}(t)$ is assumed to be a purely random, Gaussian stochastic process with average value zero and a second moment given by

$$\langle\tilde{p}(t)\tilde{p}(s)\rangle=2M^2D\delta(t-s) \tag{45}$$

in which M is the mass, as in (44), and D is a constant. The continuity equation in the configuration space description of (44) is

$$\begin{aligned}\frac{\partial}{\partial t}f(x,t)&=-\frac{\partial}{\partial x}(\dot{x}f(x,t))\\&=-\frac{\partial}{\partial x}\frac{\tilde{p}(t)}{M}f(x,t)\\&=-\frac{\tilde{p}(t)}{M}\frac{\partial}{\partial x}f(x,t).\end{aligned} \tag{46}$$

This is again a multiplicative stochastic process with a purely random, Gaussian stochastic operator. The average equation is, therefore,

$$\frac{\partial}{\partial t}\langle f(x,t)\rangle=D\frac{\partial^2}{\partial x^2}\langle f(x,t)\rangle \tag{47}$$

which is recognized as the diffusion equation with diffusion constant D. Equations (46) and (47) are special cases of (37), (38), and (40).

It may be objected that from Brownian motion we know that (45) is not so, but that instead

$$(\langle\tilde{p}(t)\tilde{p}(s)\rangle)=MK_BT\exp\left(-\frac{\alpha}{M}|t-s|\right) \tag{48}$$

which follows from (5), and in which the rounded $(\cdots)$ denote an average over the initial value distribution in addition to the stochastic average denote by $\langle\cdots\rangle$. The second average makes (48) a stationary expression depending upon $|t-s|$.[10] Using (48) in (46) leads again to

$$\frac{\partial}{\partial t}f(x,t)=-\frac{\tilde{p}(t)}{M}\frac{\partial}{\partial x}f(x,t) \tag{49}$$

which is still a multiplicative stochastic process, but the stochastic operator is now no longer purely random, so that we cannot use our theorem for averaged multiplicative stochastic processes. However, the $\tilde{p}(t)$ in (48) and (49) is still a Gaussian process because the $u(t)$ in (1) inherits the Gaussian property from the $\tilde{F}(t)$ in (1) since (1) is a linear equation. In the Appendix it is shown that the Gaussianness of $\tilde{p}(t)$ leads to the exact result

$$\frac{\partial}{\partial t}(\langle f(xt)\rangle)=\int_0^t\frac{1}{M^2}(\langle\tilde{p}(t)\tilde{p}(s)\rangle)\,ds\frac{\partial^2}{\partial x^2}(\langle f(xt)\rangle). \tag{50}$$

Using (48) in (50) permits performance of the integration giving

$$\frac{\partial}{\partial t}(\langle f(xt)\rangle)=\frac{K_BT}{\alpha}\left[1-\exp\left(-\frac{\alpha}{M}t\right)\right]\frac{\partial^2}{\partial x^2}(\langle f(xt)\rangle) \tag{51}$$

which differs from (47) by the presence of a time dependent diffusion constant: $(K_BT/\alpha)\{1-\exp[-(\alpha/M)t]\}$. For times long compared with M/α we can neglect the exponential term, and this constitutes the multiplicative stochastic, Markov approximation. The integral in (50) can be used to define a diffusion constant when we neglect the exponential part in (51). We get

$$D'=\lim_{t\to\infty}\frac{1}{M^2}\int_0^t(\langle\tilde{p}(t)\tilde{p}(s)\rangle)\,ds \tag{52}$$

where D' will be used in an expression like (45). Because of the infinite decay tail in (48), we have taken the limit $t\to\infty$ in (52), although the greatest part of the integral comes early. Using (48) in (52) gives

$$D'=K_BT/\alpha. \tag{53}$$

Note that (52) also gives the strength of the second moment for $M^{-1}\tilde{p}(t)$ as expressed by (45) since

$$D=\lim_{t\to\infty}\frac{1}{M^2}\int_0^t\langle\tilde{p}(t)\tilde{p}(s)\rangle\,ds. \tag{54}$$

Therefore, if $D\equiv D'$ we have the multiplicative stochastic, Markov approximation for (48) and (49) given by (45) and (46). The average equation (47) or (51) is the

diffusion equation, and the connection between diffusion and Brownian motion given by

$$D = K_B T/\alpha \tag{55}$$

is Einstein's original formula (8).[18] The self-consistency of the multiplicative stochastic, Markov approximation requires that the D' we get from (52) not be too large so that diffusion is slow compared with the relaxation of (48) which is governed by the magnitude of α. Indeed, (48) decays faster for larger α which via (53) results in a smaller D' which implies a slower diffusion. Therefore, in this example, the multiplicative stochastic, Markov approximation is seen to be intrinsically self-consistent. The reciprocal relation between D' and α generalizes to the more general case of multicomponent processes.

In the next section, analogs of (52) will arise in which a stochastic quantity has a non-purely-random second moment correlation formula from which we are calculating its strength. A formula like (52) will be used to calculate the strength to be used in the replacement correlation formula which is purely random. This will be analogous to the replacement of (48) by (45) where the D in (45) satisfies (55). The presence of the infinite time limit is formal, and it will be shown that the correlation integrand actually decays significantly in a very short time interval, as was the case with (52) with (48) in the integrand.

Before proceeding further, it is worth remarking that while we can actually solve (49), given (48), by writing (50), because of the Gaussian property, it is not a generally valid procedure for situations in which the stochastic operator does not commute with itself at different times.[22] Here, commutivity is guaranteed by the simple form of (49). When there is noncommutivity, then the Gaussian property alone is not sufficient for the reduction of the averaged equation to a workable form, and the multiplicative stochastic, Markov approximation becomes essential.[22]

MICROSCOPIC MODEL OF BROWNIAN MOTION

In this section we shall bring to bear the techniques of the preceeding sections as we attempt a derivation of the Fokker–Planck equation (4), for a Brownian particle, starting from a description involving a heavy particle interacting with N fluid molecules according to Hamilton's equations of motion. This is not a new program as far as its objective is concerned. Others, using other contexts and techniques, have also made this objective their goal.[23–27] Our present context and techniques were suggested by Kubo[26] in his remarkable pioneering work on multiplicative stochastic processes. The results in this paper differ somewhat with Kubo's results because he used some simplifying assumptions which we have found unnecessary. It will be seen that the analysis presented here goes beyond that of any of the other references cited in terms of the detailed account of what is happening dynamically. Two main consequences accrue: (1) A new kind of "intrinsic diffusion" is discovered which enables us to show ergodicity for the correlation formulae which appear, and (2) a connection with the dynamical origins of critical phenomena is seen. The first point will be emphasized as it comes up later in this section, while the second point will be discussed in the section following the next section.

Our starting point is the Hamiltonian

$$H = \frac{|\mathbf{P}|^2}{2M} + \sum_{j=1}^{N} \frac{|\mathbf{p}_j|^2}{2m} + \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) + \frac{1}{2} \sum_{j \neq k}^{N} U(\mathbf{r}_j, \mathbf{r}_k) \tag{56}$$

where the heavy particle has mass M, position $\mathbf{R}$, and momentum $\mathbf{P}$, and the fluid molecules have mass m, position $\mathbf{r}_j$, and momenta $\mathbf{p}_j$ where $j = 1, 2, \ldots, N$. $\varphi(\mathbf{R}, \mathbf{r}_j)$ is the interaction potential between fluid molecule j and the heavy particle, and $U(\mathbf{r}_j, \mathbf{r}_k)$ is the interaction potential for the fluid molecules. Because our description is that of a conservative system we may use Liouville's theorem to express the continuity equation corresponding with the phase space picture for the system:

$$\frac{\partial}{\partial t} f = -i\mathbf{L} f \tag{57}$$

where $f \equiv f(\mathbf{R}\mathbf{P}\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N t)$ and $-i\mathbf{L}$ is defined by

$$-i\mathbf{L} \equiv -\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} - \sum_{j=1}^{N} \frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot (\nabla_{\mathbf{P}} - \nabla_{\mathbf{p}_j}) + \sum_{j \neq k} \nabla_{\mathbf{r}_j} U(\mathbf{r}_j, \mathbf{r}_k) \cdot \nabla_{\mathbf{p}_j}. \tag{58}$$

The Liouville operator defined by (58) will be separated into two parts:

$$-i\mathbf{L}_B \equiv -\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}}, \tag{59}$$

$$-i\mathbf{L}_R \equiv -\sum_{j=1}^{N} \frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j} + \sum_{j=1}^{N} \nabla_{\mathbf{r}_j} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{p}_j} + \sum_{j \neq k}^{N} \nabla_{\mathbf{r}_j} U(\mathbf{r}_i, \mathbf{r}_k) \cdot \nabla_{\mathbf{p}_j}. \tag{60}$$

Now, define $\hat{f}$ by

$$f \equiv \exp(-it\mathbf{L}_R)\hat{f} \tag{61}$$

where $\hat{f} \equiv \hat{f}(\mathbf{R}\mathbf{P}\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N t)$. Using (57) through (61) leads to

$$\frac{\partial}{\partial t} \hat{f} = -i\tilde{\mathbf{L}}_B(t)\hat{f} \tag{62}$$

where $\tilde{\mathbf{L}}_B(t)$ is defined by

$$-i\tilde{\mathbf{L}}_B(t) \equiv \exp(it\mathbf{L}_R)(-i\mathbf{L}_B)\exp(-it\mathbf{L}_R). \tag{63}$$

Our notation suggests that $\tilde{\mathbf{L}}_B(t)$ is a stochastic operator. Of course, it is clearly not a stochastic operator as is explicitly evident if (59) and (60) are inserted into (63). However, it acts like a stochastic operator because the noncommutivity of $\mathbf{L}_B$ and $\mathbf{L}_R$ results in extremely rapid variations in $\tilde{\mathbf{L}}_B(t)$ if N is sufficiently large. Moreover, (59) and (60) may be used to exhibit $\mathbf{L}_B(t)$ as a sum of N similar terms. This suggests that to treat $\tilde{\mathbf{L}}_B(t)$ as Gaussian for large N is not unreasonable. Therefore, we shall invoke the nonperturbative, multiplicative stochastic, Markov approximation while we treat $\tilde{\mathbf{L}}_B(t)$ as stochastic.

It shall be assumed that the average of $\hat{f}$, $\langle \hat{f} \rangle$, factors for all time as follows:

$$\langle \hat{f} \rangle = g_B(Pt) W_R^{\mathrm{eq}}(\mathbf{R}\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N) \tag{64}$$

where $W_R^{\mathrm{eq}}(\mathbf{R}_1\mathbf{r}_1\mathbf{p}_1 \cdots \mathbf{r}_N\mathbf{p}_N)$ is the canonical equilibrium

distribution for the fluid molecules in the presence of the heavy particle at $\mathbf{R}$, and is given by

$$W_R^{eq}(\mathbf{R}\mathbf{r}_1\mathbf{p}_1\cdots\mathbf{r}_N\mathbf{p}_N) \equiv \frac{1}{Q_N}\exp\left[-\beta\left(\sum_{j=1}^{N}\frac{|\mathbf{p}_j|^2}{2m}+\sum_{j=1}^{N}\varphi(\mathbf{R},\mathbf{r}_j)+\frac{1}{2}\sum_{j\neq k}^{N}U(\mathbf{r}_j,\mathbf{r}_k)\right)\right] \quad (65)$$

where Q_N the normalization constant which satisfies

$$\int\cdots\int W_R^{eq}(\mathbf{R}\mathbf{r}_1\mathbf{p}_1\cdots\mathbf{r}_N\mathbf{p}_N)\,d\mathbf{R}\,d\mathbf{r}_1\cdots d\mathbf{r}_N\,d\mathbf{p}_1\cdots d\mathbf{p}_N = 1. \quad (66)$$

The heavy particle coordinates $\mathbf{R}$ appear in (65) because the inertia of the heavy particle is so large that the fluid molecules achieve thermal equilibrium relative to the instantaneous position $\mathbf{R}$ of the heavy particle very rapidly compared with the rate of change of the position $\mathbf{R}$. This situation is analogous to the technique used to derive the Langevin equation starting with a heavy particle in a fluctuating fluid, in which case the fluid fluctuations must be computed subject to boundary conditions representing the presence of the heavy particle.[7,28,29] The response of the fluid to the presence of the heavy particle must appear in the computation if sensible results are desired.

Returning to (62) and using (64) we get, on the average,

$$\frac{\partial}{\partial t}g_B(\mathbf{P}t) = -\int_0^\infty\int\cdots N\cdots\int\int\cdots N+1\cdots\int\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)\times W_R^{eq}(\mathbf{R}\mathbf{r}^N\mathbf{p}^N)\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}\,ds\,g_B(\mathbf{P}t), \quad (67)$$

where we have integrated over the fluid variables and $\mathbf{R}$, and the quantity

$$-\int_0^\infty\int\cdots N\cdots\int\int\cdots N+1\cdots\int\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)\,W_R^{eq}(\mathbf{R}\mathbf{r}^N\mathbf{p}^N)\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}\,ds \quad (68)$$

is almost the analog of the correlation strength given in (52). The minus sign comes from $(i)^2$ and $\mathbf{r}^N$ denotes $\mathbf{r}_1\cdots\mathbf{r}_N$ whereas $d^N\mathbf{r}$ denotes $d\mathbf{r}_1\cdots d\mathbf{r}_N$, etc. The integration over the variables in W_R^{eq} corresponds with the round brackets average in (48) and provides the analog of stationarity. Note that (68) is not exactly the analog of (52) because it is still an operator. Equation (67) is what would result if $\tilde{\mathbf{L}}_B(t)$ were really a stochastic, Gaussian process for which the Markov property holds. We have implicitly assumed that the average of $\tilde{\mathbf{L}}_B(t)$ is zero in writing (67). We shall digress for a moment and explicitly demonstrate that $\tilde{\mathbf{L}}_B(t)$ has a zero average, and that (68) is stationary. The average of $\tilde{\mathbf{L}}_B(t)$ is given by

$$\langle\langle\tilde{\mathbf{L}}_B(t)\rangle\rangle \equiv \int\cdots\int\tilde{\mathbf{L}}_B(t)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} = \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B\exp(-it\mathbf{L}_R)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}. \quad (69)$$

The operator given by (69) acts upon functions of $\mathbf{P}$. Using (60) and (65) it follows that

$$\exp(-it\mathbf{L}_R)(W_R^{eq}\psi(\mathbf{P})) = W_R^{eq}\exp(-it\mathbf{L}_R)(\psi(\mathbf{P})) = W_R^{eq}\psi(\mathbf{P}) \quad (70)$$

where $\psi(\mathbf{P})$ is an arbitrary function of $\mathbf{P}$, because $\mathbf{L}_R(W_R^{eq}) = 0$ and $\mathbf{L}_R(W_R^{eq}\psi(\mathbf{P})) = \mathbf{L}_R(W_R^{eq})\psi(\mathbf{P}) + W_R^{eq}\mathbf{L}_R(\psi(\mathbf{P}))$, and $\mathbf{L}_R(\psi(\mathbf{P})) = 0$ since $\mathbf{L}_R$ does not involve $\mathbf{P}$. Therefore, we have

$$\langle\langle\mathbf{L}_B(t)\rangle\rangle = \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_BW_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}. \quad (71)$$

Expanding $\exp(it\mathbf{L}_R)$ in a power series and integrating each term by parts leads to

$$\langle\langle\tilde{\mathbf{L}}_B(t)\rangle\rangle = \int\cdots\int\mathbf{L}_BW_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} \quad (72)$$

since all but the first term in the power series give zero because W_R^{eq} vanishes at the boundaries of integration. Using (59) and (65) gives

$$i\langle\langle\tilde{\mathbf{L}}_B(t)\rangle\rangle = \int\cdots\int\left[\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}}(W_R^{eq}) + \nabla_{\mathbf{R}}(W_R^{eq})\cdot\frac{1}{\beta}\nabla_{\mathbf{P}}\right]d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} = 0 \quad (73)$$

where the second equality follows from integration by parts with respect to the coordinates $\mathbf{R}$. The stationarity relation follows from similar arguments beginning with

$$\langle\langle\tilde{\mathbf{L}}_B(t)\tilde{\mathbf{L}}_B(s)\rangle\rangle \equiv \int\cdots\int\tilde{\mathbf{L}}_B(t)\tilde{\mathbf{L}}_B(s)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} \quad (74)$$
$$= \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B\exp(-it\mathbf{L}_R)\times\exp(is\mathbf{L}_R)\mathbf{L}_B\exp(-is\mathbf{L}_R)W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}.$$

Using an argument which is like that used in going from (70) to (71), we can go in the reverse direction and get

$$\langle\langle\mathbf{L}_B(t)\mathbf{L}_B(s)\rangle\rangle = \int\cdots\int\exp(it\mathbf{L}_R)\mathbf{L}_B\exp(-it\mathbf{L}_R)\times\exp(is\mathbf{L}_R)\mathbf{L}_B\exp(-is\mathbf{L}_R)\exp(it\mathbf{L}_R)\times W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p}$$
$$= \int\cdots\int\mathbf{L}_B\exp[i(s-t)\mathbf{L}_R]\mathbf{L}_B\times\exp[-i(s-t)\mathbf{L}_R]W_R^{eq}\,d^N\mathbf{r}\,d\mathbf{R}\,d^N\mathbf{p} \quad (75)$$

where the second equality follows from an argument identical with that used to get from (71) to (72). Therefore, the quantity given by (68) is in general

$$\int_t^\infty\langle\langle\tilde{\mathbf{L}}_B(t)\tilde{\mathbf{L}}_B(s)\rangle\rangle\,ds = \int_t^\infty\langle\langle\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s-t)\rangle\rangle\,ds = \int_0^\infty\langle\langle L_B(0)L_B(s')\rangle\rangle\,ds' \quad (76)$$

where the first equality follows from (75) and the second equality follows from the change of variables $s' = s - t$. This ends our digression. The expression in (67) is an approximation to the exact behavior described by (62), and we shall analyze the detailed behavior of (68) regorously from here on, to the end of this section.

It is very convenient to get the W_R^{eq} term in (68) as far to the left as possible before attempting to perform integrations. This requires letting $\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)$ act on W_R^{eq} as is appropriate. Using (63) gives

$$-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s)W_R^{eq}g_B = -\mathbf{L}_B\exp(is\mathbf{L}_R)\mathbf{L}_B\exp(-is\mathbf{L}_R)W_R^{eq}g_B. \quad (77)$$

As is indicated in (67) there will be an integration over $\mathbf{R}$. Using (59) for $\mathbf{L}_B$ and integrating over $\mathbf{R}$ by parts shows that

$$\int\cdots\int\left(-\frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}}+\sum_{j=1}^{N}\nabla_{\mathbf{R}}\varphi(\mathbf{R},\mathbf{r}_j)\cdot\nabla_{\mathbf{P}}\right)\exp(is\mathbf{L}_R)\mathbf{L}_B\times\exp(-is\mathbf{L}_R)W_R^{eq}g_B\,d\mathbf{R}$$

$$= \int \cdots \int \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} (\exp(is\mathbf{L}_R)\mathbf{L}_B \times \exp(-is\mathbf{L}_R) W_R^{eq} g_B)\, d\mathbf{R} \tag{78}$$

where the integrated term at the boundaries vanishes because W_R^{eq} vanishes there. Equation (78) shows that the $\mathbf{L}_B$ on the left in (77) acts only through the potential term

$$-i\mathbf{L}_B' = \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}}. \tag{79}$$

Therefore, in effect (77) reduces to

$$-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \to -\mathbf{L}_B' \exp(is\mathbf{L}_R)\mathbf{L}_B \exp(-is\mathbf{L}_R) W_R^{eq} g_B, \tag{80}$$

at least after the $\mathbf{R}$ integration is performed. Returning to the justification of (70), we see that

$$\exp(-is\mathbf{L}_R) W_R^{eq} g_B = W_R^{eq} g_B. \tag{81}$$

Using (59) and (65), it is seen that

$$-i\mathbf{L}_B W_R^{eq} g_B = W_R^{eq} \left(-\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) \right) g_B. \tag{82}$$

Furthermore, we have

$$\exp(is\mathbf{L}_R) W_R^{eq} h = W_R^{eq} \exp(is\mathbf{L}_R) h, \tag{83}$$

where h is any function of the variables $\mathbf{P}$, $\mathbf{R}$, $\mathbf{r}_j$, and $\mathbf{p}_j$ for $j = 1, 2, \ldots, N$. This relation follows from the reasons given in justification of (70). Therefore, (80)—(83) give

$$\begin{aligned} &-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \\ &\to -\mathbf{L}_B' W_R^{eq} \exp(is\mathbf{L}_R) \left(-\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) \right) g_B \\ &= W_R^{eq} \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} \exp(is\mathbf{L}_R) \\ &\quad \times \left(-\frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} + \sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{j=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_j) \right) g_B \end{aligned} \tag{84}$$

where the last equality follows from a result analogous to (82) which depends upon (79):

$$-i\mathbf{L}_B' W_R^{eq} h = W_R^{eq} (-i\mathbf{L}_B') h. \tag{85}$$

The expression in (84) becomes an equality when the $\mathbf{R}$ integration is performed. Note also that the $\mathbf{P}/M \cdot \nabla_{\mathbf{R}}$ operator in (84) acts on g_B only, and because g_B depends upon $\mathbf{P}$ only the effect is zero. Therefore, (84) becomes

$$\begin{aligned} &-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \\ &\to W_R^{eq} \left(\sum_{j=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_j) \cdot \nabla_{\mathbf{P}} \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \nabla_{\mathbf{R}} \varphi(\mathbf{R}, \mathbf{r}_k) \cdot \nabla_{\mathbf{P}} + \beta \frac{\mathbf{P}}{M} \cdot \nabla_{\mathbf{R}} \sum_{k=1}^{N} \varphi(\mathbf{R}, \mathbf{r}_k) \right) g_B. \end{aligned} \tag{86}$$

Finally, since $\mathbf{L}_R$ does not contain $\mathbf{P}$, we may combine terms as follows:

$$\begin{aligned} &-\tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} g_B \\ &\to W_R^{eq} \left(\sum_{j=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j) \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k) \right) \frac{\partial}{\partial P_\mu} \left(\beta \frac{P_\nu}{M} + \frac{\partial}{\partial P_\nu} \right) g_B. \end{aligned} \tag{87}$$

Returning to (68), we have found that

$$\begin{aligned} &-\int_0^\infty \int \cdots N \cdots \int \int \cdots N+1 \cdots \int \tilde{\mathbf{L}}_B(0)\tilde{\mathbf{L}}_B(s) W_R^{eq} \\ &\quad \times d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, g_B \\ &= \int \int \cdots N \cdots \int \int \cdots N+1 \cdots \int W_R^{eq} \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j) \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k) \right) \frac{\partial}{\partial P_\mu} \left(\beta \frac{P_\nu}{M} + \frac{\partial}{\partial P_\nu} \right) \\ &\quad \times d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, ds\, g_B. \end{aligned} \tag{88}$$

If for a moment we specialize the above results to one dimension, and use the fact that $P = Mu$, then we have

$$\frac{\partial}{\partial P_\mu} \left(\beta \frac{P_\nu}{M} + \frac{\partial}{\partial P_\nu} \right) \to \frac{\partial}{\partial u} \left(\beta \frac{u}{M} + \frac{1}{M^2} \frac{\partial}{\partial u} \right) \tag{89}$$

and

$$\begin{aligned} &\int_0^\infty \int \cdots \int W_R^{eq} \left(\sum_{j=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j) \right) \exp(is\mathbf{L}_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k) \right) d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, ds \\ &\quad \to \int_0^\infty \int \cdots \int W_R^{eq} \left(\sum_{j=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_j) \right) \exp(isL_R) \\ &\quad \times \left(\sum_{k=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_k) \right) d^N r\, dR\, d^N p\, ds, \end{aligned} \tag{90}$$

where W_R^{eq} and L_R are one-dimensional expressions in the last expression above. Comparing these results with (4), we see that we have the Fokker—Planck equation for a Brownian particle in (67), if we use the one-dimensional analogs given by (89) and (90). Using (6), it is seen that we have the identity

$$\begin{aligned} \lambda = &\int_0^\infty \int \cdots \int W_R^{eq} \sum_{j=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_j) \exp(isL_R) \\ &\times \sum_{k=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_k)\, d^N r\, dR\, d^N p\, ds. \end{aligned} \tag{91}$$

This is all reasonable since we can readily associate

$$\sum_{j=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_j) \to -\tilde{F}(0) \tag{92}$$

and

$$\exp(isL_R) \sum_{k=1}^{N} \frac{\partial}{\partial R} \varphi(R, r_k) \to -\tilde{F}(s).$$

This second association is perhaps even clearer if we reinsert $\exp(-isL_R)$ on the right of the integrand of (91), which changes nothing as was seen in going from (69) to (71). The strength of the stationary correlation, $\langle\langle \tilde{F}(0)\tilde{F}(s) \rangle\rangle$, follows from (2) and a formula like (52)

which reads

$$\lambda = \int_0^\infty \langle\langle F(0)F(s)\rangle\rangle\, ds. \tag{93}$$

In Eq. (88), we actually have the three-dimensional generalization of (4) which gives

$$\lambda_{\mu\nu} \equiv \int_0^\infty \cdots \int W_R^{eq} \left(\sum_{j=1}^N \frac{\partial}{\partial R_\mu}\varphi(\mathbf{R}, \mathbf{r}_j)\right) \exp(isL_R) \times \left(\sum_{k=1}^N \frac{\partial}{\partial R_\nu}\varphi(\mathbf{R}, \mathbf{r}_k)\right) d^N\mathbf{r}\, d\mathbf{R}\, d^N\mathbf{p}\, ds \tag{94}$$

where $\lambda_{\mu\nu}$ is the friction tensor,[7] and it is useful in describing rotational Brownian motion if the potential φ is not spherically symmetric.[29]

It is to be especially noted that $\exp(isL_R)$ appears in (94) and not the full Liouville evolution operator $\exp(isL)$. This point has been emphasized by Mori,[30,31] who also gets this type of result from a different approach. Other treatments involve $\exp(isL)$ in analogous expressions, and lead to certain technical difficulties, sometimes referred to as the "plateau value problem."[23,24,27] The relationship of (94) to Kubo's transport coefficient formula may be found in the references just cited.

ERGODICITY

A phase space function $f(q_1 \cdots q_N p_1 \cdots p_N t)$ is said to be ergodic if

$$\lim_{s\to\infty} \langle f(q_1 \cdots q_N p_1 \cdots p_N 0) f(q_1 \cdots q_N p_1 \cdots p_N s)\rangle = 0 \tag{95}$$

where $\langle \cdots \rangle$ denotes the canonical, initial value average.[32] We would like to show that the force on the Brownian particle $\sum_{j=1}^N \partial/\partial R_\nu \varphi(R, r_j)$ in Eq. (94) is ergodic in the sense of (95). Furthermore, if the vanishing of the correlation function in (94) is fast enough, then the integral over s will be finite. To show ergodicity it is necessary to analyze the detailed structure of $\exp(isL_R)$. In doing so, we will discover a phenomenon which we shall call "intrinsic diffusion." This intrinsic diffusion has interest in its own right, independently of our particular context here.[33]

The time ordered exponential for a time dependent operator which does not commute with itself at different times is defined by

$$\underset{\leftarrow}{T} \exp\left(\int_0^s \mathbf{O}(s')\, ds'\right) \equiv \sum_{n=1}^\infty \int_0^s \int_0^{s_1} \int_0^{s_2} \cdots \int_0^{s_{n-2}} \int_0^{s_{n-1}} \mathbf{O}(s_1)\mathbf{O}(s_2)\cdots\mathbf{O}(s_{n-1})\mathbf{O}(s_n) \times ds_n\, ds_{n-1} \cdots ds_2\, ds_1. \tag{96}$$

Given an operator of the form $\exp[is(\mathbf{A}+\mathbf{B})]$ where $\mathbf{A}$ and $\mathbf{B}$ are noncommuting differential operators, we have the following disentanglement theorem:

$$\exp[is(\mathbf{A}+\mathbf{B})] = \exp(is\mathbf{A}) \underset{\leftarrow}{T} \exp\left[i\int_0^s \exp(-is'\mathbf{A})\mathbf{B} \times \exp(is'\mathbf{A})\, ds'\right]. \tag{97}$$

Both sides of (97) are clearly equal for $s=0$, and differentiation of both sides for $s\neq 0$ gives identical results, proving the validity of (97).

When (97) is applied to $\exp(isL_R)$, where we use (60), we get

$$\exp(isL_R) = \exp\left(s\sum_{j=1}^N \frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right) \underset{\leftarrow}{T} \exp\left[-\int_0^s \exp\left(-s\sum_{k=1}^N \frac{\mathbf{p}_k}{m}\cdot\nabla_{\mathbf{r}_k}\right) \times\left(\sum_{l=1}^N \nabla_{\mathbf{r}_l}\varphi(\mathbf{R}, \mathbf{r}_l)\cdot\nabla_{\mathbf{p}_l} + \sum_{l\neq i}^N \nabla_{\mathbf{r}_l} U(\mathbf{r}_l, \mathbf{r}_i)\cdot\nabla_{\mathbf{p}_l}\right) \times\exp\left(s'\sum_{k'=1}^N \frac{\mathbf{p}_{k'}}{m}\cdot\nabla_{\mathbf{r}_{k'}}\right) ds'\right]. \tag{98}$$

The expression in (98) will be studied in detail in this paper with respect to the leading term only. This term is

$$\exp\left(s\sum_{j=1}^N \frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right). \tag{99}$$

The detailed analysis of this term will indicate how the analysis goes for higher-order terms, although in this paper no explicit expressions for the higher-order terms will be offered.

Returning to (94), we see that we need to calculate the canonical average of expression (99). We shall perform the momenta integrations first. The leading term in (99) gives

$$(2\pi m K_B T)^{-3N/2} \int \cdots \int \exp\left(-\beta\sum_{k=1}^N \frac{|\mathbf{p}_j|^2}{2m}\right) \times \exp\left(s\sum_{j=1}^N \frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right) d^N\mathbf{p} = (2\pi m K_B T)^{-3N/2} \prod_{j=1}^N \int\int\int \exp\left(-\beta\frac{|\mathbf{p}_j|^2}{2m}\right) \exp\left(s\frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j}\right) d\mathbf{p}_j. \tag{100}$$

For a fixed j, we shall now consider the integral over the x component of $\mathbf{p}_j$ because the other components and the other momenta integrals all work out similarly. We have, therefore, as a typical integral

$$(2\pi m K_B T)^{-1/2} \int_{-\infty}^{-\infty} \exp\left(-\beta\frac{p_{jx}^2}{2m}\right) \exp\left(s\frac{p_{jx}}{\partial x}\frac{\partial}{\partial x}\right) dp_{jx} = \sum_{n=0}^\infty \frac{[(s/m)(\partial/\partial x)]^n}{n!}\langle p_{jx}^n\rangle \tag{101}$$

where

$$\langle p_{jx}^n\rangle \equiv (2\pi m B K_B T)^{-1/2} \int_{-\infty}^\infty p_{jx}^n \exp\left(-\beta\frac{p_{jx}^2}{2m}\right) dp_{jx}.$$

These Gaussian integrals are well known and are given by

$$\langle p_{jx}^n\rangle = 0 \qquad \text{for } n = 2m+1 \text{ where } m = 0, 1, 2, \cdots$$

and

$$\langle p_{jx}^n\rangle = \frac{(2m)!}{2^m m!}\langle p_{jx}^2\rangle^m \quad \text{for } n = 2m \text{ where } m = 0, 1, 2, \cdots. \tag{102}$$

Inserting these averages into (101) gives

$$(2\pi m K_B T)^{-1/2} \int_{-\infty}^\infty \exp\left(-\beta\frac{p_{jx}^2}{2m}\right) \exp\left(s\frac{p_{jx}}{m}\frac{\partial}{\partial x}\right) dp_{jx} = \exp\left(s^2\frac{K_B T}{2m}\frac{\partial^2}{\partial x^2}\right) \tag{103}$$

because $\langle p_{jx}^2\rangle = mK_B T$. Returning to (100), we get

$$(2\pi m K_B T)^{-3N/2} \prod_{j=1}^{N} \iiint \exp\left(-\beta \frac{|\mathbf{p}_j|^2}{2m}\right) \exp\left(s \frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j}\right) d\mathbf{p}_j = \prod_{j=1}^{N} \exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_j}\right). \quad (104)$$

If only the leading term in (99) is used in expression (94), then the canonical momenta averages give

$$\lambda^0_{\mu\nu} = \int_0^\infty \cdots \int W^{eq}_*(\mathbf{R}, \mathbf{r}_1 \cdots \mathbf{r}_N) \left(\sum_{j=1}^{N} \frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j)\right) \times \prod_{l=1}^{N} \exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_l}\right) \left(\sum_{k=1}^{N} \frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_k)\right) d^N\mathbf{r}\, d\mathbf{R}\, ds \quad (105)$$

where $W^{eq}_*(\mathbf{R}, \mathbf{r}_1 \cdots \mathbf{r}_N)$ is the coordinate dependent factor in W^{eq}_R, and the superscript on $\lambda^0_{\mu\nu}$ indicates the lowest order truncation of the series implicit in (98) by virtue of (96). A typical term in (105) has an integrand factor such as

$$\exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_l}\right) \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_l)\right). \quad (106)$$

We shall express (106) in a different form which is suggested by an analogy with diffusion. It is worthwhile to digress for a moment in order to make the analogy clear.

The diffusion equation in three dimensions is

$$\frac{\partial}{\partial t} D(\mathbf{r}, t) = D \nabla^2_{\mathbf{r}} D(\mathbf{r}, t) \quad (107)$$

where D is the diffusion constant. A formal solution to (107) may be written as

$$D(\mathbf{r}, t) = \exp(tD\nabla^2_{\mathbf{r}}) D(\mathbf{r}, 0) \quad (108)$$

as is readily verified by differentiation. In addition, the solution to (107) in an infinite volume, with the initial condition $D(\mathbf{r}, 0) = \delta(\mathbf{r} - \mathbf{r}^0)$, is given by

$$D_G(\mathbf{r}, t) = (4\pi D t)^{-3/2} \exp - \frac{|\mathbf{r} - \mathbf{r}^0|^2}{4Dt} \quad (109)$$

where the subscript G indicates that this solution can be used as a Green's function, which enables us to conclude from (108) and (109) that

$$\exp(tD\nabla^2_{\mathbf{r}}) D(\mathbf{r}, 0) = (4\pi D t)^{-3/2} \iiint \exp - \frac{|\mathbf{r} - \mathbf{r}^0|^2}{4Dt} D(\mathbf{r}^0, 0)\, d\mathbf{r}^0 \quad (110)$$

for arbitrary initial distrubutions $D(\mathbf{r}^0, 0)$.

The analogy between these results for diffusion and expression (106) should be clear. The important differences are $K_B T/2m$ in (106) where D is in (108), and s^2 in (106) where t is in (108). However, remarkably enough, there is a Green's function which goes with (106) given by

$$\exp\left(s^2 \frac{K_B T}{2m} \nabla^2_{\mathbf{r}_l}\right) \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}_l)\right) = \left(4\pi \frac{K_B T}{2m} s^2\right)^{-3/2} \iiint \exp\left(-\frac{|\mathbf{r}_l - \mathbf{r}'_l|^2}{4(K_B T/2m)s^2}\right) \times \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}'_l)\right) d\mathbf{r}'_l. \quad (111)$$

The corresponding differential equation follows from (106) and is

$$\frac{\partial}{\partial s} D(\mathbf{r}, s) = 2s \frac{K_B T}{2m} \nabla^2_{\mathbf{r}}(\mathbf{r}, s) \quad (112)$$

which is analogous with (107). One may check all this by showing that the Green's function in (111) satisfies (112) with initial condition $D(\mathbf{r}, 0) = \delta(\mathbf{r} - \mathbf{r}^0)$, in an infinite volume. We shall refer to the behavior exhibited by (111) as "intrinsic diffusion" to distinguish it from true diffusion as exhibited by (110) while suggesting the marked similarities. Notice in particular, that "intrinsic diffusion" acts like true diffusion with a diffusion coefficient which grows linearly with time: $D \rightarrow (K_B T/2m)s$. Therefore, "intrinsic diffusion" smooths out coordinate dependent functions increasingly rapidly compared with true diffusion. Moreover, it increases the rate of smoothing proportionately with temperature and inverse fluid molecule mass.

Returning to (105), and using (111), we get

$$\lambda^0_{\mu\nu} = \sum_{j=1}^{N} \sum_{k=1}^{N} \int_0^\infty \cdots \int W^{eq}_* \left(\frac{\partial}{\partial R_\mu} \varphi(\mathbf{R}, \mathbf{r}_j)\right) \left(4\pi \frac{K_B T}{2m} s^2\right)^{-3/2} \times \exp\left(-\frac{|\mathbf{r}_k - \mathbf{r}'_k|^2}{4(K_B T/2m)s^2}\right) \left(\frac{\partial}{\partial R_\nu} \varphi(\mathbf{R}, \mathbf{r}'_k)\right) d^N\mathbf{r}'\, d^N\mathbf{r}\, d\mathbf{R}\, ds. \quad (113)$$

It is convenient to use a Fourier transformation representation of the potentials in evaluating further expression (113). Define $\hat{\varphi}(\rho)$ by

$$\varphi(\mathbf{R}, \mathbf{r}_k) \equiv \frac{1}{2\pi}^3 \iiint \exp[i\boldsymbol{\rho} \cdot (\mathbf{R} - \mathbf{r}_k)] \hat{\varphi}(\boldsymbol{\rho})\, d\boldsymbol{\rho} \quad (114)$$

using (111) in (113) with (114) gives

$$\lambda^0_{\mu\nu} = \sum_{j=1}^{N} \sum_{k=1}^{N} \int_0^\infty \cdots \int W^{eq}_* \left(\frac{1}{2\pi}\right)^6 (i\rho_\mu) \exp[i\boldsymbol{\rho} \cdot (\mathbf{R} - \mathbf{r}_j)] \hat{\varphi}(\rho) \times \exp\left(-s^2 \frac{K_B T}{2m} |\boldsymbol{\rho}'|^2\right) \exp[i\boldsymbol{\rho}' \cdot (\mathbf{R} - \mathbf{r}_k)] \hat{\varphi}(\boldsymbol{\rho}') \times d\boldsymbol{\rho}'\, d\boldsymbol{\rho}\, d^N\mathbf{r}\, d\mathbf{R}\, ds. \quad (115)$$

Equation (115) also follows directly from (105) using (114). In getting (115) we have used $\exp[s^2(K_B T/2m)\nabla^2_{\mathbf{r}}] \times \exp(i\boldsymbol{\rho}' \cdot \mathbf{r}) = \exp[-s^2(K_B T/2m)|\boldsymbol{\rho}'|^2]$. Either (113) or (115) shows that to this lowest order of truncation we have ergodic behavior. Note that in (115) the $\boldsymbol{\rho}' = 0$ term, which does not decay, is multiplied by $i\rho'_\nu$, which is zero. In (113) we see that qualitatively, "intrinsic diffusion" smoothes out the force at time s, for large s, so that we are left with the canonical coordinate average of the initial force times essentially a constant:

$$\lim_{s \to \infty} (\text{time integrand of } \lambda^0_{\mu\nu}) \approx \sum_{j=1}^{N} \sum_{k=1}^{N} \int \cdots \int W^{eq}_* \left(\frac{\partial}{\partial R_\mu} \varphi(R, r_j)\right) C\, d^N\mathbf{r}\, d\mathbf{R} = 0 \quad (116)$$

where C is the constant corresponding with the smoothed force at time s, and the second equality follows from a result similar to (73). In addition, (115) may be integrated over s explicitly giving

$$\lambda^0_{\mu\nu} = \sum_{j=1}^{N}\sum_{k=1}^{N}\int\cdots\int W^{eq}_{*}\left(\frac{1}{2\pi}\right)^6 (i\rho_\mu)\exp[i\rho\cdot(\mathbf{R}-\mathbf{r}_j)]\hat{\varphi}(\rho)$$
$$\times\left(\frac{\pi m}{2K_BT|\rho'|^2}\right)^{1/2}(i\rho'_\nu)\exp[i\rho'\cdot(\mathbf{R}-\mathbf{r}_k)]\hat{\varphi}(\rho')$$
$$\times d\rho'\,d\rho\,d^N\mathbf{r}\,d\mathbf{R}. \qquad (117)$$

As long as $\hat{\varphi}(0)$ is finite, the $(|\rho'|^2)^{1/2}$ denominator in (117) does not create a divergence because of the factor $(i\rho'_\nu)$. If $\varphi(\mathbf{R},\mathbf{r}_k)$ is spherically symmetric, (114) may be inverted to show that $\hat{\varphi}(0)=4\pi\int_0^\infty r^2\varphi(r)\,dr$, which is finite for a large class of physically reasonable potentials, which do not possess too terribly singular hard cores, and which tail off rapidly with increased separation of the interacting particles. The presence of W^{eq}_{*} in (117) makes it effectively impossible to perform the coordinate integrals in general. We will end our present discussion of $\lambda^0_{\mu\nu}$ by approximating the coordinate integrals for high temperatures.

At sufficiently high temperatures we shall approximate W^{eq}_{*} by $V^{-(N+1)}$, where V is the volume of our system, which volume we have been taking to be essentially infinite during much of the preceeding analysis. Although (113) is valid only for an infinite V, since the Green's function in its integrand obtains only for an infinite V, (117) is valid for finite V since it follows from (105) and (114) without any restriction on V. The approximation for W^{eq}_{*} by $V^{-(N+1)}$ requires that the potential have a hard core repulsion which, while very large, is finite. The limit $V\to\infty$ is accompanied by $N\to\infty$ while N/V remains equal to a constant $\hat{n}$. This is the thermodynamic limit. With the thermodynamic limit the coordinate integrals in (117) can be performed, and we get

$$\lambda^0_{\mu\nu} \approx \lim_{\text{thermo}} V^{-(N+1)}\sum_{j=1}^{N}\sum_{k=1}^{N}\int\cdots\int\left(\frac{1}{2\pi}\right)^6(i\rho_\mu)$$
$$\times\exp[i\rho\cdot(\mathbf{R}-\mathbf{r}_j)]\hat{\varphi}(\rho)\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho'|}(i\rho'_\nu)$$
$$\times\exp[i\rho'\cdot(\mathbf{R}-\mathbf{r}_k)]\hat{\varphi}(\rho')\,d\rho'\,d\rho\,d^N\mathbf{r}\,d\mathbf{R}$$
$$=\hat{n}\iiint\frac{1}{2\pi}{}^3(\rho_\mu\rho_\nu)|\hat{\varphi}(\rho)|^2\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho|}\,d\rho$$
$$+\hat{n}^2\iiint\delta(\rho)(\rho_\mu\rho_\nu)|\hat{\varphi}(\rho)|^2\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho|}\,d\rho$$
$$=\hat{n}\iiint\frac{1}{2\pi}{}^3(\rho_\mu\rho_\nu)|\hat{\varphi}(\rho)|^2\left(\frac{\pi m}{2K_BT}\right)^{1/2}\frac{1}{|\rho|}\,d\rho. \qquad (118)$$

The expression given by the second equality has a term proportional to $\hat{n}$ which comes from the double sum $\sum_j\sum_k$ when $j=k$, and a term proportional to $\hat{n}^2$ which comes when $j\neq k$. The $\mathbf{R}$ integration produced a factor $\delta(\rho+\rho')$ which converted $\hat{\varphi}(\rho)\hat{\varphi}(\rho')$ into $\hat{\varphi}(\rho)\hat{\varphi}(-\rho)$ $=\hat{\varphi}(\rho)\hat{\varphi}^*(\rho)\equiv|\hat{\varphi}(\rho)|^2$ as is seen using (114). The $|\rho|$ denominator in each term causes no trouble because of compensating numerator factors in $\rho_\mu\rho_\nu$, which also explain how the $\hat{n}^2$ term vanishes. If $|\hat{\varphi}(\rho)|^2$ vanishes for large $|\rho|$ sufficiently rapidly, then the remaining integral is finite. In general, when W^{eq}_{*} is present and no approximation is used the value of $\lambda^0_{\mu\nu}$ does not have such simple $\hat{n}$ or T dependence.

These techniques need to be extended for the analysis of higher order terms in (94) using (98).

CRITICAL BEHAVIOR

That something can be said about critical behavior within the context of this paper follows from the observation that a Brownian particle can be used as a probe which manifests the state of a fluid. If the fluid passes through a phase transition, the Brownian particle should exhibit noticeably altered behavior. In particular, for high enough temperatures the fluid will be a liquid or gas, and the Brownian motion should be normal with a finite value for $\lambda_{\mu\nu}$. However, if we freeze the fluid, we should expect that $\lambda_{\mu\nu}\to\infty$. Using (6) and (8), we see that this implies a vanishing diffusion constant D.[34]

If a complete analysis of (94) using (98) were possible, we would end up with the infinite series: $\lambda_{\mu\nu}=\lambda^0_{\mu\nu}+\lambda^1_{\mu\nu}+\lambda^2_{\mu\nu}+\cdots$ in which the superscripts indicate the number of times a potential appears in the corresponding term. We suspect that intrinsic diffusion will result in each term being finite, as was seen for $\lambda^0_{\mu\nu}$. When $T=0$, however, we have a special case in which each term is in fact infinite. For $\lambda^0_{\mu\sigma}$, this is seen in (115) because the exponential can no longer damp out the integrand when $T=0$. Consequently, $\lambda_{\mu\nu}$ diverges for $T=0$; a fact consistent with intuitive expectations. For $T\neq0$ each term in $\lambda_{\mu\nu}=\lambda^0_{\mu\nu}+\lambda^1_{\mu\nu}+\lambda^2_{\mu\nu}+\cdots$ will be finite, or at least this is plausible following our analysis of $\lambda^0_{\mu\nu}$, and if the temperature is sufficiently large, we expect the series to be summable. This expectation is based upon qualitative analysis of (94) using (98) which suggests that the $\lambda_{\mu\nu}$ series goes like a series in powers of the ratio of potential energy and thermal energy. For large temperatures this ratio gets small and the series converges. The possibility exists that each term in $\lambda_{\mu\nu}=\lambda^0_{\mu\nu}+\lambda^1_{\mu\nu}+\lambda^2_{\mu\nu}+\cdots$ is finite while the sum diverges, if the temperature is small, but nonzero. This suggests that there exists a temperature T_c such that for $T>T_c$ the series sums while for $T\leq T_c$ the series diverges, even though it is comprised of finite terms. If T_c exists, we identify it as the critical temperature for the fluid. It is desirable to try to achieve a rigorous basis for the analysis of (94) using (98) so that these conjectures may be tested.

CONCLUDING REMARKS

The theory of multiplicative stochastic processes has provided a method for nonperturbative approximate solution of complicated dynamical equations. It has been shown how to interpret an exact dynamical quantity as a stochastic quantity. By such an interpretation an averaged equation is written which serves as a nonperturbative approximation for the original dynamics. In this manner we have derived the Fokker–Planck equation for Brownian motion, starting from the exact dynamics for a heavy particle moving in a molecular fluid.

The discovery of "intrinsic diffusion" has permitted an analysis of the ergodicity of the force autocorrelation function which was derived. Because Brownian motion leads to ordinary diffusion, "intrinsic diffusion" and ordinary diffusion are connected by our analysis. "Intrinsic diffusion" will also arise in other contexts.[33]

The analysis of Brownian motion in this paper leads to a calculation of λ, the dissipative constant, in terms of the interparticle potentials. The calculation involves the time integral of a force autocorrelation function which connects λ with the dynamics of the system. A conjectured relationship between λ and critical phenomena is presented, which if eventually justified rigorously, would provide a dynamical basis for the understanding of some aspects of critical behavior.

In our other work on the quantum mechanical density matrix,[3,5] the problem of calculating the matrices, $Q_{\alpha\beta\mu\nu}$, which are the analogs of λ, has been raised. We shall pursue this problem in another paper.

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APPENDIX: DERIVATION OF (50) FROM (48) AND (49).

The correlation formula in (48) follows directly from the solution to Eqs. (1) and (2). In addition, the Gaussian property of $\tilde{F}(t)$ in (1) is inherited by $\tilde{p}(t)$ in (48).[11] This implies

$$\langle\langle \tilde{p}(t_1)\cdots\tilde{p}(t_{2m-1})\rangle\rangle = 0 \quad \text{for } m = 1, 2, \cdots \tag{A1}$$

and

$$\langle\langle \tilde{p}(t_1)\cdots\tilde{p}(t_{2m})\rangle\rangle = \frac{1}{2^m m!}\sum_{p\in S_{2m}}\prod_{j=1}^{m}\langle\langle \tilde{p}(t_{p(2j-1)})\tilde{p}(t_{p(2j)})\rangle\rangle$$

$$= \frac{(MK_BT)^m}{2^m m!}\sum_{p\in S_{2m}}\prod_{j=1}^{m}\times\exp\left[-\frac{\alpha}{M}\left|t_{p(2j)}-t_{p(2j-1)}\right|\right]$$

$$\text{for } m = 1, 2, \cdots \tag{A2}$$

The formal solution to (49) is

$$f(x,t) = \exp\left(-\int_0^t \frac{\tilde{p}(s)}{M}\,ds\frac{\partial}{\partial x}\right)f(x,0), \tag{A3}$$

as is verified by substitution and differentiation. Expanding the exponential and averaging gives

$$\langle\langle f(x,t)\rangle\rangle = \left[\left\langle\sum_{n=0}^{\infty}\left(-\frac{1}{M}\right)^n\frac{1}{n!}\left(\int_0^t\tilde{p}(s)\,ds\right)^n\frac{\partial^n}{\partial x^n}\right\rangle\right]f(x,0). \tag{A4}$$

Using (A1) and (A2) in (A4) gives

$$\langle\langle f(x,t)\rangle\rangle = \sum_{m=0}^{\infty}\left(-\frac{1}{M}\right)^{2m}\frac{1}{(2m)!}\frac{(MK_BT)^m}{2^m m!}\sum_{p\in S_{2m}}\prod_{j=1}^{m}\int_0^t\int_0^t\times\exp\left(-\frac{\alpha}{M}\left|t_{p(2j)}-t_{p(2j-1)}\right|\right)dt_{p(2j)}\,dt_{p(2j-1)}\times\frac{\partial^{2m}}{\partial x^{2m}}f(x,0)$$

$$= \sum_{m=0}^{\infty}\left(\frac{K_BT}{M}\right)^{2m}\frac{1}{2^m m!}\left(\int_0^t\int_0^t\exp\left[-\frac{\alpha}{m}\left|s-s'\right|\right]ds\,ds'\right)^m\times\left(\frac{\partial^2}{\partial x^2}\right)^m f(x,0)$$

$$= \sum_{m=0}^{\infty}\frac{1}{2^m m!}\frac{1}{M^{2m}}\left(\int_0^t\int_0^t\langle\langle \tilde{p}(s)\tilde{p}(s')\rangle\rangle\,ds\,ds'\right)^m\times\left(\frac{\partial^2}{\partial x^2}\right)^m f(x,0). \tag{A5}$$

Therefore,

$$\frac{\partial}{\partial t}\langle\langle f(x,t)\rangle\rangle = \int_0^t\frac{1}{M^2}\langle\langle \tilde{p}(t)\tilde{p}(s)\rangle\rangle\,ds\frac{\partial^2}{\partial x^2}\langle\langle f(xt)\rangle\rangle \tag{A6}$$

which is (50), and which follows from (A5) by differentiation, followed by rearrangement of terms.

Equation (A6) can be integrated to give (51) of the text. The solution to (51) is given by

$$\langle\langle f(xt)\rangle\rangle = \left\{4\pi\frac{K_BT}{\alpha}\left[t-\frac{M}{\alpha}+\frac{M}{\alpha}\exp\left(-\frac{\alpha}{M}t\right)\right]\right\}^{-1/2}\times\exp\left(-\frac{\alpha}{4K_BT}\frac{(x-x_0)^2}{\{t-(M/\alpha)+(M/\alpha)\exp[-(\alpha/M)t]\}}\right) \tag{A7}$$

if $\langle\langle f(x,0)\rangle\rangle = \delta(x-x_0)$. This expression can be checked by substitution. It leads to the Orstein–Fürth formula[35]

$$\langle\langle (x(t)-x_0)^2\rangle\rangle = \frac{2MK_BT}{\alpha^2}\left[\frac{\alpha}{M}t-1+\exp\left(-\frac{\alpha}{M}t\right)\right]. \tag{A8}$$

Note also that for the short times, $t < M/\alpha$, that (A7) reduces to

$$\left(4\pi\frac{K_BT}{2M}t^2\right)^{-1/2}\exp\left(-\frac{(x-x_0)^2}{4(K_BT/2M)t^2}\right) \tag{A9}$$

which is the Green's function for intrinsic diffusion in the text. However, for long time, $t > M/\alpha$, (A7) becomes the one-dimensional analog of (109) in the text which is valid for ordinary diffusion. The intrinsic diffusion Green's function has the form (A9) for all times!

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Application of cumulant techniques to multiplicative stochastic processes

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The use of cumulant techniques for analyzing time dependent, stochastic matrix expressions of the form $\langle \underset{\sim}{T} \exp[\int_0^t \tilde{\mathbf{B}}(S)dS] \rangle$ is explained. Because cumulants are complicated expressions when $\tilde{\mathbf{B}}(t)$ does not commute with itself at unequal times, we explicitly work out cumulant expressions up to fourth order. The fourth order terms can be used to demonstrate that noncommutivity prevents the generalization, to time-dependent, stochastic matrices which do not commute with themselves at unequal times, of the result which applies to commuting stochastic processes that states: If the stochastic process is Gaussian, then its cumulant expansion truncates after the second cumulant. Furthermore, it is argued that if the stochastic matrix process is both Gaussian *and* purely random then the cumulant expansion does truncate after the second cumulant, after all. The significance of this result with respect to the application of approximation involving cumulants is mentioned.

INTRODUCTION

It is the purpose of this paper to apply cumulant techniques to the analysis of multiplicative stochastic processes.[1] When the stochastic matrices, which appear in the differential equations defining a particular multiplicative stochastic process, have special properties, the use of cumulants can lead to significant simplifications in the analysis of solutions to the differential equations. In general, when no special conditions are imposed on the properties of the stochastic matrices, cumulant expressions contain all of the information of the original problem, but without any particular advantages for further analysis. Kubo[2] has introduced cumulant techniques for the study of multiplicative stochastic processes, and he has attempted to approach the problem in as general a setting as possible. Fox[1] has studied multiplicative stochastic processes without using cumulant techniques, and has restricted his approach to the problem to the use of stochastic matrices which are purely random and Gaussian. It will be demonstrated in this paper that the restriction to purely random, Gaussian, stochastic matrices corresponds with the special conditions alluded to earlier for which cumulant techniques are most useful.

In the course of this paper we will show how the utility of cumulant techniques is related to the Gaussian property of the stochastic matrices. When the stochastic matrices are time independent, the Gaussian property alone guarantees major simplifications in analysis if cumulants are used. When the stochastic matrices are time dependent and do not commute for unequal times, then the Gaussian property alone is insufficient, and must be augmented by the purely random property if efficacy is to be achieved using cumulant methods. It is this last point that requires emphasis when one is using approximation methods which rely upon cumulants expansions.

TIME ORDERING AND CUMULANTS

Consider a multiplicative stochastic process described by[1]

$$\frac{d}{dt}a_\alpha(t) = A_{\alpha\alpha'}a_{\alpha'}(t) + \tilde{A}_{\alpha\alpha'}(t)a_{\alpha'}(t) \tag{1}$$

in which $A_{\alpha\alpha'} = -A_{\alpha'\alpha}$, $\tilde{A}_{\alpha\alpha'}(t) = -\tilde{A}_{\alpha'\alpha}(t)$, $\tilde{A}_{\alpha\alpha'}(t)$ is a stochastic matrix with averaged value zero, $\alpha = 1, 2, \ldots, N$, and repeated indices are summed. If $\tilde{A}_{\alpha\alpha'}(t)$ had a nonzero averaged value, we could include its averaged value in the term $A_{\alpha\alpha'}$ and start over again with $\tilde{A}_{\alpha\alpha'}(t) - \langle \tilde{A}_{\alpha\alpha'}(t) \rangle$ as the stochastic matrix, where $\langle \cdots \rangle$ denotes stochastic averaging. We would then have a process such as described by (1) with the average value of $\tilde{A}_{\alpha\alpha'}(t)$ equal to zero. A useful manner for obtaining the solution to (1) is to use the transformation

$$a_\alpha(t) = [\exp(t\mathbf{A})]_{\alpha\alpha'}b_{\alpha'}(t). \tag{2}$$

Consequently, the b_α's satisfy

$$\begin{aligned}\frac{d}{dt}b_\alpha(t) &= [\exp(-t\mathbf{A})]_{\alpha\beta}\tilde{A}_{\beta\beta'}(t)[\exp(t\mathbf{A})]_{\beta'\alpha'}b_{\alpha'}(t) \\ &\equiv \tilde{B}_{\alpha\alpha'}(t)b_{\alpha'}(t)\end{aligned} \tag{3}$$

where the second equality defines $\tilde{\mathbf{B}}(t)$. Note that the averaged value of $\tilde{\mathbf{B}}(t)$ is zero since it is linear in the matrix elements of $\tilde{\mathbf{A}}(t)$. In general, $\mathbf{A}$ and $\tilde{\mathbf{A}}(t)$ will not commute, neither will $\tilde{\mathbf{A}}(t)$ and $\tilde{\mathbf{A}}(s)$ nor $\tilde{\mathbf{B}}(t)$ and $\tilde{\mathbf{B}}(s)$ for $t \neq s$.

The formal solution to (3) must be written with a time ordered exponential[3] defined by

$$\begin{aligned}b_\alpha(t) &= [\underset{\sim}{T}\exp(\textstyle\int_0^t \tilde{\mathbf{B}}(s)\,ds)]_{\alpha\alpha'}b_{\alpha'}(0) \\ &\equiv \sum_{n=0}^{\infty}\int_0^t\int_0^{t_1}\int_0^{t_2}\cdots\int_0^{t_{n-2}}\int_0^{t_{n-1}}[\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\cdots \\ &\quad \tilde{B}_{\mu_{n-2}\mu_{n-1}}(t_{n-1})\tilde{B}_{\mu_{n-1}\alpha'}(t_n)]\,dt_n\,dt_{n-1}\cdots dt_2\,dt_1 b_{\alpha'}(0)\end{aligned} \tag{4}$$

where the $n=0$ term is defined to be 1. If $\tilde{\mathbf{B}}(t)$ and $\tilde{\mathbf{B}}(s)$ commuted for $t \neq s$, then (4) would reduce to an ordinary exponential

$$\sum_{n=0}^{\infty}\frac{1}{n!}\int_0^t\cdots n\cdots\int_0^t[\tilde{B}_{\alpha\mu_1}(S_1)\cdots\tilde{B}_{\mu_{n-1}\alpha'}(S_n)]\,dS_n\cdots dS_1 b_{\alpha'}(0).$$

If $\tilde{\mathbf{B}}(t)$ is in fact time independent, then all time integrations are easily performed giving the ordinary exponential

$$\sum_{n=0}^{\infty}\frac{1}{n!}t^n[(\tilde{B})^n]_{\alpha\alpha'}b_{\alpha'}(0).$$

Cumulants arise when one wishes to perform the stochastic average of an expression like (4) or its more simple forms given above, at the end of the preceeding

paragraph. Historically speaking, cumulants arose in statistics and were known as Thiele semi-invariants.[4]

Suppose that we have a time independent stochastic variable $\tilde{X}$ and we are interested in calculating $\langle \exp(\tilde{X}) \rangle$, where $\tilde{X}$ may be either a scalar or a matrix stochastic quantity determined by the distribution function for its values. The cumulants for $\tilde{X}$ are defined by

$$\langle \exp(\tilde{X}) \rangle = \left\langle \sum_{n=0}^{\infty} \frac{1}{n!} (\tilde{X})^n \right\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \langle (\tilde{X})^n \rangle$$
$$\equiv \exp\left(\sum_{n=1}^{\infty} \frac{1}{n!} \langle (\tilde{X})^n \rangle_c \right) \tag{5}$$

where $\langle \cdots \rangle_c$ denotes the cumulant average. Cumulant averaging is by definition a homogeneous process with respect to multiplication of $\tilde{X}$ by a constant, just as is the case with ordinary averaging. Therefore, $\langle (\lambda \tilde{X})^n \rangle_c = \lambda^n \langle (\tilde{X})^n \rangle_c$, and

$$\langle \exp(\lambda \tilde{X}) \rangle = \exp\left(\sum_{n=1}^{\infty} \frac{\lambda^n}{n!} \langle (\tilde{X})^n \rangle_c \right). \tag{6}$$

Differentiating (6) n times with respect to λ, followed by setting $\lambda = 0$, gives for $n = 1, 2, 3, 4, \cdots$

$$\begin{aligned}
&\langle \tilde{X} \rangle = \langle \tilde{X} \rangle_c, \\
&\langle (\tilde{X})^2 \rangle = \langle (\tilde{X})^2 \rangle_c + \langle \tilde{X} \rangle_c^2, \\
&\langle (\tilde{X})^3 \rangle = \langle (\tilde{X})^3 \rangle_c + 3\langle (\tilde{X})^2 \rangle_c \langle \tilde{X} \rangle_c + \langle \tilde{X} \rangle_c^3, \\
&\langle (\tilde{X})^4 \rangle = \langle (\tilde{X})^4 \rangle_c + 4\langle (\tilde{X})^3 \rangle_c \langle \tilde{X} \rangle_c + 3\langle (\tilde{X})^2 \rangle_c^2 + 6\langle (\tilde{X})^2 \rangle_c \langle \tilde{X} \rangle_c^2 + \langle \tilde{X} \rangle_c^4 \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot
\end{aligned} \tag{7}$$

Starting with the first line, these equations may be successively inverted to give expressions for cumulant averages in terms of ordinary stochastic averages:

$$\begin{aligned}
&\langle \tilde{X} \rangle_c = \langle \tilde{X} \rangle, \\
&\langle (\tilde{X})^2 \rangle_c = \langle (\tilde{X})^2 \rangle - \langle \tilde{X} \rangle^2, \\
&\langle (\tilde{X})^3 \rangle_c = \langle (\tilde{X})^3 \rangle - 3\langle (\tilde{X})^2 \rangle \langle \tilde{X} \rangle + 2\langle \tilde{X} \rangle^3, \\
&\langle (\tilde{X})^4 \rangle_c = \langle (\tilde{X})^4 \rangle - 4\langle (\tilde{X})^3 \rangle \langle \tilde{X} \rangle - 3\langle (\tilde{X})^2 \rangle^2 + 12\langle (\tilde{X})^2 \rangle \langle \tilde{X} \rangle^2 - 6\langle \tilde{X} \rangle^4 \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot \\
&\quad \cdot \qquad \cdot
\end{aligned} \tag{8}$$

It is possible to define cumulants even when we are dealing with time-dependent stochastic matrices which do not commute at unequal times.[2] One gets time-ordered cumulants defined by

$$\left\langle \underset{\leftarrow}{T} \exp\left(\int_0^t \tilde{\mathbf{B}}(S)\, dS \right) \right\rangle \equiv \underset{\leftarrow}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \int_0^{t_1} \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} \times \langle \tilde{\mathbf{B}}(t_1) \tilde{\mathbf{B}}(t_2) \cdots \tilde{\mathbf{B}}(t_{n-1}) \tilde{\mathbf{B}}(t_n) \rangle_c \times dt_n\, dt_{n-1} \cdots dt_2\, dt_1 \right). \tag{9}$$

Because it is so easy to misinterpret the precise meaning of (9), we introduce here the following notational scheme which permits unambiguous rendering of (9). Define $g_{\alpha\beta}^{(n)}(t_1)$ by

$$g_{\alpha\beta}^{(n)}(t_1) \equiv \int_0^{t_1} \int_0^{t_2} \cdots \int_0^{t_{n-2}} \int_0^{t_{n-1}} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \cdots \tilde{B}_{\mu_{n-2}\mu_{n-1}}(t_{n-1}) \tilde{B}_{\mu_{n-1}\beta}(t_n) \rangle_c\, dt_n\, dt_{n-1} \cdots dt_3\, dt_2. \tag{10}$$

Therefore,

$$\left\langle \underset{\leftarrow}{T} \exp\left(\int_0^t \tilde{\mathbf{B}}(S)\, dS \right) \right\rangle = \underset{\leftarrow}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \mathbf{g}^{(n)}(t_1)\, dt_1 \right). \tag{11}$$

As before, we can introduce a parameter λ, and using (10) leads to

$$\left\langle \underset{\leftarrow}{T} \exp\left(\int_0^t \lambda \tilde{\mathbf{B}}(S)\, dS \right) \right\rangle = \underset{\leftarrow}{T} \exp\left(\sum_{n=1}^{\infty} \int_0^t \lambda^n \mathbf{g}^{(n)}(t_1)\, dt_1 \right). \tag{12}$$

Differentiating (12) with respect to λ, n times, followed by setting $\lambda = 0$, gives for $n = 1, 2, 3, 4, \cdots$

$$\int_0^t \langle \tilde{B}_{\alpha\beta}(t_1) \rangle\, dt_1 = \int_0^t g_{\alpha\beta}^{(1)}(t_1)\, dt_1 = \int_0^t \langle \tilde{B}_{\alpha\beta}(t_1) \rangle_c\, dt_1,$$

$$\begin{aligned}
\int_0^t \int_0^{t_1} \langle \tilde{B}_{\alpha\mu}(t_1) \tilde{B}_{\mu\beta}(t_2) \rangle\, dt_2\, dt_1 &= \int_0^t g_{\alpha\beta}^{(2)}(t_1)\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(1)}(t_1) g_{\mu\beta}^{(1)}(t_2)\, dt_2\, dt_1 \\
&= \int_0^t \int_0^{t_1} \langle \tilde{B}_{\alpha\mu}(t_1) \tilde{B}_{\mu\beta}(t_2) \rangle_c\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \langle \tilde{B}_{\alpha\mu}(t_1) \rangle_c \langle \tilde{B}_{\mu\beta}(t_2) \rangle_c\, dt_2\, dt_1,
\end{aligned}$$

$$\begin{aligned}
&\int_0^t \int_0^{t_1} \int_0^{t_2} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\beta}(t_3) \rangle\, dt_3\, dt_2\, dt_1 \\
&\quad = \int_0^t g_{\alpha\mu}^{(3)}(t_1)\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(2)}(t_1) g_{\mu\beta}^{(1)}(t_2) + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(1)}(t_1) g_{\mu\beta}^{(2)}(t_2)\, dt_2\, dt_1 \\
&\qquad + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\beta}^{(1)}(t_3)\, dt_3\, dt_2\, dt_1 \\
&\quad = \int_0^t \int_0^{t_1} \int_0^{t_2} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\beta}(t_3) \rangle_c\, dt_3\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \int_0^{t_1} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(S_2) \rangle_c \langle \tilde{B}_{\mu_2\beta}(t_2) \rangle_c\, dt_2\, dS_2\, dt_1 \\
&\qquad + \int_0^t \int_0^{t_1} \int_0^{t_2} \langle B_{\alpha\mu_1}(t_1) \rangle_c \langle B_{\mu_1\mu_2}(t_2) B_{\mu_2\beta}(t_3) \rangle_c\, dt_3\, dt_2\, dt_1 + \int^t \int^{t_1} \int^{t_2} \langle B_{\alpha\mu_1}(t_1) \rangle_c \langle B_{\mu_1\mu_2}(t_2) \rangle_c \langle B_{\mu_2\beta}(t_3) \rangle_c\, dt_3\, dt_2\, dt_1,
\end{aligned}$$

$$\begin{aligned}
&\int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\mu_3}(t_3) \tilde{B}_{\mu_3\beta}(t_4) \rangle\, dt_4\, dt_3\, dt_2\, dt_1 \\
&\quad = \int_0^t g_{\alpha\beta}^{(4)}(t_1)\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(3)}(t_1) g_{\mu\beta}^{(1)}(t_2)\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(1)}(t_1) g_{\mu\beta}^{(3)}(t_2)\, dt_2\, dt_1 \\
&\qquad + \int_0^t \int_0^{t_1} g_{\alpha\mu}^{(2)}(t_1) g_{\mu\beta}^{(2)}(t_2)\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(2)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\beta}^{(1)}(t_3)\, dt_3\, dt_2\, dt_1 \\
&\qquad + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(2)}(t_2) g_{\mu_2\beta}^{(1)}(t_3)\, dt_3\, dt_2\, dt_1 + \int_0^t \int_0^{t_1} \int_0^{t_2} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\beta}^{(2)}(t_3)\, dt_3\, dt_2\, dt_1 \\
&\qquad + \int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} g_{\alpha\mu_1}^{(1)}(t_1) g_{\mu_1\mu_2}^{(1)}(t_2) g_{\mu_2\mu_3}^{(1)}(t_3) g_{\mu_3\beta}^{(1)}(t_4)\, dt_4\, dt_3\, dt_2\, dt_1 \\
&\quad = \int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} \langle \tilde{B}_{\alpha\mu_1}(t_1) \tilde{B}_{\mu_1\mu_2}(t_2) \tilde{B}_{\mu_2\mu_3}(t_3) \tilde{B}_{\mu_3\beta}(t_4) \rangle_c\, dt_4\, dt_3\, dt_2\, dt_1
\end{aligned}$$

$$
\begin{aligned}
&+\int_0^t\int_0^{t_1}\int_0^{s_2}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle_c\,dt_2\,dS_3\,dS_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle_c\,dS_3\,dt_2\,dS_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_2)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_3)\rangle_c\,dt_3\,dt_2\,dS_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_3)\rangle_c\,dt_3\,dS_3\,dt_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1\\
&+\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle_c\langle\tilde{B}_{\mu_1\mu_2}(t_2)\rangle_c\langle\tilde{B}_{\mu_2\mu_3}(t_3)\rangle_c\langle\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1. \qquad (13)
\end{aligned}
$$

Especially notice the limits of integration in several of the terms which contribute to the third and fourth order expressions. By successively inverting these equations we get expressions for the cumulants in terms of the ordinary stochastic averages:

$$
\begin{aligned}
&\int_0^t\langle\tilde{B}_{\alpha\beta}(t_1)_c\,dt_1=\int_0^t\langle\tilde{B}_{\alpha\beta}(t_1)\rangle\,dt_1,\\
&\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle_c\,dt_2\,dt_1=\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle\,dt_2\,dt_1-\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\rangle\langle\tilde{B}_{\mu\beta}(t_2)\rangle\,dt_2\,at_1,\\
&\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle_c\,dt_3\,dt_2\,dt_1\\
&\qquad=\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle\,dt_3\,dt_2\,dt_1-\int_0^t\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\beta}(t_2)\rangle\,dt_2\,dS_2\,dt_1\\
&\qquad\quad-\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t)\rangle\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle\,dt_3\,dt_2\,dt_1+\int_0^t\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(t_2)\rangle\langle\tilde{B}_{\mu_2\beta}(t_3)\rangle\,dt_3\,dt_2\,dt_1,\\
&\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c\,dt_4\,dt_3\,dt_2\,dt_1\\
&\qquad=\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle\,dt_4\,dt_3\,dt_2\,dt_1\\
&\qquad\quad-\int_0^t\int_0^{t_1}\int_0^{s_2}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\qquad\quad+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\qquad\quad+\int_0^t\int_0^{t_1}\int_0^{s_2}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(S_2)\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\qquad\quad-\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_1}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(S_3)\rangle\langle\tilde{B}_{\mu_3\beta}(t_2)\rangle\,dt_2\,dS_3\,dS_2\,dt_1\\
&\qquad\quad-\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle\,dt_4\,dt_3\,dt_2\,dt_1\\
&\qquad\quad-\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle\,dS_3\,dt_2\,dS_2\,dt_1\\
&\qquad\quad+\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\rangle\langle\tilde{B}_{\mu_1\mu_2}(S_2)\rangle\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle\,dS_3\,dt_2\,dS_2\,dt_1. \qquad (14)
\end{aligned}
$$

Again, especially notice the limits of integration in several of the terms which contribute to the third and fourth order expressions. By studying the special cases in which either $\tilde{\mathbf{B}}(t)$ commutes for unequal times, or $\tilde{\mathbf{B}}$ is time independent, it may be shown that (14) reduces to (8), and (13) reduces to (7). It should by now be clear how to obtain the higher order cumulants for $\tilde{\mathbf{B}}(t)$ when it does not commute with itself for unequal times, even though the expressions become quite complicated.

THE GAUSSIAN PROPERTY

Throughout this discussion of the Gaussian property, it is convenient to invoke the condition that the averaged value of $\tilde{\mathbf{B}}(t)$ is zero. This simplifies considerations without loss of generality, as was explained at the beginning of the last section. The analogous condition for $\tilde{X}$ is that $\langle\tilde{X}\rangle=0$.

Suppose that $\tilde{X}$ is Gaussian with averaged value zero. Then it is known that the moments of $\tilde{X}$ satisfy[5]

$$
\begin{aligned}
&\langle(\tilde{X})^{2m+1}\rangle=0 \quad \text{for } m=0,1,2,\cdots, \qquad (15)\\
&\langle(\tilde{X})^{2m}\rangle=1\times3\times5\times\cdots\times(2m-1)\langle(\tilde{X})^2\rangle^m \quad \text{for } m=1,2,\cdots.
\end{aligned}
$$

If we return to (8) we see that

$$
\langle\tilde{X}\rangle_c=0,\quad \langle(\tilde{X})^2\rangle_c=\langle(\tilde{X})^2\rangle, \qquad (16)
$$

$$
\langle(\tilde{X})^3\rangle_c=0,\quad \langle(\tilde{X})^4\rangle_c=0.
$$

The last result follows from the cancellation of the two nonvanishing terms: $\langle(\tilde{X})^4\rangle$ and $-3\langle(\tilde{X})^2\rangle^2$, as may be seen using the second equation in (15). It may be proved generally that all cumulants of order higher than four also vanish. The proof may be performed by the method of induction. We assume it is true that except for the nonvanishing, second order cumulant, all cumulants up to and including order $2m$ for $m>2$ vanish. We shall now show that cumulants of order $2m+1$ and $2m+2$ also vanish.

The cumulant of order $2m+1$ will be expressible as an expansion in terms of the moments of $\tilde{X}$ up to order $2m+1$ as is indicated by (8). The leading term will be $\langle(\tilde{X})^{2m+1}\rangle$ which is zero according to (15). All other terms in the expansion will involve products of lower order moments in which at least one factor is an odd order, lower than $2m+1$ order moment. By (15), such moments vanish and we conclude that $\langle(\tilde{X})^{2m+1}\rangle_c=0$.

The consideration of the cumulant of order $2m+2$ is best pursued using the relationships given by (7). These relationships show that $\langle(\tilde{X})^{2m+2}\rangle$ may be expressed in terms of cumulants of order less than or equal to $2m+2$. The Gaussian properties given by (15) show that $\langle(\tilde{X})^{2m+2}\rangle$ is nonvanishing. Its expansion, according to

(7), in terms of cumulants begins with $\langle(\tilde{X})^{2m+2}\rangle_c$, which we wish to compute, and involves other terms, each of which is a product of lower order cumulants. By hypothesis, all lower order cumulant, except the second order and $2m+1$ order cumulants, vanish, and we have already seen that the cumulant of order $2m+1$ also vanishes. Therefore, all products vanish except the single term which is the product of $m+1$ second order cumulants. Therefore, it follows that $\langle(\tilde{X})^{2m+2}\rangle = \langle(\tilde{X})^{2m+2}\rangle_c + C\langle(\tilde{X})^2\rangle_c^{m+1}$ where C is a coefficient which has to be determined. Looking at (6), it may be seen that the $\langle(\tilde{X})^2\rangle_c^{m+1}$ term comes from the $m+1$ term in the expansion of the exponential on the right-hand side of (6). Such a term has a factor of $1/(m+1)!$ associated with it. Each factor of $\langle(\tilde{X})^2\rangle_c$ has associated with it a factor $1/2!$ as is directly evident in (6). Therefore, $\langle(\tilde{X})^2\rangle_c^{m+1}$ will have a factor, overall, of $[1/(m+1)!](1/2!)^{m+1}$. This must be multiplied by $(2m+2)!$ to get C as a result of the $2m+2$ fold differentiation of λ^{2m+2}. Consequently, $C=(2m+2)!/(m+1)!\,2^{m+1}$. Using (15), it is seen that $\langle(\tilde{X})^{2m+2}\rangle = 1\times3\times5\times\cdots\times(2m+1)\langle(\tilde{X})^2\rangle^{m+1}$. Therefore,

$$\begin{aligned}\langle(\tilde{X})^{2m+2}\rangle_c &= 1\times3\times5\times\cdots\times(2m+1)\langle(\tilde{X})^2\rangle^{m+1} \\ &\quad - \frac{(2m+2)!}{(m+1)!\,2^{m+1}}\langle(\tilde{X})^2\rangle_c^{m+1} \\ &= 0 \end{aligned} \tag{17}$$

since $\langle(\tilde{X})^2\rangle = \langle(\tilde{X})^2\rangle_c$. This completes the proof.

The conclusion is that if $\tilde{X}$ is Gaussian, with averaged value zero, then

$$\langle\exp[\tilde{X}]\rangle = \exp[\tfrac{1}{2}\langle(\tilde{X})^2\rangle] \tag{18}$$

which is especially simple. The cumulant expansion reduces to a single term!

Before attempting to generalize this result for consideration of stochastic matrices which do not commute for unequal times, it is worthwhile to observe that if $\tilde{X}$ is replaced by a scalar, time dependent stochastic quantity, $\tilde{F}(t)$, then the Gaussian property again leads to great simplifications. We make this digression in order to point out that time dependence, *per se*, does not lead to complications. The complications which will arise in our discussion of stochastic matrices, which depend upon time but which do not commute for unequal times, come from the noncommutivity.

Suppose $\tilde{F}(t)$ has averaged value zero, and is Gaussian. It can then be shown that[6]

$$\langle\exp[\textstyle\int_0^t \tilde{F}(S)\,dS]\rangle = \exp[\tfrac{1}{2}\int_0^t\int_0^t\langle\tilde{F}(S_1)\tilde{F}(S_2)\rangle\,dS_1\,dS_2]. \tag{19}$$

Equation (19) is the time dependent generalization of (18) for a time-dependent, scalar, stochastic process. Again, the cumulant expansion reduces to a single term.

The generalization of this result to time-dependent stochastic matrices which do not commute at unequal times cannot be made. The Gaussian property for $\tilde{\mathbf{B}}(t)$ is expressed by[1]

$$\langle\tilde{B}_{\mu_1\nu_1}(t_1)\cdots\tilde{B}_{\mu_{2m+1}\nu_{2m+1}}(t_{2m+1})\rangle = 0 \quad \text{for } m=0,1,2,\cdots, \tag{20}$$

$$\langle\tilde{B}_{\mu_1\nu_1}(t_1)\cdots\tilde{B}_{\mu_{2m}\nu_{2m}}(t_{2m})\rangle = \frac{1}{2^m m!} \times \sum_{p\in S_{2m}}\prod_{j=1}^{m}\langle\tilde{B}_{\mu_{p(2j-1)}\nu_{p(2j-1)}}(t_{p(2j-1)})\tilde{B}_{\mu_{p(2j)}\nu_{p(2j)}}(t_{p(2j)})\rangle$$
for $m=1,2,\cdots$,

where $\sum_{p\in S_{2m}}$ is the sum over all permutations p in the symmetric group of order $(2m)!$, S_{2m}. Even though we can think of a Gaussian $\tilde{\mathbf{B}}(t)$ in the sense of (20), the Gaussian property alone will prove insufficient for the reduction of (9) to a form analogous with (18) or (19). It is necessary that $\tilde{\mathbf{B}}(t)$ be Gaussian *and* purely random in order to write

$$\langle\underset{\leftarrow}{T}\exp[\textstyle\int_0^t\tilde{\mathbf{B}}(S)\,dS]\rangle = \underset{\leftarrow}{T}\exp[\int_0^t\int_0^{t_1}\langle\tilde{\mathbf{B}}(t_1)\tilde{\mathbf{B}}(t_2)\rangle\,dt_2\,dt_1]. \tag{21}$$

The purely random property is defined by[1]

$$\langle\tilde{B}_{\alpha\beta}(t)\tilde{B}_{\mu\nu}(S)\rangle = 2Q_{\alpha\beta\mu\nu}\delta(t-S) \tag{22}$$

in which the time delta function characterizes the purely random property. Defining $R_{\alpha\beta}$ by $R_{\alpha\beta}\equiv Q_{\alpha\theta\theta\beta}$, wherein summation over θ is implicit, Eq. (21) becomes

$$\langle\underset{\leftarrow}{T}\exp[\textstyle\int_0^t\tilde{\mathbf{B}}(S)\,dS]\rangle_{\alpha\beta} = [\exp(\mathbf{R}t)]_{\alpha\beta} \tag{23}$$

which is especially simple. We shall now proceed to demonstrate why Gaussianness alone is insufficient for the justification of (23) or (21).

That Gaussianness alone does not result in the vanishing of all but the second order cumulants of $\tilde{\mathbf{B}}(t)$ may be seen by studying (13) and (14). First of all, because $\langle\tilde{\mathbf{B}}(t)\rangle = 0$ is assumed, the expressions in (13) and (14) simplify greatly. We get immediately

$$\begin{aligned}&\int_0^t\langle\tilde{B}_{\alpha\beta}(t_1)\rangle_c\,dt_1 = 0, \\ &\int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle_c\,dt_2\,dt_1 \\ &= \int_0^t\int_0^{t_1}\langle\tilde{B}_{\alpha\mu}(t_1)\tilde{B}_{\mu\beta}(t_2)\rangle\,dt_2\,dt_1, \\ &\int_0^t\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\beta}(t_3)\rangle_c\,dt_3\,dt_2\,dt_1 = 0.\end{aligned} \tag{24}$$

Differentiation of these equations with respect to time leads to equations for the integrands. Difficulty arises with the fourth order term. From (14) we get

$$\begin{aligned}&\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c \\ &\quad\times dt_4\,dt_3\,dt_2\,dt_1 \\ &= \int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle \\ &\quad\times dt_4\,dt_3\,dt_2\,dt_1 \\ &\quad - \int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(S_2)\rangle \\ &\quad\times\langle\tilde{B}_{\mu_2\mu_3}(t_2)\tilde{B}_{\mu_3\beta}(S_3)\rangle\,dS_3\,dt_2\,dS_2\,dt_1.\end{aligned} \tag{25}$$

It can be seen that this is nonvanishing if $\tilde{\mathbf{B}}(t)$ is not purely random by considering the special case in which

$$\langle\tilde{B}_{\alpha\beta}(t)\tilde{B}_{\mu\nu}(S)\rangle = 2Q_{\alpha\beta\mu\nu}\varphi(t-S), \tag{26}$$

wherein $\varphi(t-S)$ is not a delta function, but instead is nonvanishing for nonzero values of $|t-S|$. For example, $\varphi(t-S)$ may be proportional to $\exp(-\alpha|t-S|)$. Using the two symmetries $Q_{\alpha\beta\mu\nu}=Q_{\mu\nu\alpha\beta}$ and $\varphi(t-S)=\varphi(S-t)$, the Gaussian property, as expressed by (20), leads to the following expression for (25):

$$\begin{aligned}&\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\langle\tilde{B}_{\alpha\mu_1}(t_1)\tilde{B}_{\mu_1\mu_2}(t_2)\tilde{B}_{\mu_2\mu_3}(t_3)\tilde{B}_{\mu_3\beta}(t_4)\rangle_c \\ &\quad\times dt_4\,dt_3\,dt_2\,dt_1\end{aligned}$$

$$= 4\int_0^t\int_0^{t_1}\int_0^{t_2}\int_0^{t_3}\{Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta}\varphi(t_1-t_2)\varphi(t_3-t_4)$$
$$+ Q_{\alpha\mu_1\mu_2\mu_3}Q_{\mu_1\mu_2\mu_3\beta}\varphi(t_1-t_3)\varphi(t_2-t_4)$$
$$+ Q_{\alpha\mu_1\mu_3\beta}Q_{\mu_1\mu_2\mu_2\mu_3}\varphi(t_1-t_4)\varphi(t_2-t_3)\}\,dt_4\,dt_3\,dt_2\,dt_1$$
$$- 4\int_0^t\int_0^{t_1}\int_0^{t_1}\int_0^{t_2}Q_{\alpha\mu_1\mu_1\mu_2}Q_{\mu_2\mu_3\mu_3\beta}\varphi(t_1-S_2)\varphi(t_2-S_3)$$
$$\times\, dS_3\,dt_2\,dS_2\,dt_1. \qquad (27)$$

The factors of 4 come from 2^2 as indicated by (26). The negative term is the negative term in (25) replaced by (26). The three preceeding positive terms are the $m=2$ case of the second equation in (20). There are 24 permutations to sum over, but only three distinct terms occur as a result of the two symmetries mentioned above. Only the first positive term in the right-hand side of (27) contains a matrix expression which matches the matrix expression of the negative term. The other two positive terms cannot be cancelled out at all! However, if $\varphi(t-S)\equiv\delta(t-S)$ then study of these extra two terms will show that their integrals vanish as a result of the time-ordered upper limits of integration,[7] and the remaining positive and negative two terms will exactly cancel! When $\varphi(t-S)\neq\delta(t-S)$, the above vanishing of integrals and cancellation of nonvanishing integrals fails to occur.

That the purely random property ultimately leads to (23) will not be proved here since it has been proved in another paper.[1] However, here it has been shown that without the purely random property, already the fourth order cumulant will not vanish for time dependent stochastic matrices which do not commute at unequal times. Consequently, the cumulant expansion will not truncate to a single term, but will involve all even order cumulants. Thus, no real simplification is achieved using cumulants.

APPROXIMATION PROCEDURES

Various physical problems involve computation of a quantity of the form

$$\langle \underline{T}\exp[\textstyle\int_0^t \mathbf{O}(S)\,dS]\rangle, \qquad (28)$$

wherein $\mathbf{O}(S)$ is an operator parameterized by S, which may or may not be the time variable, and $\langle\cdots\rangle$ denotes some kind of averaging such as a canonical average over some or all of the variables $\mathbf{O}(S)$ depends upon, or a ground state expectation value, or some other "averaging." Many times one sees in the literature the introduction of cumulant techniques in order to handle the computation of (28). Often it is argued that to good approximation $\mathbf{O}(S)$ behaves as if it were Gaussian, and then the cumulant expansion is truncated after the second cumulant. However, the validity of such approximations also requires that it be demonstrated that to good approximation $\mathbf{O}(S)$ behaves as if it were also purely random. Then, and only then, the truncation of the cumulant expansion is a good approximation.

One application of this kind of approximation procedure in which both Gaussianness and pure randomness were considered has been presented by the author in another paper.[6]

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Critique of the generalized cumulant expansion method

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The method of ordered cumulants is presented for the solution of multiplicative stochastic processes. The relationship between this method and the irreducible cluster integral method of Mayer, which is used in the theory of the imperfect gas, is elucidated. The cluster property of ordered cumulants is proved. A critique of the literature in this area is presented which exposes some errors in the formulas. Several examples are indicated for the application of the ordered cumulant method.

1. INTRODUCTION

Many physical processes may be mathematically modelled by stochastic operator (differential, matrix, commutator, etc.) equations. Linear stochastic operator equations usually are of two major types, the inhomogeneous or "additive" stochastic processes with the canonical form

$$\frac{d}{dt}\mathbf{a}(t) = \mathbf{G}\mathbf{a}(t) + \tilde{\mathbf{F}}(t), \tag{1}$$

and the homogeneous or "multiplicative" stochastic processes with the canonical form

$$\frac{d}{dt}\mathbf{a}(t) = \mathbf{A}\mathbf{a}(t) + \tilde{\mathbf{A}}(t)\mathbf{a}(t). \tag{2}$$

The vector $\mathbf{a}(t)$ is the quantity for which each equation is solved, $\mathbf{G}$ and $\mathbf{A}$ are t-independent operators, and $\tilde{\mathbf{F}}(t)$ is a stochastic vector whereas $\tilde{\mathbf{A}}(t)$ is a stochastic operator. Additive stochastic processes have a long history and are now well understood, but multiplicative stochastic processes have only been studied relatively recently and their solution will be the subject of this paper.

Before commencing with the formulation of the solution of multiplicative stochastic processes, it is useful, for purposes of comparison, to briefly review the applications of additive stochastic processes. Their prototype is Langevin's equation for Brownian motion.[1] Uhlenbeck and Ornstein,[2] and Wang and Uhlenbeck[3] extended Lagevin's equation to the Brownian motion of a harmonic oscillator and other more complicated systems. Onsager and Machlup[4] used this extended version of Langevin's equation as the basis of their theory of irreversible thermodynamics. de Groot and Mazur[5] began the development of a completely general theory of Markovian stochastic processes which was completed by Fox and Uhlenbeck.[6] This theory extended applicability of additive stochastic processes to hydrodynamics in precisely the manner suggested by Landau and Lifshitz,[7] and it also provided a basis for the stochastic Boltzmann equation. The non-Markovian extension of the theory was subsequently established by Hauge and Martin-Löf.[8] Recently achieved applications of additive stochastic processes include problems in binary mixtures,[9] light scattering,[10] "long time tails" for autocorrelation functions,[8] and laser theory.[11] Quite recently, a nonlinear version of additive stochastic processes has also been presented by Keizer.[12]

Multiplicative stochastic processes, in the special case of differential equations with stochastic coefficients, have been studied for several decades by many people, especially by probability theorists. The emphasis in this paper, however, will be placed on the ordered cumulant method which was pioneered by Kubo.[13] A detailed account of spin relaxation theory based upon Kubo's work has been presented by Freed,[14] and Fox[15] has studied the stochastic Schrödinger equation and its associated density matrix equation using Kubo's methods. An almost independent development, stemming from the work on stochastic differential equations with stochastic coefficients, has been published by van Kampen.[16]

In the remainder of this paper a review of the ordered cumulant method of solution of multiplicative stochastic processes will be presented. The relationship between this method and the irreducible cluster integral method of Mayer, used in the theory of the imperfect gas, will be elucidated. The cluster property for the nth order, ordered cumulant will be proved. A critique of the present literature on this subject will be given which exposes some correctable errors. Finally, the paper will conclude will a representative selection of examples.

2. ORDERED CUMULANTS

In Eq. (2) it is assumed that the various nth order moments of $\tilde{\mathbf{A}}(t)$ are computable from an appropriately specified characteristic functional. In addition, it is assumed that $\langle\tilde{\mathbf{A}}(t)\rangle = 0$, where $\langle\cdots\rangle$ denotes averaging.

Transformation to the "interaction picture" through the equation

$$\mathbf{b}(t) \equiv \exp(-t\mathbf{A})\mathbf{a}(t)$$

leads to the equation

$$\frac{d}{dt}\mathbf{b}(t) = \tilde{\mathbf{B}}(t)\mathbf{b}(t) \tag{3}$$

in which $\tilde{\mathbf{B}}(t)$ is given by

$$\tilde{\mathbf{B}}(t) \equiv \exp(-t\mathbf{A})\tilde{\mathbf{A}}(t)\exp(t\mathbf{A}).$$

It follows that $\langle\tilde{\mathbf{B}}(t)\rangle = 0$.

The solution to (3) may be written in the form

$$\mathbf{b}(t) = \underleftarrow{T}\exp\left[\int_0^t \tilde{\mathbf{B}}(s)\,ds\right]\mathbf{b}(0) \tag{4}$$

in which the symbol $\underleftarrow{T}$ denotes t-ordering and is defined by

$$\underleftarrow{T}[\int_0^t \tilde{\mathbf{B}}(s)\,ds]^n = n!\int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \times \tilde{\mathbf{B}}(s_1)\mathbf{B}(s_2)\cdots\tilde{\mathbf{B}}(s_n). \tag{5}$$

The average of (4) leads to the introduction of the ordered cumulants $\mathbf{G}^{(n)}$ through the equation

$$\langle \mathbf{b}(t)\rangle = \langle \underleftarrow{T}\exp[\int_0^t \mathbf{B}(s)\,ds]\rangle \mathbf{b}(0) = \underleftarrow{T}\exp\left(\sum_{n=1}^{\infty}\int_0^t \mathbf{G}^{(n)}(s)\,ds\right)\mathbf{b}(0). \tag{6}$$

In (6) $\mathbf{b}(0)$ is specifically statistically independent of $\tilde{\mathbf{B}}(s)$ for all $s \geq 0$. The t-ordering symbol in the second equality is defined by

$$\underleftarrow{T}\left\{\prod_{i=1}^{k}[\int_0^t \mathbf{G}^{(l_i)}(s_i)\,ds_i]\right\} = \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{k-1}} ds_k \sum_p \mathbf{G}^{(l_{p(1)})}(s_1)\mathbf{G}^{(l_{p(2)})}(s_2) \times \cdots \mathbf{G}^{(l_{p(k)})}(s_k), \tag{7}$$

in which the sum over p is a sum over all $k!$ permutations of the integers $1, 2, \ldots, k$, and l_i is some positive integer. If $l_i = m$ for $i = 1, 2, \ldots, k$, then all $k!$ integrands in (7) are identical and the sum over permutations produces an over-all factor of $k!$, which is identical with the behavior of $\underleftarrow{T}$ expressed in (5). If an intermediate state of degeneracy exists such that m_l of the l_i's equal l and $\sum_l m_l = k$, then the sum over permutations will generate factors of $\prod_l m_l!$ for each of the distinct integrands which will occur in (7). For example,

$$\underleftarrow{T}\{\int_0^t \mathbf{G}^{(6)}(s)\,ds[\int_0^t \mathbf{G}^{(2)}(s)\,ds]^2\} = 2!\{\int_0^t ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\{\mathbf{G}^{(6)}(s_1)\mathbf{G}^{(2)}(s_2)\mathbf{G}^{(2)}(s_3) + \mathbf{G}^{(2)}(s_1)\mathbf{G}^{(6)}(s_2)\mathbf{G}^{(2)}(s_3) + \mathbf{G}^{(2)}(s_1)\mathbf{G}^{(2)}(s_2)\mathbf{G}^{(6)}(s_3)\}\}. \tag{8}$$

The mth order moment operator $\mathbf{A}^{(m)}$ is defined through the equation

$$\left\langle \underleftarrow{T}\exp\left(\int_0^t \tilde{\mathbf{B}}(s)\,ds\right)\right\rangle = \sum_{m=0}^{\infty}\frac{1}{m!}\left\langle \underleftarrow{T}\left\{\left(\int_0^t \tilde{\mathbf{B}}(s)\,ds\right)^m\right\}\right\rangle = \sum_{m=0}^{\infty}\int_0^t \mathbf{A}^{(m)}(s)\,ds, \tag{9}$$

in which $\int_0^t \mathbf{A}^{(0)}(s)\,ds = \mathbf{1}$ by convention. The moments and the ordered cummulants are related by the identity

$$\int_0^t \mathbf{A}^{(m)}(s)\,ds = \sum_{\substack{\text{partitions}\\ \text{of } m}} \underleftarrow{T}\left\{\prod_{l=1}^{\infty}\frac{1}{m_l!}\left(\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^{m_l}\right\}, \tag{10}$$

in which the sum over *partitions of* m is specified by $\sum_{l=1}^{\infty} l m_l = m$, and which is proved by the sequence of identities

$$\sum_{m=0}^{\infty}\int_0^t \mathbf{A}^{(m)}(s)\,ds = \sum_{m=0}^{\infty}\sum_{\substack{\text{partitions}\\ \text{of } m}} \underleftarrow{T}\left\{\prod_{l=1}^{\infty}\frac{1}{m_l!}\left(\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^{m_l}\right\}$$
$$= \sum_{m=0}^{\infty}\sum_{\substack{\text{compositions}\\ \text{of m}}} \underleftarrow{T}\left\{\prod_{l=1}^{\infty}\frac{1}{m_l!}\left(\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^{m_l}\right\}$$
$$= \sum_{m=0}^{\infty}\frac{1}{m!}\underleftarrow{T}\left\{\left(\sum_{l=1}^{\infty}\int_0^t \mathbf{G}^{(l)}(s)\,ds\right)^m\right\}$$
$$= \underleftarrow{T}\exp\left(\sum_{n=1}^{\infty}\int_0^t \mathbf{G}^{(n)}(s)\,ds\right). \tag{11}$$

The sum over *compositions of* m in the second equality is defined by $\sum_{l=1}^{\infty} m_l = m$. The second equality is the crux of the proof, and follows from the fact that following $\sum_{l=1}^{\infty}$, a sum over partitions of m or a sum over compositions of m lead to equivalent series which differ only in the sequence of occurrence of their summands. The third equality is just the multinomial expansion which still holds in the presence of $\underleftarrow{T}$.

Using (7) in (10) gives expressions for the mth order moments in terms of ordered cumulants of order less than or equal to m. It is possible to invert these expressions and express the mth order, ordered cumulant in terms of moments of order less than or equal to m. The first three terms of each type of expression are listed below:

$$\begin{aligned}
\int_0^t \mathbf{A}^{(1)}(s)\,ds &= \int_0^t \mathbf{G}^{(1)}(s)\,ds,\\
\int_0^t \mathbf{A}^{(2)}(s)\,ds &= \int_0^t \mathbf{G}^{(2)}(s)\,ds + \tfrac{1}{2}\underleftarrow{T}\{[\int_0^t \mathbf{G}^{(1)}(s)\,ds]^2\},\\
\int_0^t \mathbf{A}^{(3)}(s)\,ds &= \int_0^t \mathbf{G}^{(3)}(s)\,ds + \underleftarrow{T}\{\int_0^t ds_1\int_0^t ds_2\mathbf{G}^{(2)}(s_1)\times\mathbf{G}^{(1)}(s_2)\} + (1/3!)\underleftarrow{T}\{[\int_0^t \mathbf{G}^{(1)}(s)\,ds]^3\}.
\end{aligned} \tag{12}$$

$$\begin{aligned}
\int_0^t \mathbf{G}^{(1)}(s)\,ds &= \int_0^t \mathbf{A}^{(1)}(s)\,ds,\\
\int_0^t \mathbf{G}^{(2)}(s)\,ds &= \int_0^t \mathbf{A}^{(2)}(s)\,ds - \tfrac{1}{2}\underleftarrow{T}\{[\int_0^t \mathbf{A}^{(1)}(s)\,ds]^2\},\\
\int_0^t \mathbf{G}^{(3)}(s)\,ds &= \int_0^t \mathbf{A}^{(3)}(s)\,ds - \underleftarrow{T}\{\int_0^t ds_1\int_0^t ds_2\mathbf{A}^{(2)}(s_1)\mathbf{A}^{(1)}(s_2)\}\\
&\quad + \underleftarrow{T}\{[\int_0^t \mathbf{A}^{(1)}(s)\,ds]\tfrac{1}{2}\underleftarrow{T}\{[\int_0^t \mathbf{A}^{(1)}(s)\,ds]^2\}\}\\
&\quad - (1/3!)\underleftarrow{T}\{[\int_0^t \mathbf{A}^{(1)}(s)\,ds]^3\}.
\end{aligned} \tag{13}$$

In order to arrive at a general expression for $\int_0^t \mathbf{G}^{(n)}(s)\,ds$, it is necessary to introduce a shorthand notation. This is most easily achieved if all expression are written out with all integrals explicit. For example,

$$\begin{aligned}
\int_0^t \mathbf{A}^{(3)}(s)\,ds &= \int_0^t ds_1\int_0^{s_1} ds_2\int_0^{s_2} ds_3\langle\tilde{\mathbf{B}}(s_1)\tilde{\mathbf{B}}(s_2)\tilde{\mathbf{B}}(s_3)\rangle,\\
\underleftarrow{T}\{\int_0^t ds_1\int_0^t ds_2\,\mathbf{A}^{(2)}(s_1)\mathbf{A}^{(1)}(s_2)\}&\\
&= \int_0^t ds_1\int_0^{s_1} ds_2\int_0^{s_2} ds_3\{\langle\tilde{\mathbf{B}}(s_1)\tilde{\mathbf{B}}(s_2)\rangle\langle\tilde{\mathbf{B}}(s_3)\rangle + \langle\tilde{\mathbf{B}}(s_1)\tilde{\mathbf{B}}(s_3)\rangle\langle\tilde{\mathbf{B}}(s_2)\rangle + \langle\tilde{\mathbf{B}}(s_1)\rangle\langle\tilde{\mathbf{B}}(s_2)\tilde{\mathbf{B}}(s_3)\rangle\},\\
\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)\tfrac{1}{2}\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)^2\}\}&\\
&= \int_0^t ds_1\int_0^{s_1} ds_2\int_0^{s_2} ds_3\{2\langle\tilde{\mathbf{B}}(s_1)\rangle\langle\tilde{\mathbf{B}}(s_2)\rangle\langle\tilde{\mathbf{B}}(s_3)\rangle + \langle\tilde{\mathbf{B}}(s_1)\rangle\langle\tilde{\mathbf{B}}(s_3)\rangle\langle\tilde{\mathbf{B}}(s_2)\rangle\}.
\end{aligned} \tag{14}$$

A natural abbreviation for the right-hand sides of these equations is

$$\begin{aligned}
&\langle 123\rangle,\\
&\langle 1\rangle\langle 23\rangle + \langle 12\rangle\langle 3\rangle + \langle 13\rangle\langle 2\rangle,\\
&2\{\langle 1\rangle\langle 2\rangle\langle 3\rangle\} + \langle 1\rangle\langle 3\rangle\langle 2\rangle,
\end{aligned} \tag{15}$$

respectively. Denoting $\int_0^t \mathbf{G}^{(n)}(s)\,ds$ by $\langle 12\cdots n\rangle_c$, where c stands for cumulant, the equations in (13) may be given in shorthand by[17]

$$\begin{aligned}
\langle 1\rangle_c &= \langle 1\rangle,\\
\langle 12\rangle_c &= \langle 12\rangle - \langle 1\rangle\langle 2\rangle,\\
\langle 123\rangle_c &= \langle 123\rangle - \langle 1\rangle\langle 23\rangle - \langle 12\rangle\langle 3\rangle - \langle 13\rangle\langle 2\rangle + \langle 1\rangle\langle 2\rangle\langle 3\rangle + \langle 1\rangle\langle 3\rangle\langle 2\rangle.
\end{aligned} \tag{16}$$

This shorthand notation permits the writing out of

$\int_0^t \mathbf{G}^{(4)}(s)\,ds$, which would otherwise be much too unwieldy:

$$\begin{aligned}\langle 1234\rangle_c = &\langle 1234\rangle - \langle 1\rangle\langle 234\rangle - \langle 123\rangle\langle 4\rangle - \langle 124\rangle\langle 3\rangle \\ &- \langle 134\rangle\langle 2\rangle - \langle 12\rangle\langle 34\rangle - \langle 13\rangle\langle 24\rangle - \langle 14\rangle\langle 23\rangle \\ &+ \langle 1\rangle\langle 2\rangle\langle 34\rangle + \langle 1\rangle\langle 3\rangle\langle 24\rangle + \langle 1\rangle\langle 4\rangle\langle 23\rangle \\ &+ \langle 1\rangle\langle 23\rangle\langle 4\rangle + \langle 1\rangle\langle 24\rangle\langle 3\rangle + \langle 1\rangle\langle 34\rangle\langle 2\rangle \\ &+ \langle 12\rangle\langle 3\rangle\langle 4\rangle + \langle 13\rangle\langle 2\rangle\langle 4\rangle + \langle 14\rangle\langle 2\rangle\langle 3\rangle \\ &+ \langle 12\rangle\langle 4\rangle\langle 3\rangle + \langle 13\rangle\langle 4\rangle\langle 2\rangle + \langle 14\rangle\langle 3\rangle\langle 2\rangle \\ &- \langle 1\rangle\langle 2\rangle\langle 3\rangle\langle 4\rangle - \langle 1\rangle\langle 2\rangle\langle 4\rangle\langle 3\rangle - \langle 1\rangle\langle 3\rangle\langle 2\rangle\langle 4\rangle \\ &- \langle 1\rangle\langle 3\rangle\langle 4\rangle\langle 2\rangle - \langle 1\rangle\langle 4\rangle\langle 2\rangle\langle 3\rangle - \langle 1\rangle\langle 4\rangle\langle 3\rangle\langle 2\rangle. \end{aligned} \tag{17}$$

The pattern that is exhibited in (16) and (17) has the general form,[16,17] known as van Kampen's rules:

$$\begin{aligned}\int_0^t \mathbf{G}^{(n)}(s)\,ds &= \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \langle 12\cdots n\rangle_c \\ &= \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \\ &\quad \times \sum_{\substack{\text{ordered}\\ \text{partitions}\\ \text{of } n}} (-1)^{k-1} \sum_p \prod_{i=1}^{k} \langle\{l_{p(i)}\}\rangle, \end{aligned} \tag{18}$$

in which the sum over *ordered partitions of n* involves partitions of the first n positive integers into m_l groups of l integers each, such that $\sum_{l=1}^{\infty} l m_l = n$ and such that in each group the l integers increase from left to right. k is defined for each particular partition by $k = \sum_{l=1}^{\infty} m_l$, which is the total number of groups in the partition. $\langle\{l_i\}\rangle$ denotes the shorthand for the integrand of a moment with l_i factors. $\langle\{l_1\}\rangle$ always contains the integer 1 in its group of integers. P is a permutation of the $k-1$ integers $2,3,\ldots,k$, so that $P(1)=1$ always holds. Equations (16) and (17) may be seen to be special cases of (18).

3. THE CLUSTER PROPERTY

In the Mayer theory of the imperfect gas,[18–23] the partition function for N gas molecules is given by

$$Q_N = N! \sum_{\substack{\text{partitions}\\ \text{of } N}} \prod_{l=1}^{N} \frac{1}{m_l!} (V b_l)^{m_l}, \tag{19}$$

in which the *partitions of N* are specified by $\sum_{l=1}^{\infty} l m_l = N$, V is the volume and b_l is determined by the linked, or irreducible, cluster integrals. The grand canonical partition function, Q, is defined by

$$Q = \sum_{N=0}^{\infty} \frac{1}{N!} Z^N Q_N.$$

Using an argument patterned after (11) gives

$$\begin{aligned} Q &= \sum_{N=0}^{\infty} \sum_{\substack{\text{partitions}\\ \text{of } N}} \prod_{l=1}^{\infty} \frac{1}{m_l!} (V b_l Z^l)^{m_l} \\ &= \sum_{N=0}^{\infty} \sum_{\substack{\text{compositions}\\ \text{of } N}} \prod_{l=1}^{\infty} \frac{1}{m_l!} (V b_l Z^l)^{m_l} \\ &= \sum_{N=0} \frac{1}{N!} \left(\sum_{l=1}^{\infty} V b_l Z^l \right)^N \\ &= \exp\left(V \sum_{l=1}^{\infty} b_l Z^l \right). \end{aligned} \tag{20}$$

The sum over *partitions of N* was specified for (19), and the sum over *compositions of N* is defined by $\sum_{l=1}^{\infty} m_l = N$. The third equality follows from the multinomial expansion. The very strong similarity between (20) and (11) suggests that the ordered cumulants possess a cluster property on analogy with the b_l's which are their counterparts. In the remainder of this section, the cluster property for $\int_0^t \mathbf{G}^{(n)}(s)\,ds$ will be proved, and the proof will use Eq. (18).

In order for the cluster property for ordered cumulants to hold, it is necessary that the moments possess the factorization property, which may be expressed by

$$\begin{aligned}&\langle \tilde{\mathbf{B}}(t_1)\tilde{\mathbf{B}}(t_2)\cdots\tilde{\mathbf{B}}(t_j)\tilde{\mathbf{B}}(t_{j+1})\cdots\tilde{\mathbf{B}}(t_n)\rangle \\ &\quad = \langle \tilde{\mathbf{B}}(t_1)\cdots\tilde{\mathbf{B}}(t_j)\rangle\langle \tilde{\mathbf{B}}(t_{j+1})\cdots\tilde{\mathbf{B}}(t_n)\rangle \end{aligned} \tag{21}$$

whenever $|t_{j+1} - t_j| \gg \tau$ and the time variables are ordered by $t_1 > t_2 > \cdots > t_n$. τ is the correlation time for $\tilde{\mathbf{B}}$, and the factorization property is strictly an identity only asymptotically. When τ is sufficiently short, however, factorization for intervals, $|t_{j+1} - t_j|$, which are not asymptotically large, may be a very good approximation.

Referring to (18), suppose that two time variables, s_j and s_k, satisfy $|s_j - s_k| \gg \tau$ and $k > j$. Because the time integrals are ordered as is specified by the limits of integration, the integrand involves time domains including $|s_j - s_{j+1}| \gg \tau$, so that if k is not $j+1$, then $|s_j - s_k| \gg \tau$ implies that $|s_j - s_{j+1}| \gg \tau$ obtains for the integrand. Therefore, consideration of the special case, $|s_j - s_{j+1}| \gg \tau$, is in fact general enough to cover all cases. For $|s_j - s_{j+1}| \gg \tau$, two cases arise in the analysis of (18): Either s_j and s_{j+1} are in the same moment, or s_j and s_{j+1} are in distinct moments. In the first case, the moment in question has the abbreviated form $\langle q\cdots j\, j+1\cdots r\rangle$ because the integers in any moment in (18) are arranged so that they increase from left to right. The factorization property implies

$$\langle q\cdots j\, j+1\cdots r\rangle = \langle q\cdots j\rangle\langle j+1\cdots r\rangle. \tag{22}$$

If $\langle q\cdots j\, j+1\cdots r\rangle$ was originally a factor in a product containing k factors, then the product contains $k+1$ factors when the right-hand side of (22) is substituted for the left-hand side. These $k+1$ factors satisfy all the conditions required for them to be a term in $\langle 12\cdots n\rangle_c$, but with the sign $(-1)^k$ rather than the sign $(-1)^{k-1}$ which attends the term containing the factor $\langle q\cdots j\, j+1\cdots r\rangle$. Therefore, these two terms cancel identically when (22) is used, and the first case is completed. In the second case, s_j is in one moment, $\langle q\cdots j\, l\cdots r\rangle$, and s_{j+1} is in another moment, $\langle g\cdots i\, j+1\cdots h\rangle$. According to the rules attending (18), $s_i > s_j > s_{j+1} > s_l$. Therefore, $|s_j - s_{j+1}| \gg \tau$ implies the two factorizations

$$\begin{aligned}&\langle q\cdots j\, l\cdots r\rangle = \langle q\cdots j\rangle\langle l\cdots r\rangle, \\ &\langle g\cdots i\, j+1\cdots h\rangle = \langle g\cdots i\rangle\langle j+1\cdots h\rangle. \end{aligned} \tag{23}$$

As in the first case, either of these factorization produces factors which are identical with factors in terms in $\langle 12\cdots n\rangle_c$. However, in this case, four terms rather than two, must be simultaneously considered. Suppose that the original term containing both $\langle q\cdots j\, l\cdots r\rangle$ and $\langle g\cdots i\, j+1\cdots h\rangle$ and k factors. It

also has the sign $(-1)^{k-1}$. $\langle 12\cdots n\rangle_c$ also contains a term with $k+1$ factors, all of which are identical with the factors in the original term except that $\langle q\cdots j\, l\cdots r\rangle$ is replaced by $\langle q\cdots j\rangle\langle l\cdots r\rangle$, and $\langle g\cdots i\, j+1\cdots h\rangle$ is unchanged. This term has the sign $(-1)^k$. Similarly, there is another term with sign $(-1)^k$ and $k+1$ factors, all of which are identical with the factors in the original term except that $\langle g\cdots i\, j+1\cdots h\rangle$ is replaced $\langle g\cdots i\rangle \times\langle j+1\cdots h\rangle$, and $\langle q\cdots j\, l\cdots r\rangle$ is unchanged. $\langle 12\cdots n\rangle_c$ also has a term with $k+2$ factors and sign $(-1)^{k+1}$ in which all the factors are identical with the factors in the original term except that both $\langle q\cdots j\, l\cdots r\rangle$ and $\langle g\cdots i\, j+1\cdots h\rangle$ are replaced by $\langle q\cdots j\rangle\langle l\cdots r\rangle$ and $\langle g\cdots i\rangle\langle j+1\cdots h\rangle$ respectively. Now, if the right-hand side of (23) is used in place of the left-hand side of (23) in the original term and in these three related other terms, then four identical terms are obtained with two of one sign and two of the opposite sign. Therefore, the four terms cancel identically, and case two is completed.

The consequence of this theorem is that $\langle 12\cdots n\rangle_c$, as defined by (18), vanishes unless all n s_i's are "clustered" together relative to the scale τ. Closer examination of the details suggests that there are terms in $\langle 12\cdots n\rangle_c$ as expressed in (18) which are comprised of sufficiently many "short overlaps" that they permit s_1 and s_n to be as far apart as roughly $\frac{1}{2}n\tau$. However, τ is usually defined to be a time long enough so that $\langle 12\rangle$ falls to only a few percent of its value when $s_1 = s_2$. If τ is the time for which $\langle 12\rangle$ is only $\frac{1}{10}$ its equal time value, then terms permitting s_1 and s_n to be apart by as much as $\frac{1}{2}n\tau$ are also porportional to a factor of order $(1/10)^{n/2}$.

The cluster property for $\langle 12\cdots n\rangle_c$ can be used to prove that, for $t\gg\tau$, $\int_0^t \mathbf{G}^{(n)}(s)\,ds$ has the simple form

$$\lim_{t\gg\tau}\int_0^t \mathbf{G}^{(n)}(s)\,ds = \int_0^t \exp(-t'\mathrm{A})\mathbf{M}^{(n)}\exp(t'\mathrm{A})\,dt' \qquad (24)$$

in which $\mathbf{M}^{(n)}$ is t'-independent. The exponential-of-A factors stem from the interaction picture which is being used throughout this paper. The proof of (24) goes as follows: Consider the t derivative of $\int_0^t \mathbf{G}^{(n)}(s)\,ds$ which is $\mathbf{G}^{(n)}(t)$, and consider the t derivative of the right-hand side of (18), which converts s_1 into t. The cluster property of $\langle 12\cdots n\rangle_c$ with $s_1\equiv t$ requires that all time variables be close to t relative to τ. The leading factor in every term in the t derivative of the right-hand side of (18) has the form $\langle\tilde{\mathbf{B}}(t)\cdots\rangle$. Using the definition of $\tilde{\mathbf{B}}(t)$ shows that $\langle\tilde{\mathbf{B}}(t)\cdots\rangle = \exp(-t\mathrm{A})\langle\tilde{\mathbf{A}}(t)\exp(t\mathrm{A})\cdots\rangle$. Additionally, every term also ends with a factor which is farthest to the right of the form $\langle\cdots\tilde{\mathbf{B}}(s_j)\rangle$, where $j=2,3\cdots n$ but $j\neq 1$. This factor may be written as $\langle\cdots\exp(-s_j\mathrm{A})\tilde{\mathbf{A}}(s_j)\rangle\exp(s_j\mathrm{A})$ and $\exp(s_j\mathrm{A})$ may be approximated by $\exp(t\mathrm{A})$ because of the cluster property if $\tau\mathrm{A}$ is sufficiently small. After removal of the leading exponential, $\exp(-t\mathrm{A})$, and the tailing exponential, $\exp(t\mathrm{A})$, the residual terms integrate to a t-independent expression when $t\gg\tau$. This expression will be called $\mathbf{M}^{(n)}$.

4. THE SOLUTION

It has now been demonstrated that the solution to (2), when averaged, is given by

$$\langle\mathbf{b}(t)\rangle = \underset{\leftarrow}{T}\exp\left(\sum_{n=1}^{\infty}\int_0^t \mathbf{G}^{(n)}(s)\,ds\right)\mathbf{b}(0)$$

and that

$$\mathbf{G}^{(n)}(t) \underset{t\gg\tau}{\rightarrow} \exp(-t\mathrm{A})\mathbf{M}^{(n)}\exp(t\mathrm{A}).$$

$\langle\mathbf{b}(t)\rangle$ is also equal to $\exp(-t\mathrm{A})\langle\mathbf{a}(t)\rangle$. Therefore, the above solution is equivalent to the solution to

$$\frac{d}{dt}\langle\mathbf{a}(t)\rangle = \mathrm{A}\langle\mathbf{a}(t) + \exp(t\mathrm{A})\sum_{n=1}^{\infty}\mathbf{G}^{(n)}(t)\exp(-t\mathrm{A})\langle\mathbf{a}(t)\rangle, \qquad (25)$$

which for $t\gg\tau$ is very well approximated by

$$\frac{d}{dt}\langle\mathbf{a}(t)\rangle = \mathrm{A}\langle\mathbf{a}(t)\rangle + \sum_{n=1}^{\infty}\mathbf{M}^{(n)}\langle\mathbf{a}(t)\rangle, \qquad (26)$$

which has a simple exponential solution. Because $\langle\tilde{\mathbf{B}}(t)\rangle = 0$, it follows that $\mathbf{M}^{(1)} = 0$, as well as $\mathbf{G}^{(1)}(t) = 0$. $\mathbf{M}^{(2)}$, which is often a good approximation to $\sum_{n=1}^{\infty}\mathbf{M}^{(n)}$ by itself, is given explicitly by

$$\mathbf{M}^{(2)} = \int_0^t\langle\tilde{\mathbf{A}}(t)\exp((t-s)\mathrm{A})\mathbf{A}(s)\rangle\exp((s-t)\mathrm{A})\,ds, \qquad (27)$$

where $t\gg\tau$.

Two special cases are worth mentioning at this point. If $\tilde{\mathbf{A}}(t)$ is determined by a Gaussian characteristic functional which is consequently an even functional, then only the even order, ordered cumulants are nonvanishing. However, unlike the fully commutative situation in which the cumulants for a Gaussian process vanish after the second cumulant, the higher order, ordered cumulants do not vanish.[15] They do, of course, satisfy the cluster property as may be observed directly by writing out (18) for the Gaussian case explicitly. The second special case is the case in which the autocorrelation function for $\tilde{\mathbf{A}}(t)$ is porportional to a delta function in the time variables. In this case, the higher order, ordered cumulants all vanish after $n=2$, because of the cluster property.

5. COMMENTARY

It may be asked why van Kampen's rules[16] for the construction of the ordered cumulants were necessary when it is the case that Kubo's basic paper[13] on the subject appeared nearly twelve years earlier. Indeed, Eq. (6.9) of Kubo's paper[13] purports to be a closed form formula for ordered cumulants. The formula is an extention to ordered operators of a formula for commuting quantities which was worked out by Meeron.[24] In the commutative case Meeron's formula is unquestionably correct. In Kubo's formula there is an index j which may be restricted to just one value for the context of this paper, and the ordering operation, Q, in his formula corresponds with $\underset{\leftarrow}{T}$ here. Rewriting Kubo's general formula for just one value of j and with $\underset{\leftarrow}{T}$ replacing Q, and with a few changes of variables, gives the formula

$$\int_0^t \mathbf{G}^{(n)}(s)\,ds = \sum_{\substack{\text{partitions}\\ \text{of } n}}(-1)^{p-1}(p-1)! \times\underset{\leftarrow}{T}\left\{\prod_{l=1}^{\infty}\frac{1}{m_l!}\left(\int_0^t \mathbf{A}^{(l)}(s)\,ds\right)^{m_l}\right\}, \qquad (28)$$

in which the sum over partitions is specified by $\sum_{l=1}^{\infty} l m_l = n$ and $p = \sum m_l$, and which more recently appeared in a paper by Fox.[25] A combinational procedure for the derivation of (28) was presented, and Fox did not then know that the formula, in a somewhat more general form, had already appeared in the literature.[13] In fact the equivalent of (28) had also been used by Freed[14] for $n = 1, 2, 3, 4$ in his Eqs. (2.14a)–(2.14d). Are Eqs. (28) and (18) equivalent? The answer is no.

The nature of the error is somewhat subtle because only a slight, but very significant, difference exists between formulas (18) and (28). It is easiest to see the difference by example. If the $n = 3$ case in equation (13) is compared with the $n = 3$ case in (28), then two expressions are obtained for $\int_0^t \mathbf{G}^{(3)}(s)\,ds$ which contain some identical terms, and some nonidentical terms. Ignoring the identical terms, from (13) one gets

$$\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)\tfrac{1}{2}\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)^2\}\} - (1/3!)\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)^3\} \tag{29}$$

whereas from (28) one gets instead

$$2\underleftarrow{T}\{(1/3!)(\int_0^t \mathbf{A}^{(1)}(s)\,ds)^3\}. \tag{30}$$

By using the shorthand notation of Sec. 2 of this paper and working out all the integrals, (29) and (30) become (31) and (32) respectively

$$\langle 1\rangle\langle 2\rangle\langle 3\rangle + \langle 1\rangle\langle 3\rangle\langle 2\rangle, \tag{31}$$

$$2\{\langle 1\rangle\langle 2\rangle\langle 3\rangle\}. \tag{32}$$

Generally, the factor $(p-1)!$ in (28) corresponds with $(p-1)!$ permuted terms in (18). van Kampen[16] even suggests using an expression like (28) as a mnemonic device for remembering (18), provided one replaces the $(p-1)!$ by $(p-1)!$ permutations of the $p-1$ moments following the moment which contains 1. In Fox's paper[25] the error arises from the incorrect identity

$$\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)\tfrac{1}{2}\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)^2\}\} = (3/3!)\underleftarrow{T}\{(\int_0^t \mathbf{A}^{(1)}(s)\,ds)^3\}, \tag{33}$$

which would render (29) and (30) equal. An identity such as (33) is discussed by Fox,[25] and is in fact valid in the appropriate context, but that context requires a very different meaning for $\mathbf{A}^{(1)}$ than its meaning here. While the discrepancy is exhibited here for $n = 3$, it does not show up until $n = 6$ if $\langle \tilde{\mathbf{A}}(t)\rangle = 0$. Since both Freed[14] and Fox[25] assumed $\langle \tilde{\mathbf{A}}(t)\rangle = 0$ in their subsequent calculations, and both only looked explicitly at $n = 2$ and $n = 4$ results, they got the correct results.

The cluster property of the ordered cumulants, which is of such fundamental importance as far as the utility of the ordered cumulant method is concerned, also has a somewhat confused literature. van Kampen[16] barely mentions it. Freed[14] makes very interesting use of it, but bases its validity upon general results in the Kubo[13] paper. In the Kubo paper, the important equation in this regard is (6.7). It is not difficult to show that for $\underleftarrow{T}$ ordering, counter examples to Eq. (6.7) can be constructed, and that even though the cluster property is nevertheless true, Kubo's argument does not justify it. The argument in the present paper is offered to remedy this situation. In a very clear and concise paper, Terweil[26] demonstrates the connection between the ordered cumulant method and the Zwanzig projection operator technique. In that paper, he proves a cluster property for the "partial kernels" which arise in the projection operator approach. His proof should be compared with the proof here. His proof does not, however, establish directly the cluster property for the ordered cumulants.

Yoon, Deutch, and Freed[27] have also compared the ordered cumulant method with the projection operator method, and their considerations are deducible from Terweil's paper, although their context is very different, and very interesting.

6. EXAMPLES

In addition to the examples discussed by Kubo,[13] van Kampen,[16] and Freed,[14] a few other representative examples will be sketched here. The examples will be treated to the extent that they are made to have the form of (2).

Example 1: The stochastic, standing wave equation[28]:

$$\frac{d^2}{dx^2} v(x) + k^2[1 + \tilde{\phi}(x)]v(x) = 0.$$

Replace $v(x)$ by

$$v(x) = A(x)\exp(ikx) + B(x)\exp(-ikx),$$

in which $A(x)$ and $B(x)$ are subject to the auxillary condition

$$\frac{dA}{dx}\exp(ikx) + \frac{dB}{dx}\exp(-ikx) = 0.$$

It then follows that

$$\frac{d}{dx}\begin{pmatrix} A(x) \\ B(x)\end{pmatrix} = i\frac{k}{2}\tilde{\phi}(x)\begin{pmatrix} 1 & \exp(-2ikx) \\ -\exp(2ikx) & -1\end{pmatrix}\begin{pmatrix} A(x) \\ B(x)\end{pmatrix}.$$

This is the form of (2) if x is changed to t, $A = 0$, and $a(t)$ and $\tilde{A}(t)$ are complex valued.

Example 2: The stochastic Schrödinger equation[29]:

$$i\hbar\frac{\partial}{\partial t}\psi = (\mathbf{H}^\circ + \tilde{\mathbf{H}}(t))\psi$$

Expand ψ in terms of the eigenstates of $\mathbf{H}^\circ$, $\mathbf{H}^\circ\,|\,\alpha\rangle = E_\alpha\,|\,\alpha\rangle$:

$$\psi(t) = \sum_\alpha C_\alpha(t)\,|\,\alpha\rangle.$$

The Schrödinger equation becomes

$$i\hbar\frac{d}{dt}C_\alpha(t) = E_\alpha C_\alpha(t) + \tilde{H}_{\alpha\alpha'}(t)C_{\alpha'}(t),$$

in which $\tilde{H}_{\alpha\alpha'}(t) = \langle\alpha\,|\,\tilde{\mathbf{H}}(t)\,|\,\alpha'\rangle$. This is also a complex realization of (2) with a diagonal $\mathbf{A}$.

Example 3: The stochastic density matrix equation[29]:

By using the previous example and defining the density matrix by

$$\rho_{\alpha\beta}(t) = C_\beta^*(t)C_\alpha(t)$$

the density matrix equation is

$$i\hbar\frac{d}{dt}\rho_{\alpha\beta} = (E_\alpha - E_\beta)\rho_{\alpha\beta} + \tilde{L}_{\alpha\beta\alpha'\beta'}(t)\rho_{\alpha'\beta'},$$

where $\tilde{L}_{\alpha\beta\alpha'\beta'}(t) \equiv \delta_{\beta\beta'}\tilde{H}_{\alpha\alpha'}(t) - \delta_{\alpha\alpha'}\tilde{H}_{\beta'\beta}(t)$. This can also be written equivalently

$$i\hbar\frac{\partial}{\partial t}\rho = [\mathbf{H}^{\circ}, \rho] + [\tilde{\mathbf{H}}(t), \rho].$$

Example 4: Equation of motion for a magnetic moment in a stochastic magnetic field:

$$\frac{d}{dt}\mathbf{m} = -\frac{e}{2mc}[\mathbf{B} + \tilde{\mathbf{B}}(t)] \times \mathbf{m}.$$

Example 5: Reduced density matrix equation:

$$i\hbar\frac{\partial}{\partial t}\rho = [\mathbf{H}^{s} + \mathbf{H}^{R} + \mathbf{H}^{I}, \rho],$$

where $\mathbf{H}^{s}$ is a system Hamiltonian, $\mathbf{H}^{R}$ is a reservoir Hamiltonian, and $\mathbf{H}^{I}$ is the interaction Hamiltonian. No explicit stochasticity appears. However, reduction of the full density matrix by tracing over the reservoir states can be treated as averaging, and associated ordered cumulants can then be defined in a natural way. Another paper doing this in detail will be forthcoming.

Generally, the effect of $\mathbf{M}^{(2)}$, which appears in (26), is to create dissipative behavior for the averaged equations in these examples. Each example is in fact time reversal invariant before averaging is performed, so that averaging is the sole source of dissipation.

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Fluctuating hydrodynamics explanation of the Alder–Wainwright velocity autocorrelation computer experiments

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Shortly after Alder and Wainwright[1] published a summary of their work on computer simulated dynamics, in which long time tails were observed for the velocity autocorrelation function, a variety of theoretical papers appeared which claimed to explain the phenomenon. Dorfman and Cohen[2] presented a kinetic theory justification of the results of Alder and Wainwright. Zwanzig and Bixon[3] presented a hydrodynamical theory which also explained the long time tail behavior of the autocorrelation function. A semikinetic, semihydrodynamical theory was also presented by Ernst, Hauge, and van Leeuwen,[4] which also explained the long time tails. Another semihydrodynamical approach, the mode coupling theory, was used to explain these same results by Kawasaki[5] and also by Pomeau.[6]

A closely related problem is the problem of the velocity autocorrelation function for a Brownian particle immersed in a fluctuating fluid. The Landau–Liftshitz theory[7] of fluctuating hydrodynamics, as formulated by Fox and Uhlenbeck,[8] has been applied successfully to this problem by Chow and Hermans,[9] and by Hauge and Martin-Löf.[10] Both groups showed long time tail behavior of the type observed by Alder and Wainwright.

It is the purpose of this note to make an observation which appears to have been overlooked so far. The fluctuating hydrodynamic theory directly yields the Alder and Wainwright result through the autocorrelation function of the fluid velocity field, without the introduction of a Brownian particle. The advantage of this approach is its simplicity, because the computation of the free fluid velocity field autocorrelation is rather easy compared with the calculation of the corresponding velocity autocorrelation function for the Brownian particle.

The velocity field satisfies the following linearized, Navier–Stokes equation[7,8]:

$$\rho_0 \frac{\partial v_i}{\partial t} = -\frac{\partial \rho}{\partial x_i} + \eta \nabla^2 v_i + \frac{\partial}{\partial x_j} \tilde{S}_{ij}, \tag{1}$$

in which $\tilde{S}_{ij}$ is the fluctuating stress tensor which has the correlation formula

$$\langle \tilde{S}_{ik}(\mathbf{x}, t) \tilde{S}_{jl}(\mathbf{x}', t') \rangle = 2K_B T \eta (\delta_{ij}\delta_{kl} + \delta_{il}\delta_{kj}) \delta(t - t') \times \delta(\mathbf{x} - \mathbf{x}'), \tag{2}$$

in which K_B is Boltzmann's constant, T is the temperature, and η is the shear viscosity. In the above, restriction to the incompressible case is implicit, although not necessary. Szu, Szu, and Hermans[11] have treated the autocorrelation functions for fluctuating hydrodynamics in some detail; so we quote their result for the velocity autocorrelation function of the free fluid, although the derivation, using Fourier transformations, from (1) and (2) is quick and easy. The result is according to Eq. (24) of Szu *et al.*,

$$\langle v_i(\mathbf{x}, t) v_j(\mathbf{x}, t') \rangle = \tfrac{2}{3} K_B T (1/\rho_0) (4\pi\nu |t - t'|)^{-3/2} \tag{3}$$

in which $\nu = \eta/\rho_0$. This is precisely the formula which provides an explanation of the Alder–Wainwright observations, according to the earlier theories.[2–6]

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Fluctuation Theories and Non-Stationary Markov Processes

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Abstract

The theory of fluctuations for systems near equilibrium has given rise to two developments which concern generalizing the theory in two distinct ways. One of these developments is focused on the theory of fluctuations far from equilibrium where the dynamics may be non-linear. The other development has dealt with extending the class of fluctuating forces to include forces with non-delta function autocorrelations. It is shown here that both of these developments lead to the same class of Fokker-Planck equations and that class corresponds with the theory of non-stationary, Markov processes.

I. Introduction

Over an extended period of time, Langevin's[1] theory of Brownian motion has developed into a remarkably general theory for non-equilibrium processes. The early work of Uhlenbeck and Ornstein,[2] which applied Langevin's theory to the harmonic oscillator, provided the basis upon which Onsager and Machlup[3] were able to establish a stochastic foundation for irreversible thermodynamics. Subsequently, Landau and Lifshitz suggested how to extend this theory even further when they presented equations for hydrodynamic[4] fluctuations and for electro magnetic[5] fluctuations. These suggestions gave rise to a general formulation which Fox and Uhlenbeck[6] showed was equivalent to the theory of Stationary, Markov processes.

General though this theory is, it is certainly not universal, and is limited in two distinct, physical ways. First of all, the applications mentioned above, as well as all others, are confined to systems which are dynamically close to full equilibrium. This implies that the equations are linear equations. Secondly, on the time scale determined by the relaxation time for the system, the correlation time for the fluctuating forces is negligibly short, as is manifested mathematically by a fluctuating force autocorrelation formula involving a delta function of the time variables. The general situation is exhibited by the equations[6]

$$\frac{d}{dt}\,\underset{\sim}{a}(t) = \underset{\sim}{A}\,\underset{\sim}{a}(t) + \underset{\sim}{S}\,\underset{\sim}{a}(t) + \tilde{\underset{\sim}{F}}(t) \tag{1}$$

$$\langle \tilde{\underset{\sim}{F}}(t) \rangle = 0 \text{ and } \quad \langle \tilde{\underset{\sim}{F}}(t)\, \tilde{\underset{\sim}{F}}^{\dagger}(s) \rangle = 2\,\underset{\sim}{Q}\,\delta(t-s) \tag{2}$$

in which $\underset{\sim}{a}(t)$ is a vector valued, N-component process, $\underset{\sim}{A}$ is an N x N anti-symmetric matrix, $\underset{\sim}{S}$ is an N x N symmetric matrix, $\tilde{\underset{\sim}{F}}(t)$ is a vector valued fluctuating force, and $\langle \cdots \rangle$ denotes stochastic averaging. $\underset{\sim}{Q}$ is an N x N

symmetric correlation matrix. Near equilibrium, the entropy of the system is given by the quadratic form

$$S(t) = S_o - \frac{1}{2} \underset{\sim}{a}^{\dagger}(t) \underset{\sim}{E} \underset{\sim}{a}(t) \tag{3}$$

in which $\underset{\sim}{E}$ is the N x N, symmetric, entropy matrix. A fluctuation dissipation relation exists and takes the form

$$-2\underset{\sim}{Q} = (\underset{\sim}{A}+\underset{\sim}{S})\underset{\sim}{E}^{-1} + \underset{\sim}{E}^{-1}(\underset{\sim}{A}^{\dagger}+\underset{\sim}{S}^{\dagger}) \tag{4}$$

in which † denotes the matrix adjoint.

The limitations of the theory have prompted two developments which are aimed at extending the domain of applicability. The first development, which began slightly earlier, concerns establishment of a theory of fluctuations for systems far from equilibrium in which case the dynamics are generally non-linear. van Kampen[7] initiated this development using a master equation basis which has more recently been clarified by Kubo[8] et.al.. In addition, an equivalent, Langevin-like, fluctuating force theory has been proposed by Keizer,[9] Nitzan[10] et.al., and Portnow and Kitahara.[11] The second development concerns the linear, near equilibrium theory in the case for which the fluctuating force autocorrelation formula involves an extended time dependence which is not properly represented by a sharp delta function. Zwanzig's[12] projection operator method is the key to this development, although it was Mori[13] who achieved a general formulation. These two developments proceeded quite independently, motivated by distinct physical causes, so it is rather surprising that when they are viewed as formal mathematical structures, that they are found to correspond to the same structure. Namely, both correspond to slightly different forms from the theory of non-stationary, Markov processes.

It is the purpose of this paper to exhibit this developmental convergence of mathematical structures. In doing so, the opportunity arises, on the one hand, to show that the master equation approach and the fluctuating force approach to non-linear processes are connected in a direct way, previously not exhibited in the literature; and, on the other hand, to clarify serious, long established confusion in the literature regarding putatively non-Markovian processes which turn out to be really non-stationary, Markov processes.

II. Stochastic Probability Flows

An exceedingly useful lemma exists which provides the basis for the unification of the two developments described above. It was used earliest by Kubo,[14] and its utility in constructing Fokker-Planck equations has been stressed by Fox,[15,16] but it was van Kampen[17,18] who first explicity provided a proof of its validity.

It will subsequently be shown that both developments lead to equations with the form

$$\frac{d}{dt}\,\underset{\sim}{a}(t) = \underset{\sim}{\bar{M}}(t)\;\underset{\sim}{a}(t) + \underset{\sim}{\tilde{g}}(t) \tag{5}$$

in which $\underset{\sim}{a}(t)$ is a vector valued, N-component process, $\underset{\sim}{\bar{M}}(t)$ is an NxN, time dependent matrix, and $\underset{\sim}{\tilde{g}}(t)$ is a vector valued fluctuating force satisfying

$$\langle\underset{\sim}{\tilde{g}}(t)\rangle = 0 \text{ and } \langle\underset{\sim}{g}(t)\;\underset{\sim}{\tilde{g}}^{\dagger}(s)\rangle = \underset{\sim}{\Gamma}(t-s) \tag{6}$$

in which $\underset{\sim}{\Gamma}(t-s)$ is an NxN time dependent matrix of correlations. The similarities and difference between (1) and (2), and (5) and (6) should be evident.

The lemma stated below provides a procedure for the construction of the Fokker-Planck equation which corresponds with (5) and (6), and it does so by considering a stochastic probability flow in a "phase space" determined by the N-component vector process, a(t).

Lemma: Given the sharp initial condition at $t = o$, $\underset{\sim}{a}(o) = \underset{\sim}{a}_o$, the associated conditional probability distribution, $P(\underset{\sim}{a},t)$, conditioned by the initial condition, $P(\underset{\sim}{a},o) = \delta(\underset{\sim}{a} - \underset{\sim}{a}_o)$, is equal to the stochastic average of the "phase space" distribution, $\rho(\underset{\sim}{a},t)$, which satisfies the continuity equation

$$\frac{\partial}{\partial t}\rho(\underset{\sim}{a},t) = -\frac{\partial}{\partial \underset{\sim}{a}}\cdot(\dot{\underset{\sim}{a}}\,\rho(\underset{\sim}{a},t)) \tag{7}$$

in which $\dot{\underset{\sim}{a}}$ denotes the time derivative of $\underset{\sim}{a}(t)$ as given by (5), and $\frac{\partial}{\partial \underset{\sim}{a}}\cdot$ denotes the N-dimensional gradient operator. The stochastic probability flow resulting from insertion of (5) into (7), the average of which yields the desired Fokker-Planck equation, is

$$\frac{\partial}{\partial t}\rho(\underset{\sim}{a},t) = -\frac{\partial}{\partial \underset{\sim}{a}}\cdot(\overline{\underset{\sim}{M}}(t)\underset{\sim}{a}\rho(\underset{\sim}{a},t)) - \frac{\partial}{\partial \underset{\sim}{a}}\cdot(\tilde{\underset{\sim}{g}}(t)\,\rho(\underset{\sim}{a},t)) \tag{8}$$

The proof of this lemma is to be found in reference 17 where the stochastic setting has a more rigorous, modern mathematical flavor.

It is proved in appendix A that the average of (8) can be worked out exactly when $\tilde{\underset{\sim}{g}}(t)$ is Gaussian as it usually is in both developments. The result is the non-stationary Fokker-Planck equation

$$\begin{aligned}\frac{\partial}{\partial t}\langle\rho(\underset{\sim}{a},t)\rangle &= -\frac{\partial}{\partial \underset{\sim}{a}}\cdot(\overline{\underset{\sim}{M}}(t)\underset{\sim}{a}\langle\rho(\underset{\sim}{a},t)\rangle) \\ &+ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\int_o^t ds\;\underset{\sim}{\Gamma}(t-s)\;\underset{\rightarrow}{T}\exp\left[\int_s^t \overline{\underset{\sim}{M}}(t')^{\dagger}dt'\right]\cdot\frac{\partial}{\partial \underset{\sim}{a}}\langle\rho(\underset{\sim}{a},t)\rangle\end{aligned} \tag{9}$$

Notice especially that the second term on the right-hand side of (9) involves a time integration over s which appears only in the matrix coefficients and not in $\langle\rho(\underset{\sim}{a},t)\rangle$ to its right. It is for this reason that (9) is a non-stationary Fokker-Planck equation and does not involve a memory kernel which would convert it into an integro-differential equation. The derivation of (9) given in the appendix exhibits several useful operator calculus identities and explains the origin of the reverse time ordered exponential, denoted by

$\underset{\rightarrow}{T}$ exp[...], found in (9).

It should also be noted that equations of the type given by (9) are identical with Kolmogorov's forward equation for non-stationary Markov processes.[19]

The solution to (9) is not difficult and yields an explicit formula for $P(\underset{\sim}{a},t) \equiv \langle \rho(\underset{\sim}{a},t) \rangle$. Define $\underset{\sim}{\gamma}(t)$ by

$$\underset{\sim}{\gamma}(t) = \int_0^t ds\ \underset{\sim}{\Gamma}(t-s)\ \underset{\rightarrow}{T} \exp\left[\int_s^t \overline{\underset{\sim}{M}}^{\dagger}(t')dt'\right] \tag{10}$$

and $\underset{\sim}{\Sigma}(t)$, the covariance matrix, by

$$\underset{\sim}{\Sigma}(t) = \langle \underset{\sim}{a}(t)\ \underset{\sim}{a}^{\dagger}(t) \rangle \tag{11}$$

Together, (10), (11), and (12) yield

$$\frac{d}{dt}\underset{\sim}{\Sigma}(t) = \overline{\underset{\sim}{M}}(t)\ \underset{\sim}{\Sigma}(t) + \underset{\sim}{\Sigma}(t)\ \overline{\underset{\sim}{M}}^{\dagger}(t) + \underset{\sim}{\gamma}(t) + \underset{\sim}{\gamma}^{\dagger}(t) \tag{12}$$

the solution to which is

$$\underset{\sim}{\Sigma}(t) = \int_0^t ds\ \underset{\leftarrow}{T} \exp\left[\int_s^t \overline{\underset{\sim}{M}}(t')dt'\right] (\underset{\sim}{\gamma}(s) + \underset{\sim}{\gamma}^{\dagger}(s))\ \underset{\rightarrow}{T} \exp\left[\int_s^t \overline{\underset{\sim}{M}}^{\dagger}(t')dt'\right] \tag{13}$$

The solution to (9) can now be written

$$P(\underset{\sim}{a},t) = \left((2\pi)^N \det(\underset{\sim}{\Sigma}(t))\right)^{-\frac{1}{2}} \exp\left[-\frac{1}{2}(\underset{\sim}{a} - \overline{\underset{\sim}{M}}(t)\underset{\sim}{a}_o)^{\dagger}\underset{\sim}{\Sigma}^{-1}(t)(\underset{\sim}{a} - \overline{\underset{\sim}{M}}(t)\underset{\sim}{a}_o)\right] \tag{14}$$

in which $\det(\underset{\sim}{\Sigma}(t))$ denotes the determinant of the covariance matrix. $P(\underset{\sim}{a},t)$ will satisfy the non-stationary, Chapman-Kolmogorov equation[19] for non-stationary, Markov processes.

III. Fluctuations Far From Equilibrium

The description of fluctuations far from equilibrium is based upon taking the "thermodynamic limit" of a master equation description of the underlying process. In both van Kampen's[7] pioneering work and Kubo's[8] more recent extention, this limit is referred to as the limit of a large "system-size"

parameter. Regardless of how one expresses it, the result is that in the limit of a very large system, the master equation description goes over into a Fokker-Planck equation description. For the special case of a system of chemical reactions obeying the McQuarrie[20] master equation, Kurtz[21] has proved, with all the rigor one would like, that the limit of a very large volume yields a Fokker-Planck equation. In the general case, the situation is not so well established, and Fox and Kac[22] have recently explored another special case in which delicate questions regarding initial distributions and scaling have been broached, although not with the same degree of rigor as in Kurtz' work. Nevertheless, the resulting Fokker-Planck equations, whether rigorously justified or not, has the form

$$\frac{\partial}{\partial t} P(\underset{\sim}{n},t) = - \frac{\partial}{\partial \underset{\sim}{n}} \cdot (\underset{\sim}{H}(t) \; \underset{\sim}{n} \; P(\underset{\sim}{n},t)) + \frac{\partial}{\partial \underset{\sim}{n}} \cdot \underset{\sim}{\gamma}(t) \cdot \frac{\partial}{\partial \underset{\sim}{n}} P(\underset{\sim}{n},t) \tag{15}$$

in which $\underset{\sim}{n}$ is an N-component vector valued process, $\underset{\sim}{H}(t)$ is an NxN matrix, and $\underset{\sim}{\gamma}(t)$ is an NxN matrix, not to be confused, yet, with the $\underset{\sim}{\gamma}(t)$ in (10).

This Fokker-Planck equation describes the time evolution of the distribution function for the deviations around the deterministic solution, $\bar{\underset{\sim}{n}}(t)$, which is also deduced from the large "system-size" limit of the underlying master equation. In general, $\bar{\underset{\sim}{n}}(t)$ satisfies a non-linear rate equation of the form

$$\frac{d}{dt} \bar{\underset{\sim}{n}}(t) = \underset{\sim}{K}[\bar{\underset{\sim}{n}}(t)] \tag{16}$$

in which $\underset{\sim}{K}$ is a vector valued functional of $\bar{\underset{\sim}{n}}(t)$. The matrix $\underset{\sim}{H}(t)$ which appears in (15) is the first derivative of $\underset{\sim}{K}$ with respect to $\bar{\underset{\sim}{n}}(t)$ at time t. Since this differentiation is carried out component by component, on a vector by a vector, $\underset{\sim}{H}(t)$ is a <u>matrix</u> functional of $\bar{\underset{\sim}{n}}(t)$. The derivation of (15) from the underlying master equation also shows that $\underset{\sim}{\gamma}(t)$ is a functional of $\bar{\underset{\sim}{n}}(t)$. Thus both $\underset{\sim}{H}(t)$ and $\underset{\sim}{\gamma}(t)$ acquire their time dependence from that of $\bar{\underset{\sim}{n}}(t)$, the deterministic solution to (16).

Although van Kampen[23] has repeatedly expressed the view that there does not exist an equivalent fluctuating force formulation of this theory, Nitzan[10] et.al., and Portnow and Kitahara[11] have both shown that a Langevin-like formulation for fluctuations near steady states which are far from equilibrium is possible, and Keizer[9] has presented a phenomenologically grounded theory of Langevin-like structure for the entire non-equilibrium domain. Each of these cases utilizes an equation of the type given by (5) above with the added specialization that in place of (6) one has

$$\langle \underset{\sim}{\tilde{g}}(t)\ \underset{\sim}{\tilde{g}}^{\dagger}(s)\rangle = 2\underset{\sim}{\gamma}(t)\ \delta(t-s) \tag{17}$$

in which $\underset{\sim}{\gamma}(t)$ is the $\underset{\sim}{\gamma}(t)$ in (15). Consequently, in (9), which ironically enough was achieved using the lemma van Kampen proved, $\underset{\sim}{\Gamma}(t-s)$ must be replaced by $2\underset{\sim}{\gamma}(t)\ \delta(t-s)$ which greatly simplifies the integration. Indeed, (10) now yields $\underset{\sim}{\gamma}(t) = \underset{\sim}{\gamma}(t)$. Therefore, after completing the derivation of the Fokker-Planck equation from the master equation using the thermodynamic limit, it is always possible to insert the $\underset{\sim}{\gamma}(t)$ acquired in the derivation into the right-hand side of (17) which coupled with (5) provides an equivalent fluctuating force formulation of the problem, and which yields the same Fokker-Planck equation through (9), simplified by (17) in place of (6).

At arbitrary times, there is no direct connection between the covariance of fluctuations, $\underset{\sim}{\gamma}(t)$, and the dissipation matrix, $\underset{\sim}{H}(t)$, as there is near equilibrium as is exhibited by the fluctuation dissipation relation (4). Each is determined directly from the underlying master equation. However, equation (12) shows that at equilibrium or at a steady state, where $\frac{d}{dt}\underset{\sim}{\Sigma}(t) = 0$,

$$-2\underset{\sim}{\gamma} = \underset{\sim}{H}\underset{\sim}{\Sigma} + \underset{\sim}{\Sigma}\underset{\sim}{H}^{\dagger} \tag{18}$$

in which $\underset{\sim}{H}$ has replaced $\underset{\sim}{\bar{M}}$ and $2\underset{\sim}{\gamma}$ has replaced $\underset{\sim}{\gamma} + \underset{\sim}{\gamma}^{\dagger}$ because (17) implies $\underset{\sim}{\gamma} = \underset{\sim}{\gamma}^{\dagger}$. This is very close to (4), which becomes even more apparent when the argument of the exponential in (14) is compared with (3). In (18), the

value of $\underset{\sim}{\Sigma}$ depends upon whether the system is at equilibrium or at one of possibly several steady states. Similarly, the values of $\underset{\sim}{\gamma}$ and $\underset{\sim}{H}$, through their dependence on the deterministic solution, $\underset{\sim}{\bar{n}}$, depend upon where the system is when $\frac{d}{dt}\,\underset{\sim}{\Sigma}(t) = 0$. Thus, the fluctuation-dissipation relation is extended to steady states, and a Fokker-Planck description appears to be valid for all non-equilibrium states.

IV. Generalized Langevin Equations

An apparently different situation arises when the near equilibrium, linear theory is modified by replacing the delta function autocorrelation formula for the fluctuating force, (2), with a non-delta function autocorrelation such as in

$$\frac{d}{dt}\,\underset{\sim}{a}(t) = i\underset{\sim}{\Omega}\,\underset{\sim}{a}(t) - \int_o^t \underset{\sim}{\phi}(t-s)\,\underset{\sim}{a}(s)ds + \underset{\sim}{\tilde{f}}(t) \tag{19}$$

where

$$<\underset{\sim}{\tilde{f}}(t)> = 0 \text{ and } <\underset{\sim}{\tilde{f}}(t)\,\underset{\sim}{\tilde{f}}^{\dagger}(s)> = \underset{\sim}{\phi}(t-s)\cdot<\underset{\sim}{a}_o,\underset{\sim}{a}_o^{\dagger}> \tag{20}$$

Averaging is accomplished here by integrating with a canonically weighted phase space distribution, and $\underset{\sim}{a}(t)$ is an N-component vector valued process comprised of phase space coordinates and momenta. $<\underset{\sim}{a}_o,\underset{\sim}{a}_o^{\dagger}>$ is, consequently, a matrix and the subscript o denotes the initial values of the components of $\underset{\sim}{a}(t)$. When $\underset{\sim}{a}$ is the three dimensional momentum of a particle, then $<\underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}>$ yields mKT times the 3x3 identity matrix, for example. $i\underset{\sim}{\Omega}$ is a frequency matrix and $\underset{\sim}{\phi}(t-s)$ is the dissipative "memory kernel" which is generated by the fluctuation-dissipation relation (20). Such a description was originally characterized in a general way by Mori[13] using Zwanzig's[12]

projection operation method. The presence of the "memory kernel" and the non-delta correlated fluctuating forces has lead to the belief that a non-Markovian process is being described.

Only recently, Tokuyama and Mori,[24] and independently Fox,[16,25] have shown that equation (19) can always be transformed into the single time form

$$\frac{d}{dt}\,\underset{\sim}{a}(t) = i\underset{\sim}{\Omega}\;\underset{\sim}{a}(t) - \underset{\sim}{\Psi}(t)\;\underset{\sim}{a}(t) + \tilde{\underset{\sim}{g}}(t) \tag{21}$$

in which

$$\underset{\sim}{\Psi}(t) \equiv \int_0^t \langle \tilde{\underset{\sim}{g}}(s)\;\tilde{\underset{\sim}{g}}(o)\rangle \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger}\rangle^{-1}\;\underset{\sim}{M}^{-1}(s)ds \tag{22}$$

$$\tilde{\underset{\sim}{g}}(t) \equiv \underset{\sim}{M}(t)\,\frac{d}{dt}\int_0^t \underset{\sim}{M}^{-1}(t)\;\underset{\sim}{M}(t-s)\;\tilde{\underset{\sim}{f}}(s)ds \tag{23}$$

and $\underset{\sim}{M}(t)$ is defined through its Laplace transform and the Laplace transform of $\underset{\sim}{\phi}(t)$ by

$$\hat{\underset{\sim}{M}}(z) = [z\underset{\sim}{1} - i\underset{\sim}{\Omega} + \hat{\underset{\sim}{\phi}}(z)]^{-1} \tag{24}$$

Using this single time representation, Fox[16] has also shown that the lemma concerning stochastic probability flows described in part II of this paper permits the construction of the Fokker-Planck equation corresponding with (21), or its equivalent (18). The result, which is proved in appendix B, using (9), is

$$\frac{\partial}{\partial t}\,P(\underset{\sim}{a},t) = -\frac{\partial}{\partial \underset{\sim}{a}}\cdot(\dot{\underset{\sim}{M}}(t)\;\underset{\sim}{M}^{-1}(t)\;\underset{\sim}{a}\;P(\underset{\sim}{a},t))$$

$$-\frac{\partial}{\partial \underset{\sim}{a}}\cdot\dot{\underset{\sim}{M}}(t)\;\underset{\sim}{M}^{-1}(t)\langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger}\rangle\cdot\frac{\partial}{\partial \underset{\sim}{a}}\,P(\underset{\sim}{a},t) \tag{25}$$

The combination $\dot{\underset{\sim}{M}}(t)\;\underset{\sim}{M}^{-1}(t)$ is identical with $i\underset{\sim}{\Omega} - \underset{\sim}{\Psi}(t)$ as has been proved by Fox.[25] Therefore, the fluctuation-dissipation relation is again exhibited in the proportionality of the matrix coefficients for the streaming and diffusive

portions of the right-hand side of (25). If the identifications, $\dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t) \to \bar{\underset{\sim}{M}}(t)$ and $\dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t)\ \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger \rangle \to -\underset{\sim}{\gamma}(t)$ are made then

$$-(\underset{\sim}{\gamma}(t) + \underset{\sim}{\gamma}^\dagger(t)) = \bar{\underset{\sim}{M}}(t)\langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger \rangle + \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger \rangle \bar{\underset{\sim}{M}}^\dagger(t) \tag{26}$$

parallels both (4) and (18) with $\langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger \rangle$ serving the role of $\underset{\sim}{E}^{-1}$ or $\underset{\sim}{\Sigma}$ respectively.

By now, it should not be necessary to emphasize that (25) describes a <u>non-stationary, Markov process</u>, rather than a <u>non-Markovian process</u>. This is very largely a result of <u>linearity</u> of (19) which permits the transformations leading to (21).

Appendix A

Derivation of (9) from (6) and (8):

Define $R(\underset{\sim}{a},t)$ by

$$\rho(\underset{\sim}{a},t) = \underset{\leftarrow}{T} \exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a}\, ds\right] R(\underset{\sim}{a},t) \tag{A1}$$

in which $\underset{\leftarrow}{T}\exp[\ldots]$ denotes the time ordered exponential with later times to the left. $R(\underset{\sim}{a},t)$ must satisfy

$$\frac{\partial}{\partial t} R(\underset{\sim}{a},t) = -\underset{\leftarrow}{T} \exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\ \underset{\sim}{a}\, ds\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t)\ \underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a}\, ds\right] R(\underset{\sim}{a},t) \tag{A2}$$

which follows from (8) and in which $\underset{\rightarrow}{T}\exp[\ldots]$ denotes the reverse time ordered exponential with later times to the right. The reverse time ordered exponential appears because, in general, the inverse of the operator $\underset{\leftarrow}{T}\exp\left[\int_0^t \underset{\sim}{B}(s)ds\right]$ is $\underset{\rightarrow}{T}\exp\left[-\int_0^t \underset{\sim}{B}(s)ds\right]$. (A2) can be rewritten

$$\frac{\partial}{\partial t} R(\underset{\sim}{a},t) = -\underset{\rightarrow}{T}\exp\left[\int_0^t \left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\bullet\right] ds\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t)\ R(\underset{\sim}{a},t) \tag{A3}$$

in which there appears the reverse time ordered exponential of the commutator operator $\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\bullet\right]$ which acts as indicated below

$$\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\bullet\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t) = \left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t)\right] \tag{A4}$$

$$\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\bullet\right]\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s')\underset{\sim}{a},\bullet\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t) = \left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s')\underset{\sim}{a},\ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t)\right]\right] \tag{A5}$$

Higher order iterations of the commutator which appear in the ordered exponential in (A3) are interpreted in the natural way suggested by (A4) and (A5).

Now, (A4) and (A5) lead to

$$\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t)\right] = -\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\ \tilde{\underset{\sim}{g}}(t) \tag{A6}$$

and

$$\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s')\underset{\sim}{a},\frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t)\right]\right] = (-1)^2\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\ \bar{\underset{\sim}{M}}(s')\ \tilde{\underset{\sim}{g}}(t) \tag{A7}$$

Therefore, we arrive at the identity

$$\underset{\rightarrow}{T}\exp\left[\int_0^t\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\bar{\underset{\sim}{M}}(s)\underset{\sim}{a},\bullet\right]ds\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\tilde{\underset{\sim}{g}}(t) = \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\rightarrow}{T}\exp\left[-\int_0^t\bar{\underset{\sim}{M}}(s)ds\right]\tilde{\underset{\sim}{g}}(t) \tag{A8}$$

Consequently, (A3) becomes

$$\frac{\partial}{\partial t}R(\underset{\sim}{a},t) = -\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\rightarrow}{T}\exp\left[-\int_0^t\bar{\underset{\sim}{M}}(s)ds\right]\dot{\tilde{\underset{\sim}{g}}}(t)\ R(\underset{\sim}{a},t) \tag{A9}$$

If $\tilde{\underset{\sim}{g}}(t)$ is Gaussian, and because the differential operator on the right-hand side of (A8) commutes with itself at different times, the 2nd order cumulant[26] gives an exact result for the average of (A9) which is

$$\frac{\partial}{\partial t}\langle R(\underset{\sim}{a},t)\rangle = \frac{\partial}{\partial \underset{\sim}{a}}\cdot\int_0^t ds\left\langle\underset{\rightarrow}{T}\exp\left[-\int_0^t\bar{\underset{\sim}{M}}(s')ds'\right]\tilde{\underset{\sim}{g}}(t)\ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\rightarrow}{T}\exp\left[-\int_0^s\bar{\underset{\sim}{M}}(s')ds'\right]\tilde{\underset{\sim}{g}}(s)\right\rangle\langle R(\underset{\sim}{a},t)\rangle \tag{A10}$$

Especially notice that the right-hand side of (A10) does not involve a "memory kernel" structure because $\langle R(\underset{\sim}{a},t)\rangle$ is evaluated at time t and not at time s. The use of cumulants is responsible for this form for the result. Using (6) and the identities

$$\begin{aligned}\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\rightarrow}{T}\exp\left[-\int_0^s\bar{\underset{\sim}{M}}(s')ds'\right]\tilde{\underset{\sim}{g}}(s) &= \left(\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\rightarrow}{T}\exp\left[-\int_0^s\bar{\underset{\sim}{M}}(s')ds'\right]\tilde{\underset{\sim}{g}}(s)\right)^{\dagger}\\ &= \tilde{\underset{\sim}{g}}^{\dagger}(s)\left(\underset{\rightarrow}{T}\exp\left[-\int_0^s\bar{\underset{\sim}{M}}(s')ds'\right]\right)^{\dagger}\cdot\frac{\partial}{\partial \underset{\sim}{a}}\\ &= \tilde{\underset{\sim}{g}}(s)\ \underset{\leftarrow}{T}\exp\left[-\int_0^s\bar{\underset{\sim}{M}}^{\dagger}(s')ds'\right]\cdot\frac{\partial}{\partial \underset{\sim}{a}}\end{aligned} \tag{A11}$$

converts (A10) into

$$\frac{\partial}{\partial t}\langle R(\underset{\sim}{a},t)\rangle = \frac{\partial}{\partial \underset{\sim}{a}}\cdot\int_0^t ds\ \underset{\rightarrow}{T}\ \exp\left[-\int_0^t \underset{\sim}{\bar{M}}(s')ds'\right]\underset{\sim}{\Gamma}(t-s)\ \underset{\leftarrow}{T}\ \exp\left[-\int_0^s \underset{\sim}{\bar{M}}^{\dagger}(s')ds'\right]\cdot\frac{\partial}{\partial \underset{\sim}{a}}\langle R(\underset{\sim}{a},t)\rangle \tag{A12}$$

Together, (A1) and (A12) yield

$$\begin{aligned}\frac{\partial}{\partial t}\langle\rho(\underset{\sim}{a},t)\rangle &= -\frac{\partial}{\partial \underset{\sim}{a}}\cdot(\underset{\sim}{\bar{M}}(t)\underset{\sim}{a}\langle\rho(\underset{\sim}{a},t)\rangle)\\ &+ \underset{\leftarrow}{T}\ \exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{a}ds\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}}\ \underset{\rightarrow}{T}\ \exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{a}ds\right]\langle\rho(\underset{\sim}{a},t)\rangle\\ &= -\frac{\partial}{\partial \underset{\sim}{a}}\cdot(\underset{\sim}{\bar{M}}(t)\underset{\sim}{a}\langle\rho(\underset{\sim}{a},t)\rangle)\\ &+ \underset{\leftarrow}{T}\ \exp\left[-\int_0^t \left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{a},\bullet\right]ds\right]\ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}}\langle\rho(\underset{\sim}{a},t)\rangle\end{aligned} \tag{A13}$$

in which $\underset{\sim}{\bar{\Gamma}}(t)$ is representing the entire integral in (A12). The last line of (A13) has again introduced the ordered exponential of a commutator operator. Now notice that

$$\left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{a},\bullet\right]\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}} = \left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{a},\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}}\right] \tag{A14}$$

$$\begin{aligned}&= -\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}} - \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{\Gamma}}(t)\underset{\sim}{\bar{M}}^{\dagger}(s)\cdot\frac{\partial}{\partial \underset{\sim}{a}}\\ &= -\frac{\partial}{\partial \underset{\sim}{a}}\cdot\left\{\underset{\sim}{\bar{M}}(s),\bullet\right\}_{\dagger}\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}}\end{aligned}$$

in the last line of which $\{\underset{\sim}{\bar{M}},\bullet\}_{\dagger}$ has been introduced and is seen to be defined by

$$\left\{\underset{\sim}{M}(s),\bullet\right\}_{\dagger}\underset{\sim}{B}(t) \equiv \underset{\sim}{\bar{M}}(s)\ \underset{\sim}{B}(t) + \underset{\sim}{B}(t)\ \underset{\sim}{\bar{M}}^{\dagger}(s) \tag{A15}$$

Following along the lines leading to (A8), leads to the additional identity

$$\underset{\leftarrow}{T}\ \exp\left\{-\int_0^t \left[\frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{M}}(s)\underset{\sim}{a},\bullet\right]ds\right\}\ \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}} = \frac{\partial}{\partial \underset{\sim}{a}}\cdot\underset{\leftarrow}{T}\ \exp\left[\int_0^t \left\{\underset{\sim}{\bar{M}}(s),\bullet\right\}_\dagger ds\right]\underset{\sim}{\bar{\Gamma}}(t)\cdot\frac{\partial}{\partial \underset{\sim}{a}} \qquad \text{(A16)}$$

It is not difficult to prove still another useful identity:

$$\underset{\leftarrow}{T}\ \exp\left[\int_0^t \left\{\underset{\sim}{\bar{M}}(s),\bullet\right\}_\dagger ds\right]\underset{\sim}{\bar{\Gamma}}(t) = \underset{\leftarrow}{T}\ \exp\left[\int_0^t \underset{\sim}{\bar{M}}(s)ds\right]\underset{\sim}{\bar{\Gamma}}(t)\ \underset{\rightarrow}{T}\ \exp\left[\int_0^t \underset{\sim}{\bar{M}}^\dagger(s)ds\right] \qquad \text{(A17)}$$

which together with (A12) and (A13) which defined $\underset{\sim}{\bar{\Gamma}}(t)$ leads to

$$\underset{\leftarrow}{T}\ \exp\left[\int_0^t \left\{\underset{\sim}{\bar{M}}(s),\bullet\right\}_\dagger ds\right]\underset{\sim}{\bar{\Gamma}}(t) = \int_0^t ds\ \underset{\sim}{\Gamma}(t-s)\ \underset{\rightarrow}{T}\ \exp\left[\int_s^t \underset{\sim}{\bar{M}}^\dagger(s')ds'\right] \qquad \text{(A18)}$$

Using this in (A16) and then in (A13) gives (A9) and completes the proof.

Appendix B

Derivation of (25) from (9):

As is indicated in the paragraph following equation (25)

$$\underset{\sim}{\bar{M}}(t) = \dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t) = i\underset{\sim}{\Omega} - \underset{\sim}{\Psi}(t) \qquad \text{(B1)}$$

It is, therefore, sufficient to show that

$$\frac{\partial}{\partial \underset{\sim}{a}}\cdot\int_0^t ds\ \underset{\sim}{\Gamma}(t-s)\ \underset{\rightarrow}{T}\ \exp\left[\int_s^t \underset{\sim}{\bar{M}}^\dagger(s')ds'\right]\cdot\frac{\partial}{\partial \underset{\sim}{a}} = -\frac{\partial}{\partial \underset{\sim}{a}}\cdot\dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t)\langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger\rangle\cdot\frac{\partial}{\partial \underset{\sim}{a}} \qquad \text{(B2)}$$

in which $\underset{\sim}{\Gamma}(t-s)$ is determined from (6) with $\tilde{\underset{\sim}{g}}(t)$ defined by (23). Using (23) implies

$$\underset{\sim}{\Gamma}(t-s) = \left\langle\left(\underset{\sim}{M}(t)\frac{d}{dt}\int_0^t dt'\ \underset{\sim}{M}^{-1}(t)\ \underset{\sim}{M}(t-t')\ \tilde{\underset{\sim}{f}}(t')\right)\ x\right.$$

$$\left.\left(\underset{\sim}{M}(s)\frac{d}{ds}\int_0^s ds'\ \underset{\sim}{M}^{-1}(s)\ \underset{\sim}{M}(s-s')\ \tilde{\underset{\sim}{f}}(s')\right)\right\rangle$$

=

$$= \underset{\sim}{M}(t)\frac{d}{dt}\int_0^t dt' \frac{d}{ds}\int_0^s ds' \; \underset{\sim}{M}^{-1}(t)\; \underset{\sim}{M}(t-t')\langle \underset{\sim}{\tilde{f}}(t')\; \underset{\sim}{\tilde{f}}(s')^{\dagger}\rangle \underset{\sim}{M}^{\dagger}(s-s')(\underset{\sim}{M}^{-1}(s))^{\dagger}\; \underset{\sim}{M}^{\dagger}(s) \qquad \text{(B3)}$$

Now, with $\underset{\sim}{\bar{M}}(t) \equiv \underset{\sim}{\dot{M}}(t)\; \underset{\sim}{M}^{-1}(t)$ it follows from (A12), (A17), and (A18) that

$$\underset{\rightarrow}{T}\exp\left[\int_s^t \underset{\sim}{\bar{M}}^{\dagger}(s')ds'\right] = \underset{\rightarrow}{T}\exp\left[\int_s^t (\underset{\sim}{M}^{-1}(s'))^{\dagger}\; \underset{\sim}{\dot{M}}^{\dagger}(s')ds'\right]$$

$$= \underset{\leftarrow}{T}\exp\left[-\int_0^s (\underset{\sim}{M}^{-1}(s'))^{\dagger}\; \underset{\sim}{\dot{M}}^{\dagger}(s')ds'\right]\; \underset{\rightarrow}{T}\exp\left[\int_0^t (\underset{\sim}{M}^{-1}(s'))^{\dagger}\; \underset{\sim}{\dot{M}}^{\dagger}(s')ds'\right] \qquad \text{(B4)}$$

Fox[16] has proved that

$$\underset{\rightarrow}{T}\exp\left[-\int_0^t \dot{M}(s')\; M^{-1}(s')ds'\right] = M^{-1}(t) \qquad \text{(B5)}$$

which implies that (B4) may be written

$$\underset{\rightarrow}{T}\exp\left[\int_s^t \underset{\sim}{\bar{M}}^{\dagger}(s')ds'\right] = (\underset{\sim}{M}^{-1}(s))^{\dagger}\; \underset{\sim}{M}^{\dagger}(t) \qquad \text{(B6)}$$

Therefore

$$\int_0^t ds\; \underset{\sim}{\Gamma}(t-s)\; \underset{\rightarrow}{T}\exp\left[\int_s^t \underset{\sim}{\bar{M}}^{\dagger}(s')ds'\right]$$

$$= \int_0^t ds\; \underset{\sim}{M}(t)\left(\frac{d}{dt}\int_0^t dt' \frac{d}{ds}\int_0^s ds' \underset{\sim}{M}^{-1}(t)\; \underset{\sim}{M}(t-t')\langle \underset{\sim}{\tilde{f}}(t')\; \underset{\sim}{\tilde{f}}^{\dagger}(s')\rangle\; \underset{\sim}{M}^{\dagger}(s-s')(\underset{\sim}{M}^{-1}(s))^{\dagger}\right)\underset{\sim}{M}^{\dagger}(t)$$

$$= \underset{\sim}{M}(t)\int_0^t ds'\left(\frac{d}{dt}\int_0^t dt'\; \underset{\sim}{M}^{-1}(t)\; \underset{\sim}{M}(t-t')\langle \underset{\sim}{\tilde{f}}(t')\; \underset{\sim}{\tilde{f}}\; (s')\rangle\right)\underset{\sim}{M}^{\dagger}(t-s')(\underset{\sim}{M}^{-1}(t))^{\dagger}\; \underset{\sim}{M}^{\dagger}(t) \qquad \text{(B7)}$$

in which the last line follows because the preceding line is the s-integral of an exact s-differential.

The expression in the botton line of (B7) contains a quantity which may be rewritten in an equivalent but much more useful form

$$\int_0^t ds' \left(\frac{d}{dt} \int_0^t dt' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - t') \langle \underset{\sim}{\tilde{f}}(t') \underset{\sim}{\tilde{f}}^{\dagger}(s') \rangle \right) \underset{\sim}{M}^{\dagger}(t - s') \, (\underset{\sim}{M}^{-1}(t))^{\dagger}$$

$$= \left\langle \left(\frac{d}{dt} \int_0^t dt' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - t') \, \underset{\sim}{\tilde{f}}(t') \right) \left(\int_0^t ds' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - s') \, \underset{\sim}{\tilde{f}}(s') \right) \right\rangle$$

$$= \frac{1}{2} \frac{d}{dt} \left\langle \left(\int_0^t dt' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - t') \, \underset{\sim}{\tilde{f}}(t') \right) \left(\int_0^t ds' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - s') \, \underset{\sim}{\tilde{f}}(s \,) \right) \right\rangle$$

$$= \frac{1}{2} \frac{d}{dt} \left(\int_0^t ds' \int_0^t dt' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - t') \langle \underset{\sim}{\tilde{f}}(t') \, \underset{\sim}{\tilde{f}}^{\dagger}(s') \rangle \, \underset{\sim}{M}^{\dagger}(t - s') (\underset{\sim}{M}^{-1}(t))^{\dagger} \right)$$

$$= \frac{1}{2} \frac{d}{dt} \left(\int_0^t ds' \int_0^t dt' \, \underset{\sim}{M}^{-1}(t) \, \underset{\sim}{M}(t - t') \, \underset{\sim}{\phi}(t' - s') \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle \, \underset{\sim}{M}^{\dagger}(t - s') (\underset{\sim}{M}^{-1}(t))^{\dagger} \right) \tag{B8}$$

Define $\underset{\sim}{A}(t)$ by

$$\underset{\sim}{A}(t) \equiv \int_0^t ds' \int_0^t dt' \, \underset{\sim}{M}(t - t') \, \underset{\sim}{\phi}(t' - s') \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle \, \underset{\sim}{M}^{\dagger}(t - s')$$

$$= \int_0^t dr \int_0^t ds \, \underset{\sim}{M}(s) \, \underset{\sim}{\phi}(r - s) \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle \, \underset{\sim}{M}^{\dagger}(r) \tag{B9}$$

It follows that

$$\frac{d}{dt} \underset{\sim}{A}(t) = \int_0^t ds \, \underset{\sim}{M}(s) \, \underset{\sim}{\phi}(t - s) \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle \, \underset{\sim}{M}^{\dagger}(t)$$

$$+ \int_0^t dr \, \underset{\sim}{M}(t) \, \underset{\sim}{\phi}(r - t) \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle \, \underset{\sim}{M}^{\dagger}(r) \tag{B10}$$

Mori[13] has shown that

$$\underset{\sim}{\phi}(t_1 - t_2) \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle = \langle \underset{\sim}{\tilde{f}}(t_1) \, \underset{\sim}{\tilde{f}}^{\dagger}(t_2) \rangle$$

$$= \langle \underset{\sim}{\tilde{f}}(-t_2) \, \underset{\sim}{\tilde{f}}^{\dagger}(-t_1) \rangle = \langle \underset{\sim}{\tilde{f}}(-t_1) \, \underset{\sim}{\tilde{f}}^{\dagger}(-t_2) \rangle^{\dagger}$$

$$= \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^{\dagger} \rangle \, \underset{\sim}{\phi}^{\dagger}(t_2 - t_1) \tag{B11}$$

Fox[25] has also shown that

$$\dot{\underset{\sim}{M}}(t) = i\,\underset{\sim}{M}(t)\,\underset{\sim}{\Omega} - \int_0^t ds\,\underset{\sim}{M}(s)\,\underset{\sim}{\phi}(t-s) \tag{B12}$$

and

$$\dot{\underset{\sim}{M}}^{\dagger}(t) = -i\underset{\sim}{\Omega}^{\dagger}\,\underset{\sim}{M}^{\dagger}(t) - \int_0^t ds\,\underset{\sim}{\phi}^{\dagger}(t-s)\,\underset{\sim}{M}^{\dagger}(s)$$

Using (B11) in the second line of (B10), and then using (B12) leads to

$$\begin{aligned}\frac{d}{dt}\underset{\sim}{A}(t) &= (i\underset{\sim}{M}(t)\underset{\sim}{\Omega} - \dot{\underset{\sim}{M}}(t))\langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle \underset{\sim}{M}^{\dagger}(t) \\ &\quad + \underset{\sim}{M}(t)\langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle(-i\underset{\sim}{\Omega}^{\dagger}\,\underset{\sim}{M}^{\dagger}(t) - \dot{\underset{\sim}{M}}^{\dagger}(t)) \\ &= -\frac{d}{dt}(\underset{\sim}{M}(t)\langle \underset{\sim}{a}_o\underset{\sim}{a}_o\rangle \underset{\sim}{M}^{\dagger}(t))\end{aligned} \tag{B13}$$

because, as has been proved by Mori,[13]

$$\underset{\sim}{\Omega}\langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle = \langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle\underset{\sim}{\Omega}^{\dagger} \tag{B14}$$

Integrating (B13) with the initial condition $\underset{\sim}{M}(o) = \underset{\sim}{1}$ gives

$$\underset{\sim}{A}(t) = \langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle - \underset{\sim}{M}(t)\langle \underset{\sim}{a}_o\underset{\sim}{a}_o\rangle \underset{\sim}{M}^{\dagger}(t) \tag{B15}$$

Using this expression for (B9) and putting it back into the bottom line of (B8) implies that (B7) can be written

$$\begin{aligned}&\int_0^t ds\,\underset{\sim}{\Gamma}(t-s)\,\underset{\rightarrow}{T}\exp\left[\int_s^t \bar{\underset{\sim}{M}}^{\dagger}(s')ds'\right] \\ &= \underset{\sim}{M}(t)\,\frac{1}{2}\frac{d}{dt}\left(\underset{\sim}{M}^{-1}(t)\left\{\langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle - \underset{\sim}{M}(t)\langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle \underset{\sim}{M}^{\dagger}(t)\right\}(\underset{\sim}{M}^{-1}(t))^{\dagger}\right)\underset{\sim}{M}^{\dagger}(t) \\ &= \underset{\sim}{M}(t)\left(\frac{1}{2}\frac{d}{dt}\left(\underset{\sim}{M}^{-1}(t)\langle \underset{\sim}{a}_o\underset{\sim}{a}_o^{\dagger}\rangle(\underset{\sim}{M}^{-1}(t))^{\dagger}\right)\right)\underset{\sim}{M}^{\dagger}(t)\end{aligned}$$

$$= -\frac{1}{2}\Big\{\underset{\sim}{M}(t)\ \underset{\sim}{M}^{-1}(t)\ \dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t)\langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger\rangle + \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger\rangle (\underset{\sim}{M}^{-1}(t))^\dagger\ \dot{\underset{\sim}{M}}^\dagger(t)(\underset{\sim}{M}^{-1}(t))^\dagger\ \underset{\sim}{M}^\dagger(t)\Big\}$$

$$= -\frac{1}{2}(\dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t)\langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger\rangle + \langle \underset{\sim}{a}_o \underset{\sim}{a}_o^\dagger\rangle (\underset{\sim}{M}^{-1}(t))^\dagger \dot{\underset{\sim}{M}}^\dagger(t)) \qquad \text{(B16)}$$

in which the identity[16] $\dot{\underset{\sim}{M}}^{-1}(t) = -\underset{\sim}{M}^{-1}(t)\ \dot{\underset{\sim}{M}}(t)\ \underset{\sim}{M}^{-1}(t)$ and its adjoint have been used to get the penultimate line.

Because the desired quantity on the left-hand side of (B2) is a scalar, differential operator, and because the two terms in the last line of (B16) are adjoints of each other, it follows that the final step of premultiplication with $\frac{\partial}{\partial \underset{\sim}{a}}\cdot$ and postmultiplication by $\cdot\frac{\partial}{\partial \underset{\sim}{a}}$ converts (B16) into (B2), thereby completing the proof.

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Analysis of Non-stationary, Gaussian and Non-Gaussian, Generalized Langevin Equations Using Multiplicative Stochastic Processes' Methods

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Abstract

Using the methods of multiplicative stochastic processes[4,9], a thorough analysis of "non-Markovian", generalized Langevin equations is presented. For the Gaussian case, these methods are used to show that the non-stationary Fokker-Planck equation already found by Adelman[1] and others[16] is also obtainable from van Kampen's lemma[9] for stochastic probability flows. Here, results applicable to an arbitrary n-component process are obtained and the specific 2 component case of the Brownian harmonic oscillator is presented in detail in order to explicitly exhibit the matrix algebraic methods. The non-Gaussian case is presented at the end of the paper and shows that the methods already used in the Gaussian case lead directly to results for the non-Gaussian case. In order to use the methods of multiplicative stochastic processes' analysis, it is necessary to transform the "non-Markovian", generalized Langevin equation using a stochastic extension of a transformation discussed by Adelman.[1] This transformation removes the "memory kernel" term in the usual generalized Langevin equation and in the Gaussian case leads to the result that the original process was in fact not "non-Markovian" but actually non-stationary, Markovian.

I. Introduction

In this paper, the relationship between the generalized Langevin equation and the Fokker-Planck equation for the time evolution of the conditional probability distribution is elucidated. A method is exhibited which provides the results already obtained by Adelman[1] for the special case in which the stochastic driving force is Gaussian. This method has the virtue that it directly leads to the corresponding results for the non-Gaussian case, and thereby provides the general and definitive treatment Adelman discussed in the summary of his paper.

The method to be applied in this paper utilizes ordered cumulants[2,3] which were developed for the theory of multiplicative stochastic processes.[4] The generalized Langevin equation is an additive stochastic process and has been treated and derived with projection operator techniques.[5,6] Consequently, this paper will serve to illustrate the relationship between additive and multiplicative stochastic processes as well as to illustrate the alternative advantages of projection operator and cumulant techniques. While this last point has been discussed in the recent literature,[7,8] this paper provides a detailed account of the relative merits of the methods in the explicit solution to the problem of finding the conditional probability distribution for generalized Langevin equations.

Two lemmas will be presented which are necessary in order to implement the program presented in this paper. The first lemma follows from the discussion in section V of Adelman's paper,[1] and shows that the "memory kernel" of the generalized Langevin equation can always be transformed into a term without "memory". The second lemma was proved by van Kampen[9] and involves

stochastic probability flows which were discussed somewhat earlier by Fox,[10] but without the proof provided by van Kampen.

In section II of this paper, the generalized Langevin equation will be presented and briefly reviewed. A stochastic generalization of the Adelman transformation will be introduced in order to eliminated the "memory kernel". In section III, a related stochastic probability flow will be introduced, and van Kampen's lemma will be used to show that the stochastic average of the probability flow leads directly to the conditional probability distribution equation which will be referred to as the Fokker-Planck equation. In section IV a second example, the Brownian oscillator, will be presented in order to exhibit the fact that the methods used apply equally well to multi-component equations. In section V, a discussion of the non-Gaussian generalization is given, and provides the solution Adelman[1] desired.

II. Generalized Langevin Equation

The generalized Langevin equation provides a "non-Markovian" extension of Langevin's equation for Brownian motion. The equation is, in one dimension

$$\frac{d}{dt} u(t) = - \int_0^t \beta(t - s)u(s)ds + \frac{1}{m} \tilde{f}(t) \qquad (1)$$

in which u(t) is the velocity of the Brownian particle at time t, m is its mass, $\beta(t - s)$ is the dissipative "memory kernel" and $\tilde{f}(t)$ is the stochastic driving force. $\tilde{f}(t)$ is assumed to have zero mean which is denoted by $\langle \tilde{f}(t) \rangle = 0$ and has a variance given by[6,11]

$$\langle \tilde{f}(t)\tilde{f}(s) \rangle = K_B T m \, \beta(t - s) \qquad (2)$$

in which K_B is Boltzmann's constant, and T is the temperature. In order to specify the higher order moments of $\tilde{f}(t)$ it is necessary to be more specific

about what kind of process $\tilde{f}(t)$ actually is. Usually, it is assumed to be Gaussian, although this is never proved on the basis of a truly microscopic theory. If $\beta(t - s) = 2\delta(t - s)$ in which $\delta(t)$ denotes the Dirac delta function, then (1) and (2) correspond to the Markovian Langevin equation.[12] The restriction to one dimension is not necessary and is made here in order to most clearly exhibit the nature of the mathematics, and in section IV a two component equation will be treated to illustrate the extension to multi-component cases. Equation (2) is called the fluctuation-dissipation relation because it couples the variance of the stochastic force to the strength of the dissipative memory kernel.

The solution to (1) is obtained by introducing the Laplace transform of $\beta(\tau)$ which is denoted by $\hat{\beta}(z)$ and defined by

$$\hat{\beta}(z) = \int_0^\infty e^{-z\tau}\, \beta(\tau)d\tau \tag{3}$$

Using $\chi(t)$, which is defined through its Laplace transform which is

$$\hat{\chi}(z) = (z + \hat{\beta}(z))^{-1} \tag{4}$$

gives the solution for $u(t)$ as

$$u(t) = \chi(t)u(0) + \frac{1}{m}\int_0^t \chi(t - s)\tilde{f}(s)ds \quad \text{and} \quad \chi(0) = 1 \tag{5}$$

All of this is well known and has appeared in the literature many times.

By stochastically extending a transformation introduced by Adelman,[1] it is possible to convert (1) into an equilivalent equation without a memory kernel. From (5) it follows that

$$u(0) = \frac{1}{\chi(t)} \left(u(t) - \frac{1}{m} \int_0^t \chi(t - s) \tilde{f}(s) ds\right) \tag{6}$$

and that

$$\frac{d}{dt} u(t) = \frac{d}{dt} \chi(t) u(0) + \frac{1}{m} \frac{d}{dt} \int_0^t \chi(t - s) \tilde{f}(s) ds \tag{7}$$

Using (6) in (7) gives

$$\begin{aligned} \frac{d}{dt} u(t) &= \frac{\frac{d}{dt} \chi(t)}{\chi(t)} u(t) + \frac{1}{m} \chi(t) \frac{d}{dt} \int_0^t \frac{\chi(t - s)}{\chi(t)} \tilde{f}(s) ds \\ &= -\bar{\beta}(t) u(t) + \tilde{g}(t) \end{aligned} \tag{8}$$

in which the second equality defines both $\bar{\beta}(t)$ and $\tilde{g}(t)$. Note that $\langle \tilde{g}(t) \rangle = 0$. This transformation will be called Adelman's lemma.

Two points are worth emphasizing at this stage. Because equation (8) is a single time equation, without a memory kernel, it may be suspected that the original "non-Markovian" process is actually Markovian after all. This point will be expanded upon later, and at the end of the paper. Secondly, the objection may be raised that $\chi(t)$ can become zero and then negative,[13] so that division by $\chi(t)$ when it is zero is not defined. Note, however, that if the average of equation (8) is considered

$$\frac{d}{dt} \langle u(t) \rangle = \left(\frac{d}{dt} \ln \chi(t)\right) \langle u(t) \rangle \tag{9}$$

then its solution is

$$\langle u(t) \rangle = \exp\left[\int_0^t \left(\frac{d}{ds} \ell n\, \chi(s) \right) ds \right] \langle u(0) \rangle \tag{10}$$

$$= \chi(t) \langle u(0) \rangle$$

which agrees with (5) and demonstrates that the division by zero does not in fact introduce extraneous behavior. Later, it will be seen that that the variance of u(t) also behaves correctly even if $\chi(t)$ is allowed to become negative.

In Adelman's[1] use of the transformation of (1) into (8) no discussion of the stochastic driving force, $\tilde{g}(t)$, appeared. Here, it will be seen to be of great importance in the subsequent sections.

III. Stochastic Probability Flows

Associated with equation (8) and the initial condition $u(t = 0) = u(0)$ is the conditional probability distribution, $P(u,t)$, which is conditioned by the initial condition: $P(u,0) = \delta(u - u(0))$. Also associated with (8) is a "phase space" description in which $\rho(u,t)$ denotes a density of phase space points at time t determined from the initial density $\rho(u,0)$ by the equation of motion (8). Because this phase space density is conserved it satisfies a continuity equation which is

$$\frac{\partial}{\partial t} \rho(u,t) = - \frac{\partial}{\partial u} (\dot{u}\, \rho(u,t)) \tag{11}$$

in which $\dot{u}$ denotes $\frac{d}{dt} u$ and which becomes

$$\frac{\partial}{\partial t} \rho(u,t) = - \frac{\partial}{\partial u} ((-\bar{\beta}(t)u + \tilde{g}(t))\rho(u,t)) \tag{12}$$

when (8) is used. The presence of $\tilde{g}(t)$ in (12) makes (12) a multiplicative stochastic process[4,9] and ordered cumulant methods may be used to determine

$\langle \rho(u,t) \rangle$. van Kampen[9] has proved that under the conditions stipulated above, $\langle \rho(u,t) \rangle \equiv P(u,t)$. This will be called van Kampen's lemma.

The utility of van Kampen's lemma is that it provides a method for obtaining the conditional probability distribution for an equation such as (8), or equivalently, it enables one to obtain the corresponding Fokker-Planck equation. In order to use this lemma, however, it was essential that the Adelman transformation be performed in order that the "non-Markovian" generalized Langevin equation be in a form suitable for application of multiplicative stochastic process methods.

The following, somewhat lengthy, computations will provide the Fokker-Planck equation for $\langle \rho(u,t) \rangle \equiv P(u,t)$. In order to make the presentation as intelligible as possible, it will initially be assumed that $\tilde{f}(t)$ in (1) is Gaussian. As a consequence the result obtained for $P(u,t)$ will be identical with the result already presented by Adelman and others.[1] However, in section V the non-Gaussian extension will be elucidated.

Define $\phi(u,t)$ by the "interaction picture"

$$\rho(u,t) \equiv \exp\left[- \frac{\partial}{\partial u} u \int_0^t \frac{\dot{\chi}(s)}{\chi(s)} ds \right] \phi(u,t)$$
$$= \exp\left[- \frac{\partial}{\partial u} u \ln \chi(t) \right] \phi(u,t). \qquad (13)$$

$\phi(u,t)$ satisfies

$$\frac{\partial}{\partial t} \phi(u,t) = -\exp\left[\frac{\partial}{\partial u} u \ln \chi(t) \right] \frac{\partial}{\partial u} \tilde{g}(t) \exp\left[- \frac{\partial}{\partial u} u \ln \chi(t) \right] \phi(u,t) \qquad (14)$$

Identity 1: $$\exp\left[\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right] \frac{\partial}{\partial u}\, \tilde{g}(t)\, \exp\left[-\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right] = \frac{1}{m}\frac{d}{dt}\int_0^t \frac{\chi(t-s)}{\chi(t)}\, \tilde{f}(s)ds\, \frac{\partial}{\partial u} \tag{15}$$

Proof:

$$\exp\left[\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right] \frac{\partial}{\partial u}\, \tilde{g}(t)\, \exp\left[-\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right] =$$

$$\exp\left[\ell n\, \chi(t)\, \left[\frac{\partial}{\partial u}\, u\, \cdot\right]\right]\frac{\partial}{\partial u}\, \tilde{g}(t) =$$

$$\tilde{g}(t) \sum_{n=0}^{\infty} \frac{1}{n!}\, (\ell n\, \chi(t))^n \left[\frac{\partial}{\partial u}\, u, \cdot\right]^n \frac{\partial}{\partial u} =$$

$$\tilde{g}(t) \sum_{n=0}^{\infty} \frac{1}{n!}\, (\ell n\, \chi(t))^n\, (-1)^n \frac{\partial}{\partial u} = \tag{16}$$

$$\tilde{g}(t)\, \exp\, [-\ell n\, \chi(t)]\, \frac{\partial}{\partial u} =$$

$$\tilde{g}(t)\, \frac{1}{\chi(t)}\, \frac{\partial}{\partial u} =$$

$$\frac{1}{m}\frac{d}{dt}\int_0^t \frac{\chi(t-s)}{\chi(t)}\, \tilde{f}(s)ds\, \frac{\partial}{\partial u}$$

In line two of the proof, $\left[\frac{\partial}{\partial u}\, u, \cdot\right]^n$ denotes the n^{th} power or iteration of the commutator operator, $\left[\frac{\partial}{\partial u}\, u, \cdot\right]$, which is to act on the operator, $\frac{\partial}{\partial u}$, to the right. It is easily verified that $\left[\frac{\partial}{\partial u}\, u, \cdot\right]^n \frac{\partial}{\partial u} = (-1)^n \frac{\partial}{\partial u}$ which has been used to get from line three to line four. The last line follows from (8).

Therefore, (14) becomes

$$\frac{\partial}{\partial t}\, \phi(u,t) = -\frac{1}{m}\frac{d}{dt}\int_0^t \frac{\chi(t-s)}{\chi(t)}\, \tilde{f}(s)ds\, \frac{\partial}{\partial u}\, \phi(u,t) \tag{17}$$

Because $\langle \tilde{f}(t) \rangle = 0$ for all t, and because $\tilde{f}(t)$ is assumed to be Gaussian at this stage, ordered cumulant methods[4] provide an exact result involving only the $2^{\underline{nd}}$ cumulant, which gives for the average of $\phi(u,t)$

$$\frac{\partial}{\partial t} \langle \phi(u,t) \rangle =$$

$$\int_0^t ds \frac{d}{dt} \int_0^t dt' \frac{d}{ds} \int_0^s ds' \frac{\chi(t-t')}{\chi(t)} \frac{\chi(s-s')}{\chi(s)} \frac{K_B T}{m} \beta(t'-s') \frac{\partial^2}{\partial u^2} \langle \phi(u,t) \rangle \qquad (18)$$

In fact, for this simple case, the differential operator in (17) commutes with itself at different times so that ordinary cumulants are adequate. If the differential operator in (17) had been non-commuting at different times, then even its Gaussianness would not have permitted an exact expression involving only the $2^{\underline{nd}}$ cumulant.[4] Higher order, ordered cumulants would have been required, and, in fact, are going to be discussed in section V when the non-Gaussian case is discussed because non-Gaussianness also requires higher order cumulants.

In (18) the s-integration involves an integrand which is an exact differential so that

$$\int_0^t ds \frac{d}{dt} \int_0^t dt' \frac{d}{ds} \int_0^s ds' \frac{\chi(t-t')}{\chi(t)} \frac{\chi(s-s')}{\chi(s)} \frac{K_B T}{m} \beta(t'-s') =$$

$$\frac{K_B T}{m} \int_0^t ds' \frac{\chi(t-s')}{\chi(t)} \frac{d}{dt} \int_0^t dt' \frac{\chi(t-t')}{\chi(t)} \beta(t'-s') = \qquad (19)$$

$$\frac{1}{2} \frac{K_B T}{m} \frac{d}{dt} \int_0^t ds' \int_0^t dt' \frac{\chi(t-s')}{\chi(t)} \frac{\chi(t-t')}{\chi(t)} \beta(t'-s') =$$

$$\frac{1}{2} \frac{K_B T}{m} \frac{d}{dt} \{\chi^{-2}(t) A(t)\}$$

where the last line defines A(t) which can be rewritten as

$$A(t) = \int_0^t d\tau \int_0^t d\sigma\ \chi(\tau)\beta(\sigma - \tau)\chi(\sigma) \tag{20}$$

Adelman[1] has shown that

$$\frac{d}{dt} A(t) = 2\chi(t) \int_0^t d\sigma\ \beta(\sigma - t)\chi(\sigma) \tag{21}$$

$$= -2\chi(t)\dot{\chi}(t)$$

because the Laplace transforms of $\dot{\chi}(t)$ and $\int_0^t d\sigma\ \chi(\sigma)\beta(\sigma - t)$ are respectively: $z\hat{\chi}(z) - 1$ and $\hat{\chi}(z)\hat{\beta}(z) \equiv 1 - z\hat{\chi}(z)$ because (4) implies: $\hat{\beta}(z) = \hat{\chi}^{-1}(z) - z$. The solution to (21) is

$$A(t) = 1 - \chi^2(t) \tag{22}$$

which is compatible with $\chi(0) = 1$ and (20). Therefore,

$$\frac{d}{dt} \{\chi^{-2}(t)A(t)\} = -2 \frac{\dot{\chi}(t)}{\chi^3(t)} \tag{23}$$

Putting (23) into (19) and then into (18) gives

$$\frac{\partial}{\partial t} \langle \phi(u,t) \rangle = - \frac{K_B T}{m} \frac{\dot{\chi}(t)}{\chi^3(t)} \frac{\partial^2}{\partial u^2} \langle \phi(u,t) \rangle \tag{24}$$

Returning to (13) gives

$$\frac{\partial}{\partial t}\langle\rho(u,t)\rangle = -\frac{\dot{\chi}(t)}{\chi(t)}\frac{\partial}{\partial u}\left(u\langle\rho(u,t)\rangle\right) + \exp\left[-\frac{\partial}{\partial u}\, u\, \ell n\chi(t)\right]\frac{\partial}{\partial t}\langle\phi(u,t)\rangle$$

$$= -\frac{\dot{\chi}(t)}{\chi(t)}\frac{\partial}{\partial u}\left(u\langle\rho(u,t)\rangle\right) \tag{25}$$

$$-\frac{K_B T}{m}\frac{\dot{\chi}(t)}{\chi^3(t)}\exp\left[-\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right]\frac{\partial^2}{\partial u^2}\exp\left[+\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right]\langle\rho(u,t)\rangle$$

Identity 2: $$\exp\left[-\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right]\frac{\partial^2}{\partial u^2}\exp\left[\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right] = \tag{26}$$

$$\chi^2(t)\frac{\partial^2}{\partial u^2}$$

Proof:
$$\exp\left[-\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right]\frac{\partial^2}{\partial u^2}\exp\left[\frac{\partial}{\partial u}\, u\, \ell n\, \chi(t)\right] =$$

$$\exp\left[-\ell n\, \chi(t)\left[\frac{\partial}{\partial u}\, u,\ \cdot\right]\right]\frac{\partial^2}{\partial u^2} = \tag{27}$$

$$\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(\ell n\, \chi(t))^n\left[\frac{\partial}{\partial u}\, u,\ \cdot\right]^n\frac{\partial^2}{\partial u^2} =$$

$$\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(\ell n\, \chi(t))^n\,(-2)^n\frac{\partial^2}{\partial u^2} = \chi^2(t)\frac{\partial^2}{\partial u^2}$$

To get line 4 of (27), $\left[\frac{\partial}{\partial u}\, u,\ \cdot\right]^n\frac{\partial^2}{\partial u^2} = (-2)^n\frac{\partial^2}{\partial u^2}$ was used and is easily verified.

Consequently, equation (25) becomes

$$\frac{\partial}{\partial t}\langle\rho(u,t)\rangle = -\frac{\dot{\chi}(t)}{\chi(t)}\frac{\partial}{\partial u}\left(u\langle\rho\langle u,t\rangle\rangle\right) - \frac{K_B T}{m}\frac{\dot{\chi}(t)}{\chi(t)}\frac{\partial^2}{\partial u^2}\langle\rho(u,t)\rangle \tag{28}$$

or equilivalently, using (8) and van Kampen's lemma

$$\frac{\partial}{\partial t} P(u,t) = \bar{\beta}(t) \frac{\partial}{\partial u} (uP(u,t)) + \frac{K_B T}{m} \bar{\beta}(t) \frac{\partial^2}{\partial u^2} P(u,t) \tag{29}$$

which is a Fokker-Planck equation for $P(u,t)$.

Especially notice that (29) contains t-dependent coefficients in $\bar{\beta}(t)$. This means that (29) describes a non-stationary, Gaussian, Markov process because (29) is a non-stationary diffusion equation,[15] and its explicit solution which is given below can be shown to satisfy the non-stationary Chapman-Kolmogorov equation.[15] Another way to express this is to note that (29) is Kolmogorov's forward equation[15] for a non-stationary Markov process in which the diffusion coefficient is t-dependent but not u-dependent.

By direct substitution into (29) it can be seen that the solution to (29) with $P(u,0) = \delta(u - u(0))$ is given by the non-stationary Gaussian conditional probability distribution

$$P(u,t) = (2\pi\sigma^2(t))^{-\frac{1}{2}} \exp\left[- \frac{(u - \chi(t)u(0))^2}{2\sigma^2(t)} \right] \tag{30}$$

in which $\sigma^2(t)$ satisfies the equation

$$\frac{1}{2} \frac{d}{dt} \sigma^2(t) = \frac{\dot{\chi}(t)}{\chi(t)} \left(\sigma^2(t) - \frac{K_B T}{m} \right) \tag{31}$$

with initial condition $\sigma^2(0) = 0$. The solution to (31) is

$$\sigma^2(t) = \frac{K_B T}{m} (1 - \chi^2(t)) = \frac{K_B T}{m} A(t) \tag{32}$$

Equations (30) and (32) provide the complete stochastic description of the solution to (1) in the Gaussian case. Notice also that if $\chi(t)$ becomes negative, as discussed earlier, no difficulty arises.

Before proceeding to the non-Gaussian case which is given in section V, a two component case will be presented to illustrate the fact that none of the preceding considerations are limited to one component equations. These considerations will occupy section IV.

IV. "Non-Markovian" Brownian Oscillator

The traditional example for a multicomponent Langevin equation is the Brownian motion of a harmonic oscillator.[12,14] If ω denotes the unperturbed frequency of the oscillator, m its mass, p its momentum, and $y = m\omega x$ where x is its position, then the equations of motion can be written in terms of a two component vector:

$$\frac{d}{dt}\begin{pmatrix} y \\ p \end{pmatrix} = \begin{pmatrix} 0 & \omega \\ -\omega & 0 \end{pmatrix}\begin{pmatrix} y \\ p \end{pmatrix} - \int_0^t \begin{pmatrix} 0 & 0 \\ 0 & \beta(t-s) \end{pmatrix}\begin{pmatrix} y(s) \\ p(s) \end{pmatrix} ds + \begin{pmatrix} 0 \\ \tilde{f}(t) \end{pmatrix} \qquad (33)$$

in which $\beta(t - s)$ is the memory kernel and $\tilde{f}(t)$ is the stochastic driving force. As in the example of sections II and III, $\langle \tilde{f}(t) \rangle = 0$ and $\langle \tilde{f}(t)\tilde{f}(s) \rangle = K_B T m \beta(t - s)$. It will also be assumed in this section that $\tilde{f}(t)$ is Gaussian. The non-Gaussian case will be discussed in section V. Using Laplace transforms gives

$$\begin{pmatrix} \hat{y}(z) \\ \hat{p}(z) \end{pmatrix} = \left[z\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \begin{pmatrix} 0 & \omega \\ -\omega & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & \hat{\beta}(z) \end{pmatrix} \right]^{-1} \left[\begin{pmatrix} y(0) \\ p(0) \end{pmatrix} + \begin{pmatrix} 0 \\ \hat{f}(z) \end{pmatrix} \right] \qquad (34)$$

It is easily verified using the matrix adjoint method of construction that the inverse of the matrix in (34) is given by

$$\begin{pmatrix} z & -\omega \\ +\omega & z + \hat{\beta}(z) \end{pmatrix}^{-1} = \begin{pmatrix} z + \hat{\beta}(z) & \omega \\ -\omega & z \end{pmatrix} \quad \frac{1}{z(z + \hat{\beta}(z)) + \omega^2} \tag{35}$$

Let $\chi_p(t)$ be defined through its Laplace transform by

$$\hat{\chi}_p(z) \equiv (z^2 + z\hat{\beta}(z) + \omega^2)^{-1} \tag{36}$$

Because in this case $\chi_p(0) = 0$, $z\hat{\chi}_p(z)$ is the Laplace transform of $\dot{\chi}_p(t)$. Therefore, (34) can be inverse Laplace transformed into

$$\begin{pmatrix} y(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} \dot{\chi}_p(t) + \int_0^t \beta(t-s)\chi_p(s)\,ds & \omega\chi_p(t) \\ -\omega\chi_p(t) & \dot{\chi}_p(t) \end{pmatrix} \begin{pmatrix} y(0) \\ p(0) \end{pmatrix} \tag{37}$$

$$+ \begin{pmatrix} \omega \int_0^t \chi_p(t-s)\tilde{f}(s)ds \\ \int_0^t \dot{\chi}_p(t-s)\tilde{f}(s)ds \end{pmatrix}$$

It also follows that $\dot{\chi}_p(0) = 1$, which guarantees the initial value requirements. Equations (33) and (37) also imply $\ddot{\chi}_p(0) = 0$.

To perform the Adelman transformation on equation (33) it is convenient to rewrite (37) as

$$\begin{pmatrix} y(t) \\ p(t) \end{pmatrix} \equiv \underline{\underline{M}}(t) \begin{pmatrix} y(0) \\ p(0) \end{pmatrix} + \begin{pmatrix} \tilde{F}_y(t) \\ \tilde{F}_p(t) \end{pmatrix} \tag{38}$$

which defines $\underset{\sim}{M}(t)$ and $\tilde{F}_y(t)$ and $\tilde{F}_p(t)$. Therefore

$$\begin{pmatrix} y(0) \\ p(0) \end{pmatrix} = \underset{\sim}{M}^{-1}(t) \left(\begin{pmatrix} y(t) \\ p(t) \end{pmatrix} - \begin{pmatrix} \tilde{F}_y(t) \\ \tilde{F}_p(t) \end{pmatrix} \right) \tag{39}$$

and

$$\frac{d}{dt}\begin{pmatrix} y(t) \\ p(t) \end{pmatrix} = \dot{\underset{\sim}{M}}(t) \begin{pmatrix} y(0) \\ p(0) \end{pmatrix} + \frac{d}{dt} \begin{pmatrix} \tilde{F}_y(t) \\ \tilde{F}_p(t) \end{pmatrix} \tag{40}$$

Substitution of (39) into (40) gives

$$\frac{d}{dt}\begin{pmatrix} y(t) \\ p(t) \end{pmatrix} = \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \begin{pmatrix} y(t) \\ p(t) \end{pmatrix} - \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \begin{pmatrix} \tilde{F}_y(t) \\ \tilde{F}_p(t) \end{pmatrix} \tag{41}$$

$$+ \frac{d}{dt} \begin{pmatrix} \tilde{F}_y(t) \\ \tilde{F}_p(t) \end{pmatrix}$$

$$\equiv \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \begin{pmatrix} y(t) \\ p(t) \end{pmatrix} + \begin{pmatrix} \tilde{G}_y(t) \\ \tilde{G}_p(t) \end{pmatrix}$$

in which the last line defines $\tilde{G}_y(t)$ and $\tilde{G}_p(t)$. An explicit calcualtion shows that

$$\begin{pmatrix} \tilde{G}_y(t) \\ \tilde{G}_p(t) \end{pmatrix} = \underset{\sim}{M}(t) \frac{d}{dt} \int_0^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s) \begin{pmatrix} 0 \\ \tilde{f}(s) \end{pmatrix} ds \tag{42}$$

because $\frac{d}{dt}\left(\underset{\sim}{M}(t)\underset{\sim}{M}^{-1}(t)\right) = 0$ and $\frac{d}{dt}\left(\underset{\sim}{M}(t)\underset{\sim}{M}^{-1}(t)\right) = \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) + \underset{\sim}{M}(t)\frac{d}{dt}\underset{\sim}{M}^{-1}(t)$, which together imply the identity for t-dependent matrices

$$\frac{d}{dt}\underset{\sim}{M}^{-1}(t) = -\underset{\sim}{M}^{-1}(t)\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \tag{43}$$

Therefore, (41) and (42) provide the two-component analogue to (8).

To get the conditional probability distribution determined by (33) and denoted by $P(y,p,t)$ with the initial condition $P(y,p,0) = \delta(y-y(0))\delta(p-p(0))$, van Kampen's lemma is used again. Beginning with a phase space density, $\rho(y,p,t)$, the continuity equation in this case may be written as

$$\frac{\partial}{\partial t}\rho(y,p,t) = -\frac{\partial}{\partial \underset{\sim}{x}}\cdot\left(\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{x}\rho(\underset{\sim}{x},t)\right) - \frac{\partial}{\partial \underset{\sim}{x}}\cdot\left(\tilde{\underset{\sim}{G}}(t)\rho(\underset{\sim}{x}\ t)\right) \tag{44}$$

in which $\underset{\sim}{x}$ denotes the two component vector $\begin{pmatrix} y \\ p \end{pmatrix}$, and $\frac{\partial}{\partial \underset{\sim}{x}}\cdot$ denotes the two dimensional divergence operator. Equation (44) is a multiplicative stochastic process, and van Kampen's lemma asserts that $\langle\rho(\underset{\sim}{x},t)\rangle \equiv P(\underset{\sim}{x},t)$. To get $\langle\rho(\underset{\sim}{x},t)\rangle$, a sequence of identities which parallel the development in section III will be used.

Define $\phi(\underset{\sim}{x},t)$ by

$$\rho(\underset{\sim}{x},t) = \underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\phi(\underset{\sim}{x},t) \tag{45}$$

in which $\underset{\leftarrow}{T}\exp[---]$ denotes the time ordered exponential[4] which is required here because the operator $\frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}$ does not commute with itself at different times. This is the primary complication a multicomponent process creates. If $\underset{\sim}{B}(t)$ is an arbitrary time dependent operator which does not commute with itself at different times, then the inverse of $\underset{\leftarrow}{T}\exp\left[\int_0^t \underset{\sim}{B}(s)ds\right]$ is given by

$\underset{\rightarrow}{T}\exp\left[-\int_0^t \underset{\sim}{B}(s)ds\right]$ in which it must be noticed that the time ordering is in the reversed sense. Therefore,

$$\frac{\partial}{\partial t}\phi(\underset{\sim}{x},t) =$$

$$-\underset{\rightarrow}{T}\exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{\partial}{\partial \underset{\sim}{x}}\cdot\tilde{\underset{\sim}{G}}(t)\ \underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\phi(\underset{\sim}{x},t) \qquad (46)$$

Identity 3:

$$\underset{\rightarrow}{T}\exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{\partial}{\partial \underset{\sim}{x}}\cdot\tilde{\underset{\sim}{G}}(t)\ \underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right] =$$

$$\frac{d}{dt}\frac{\partial}{\partial \underset{\sim}{x}}\cdot\int_0^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s)\begin{pmatrix}0\\ \tilde{f}(s)\end{pmatrix}ds \qquad (47)$$

Proof:

$$\underset{\rightarrow}{T}\exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{\partial}{\partial \underset{\sim}{x}}\cdot\tilde{\underset{\sim}{G}}(t)\ \underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right] =$$

$$\underset{\rightarrow}{T}\exp\left[\int_0^t \left[\frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x},\ \cdot\right]ds\right]\frac{\partial}{\partial \underset{\sim}{x}}\cdot\tilde{\underset{\sim}{G}}(t) \qquad (48)$$

where the right-hand side of this equation contains the time ordered exponential of a commutator operator denoted by $\left[\frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x},\ \cdot\right]$. The first order term in this exponential contains

$$\left[\frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x},\ \frac{\partial}{\partial \underset{\sim}{x}}\cdot\tilde{\underset{\sim}{G}}(t)\right] =$$

$$-\frac{\partial}{\partial \underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\tilde{\underset{\sim}{G}}(t) \qquad (49)$$

This makes it clear that each higher order commutator will contain only the first order $\frac{\partial}{\partial \underset{\sim}{x}} \cdot$ factor, although the time dependent matrix product will become increasingly complicated. However, the result, to all orders, may be expressed by the identity

$$\underset{\rightarrow}{T} \exp\left[\int_o^t \left[\frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}, \cdot\right] ds\right] \frac{\partial}{\partial \underset{\sim}{x}} \cdot \tilde{\underset{\sim}{G}}(t) = \frac{\partial}{\partial \underset{\sim}{x}} \cdot \underset{\rightarrow}{T} \exp\left[-\int_o^t \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)ds\right]\tilde{\underset{\sim}{G}}(t) \tag{50}$$

Note that even though (48) begins with both time ordering senses represented, only one sense of time ordering is required for the commutator exponentials.

The expression $\underset{\rightarrow}{T} \exp\left[-\int_o^t \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)ds\right]$ can be simplified considerably by noting that: at t = o it gives the 2x2 identity matrix which is identical with both $\underset{\sim}{M}(0)$ and $\underset{\sim}{M}^{-1}(0)$; and it satisfies the first order differential equation

$$\frac{d}{dt}\underset{\rightarrow}{T} \exp\left[-\int_o^t \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)ds\right] = -\underset{\rightarrow}{T} \exp\left[-\int_o^t \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)ds\right]\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \tag{51}$$

wherein the derivative of the exponent appears on the right because the exponential is ordered to the right as indicated. This is identical with equation (43) for the derivative of $\underset{\sim}{M}^{-1}(t)$, and it was already noted that the ordered exponential agrees with $\underset{\sim}{M}^{-1}(0)$ at t = 0. Therefore,

$$\underset{\rightarrow}{T} \exp\left[-\int_o^t \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)ds\right] = \underset{\sim}{M}^{-1}(t) \tag{52}$$

Using (52) in (50) and using (42) gives the right-hand side of (47).

Therefore, (46) becomes

$$\frac{\partial}{\partial t}\ \phi(\underset{\sim}{x},t) = -\frac{d}{dt}\frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s) \begin{pmatrix} 0 \\ \tilde{f}(s) \end{pmatrix} ds\ \phi(\underset{\sim}{x},t) \tag{53}$$

Because $\langle \tilde{f}(t) \rangle = 0$, $\tilde{f}(t)$ is Gaussian, and the differential operator

$\frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s) \begin{pmatrix} 0 \\ \tilde{f}(s) \end{pmatrix} ds$ commutes with itself at different times, it follows that the $2^{\underline{nd}}$ cumulant is exact in this case, as in the case of free Brownian motion which was discussed earlier; and implies

$$\frac{\partial}{\partial t}\ \langle \phi(\underset{\sim}{x},t) \rangle = \tag{54}$$

$$\int_0^t ds \Big\langle \frac{d}{dt}\frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t dt' \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-t') \begin{pmatrix} 0 \\ \tilde{f}(t') \end{pmatrix} \frac{d}{ds}\frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^s ds' \underset{\sim}{M}^{-1}(s)\underset{\sim}{M}(s-s') \begin{pmatrix} 0 \\ \tilde{f}(s') \end{pmatrix} \Big\rangle \langle \phi(\underset{\sim}{x},t) \rangle$$

$$= \Big\langle \frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t ds' \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s') \begin{pmatrix} 0 \\ \tilde{f}(s') \end{pmatrix} \frac{d}{dt}\frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t dt' \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-t') \begin{pmatrix} 0 \\ \tilde{f}(t') \end{pmatrix} \Big\rangle \langle \phi(\underset{\sim}{x},t) \rangle$$

The second equality follows from the fact that the integrand in the first line is an exact differential with respect to s-integration. The last line of (54) can be treated in parallel with (19) to give

$$\frac{1}{2}\frac{d}{dt} \Big\langle \frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t ds' \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s') \begin{pmatrix} 0 \\ \tilde{f}(s') \end{pmatrix} \frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t dt' \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-t') \begin{pmatrix} 0 \\ \tilde{f}(t') \end{pmatrix} \Big\rangle \langle \phi(\underset{\sim}{x},t) \rangle \tag{55}$$

$$= \frac{1}{2} K_B T m \frac{d}{dt} \left\{ \frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t ds' \int_0^t dt' \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s')\underset{\sim}{D}(s'-t')\underset{\sim}{M}^{\dagger}(t-t')(\underset{\sim}{M}^{-1}(t))^{\dagger} \cdot \frac{\partial}{\partial \underset{\sim}{x}} \right\} \langle \phi(\underset{\sim}{x},t) \rangle$$

in which † denotes the transpose of a matrix and $\underset{\sim}{D}(s'-t')$ is defined by

$$K_B Tm \underset{\sim}{D}(s-t) \equiv \left\langle \begin{pmatrix} 0 \\ \tilde{f}(s) \end{pmatrix} (0 \;\; \tilde{f}(t)) \right\rangle = \begin{pmatrix} 0 & 0 \\ 0 & K_B Tm \beta(s-t) \end{pmatrix} \tag{56}$$

Define $\underset{\sim}{A}(t)$ by

$$\underset{\sim}{A}(t) \equiv \int_0^t ds \int_0^t dr \, \underset{\sim}{M}(s) \underset{\sim}{D}(r-s) \underset{\sim}{M}^{\dagger}(r) \tag{57}$$

Equation (54) can now be written in the form

$$\frac{\partial}{\partial t} \langle \phi(\underset{\sim}{x},t) \rangle = \frac{1}{2} K_B Tm \frac{d}{dt} \left\{ \frac{\partial}{\partial \underset{\sim}{x}} \cdot \underset{\sim}{M}^{-1}(t) \underset{\sim}{A}(t) (\underset{\sim}{M}^{-1}(t))^{\dagger} \cdot \frac{\partial}{\partial \underset{\sim}{x}} \right\} \langle \phi(\underset{\sim}{x},t) \rangle \tag{58}$$

which parallels the bottom line of (19).

To continue the parallels, the following equation for $\dot{\underset{\sim}{M}}(t)$ is required in which $\underset{\sim}{\Omega} \equiv \begin{pmatrix} 0 & \omega \\ -\omega & 0 \end{pmatrix}$

$$\frac{d}{dt} \underset{\sim}{M}(t) = \underset{\sim}{M}(t) \underset{\sim}{\Omega} - \int_0^t \underset{\sim}{M}(s) \underset{\sim}{D}(t-s) ds \tag{59}$$

This equation can be derived algebraically by looking at the Laplace transforms of each term which gives

$$\dot{\underset{\sim}{M}}(t) \to z\hat{\underset{\sim}{M}}(z) - \underset{\sim}{M}(0) = \begin{pmatrix} -\omega^2 & \omega z \\ -\omega z & -\omega^2 - z\hat{\beta}(z) \end{pmatrix} (z(z+\hat{\beta}(z))+\omega^2)^{-1} \tag{60}$$

$$\underset{\sim}{M}(t)\underset{\sim}{\Omega} \to \hat{\underset{\sim}{M}}(z)\underset{\sim}{\Omega} = \begin{pmatrix} -\omega^2 & \omega(z+\hat{\beta}(z)) \\ -\omega z & -\omega^2 \end{pmatrix} (z(z+\hat{\beta}(z))+\tfrac{2}{\omega})^{-1} \tag{61}$$

$$-\int_0^t \underset{\sim}{M}(s)\underset{\sim}{D}(t-s)ds \rightarrow -\hat{\underset{\sim}{M}}(z)\hat{\underset{\sim}{D}}(z) = \begin{pmatrix} 0 & -\omega\hat{\beta}(z) \\ 0 & -z\hat{\beta}(z) \end{pmatrix} \quad (z(z+\hat{\beta}(z))+\omega^2)^{-1} \qquad (62)$$

in which the right-hand side of (35) is used for $\hat{\underset{\sim}{M}}(z)$ and in which $\hat{\underset{\sim}{D}}(z) = \begin{pmatrix} 0 & 0 \\ 0 & \hat{\beta}(z) \end{pmatrix}$ has been used in (62).

With (57) and (59), it is possible to get a much more revealing expression for $\underset{\sim}{A}(t)$.

$$\frac{d}{dt}\underset{\sim}{A}(t) = \underset{\sim}{M}(t)\int_0^t dr\, \underset{\sim}{D}(r-t)\underset{\sim}{M}^{\dagger}(r) + \int_0^t \underset{\sim}{M}(s)\underset{\sim}{D}(t-s)ds\, \underset{\sim}{M}^{\dagger}(t) \qquad (63)$$

From (59) it follows that

$$\frac{d}{dt}\underset{\sim}{M}^{\dagger}(t) = -\underset{\sim}{\Omega}\underset{\sim}{M}^{\dagger}(t) - \int_0^t \underset{\sim}{D}(t-s)\underset{\sim}{M}^{\dagger}(s)ds \qquad (64)$$

because $\underset{\sim}{\Omega}$ is antisymmetric and $\underset{\sim}{D}$ is symmetric as matrices. $\underset{\sim}{D}(t-s)$ is also symmetric as a function of s and t. Therefore, (59) and (64) provide

$$\int_0^t \underset{\sim}{D}(t-r)\underset{\sim}{M}^{\dagger}(r)dr = -\underset{\sim}{\Omega}\underset{\sim}{M}^{\dagger}(t) - \dot{\underset{\sim}{M}}^{\dagger}(t) \qquad (65)$$

and

$$\int_0^t \underset{\sim}{M}(s)\underset{\sim}{D}(t-s)ds = \underset{\sim}{M}(t)\underset{\sim}{\Omega} - \dot{\underset{\sim}{M}}(t) \qquad (66)$$

When (65) and (66) are placed in (63) the result is

$$\dot{\underset{\sim}{A}}(t) = \underset{\sim}{M}(t)(-\underset{\sim}{\Omega}\underset{\sim}{M}^{\dagger}(t) - \dot{\underset{\sim}{M}}^{\dagger}(t))$$

$$+ (\underset{\sim}{M}(t)\underset{\sim}{\Omega} - \dot{\underset{\sim}{M}}(t))\underset{\sim}{M}^{\dagger}(t) \tag{67}$$

$$= -\frac{d}{dt}(\underset{\sim}{M}(t)\underset{\sim}{M}^{\dagger}(t))$$

This equation is trivially integrated with the initial condition $\underset{\sim}{A}(0) = 0$ and gives

$$\underset{\sim}{A}(t) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \underset{\sim}{M}(t)\underset{\sim}{M}^{\dagger}(t) \tag{68}$$

in striking parallel with (22). This means that (58) can be written as

$$\frac{\partial}{\partial t}\langle\phi(\underset{\sim}{x},t)\rangle = \frac{1}{2}K_B Tm\frac{d}{dt}\left(\frac{\partial}{\partial\underset{\sim}{x}}\cdot\underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial\underset{\sim}{x}}\right)\langle\phi(\underset{\sim}{x},t)\rangle \tag{69}$$

Therefore, (45) implies

$$\frac{\partial}{\partial t}\langle\rho(\underset{\sim}{x},t)\rangle = -\frac{\partial}{\partial\underset{\sim}{x}}\cdot\left(\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{x}\langle\rho(\underset{\sim}{x},t)\rangle\right)$$

$$+ \underset{\leftarrow}{T}\exp\left[-\int_0^t\frac{\partial}{\partial\underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{\partial}{\partial t}\langle\phi(\underset{\sim}{x},t)\rangle$$

$$= -\frac{\partial}{\partial\underset{\sim}{x}}\cdot(\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{x}\langle\rho(\underset{\sim}{x},t)\rangle) \tag{70}$$

$$+\frac{1}{2}K_B Tm\,\underset{\leftarrow}{T}\exp\left[-\int_0^t\frac{\partial}{\partial\underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{d}{dt}\left(\frac{\partial}{\partial\underset{\sim}{x}}\cdot\underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial\underset{\sim}{x}}\right)\cdot$$

$$\underset{\rightarrow}{T}\exp\left[\int_0^t\frac{\partial}{\partial\underset{\sim}{x}}\cdot\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\langle\rho(\underset{\sim}{x},t)\rangle$$

Identity 4:

$$\underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}}\cdot \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial \underset{\sim}{x}}\right)\cdot$$

$$\underset{\rightarrow}{T}\exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right] = \tag{71}$$

$$-2\frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\cdot\frac{\partial}{\partial \underset{\sim}{x}}$$

Proof: Closely related to (48) is the relation

$$\underset{\leftarrow}{T}\exp\left[-\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right]\frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}}\cdot \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial \underset{\sim}{x}}\right)\cdot$$

$$\underset{\rightarrow}{T}\exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x}ds\right] = \tag{72}$$

$$\underset{\leftarrow}{T}\exp\left[-\int_0^t \left[\frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x},\ \cdot\right]ds\right]\frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}}\cdot \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial \underset{\sim}{x}}\right)$$

which involves the ordered exponential of a commutator operator. The first order term in this exponential contains

$$-\left[\frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x},\ \frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}}\cdot \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial \underset{\sim}{x}}\right)\right] =$$

$$\frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}}\cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\cdot\frac{\partial}{\partial \underset{\sim}{x}}+\frac{\partial}{\partial \underset{\sim}{x}}\cdot \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}(\underset{\sim}{M}^{-1}(s))^{\dagger}\dot{\underset{\sim}{M}}^{\dagger}(s)\cdot\frac{\partial}{\partial \underset{\sim}{x}}\right) \tag{73}$$

$$\equiv \frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}}\cdot\left\{\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s),\ \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\right\}_{+}\cdot\frac{\partial}{\partial \underset{\sim}{x}}\right)$$

where the second equality defines the operator $\left\{\underset{\sim}{B}(s),\ \cdot\right\}_{+}$ to be given by

$$\{\underset{\sim}{B}(s),\ \cdot\}_+\ \underset{\sim}{E} \equiv \underset{\sim}{B}(s)\underset{\sim}{E} + \underset{\sim}{E}\underset{\sim}{B}^{+}(s) \tag{74}$$

in which $\underset{\sim}{B}(s)$ and $\underset{\sim}{E}$ are arbitrary matrices. Note that the result in (73) contains exactly two orders of $\frac{\partial}{\partial \underset{\sim}{x}}$. Therefore, the entire exponential on the right-hand side of (72) can be written as

$$\underset{\leftarrow}{T}\ \exp\left[-\int_0^t \left[\frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\underset{\sim}{x},\ \cdot\right] ds\right] \frac{d}{dt}\left(\frac{\partial}{\partial \underset{\sim}{x}} \cdot \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger} \cdot \frac{\partial}{\partial \underset{\sim}{x}}\right) =$$

$$\frac{\partial}{\partial \underset{\sim}{x}} \cdot \left[\underset{\leftarrow}{T}\ \exp\left[\int_0^t \{\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s),\ \cdot\}_+\ ds\right] \frac{d}{dt}\ (\underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger})\right] \cdot \frac{\partial}{\partial \underset{\sim}{x}} \tag{75}$$

This relation is closely related to (50), and the exponential in the right-hand side may be simplified considerably in parallel with (52).

$$\underset{\leftarrow}{T}\ \exp\left[\int_0^t \{\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s),\ \cdot\}_+\ ds\right] = \underset{\sim}{M}(t) \cdot \underset{\sim}{M}^{\dagger}(t) \tag{76}$$

because both sides agree at t = 0. and they both satisfy the first order differential equation

$$\frac{d}{dt}\ \underset{\sim}{U}(t) = \{\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t), \underset{\sim}{U}(t)\}_+ \tag{77}$$

as is readily verified. Using (43) and (76) in (75) gives

$$\underset{\leftarrow}{T}\ \exp\left[\int_0^t \{\underset{\sim}{M}(s)\underset{\sim}{M}^{-1}(s),\ \cdot\}_+\ ds\right] \frac{d}{dt}\ (\underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}) =$$

$$-\underset{\sim}{M}(t)\left(\underset{\sim}{M}^{-1}(t)\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger} + \underset{\sim}{M}^{-1}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\ \dot{\underset{\sim}{M}}^{\dagger}(t)(\underset{\sim}{M}^{-1}(t))^{\dagger}\right)\underset{\sim}{M}^{\dagger}(t) \tag{78}$$

$$= -\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) - (\underset{\sim}{M}^{-1}(t))^{\dagger}\ \dot{\underset{\sim}{M}}^{\dagger}(t)$$

It is also so that

$$\frac{\partial}{\partial \underset{\sim}{x}} \cdot \left(\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) + (\underset{\sim}{M}^{-1}(t))^{\dagger}\, \dot{\underset{\sim}{M}}^{\dagger}(t) \right) \cdot \frac{\partial}{\partial \underset{\sim}{x}} = 2\, \frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \cdot \frac{\partial}{\partial \underset{\sim}{x}} \tag{79}$$

Using (79) and (78) in (75) and (72) justifies Identity 4.

Consequently, (70) becomes

$$\frac{\partial}{\partial t} \langle \rho(\underset{\sim}{x},t) \rangle = - \frac{\partial}{\partial \underset{\sim}{x}} \cdot \left(\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{x} \langle \rho(\underset{\sim}{x},t) \rangle \right) - K_B T m \frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \cdot \frac{\partial}{\partial \underset{\sim}{x}} \langle \rho(\underset{\sim}{x},t) \rangle \tag{80}$$

Using van Kampen's lemma provides the Fokker-Planck equation for this Brownian oscillator which is

$$\frac{\partial}{\partial t} P(\underset{\sim}{x},t) = - \frac{\partial}{\partial \underset{\sim}{x}} \cdot (\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{x}P(\underset{\sim}{x},t)) - K_B T m \frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) \cdot \frac{\partial}{\partial \underset{\sim}{x}} P(\underset{\sim}{x},t) \tag{81}$$

Notice that the matrix coefficients, $\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)$, are t-dependent, so that (81) describes a non-stationary Gaussian process, which is consequently also a non-stationary Markovian process.

It may be verified by substitution in (81) that the solution satisfying the initial condition $P(y,p,0) = \delta(y-y(0))\delta(p-p(0))$ is

$$P(y,p,t) = (2\pi K_B T m)^{-1} (\det(\underset{\sim}{A}(t))^{-\frac{1}{2}} \exp\left[- \frac{1}{2K_B T m} (\underset{\sim}{x}-\underset{\sim}{M}(t)\underset{\sim}{x}(0))^{\dagger} \underset{\sim}{A}^{-1}(t) (\underset{\sim}{x}-\underset{\sim}{M}(t)\underset{\sim}{x}(0)) \right] \tag{82}$$

in which $\underset{\sim}{A}(t)$ is given by (68), $\underset{\sim}{x}(0) = \begin{pmatrix} y(0) \\ p(0) \end{pmatrix}$. The notation $\det(\underset{\sim}{A}(t))$ denotes the determinant of the matrix $\underset{\sim}{A}(t)$. Equation (82)

provides the complete stochastic description of the "non-Markovian" Brownian oscillator. Note that the result is in fact a non-stationary, Gaussian, Markov process.

V. Non-Gaussian Processes

In order for the setting for the non-Gaussian case to be as general as possible, it should be noted that most of the details involved in the analysis of the "non-Markovian" Brownian oscillator did not really depend upon the explicit 2x2 matrices used but instead depended upon only quite general matrix algebraic properties which apply equally well to systems with more than two components. Specifically, equation (33) is a special case of

$$\frac{d}{dt}\,\underset{\sim}{x}(t) = \underset{\sim}{\Omega}\underset{\sim}{x}(t) - \int_0^t \underset{\sim}{D}(t-s)\underset{\sim}{x}(s)ds + \underset{\sim}{\tilde{f}}(t) \tag{83}$$

in which $\underset{\sim}{x}(t)$ denotes an n-component vector, $\underset{\sim}{\Omega}$ denotes an nxn antisymmetric matrix, and $\underset{\sim}{D}(t-s)$ denotes a symmetric, nxn matrix "memory kernel". The process is driven by a stochastic vector force, $\underset{\sim}{\tilde{f}}(t)$, which will generally have n components. The fluctuation-dissipation relation is now

$$\langle \underset{\sim}{\tilde{f}}(t)\ \underset{\sim}{\tilde{f}}(s)^{\dagger} \rangle = K_B T\ \underset{\sim}{D}(t-s) \tag{84}$$

The Adelman transformation converts (83) into

$$\frac{d}{dt}\,\underset{\sim}{x}(t) = \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{x}(t) + \underset{\sim}{M}(t)\,\frac{d}{dt}\int_0^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s)\underset{\sim}{\tilde{f}}(s)ds \tag{85}$$

in which $\underset{\sim}{M}(t)$ is defined through its Laplace transform, $\hat{\underset{\sim}{M}}(z)$, which is given by

$$\hat{\underset{\sim}{M}}(z) = [z\,\underset{\sim}{1} - \underset{\sim}{\Omega} + \hat{\underset{\sim}{D}}(z)]^{-1} \tag{86}$$

where $\underline{1}$ is the nxn identity matrix and $\hat{\underline{D}}(z)$ is the Laplace transform of $\underline{D}(t-s)$. It is now possible to proceed in the Gaussian case from (44) to (58) without alteration because those steps in the 2x2 case did not use the explicit 2x2 nature of the matrices involved. All that must be shown is that equation (59) can be justified for the nxn case because equations (60)-(62) explicitly involve the 2x2 case matrices. The analogues of (60)-(62) are

$$\dot{\underline{M}}(t) \to z\hat{\underline{M}}(z) - \underline{1} = z[z\,\underline{1} - \underline{\Omega} + \hat{\underline{D}}(z)]^{-1} - \underline{1} \tag{87}$$

$$= [z\,\underline{1} - \underline{\Omega} + \hat{\underline{D}}(z)]^{-1}\,(\underline{\Omega} - \hat{\underline{D}}(z))$$

$$\underline{M}(t)\underline{\Omega} \to \hat{\underline{M}}(z)\underline{\Omega} = [z\,\underline{1} - \underline{\Omega} + \underline{D}(z)]^{-1}\,\underline{\Omega} \tag{88}$$

$$-\int_0^t \underline{M}(s)\underline{D}(t-s)ds \to -\hat{\underline{M}}(z)\hat{\underline{D}}(z) = -[z\,\underline{1} - \underline{\Omega} + \hat{\underline{D}}(z)]^{-1}\,\hat{\underline{D}}(z) \tag{89}$$

Therefore, it clearly follows that

$$\frac{d}{dt}\underline{M}(t) = \underline{M}(t)\underline{\Omega} - \int_0^t \underline{M}(s)\underline{D}(t-s)ds \tag{90}$$

Now one may proceed from (63) all the way to (82) without alteration in the argument, provided that the left-hand side of (82) is written as $P(\underline{x},t)$ in which $\underline{x}$ denotes an n-component vector, and the right-hand side contains $(2\pi K_B T)^{-n/2}$.

For the non-Gaussian case, the critical step is the step from equation (53) to equation (54), or their analogues in the n-component case. The second cumulant will no longer be exact and higher order cumulants will be required. Explicit combinatorial formulae exist[4] for all of the higher order cumulants so that it is possible to write out explicit formulae that generalize equation

(54). Because $\langle \underset{\sim}{\tilde{f}}(t) \rangle = 0$, only even order cumulants will be non-vanishing. Because the differential operator

$$- \frac{d}{dt} \frac{\partial}{\partial \underset{\sim}{x}} \cdot \int_0^t \underset{\sim}{M}^{-1}(t) \underset{\sim}{M}(t-s) \underset{\sim}{\tilde{f}}(s) ds$$

commutes with itself at different times, only ordinary cumulants are required and ordered cumulants simply reduce to ordinary cumulants. Whereas the second cumulant which occurs in (54) is second order in $\frac{\partial}{\partial \underset{\sim}{x}}$, the n^{th} cumulant will be n^{th} order in $\frac{\partial}{\partial \underset{\sim}{x}}$ as was suggested by Adelman.[1] The analogue of (54) will have the form

$$\frac{\partial}{\partial t} \langle \phi(\underset{\sim}{x},t) \rangle = \sum_{n=1}^{\infty} \underset{\sim}{G}^{(2n)}(t) \langle \phi(\underset{\sim}{x},t) \rangle \tag{91}$$

in which $\underset{\sim}{G}^{(2n)}(t)$ denotes the $2n^{th}$ cumulant and $\underset{\sim}{G}^{(2)}(t)$ is identically given by (54). In order to subsequently get the equation for $\langle \rho(\underset{\sim}{x},t) \rangle$ it will be necessary to compute the analogue of Identity 4 for the higher cumulants

$$\underset{\leftarrow}{T} \exp\left[- \int_0^t \frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(s) \underset{\sim}{M}^{-1}(s) \underset{\sim}{x} ds \right] \underset{\sim}{G}^{(2n)}(t) \underset{\rightarrow}{T} \exp\left[\int_0^t \frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(s) \underset{\sim}{M}^{-1}(s) \underset{\sim}{x} ds \right]$$

Because $\underset{\sim}{G}^{(2n)}(t)$ is of order 2n in $\frac{\partial}{\partial \underset{\sim}{x}}$, the expression above will also turn out to be of order 2n in $\frac{\partial}{\partial \underset{\sim}{x}}$ because the exponentials contain the combination

$$\frac{\partial}{\partial \underset{\sim}{x}} \cdot \dot{\underset{\sim}{M}}(s) \underset{\sim}{M}^{-1}(s) \underset{\sim}{x}$$

The final result will always involve infinitely many higher cumulants, so that approximations through truncation of the cumulant series will be required. Closed form solutions to these generalized Fokker-Planck equations which possess higher than 2^{nd} order derivatives in x are not known for either the entire cumulant series

or for its truncations. However, the generalized Fokker-Planck equations readily generate equations for the moments of the original stochastic process $\underset{\sim}{x}$, and these moment equations usually permit elementary solutions.

It must be emphasized that for the Gaussian case, equation (29) for the free Brownian motion has been obtained by several others[16] as well as by Adelman[1], and that equation (81), in a somewhat different but equivalent form, has been obtained by Adelman.[1] However, the methods used here also readily develop into a description of non-Gaussian processes. Although that description is perhaps combinatorially complicated, it is nevertheless known explicitly.[4] The virtues of the multiplicative stochastic process approach, with its use of ordered and ordinary cumulants, may be exhibited in many other contexts as well. Moreover, the use of time ordering and related operator calculus techniques, which usually appear only in quantum mechanical contexts, should also be noted. These methods enjoy a broad applicability in classical contexts as has been exhibited here.

It is to be especially noted that for the Gaussian cases the Adelman transformation, in its extended, stochastic form, results in a non-stationary Fokker-Planck equation which describes a non-stationary, Gaussian, Markovian process. This is inspite of the fact that projection operator techniques which give rise to the "memory kernel" equations have led many authors[1] and other workers to refer to those processes as non-Markovian. However, all the memory kernel really does is produce a non-stationary, Markovian process.[15] The methods of multiplicative stochastic process analysis make this fact especially transparent and suggest that these methods are more fundamental. The point will be reinforced in other contexts in subsequent papers.

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REMOVAL OF THE MEMORY KERNEL IN GENERALIZED LANGEVIN EQUATIONS

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Abstract

The connection between the memory kernel form of Mori's generalized Langevin equation and the memoryless form derived by Tokuyama and Mori and by Fox is exhibited in an especially transparent and short form.

Removal of the Memory Kernel in Generalized Langevin Equations

Recently, Tokuyama and Mori[1] showed that the generalized Langevin equation which was earlier derived by Mori[2] with a memory kernel

$$\frac{d}{dt}\underset{\sim}{A}(t) = i\underset{\sim}{\Omega}\underset{\sim}{A}(t) - \int_0^t \underset{\sim}{\phi}(s)\underset{\sim}{A}(t-s)ds + \underset{\sim}{f}(t) \tag{1}$$

can also be written in the "frequency modulated" form

$$\frac{d}{dt}\underset{\sim}{A}(t) = i\underset{\sim}{\Omega}\underset{\sim}{A}(t) - \underset{\sim}{\Psi}(t)\underset{\sim}{A}(t) + \underset{\sim}{g}(t) \tag{2}$$

in which all terms are evaluated at the same time t. $\underset{\sim}{A}(t)$ represents a vector of dynamical variables and satisfies the Liouville equation

$$\frac{d}{dt}\underset{\sim}{A}(t) = i\underset{\sim}{L}\underset{\sim}{A}(t) \tag{3}$$

where $\underset{\sim}{L}$ is the Liouville operator.

The quantities which appear in equations (1) and (2) are determined by the Liouville operator, $\underset{\sim}{L}$, and the inner product

$$(\underset{\sim}{F},\underset{\sim}{G}^{\dagger}) \equiv \langle \underset{\sim}{F},\underset{\sim}{G}^{\dagger} \rangle \tag{4}$$

where $\langle --- \rangle$ denotes averaging with respect to the classical mechanical canonical distribution, and $\underset{\sim}{F}$ and $\underset{\sim}{G}$ are arbitrary column vectors of dynamical variables with $\dagger$ denoting the adjoint operation. Quantum mechanical analogues of this inner product and the corresponding formulae for the quantities in equations (1) and (2) exist[1,2] but will not be explicitly given here. In both (1) and (2), $\underset{\sim}{\Omega}$ is defined by

$$i\underset{\sim}{\Omega} \equiv (i\underset{\sim}{L}\underset{\sim}{A},\underset{\sim}{A}^{\dagger})\cdot(\underset{\sim}{A},\underset{\sim}{A}^{\dagger})^{-1} \tag{5}$$

where $\underset{\sim}{A}$ denotes the column vector dynamical variables, $\underset{\sim}{A}$, at t = o. In (1), $\underset{\sim}{\phi}(t-s)$ is defined by the generalized fluctuation-dissipation relation

$$(\underset{\sim}{f}(t),\underset{\sim}{f}^{\dagger}(s)) = \underset{\sim}{\phi}(t-s)\ (\underset{\sim}{A},\underset{\sim}{A}^{\dagger}) \tag{6}$$

In (2), $\underset{\sim}{\Psi}(t)$ is defined by

$$\underset{\sim}{\Psi}(t) \equiv \int_{o}^{t} \underset{\sim}{\psi}(s)ds \tag{7}$$

where $\underset{\sim}{\psi}(t)$ is given by an alternative fluctuation-dissipation relation

$$\underset{\sim}{\psi}(t) = (\underset{\sim}{g}(t),\underset{\sim}{g}(o)^{\dagger})\cdot(\underset{\sim}{A}(t),\underset{\sim}{A}^{\dagger})^{-1} \tag{8}$$

Also recently, Fox[3] has shown that the generalized Langevin equation with a memory kernel can always be transformed into a memoryless form. The purpose of Fox's work was to provide a general methodology for obtaining the generalized Fokker-Planck equations which attend a generalized Langevin equation description, and removal of the memory kernel in favor of the memoryless form greatly facilitated this objective. However, it also provides a more direct and transparent rendering of the results of Tokuyama and Mori which were derived by a special projection operator method. It is the purpose of this paper to exhibit the shorter method of Fox in the hope of bringing the result to the attention of a wider readership and with the aim of providing a unifying approach to non-equilibrium statistical mechanics. The earlier theory of Mori[1] has already provided useful methods for computation of time correlation formulae and transport coefficients, and the added perspective of the memoryless form of the generalized Langevin equation can be illuminating[2,3].

The transformation used by Fox[3] begins with equation (1) and the fluctuation-dissipation relation in equation (6). The $\underset{\sim}{\Omega}$ in (1), which is defined by (5), is t-independent because L is t-independent and $\underset{\sim}{A}$ denotes $\underset{\sim}{A}(o)$. The solution to (1) may be written

$$\underset{\sim}{A}(t) = \underset{\sim}{M}(t)\underset{\sim}{A}(o) + \int_o^t \underset{\sim}{M}(t-s)\underset{\sim}{f}(s)ds \tag{9}$$

where $\underset{\sim}{M}(t)$ is defined[4] through its Laplace transform, $\hat{\underset{\sim}{M}}(z)$, which is given by

$$\hat{\underset{\sim}{M}}(z) = [z\underset{\sim}{1} - i\underset{\sim}{\Omega} + \hat{\underset{\sim}{\phi}}(z)]^{-1} \tag{10}$$

in which $\underset{\sim}{1}$ is the identity matrix, and $\hat{\underset{\sim}{\phi}}(z)$ is the Laplace transform of $\underset{\sim}{\phi}(t)$. By writing

$$\int_o^t \underset{\sim}{M}(t-s)\underset{\sim}{f}(s)ds = \underset{\sim}{M}(t) \int_o^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s)\underset{\sim}{f}(s)ds \tag{11}$$

and using the seemingly pointless identity

$$\dot{\underset{\sim}{M}}(t) = \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t) \tag{12}$$

the time derivative of (9) becomes

$$\frac{d}{dt}\underset{\sim}{A}(t) = \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{A}(t) + \underset{\sim}{M}(t)\frac{d}{dt}\int_o^t \underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s)\underset{\sim}{f}(s)ds \tag{13}$$

$$= \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)\underset{\sim}{A}(t) + \underset{\sim}{g}(t)$$

in which the last equality defines $\underset{\sim}{g}(t)$. This is clearly the memoryless form of (1), although it is not yet quite in the form of (2) given by Tokuyama and Mori.

Note that $\underset{\sim}{g}(o) = \underset{\sim}{f}(o)$, so that

$$(\underset{\sim}{g}(t),\underset{\sim}{g}^{\dagger}(o)) = \underset{\sim}{M}(t)\,\frac{d}{dt}\int_{o}^{t}\underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s)(\underset{\sim}{f}(s),\underset{\sim}{f}^{\dagger}(o))ds \tag{14}$$

$$= \underset{\sim}{M}(t)\,\frac{d}{dt}\int_{o}^{t}\underset{\sim}{M}^{-1}(t)\underset{\sim}{M}(t-s)\underset{\sim}{\phi}(s)\cdot(\underset{\sim}{A},\underset{\sim}{A}^{\dagger})ds$$

in which (6) has been used. From (10), it is straight-forward to show[3] that

$$\frac{d}{dt}\underset{\sim}{M}(t) = \underset{\sim}{M}(t)\underset{\sim}{\Omega} - \int_{o}^{t}\underset{\sim}{M}(s)\underset{\sim}{\phi}(t-s)ds \tag{15}$$

$$= \underset{\sim}{M}\underset{\sim}{\Omega} - \int_{o}^{t}\underset{\sim}{M}(t-s)\underset{\sim}{\phi}(s)ds$$

which implies

$$\int_{o}^{t}\underset{\sim}{M}(t-s)\underset{\sim}{\phi}(s)ds = \underset{\sim}{M}(t)\underset{\sim}{\Omega} - \frac{d}{dt}\underset{\sim}{M}(t) \tag{16}$$

Putting (16) into (14) yields

$$\left(\underset{\sim}{g}(t),\underset{\sim}{g}^{\dagger}(o)\right) = \underset{\sim}{M}(t)\,\frac{d}{dt}\left(\underset{\sim}{M}^{-1}(t)\left(\underset{\sim}{M}(t)\underset{\sim}{\Omega} - \dot{\underset{\sim}{M}}(t)\right)\right)\cdot\left(\underset{\sim}{A},\underset{\sim}{A}^{\dagger}\right) \tag{17}$$

$$= -\,\underset{\sim}{M}(t)\,\frac{d}{dt}\left(\underset{\sim}{M}^{-1}(t)\dot{\underset{\sim}{M}}(t)\right)\cdot\left(\underset{\sim}{A},\underset{\sim}{A}^{\dagger}\right)$$

Define $\underset{\sim}{\psi}(t)$ by

$$\underset{\sim}{\psi}(t) \equiv \left(\underset{\sim}{g}(t),\underset{\sim}{g}^{\dagger}(o)\right)\left(\underset{\sim}{A},\underset{\sim}{A}^{\dagger}\right)^{-1}\underset{\sim}{M}^{-1}(t) \tag{18}$$

$$= -\,\underset{\sim}{M}(t)\left[\frac{d}{dt}\left(\underset{\sim}{M}^{-1}(t)\dot{\underset{\sim}{M}}(t)\right)\right]\underset{\sim}{M}^{-1}(t)$$

Therefore,

$$\underset{\sim}{\Psi}(t) \equiv \int_o^t \underset{\sim}{\psi}(s)ds = -\int_o^t \underset{\sim}{M}(s)\left[\frac{d}{ds}\left(\underset{\sim}{M}^{-1}(s)\dot{\underset{\sim}{M}}(s)\right)\right]\underset{\sim}{M}^{-1}(s)ds \tag{19}$$

$$= \underset{\sim}{M}(o)\underset{\sim}{M}^{-1}(o)\dot{\underset{\sim}{M}}(o)\underset{\sim}{M}^{-1}(o) - \underset{\sim}{M}(t)\underset{\sim}{M}^{-1}(t)\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)$$

$$+ \int_o^t \dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s)ds$$

$$+ \int_o^t \underset{\sim}{M}(s)\underset{\sim}{M}^{-1}(s)\dot{\underset{\sim}{M}}(s)\frac{d}{ds}\underset{\sim}{M}^{-1}(s)ds$$

$$= \dot{\underset{\sim}{M}}(o)\underset{\sim}{M}^{-1}(o) - \dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t)$$

because the last two integrals on the right-hand side of the third equality cancel each other when we use the identity[3]

$$\frac{d}{ds}\underset{\sim}{M}^{-1}(s) = -\underset{\sim}{M}^{-1}(s)\dot{\underset{\sim}{M}}(s)\underset{\sim}{M}^{-1}(s) \tag{20}$$

From (1) and (13) it follows that

$$\dot{\underset{\sim}{M}}(o)\underset{\sim}{M}^{-1}(o) \equiv i\underset{\sim}{\Omega} \tag{21}$$

Therefore, (19) implies

$$\dot{\underset{\sim}{M}}(t)\underset{\sim}{M}^{-1}(t) = i\underset{\sim}{\Omega} - \underset{\sim}{\Psi}(t) \tag{22}$$

and this identity converts (13) into (2).

It is often remarked that equations with memory kernels such as the generalized Langevin equation, describe non-Markovian processes[5]. The Fokker-Planck analysis of Fox[3] which uses the memoryless form of the generalized Langevin equation (13) has shown that these processes are in fact non-stationary, Markovian processes.

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A remark on the theory of fluctuations far from thermodynamic equilibrium

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Dedicated to the memory

of Lars Onsager

Introduction

Lars Onsager provided the foundation for a universal theory of non-equilibrium processes which are close to equilibrium in 1931 when he published the paper[1] which contained the celebrated reciprocal relations[2]. Twenty-two years later, Onsager and Machlup[3] provided a stochastic basis for the reciprocal relations when they generalized the stochastic treatment of Brownian motion which was established by Langevin[4] and greatly clarified by Uhlenbeck and Ornstein[5]. This development culminated in the application of these ideas to the linearized Boltzmann equation[6] which leads to an infinitely dimensional stationary Markov process.

The universal character of Onsager's theory is exhibited by the so-called fluctuation-dissipation theorem which connects the variance of the stochastic force with the strength of the dissipative parameter which governs the approach to equilibrium. For Brownian motion, the Langevin equation is

$$M\frac{d}{dt}u(t) = -\alpha u(t) + \tilde{F}(t) \qquad (1)$$

where M is the mass, $u(t)$ is the velocity at time t, and α is the dissipative drag coefficient. $\tilde{F}(t)$ is the stochastic force acting on the Brownian particle and has the properties

$$\langle \tilde{F}(t) \rangle = 0 \qquad (2)$$

and

$$\langle \tilde{F}(t)\tilde{F}(s) \rangle = 2\lambda\delta(t-s) \qquad (3)$$

where $\langle \ldots \rangle$ denotes averaging. The fluctuation-dissipation theorem in this case is

$$\lambda = KT\alpha \qquad (4)$$

This became a paradigm for the many applications of Onsager's theory, notably to hydrodynamical fluctuations[7], fluctuations in the Boltzmann equation[6], and fluctuations in electromagnetic fields[8].

In each case the fluctuation-dissipation relations are independent of the underlying microscopic theory, i.e. are of thermodynamical character.

In 1961, van Kampen[9] attempted the establishment of a fluctuation theory which would apply far from equilibrium where the dynamics is usually non-linear. It was not clear that a universal theory for far from equilibrium processes could be established and difficulties remained even after 1973 when Kubo et al.[10] reviewed van Kampen's theory and provided an alternative treatment.

In order to clarify the situation, we have considered the case of a plane mirror in a Knudsen gas in the range of velocities of the order of gas molecule velocities, i.e. far from the regime where the ordinary theory of Brownian motion is applicable.

This example was suggested to us by George Uhlenbeck and is particularly appropriate since ordinary Brownian motion, as mentioned above, is at the root of the Onsager, near-equilibrium theory.

Fluctuations of the Velocity of a Plane Mirror Moving Rapidly in a Knudsen Gas

Consider a plane mirror of cross-sectional area A immersed in a Knudsen gas, i.e. a gas which is so dilute that after its molecules strike the mirror, from which they are perfectly reflected, they almost never hit the mirror again

and make so few collisions with other gas molecules that the distribution of velocities remains unaffected. It is also assumed that the Knudsen gas is initially in thermal equilibrium at temperature T so that the velocity distribution is Maxwellian, and remains Maxwellian. The mirror will, consequently, experience a Brownian motion. The time evolution of the velocity distribution of the mirror is thus described by the linear Boltzmann equation[11] which can be written in the form

$$\frac{\partial}{\partial t}P(v_x,t) = \int_{-\infty}^{\infty}\{R(v_x,v_x')P(v_x',t)-R(v_x',v_x)P(v_x,t)\}dv_x' \qquad (5)$$

in which $R(v_x',v_x)$ is defined by

$$R(v_x',v_x) = (2\pi\frac{KT}{m})^{-1/2}A\frac{N}{V}\left(\frac{M+m}{2m}\right)^2 \exp\{-\frac{\left(\frac{M+m}{2}v_x' - \frac{M-m}{2}v_x\right)^2}{2mKT}\}|v_x-v_x'| \qquad (6)$$

M is the mass of the mirror, m is the mass of a gas molecule, K is Boltzmann's constant, N is the total number of gas molecules in volume V, and conservation of linear momentum and kinetic energy have been used to obtain this explicit formula for $R(v_x',v_x)$. Equations (5) and (6) have the form of a linear master equation of the type which underlies van Kampen's general treatment.

Near equilibrium, when the velocity of the mirror is small compared to the molecular velocities and in the case of small mass ratio

$$\mu = \frac{m}{M} \qquad (7)$$

it is known[11] that to lowest order in μ the linear Boltzmann equation can be approximated by a Fokker-Planck equation which is consistent with the Langevin equation (1) with appropriately defined constants, α and λ.

Thus, near equilibrium we have two equivalent ways of treating Browian motion: (a) by the Langevin equation, and (b) by the Fokker-Planck equation.

Away from equilibrium, it is easier to pursue the Fokker-Planck approach, bypassing the Langevin description, and starting with the master equation. On the other hand, Keizer[12] has proposed a modified Langevin treatment which leads to equivalent results and is closer in spirit to Onsager's work. The problem is to solve the initial value problem for the Boltzmann equation, i.e. to find $P(v_x;t)$ given $P(v_x;0)$.

Near equilibrium and for small mass ratio μ an approximate solution to lowest order in μ is obtained by solving a Fokker-Planck equation already mentioned above. What remains to be done is to see whether a similar simplification can be given far from equilibrium.

First of all, from (5) by direct averaging, i.e. with respect to $P(v_x;t)$, we obtain

$$M\frac{d}{dt}\langle v_x(t)\rangle = A\frac{N}{V}\frac{2}{(1+\mu)m}\left(2\pi mKT\right)^{-1/2}\int_{-\infty}^{\infty}d\xi\left\langle \exp\left\{-\frac{(\xi+mv_x(t))^2}{2mKT}\right\}\right\rangle \xi|\xi|$$

and hence neglecting fluctuations

$$M\frac{d}{dt}\langle v_x(t)\rangle = A\frac{N}{V}\frac{2}{(1+\mu)m}\left(2\pi mKT\right)^{-1/2}\int_{-\infty}^{\infty}d\xi\,\exp\left\{-\frac{(\xi+m\langle v_x(t)\rangle)^2}{2mKT}\right\}\xi|\xi| \qquad (8)$$

It is not difficult to show that this transcedental dependence upon $\langle v_x(t)\rangle$ leads to the Rayleigh form:

$$M\frac{d}{dt}\langle v_x(t)\rangle \simeq -\frac{8}{\sqrt{2\pi}}(mKT)^{1/2}A\frac{N}{V}\frac{1}{1+\mu}\langle v_x(t)\rangle \qquad (9)$$

when $\langle v_x(0)\rangle$ is small compared with $\left(\frac{KT}{m}\right)^{1/2}$, and to the Newtonian form:

$$M\frac{d}{dt}\langle v_x(t)\rangle \simeq -2A\frac{N}{V}\frac{m}{1+\mu}|\langle v_x(t)\rangle|\langle v_x(t)\rangle \qquad (10)$$

when $\langle v_x(0)\rangle$ is of the order of $\left(\frac{KT}{m}\right)^{1/2}$, or larger.

To insure that at t=0 the fluctuations are negligible it is convenient and natural to take

$$P(v_x,0)=\delta(v_x-v_x(0)) \tag{11}$$

i.e. the initial velocity is sharply prescribed so that $\langle v_x(0)\rangle=v_x(0)$

However, this initial distribution will spread in time (for $t\to\infty$ it must approach the Maxwellian distribution) and the validity of (8) depends on fluctuations about the average remaining small.

As long as one is far away from equilibrium, i.e. $v_x(0)$ is of the order of $\left(\frac{KT}{m}\right)^{1/2}$, "small" means that deviations from the average are small compared to it.

Near equilibrium (i.e. $v_x(0)$ of the order $\left(\frac{KT}{M}\right)^{1/2}$) the above statement has to be modified.

Before proceeding with the discussion it will be convenient to introduce dimensionless variables.

$$v_x' = \sqrt{\frac{KT}{M}}\, v, \qquad v_x = \sqrt{\frac{KT}{M}}\, u, \quad t = \frac{V}{AN}\sqrt{\frac{M}{KT}}\, \tau \tag{12}$$

and in these variables the Boltzmann equation[5] becomes

$$\frac{\partial}{\partial \tau}\, p(u;\tau) = \left(\frac{1+\mu}{2\mu}\right) 2 \int_{-\infty}^{\infty} \Big[p(v;\tau)\, \phi_o\left(\frac{1+\mu}{2\sqrt{\mu}}\, u - \frac{1-\mu}{2\sqrt{\mu}}\, v\right)$$

$$- p(u;\tau)\phi_o\left(\frac{1+\mu}{2\sqrt{\mu}}\, v - \frac{1-\mu}{2\sqrt{\mu}}\, u\right)\Big] |u-v|\, dv \tag{13}$$

where

$$p(u;\tau) = \sqrt{\frac{KT}{M}}\, P\left(\sqrt{\frac{KT}{M}}\, u \;;\; \frac{V}{AN}\sqrt{\frac{M}{KT}}\, \tau\right) \tag{14}$$

and

$$\phi_o(u) = \frac{1}{\sqrt{2\pi}} \exp\ (-u^2/2). \tag{15}$$

Away from equilbrium where $u\sqrt{\mu}$ is of order 1 we set

$$p(u;\tau) = p\left(\frac{w(\tau)}{\sqrt{\mu}} + \xi;\tau\right) = \bar{p}(\xi;\tau) \tag{16}$$

where $w(\tau)$ is to be determined a little later.

The motivation behind this substitution is the following; one expects the average (mean) to be of the order $1/\sqrt{\mu}$ so that the distribution of u would be centered about $w(\tau)/\sqrt{\mu}$, and one hopes that the deviation from the mean will be of order 1.

Such a hope can only be justified if at $\tau=0$ the (initial) distribution about $u(0) = w(0)/\sqrt{\mu}$ has width of order 1 and to simplify matters we shall first assume that

$$p(u;0)=\delta\left(u-\frac{w(0)}{\sqrt{\mu}}\right) \tag{17}$$

or, equivalently,

$$\bar{p}\,(\xi;0) = \delta(\xi). \tag{18}$$

This is merely a translation of (11) into dimensionless terms.

Strictly speaking one must now prove that the width of $\bar{p}\,(\xi;\tau)$ will be of order 1 for all $\tau>0$ (in an analogous problem concerning the birth-death model of chemical reactions such a proof has, in fact, been given by Kurtz)[13] but we shall be content here by showing that the assumption that the width of $\bar{p}(\xi;\tau)$ remains of order 1 leads to a consistent theory.

In terms of $\bar{p}(\xi;t)$ the Boltzmann equation assumes, upon setting,

$$v=\zeta+\frac{w(\tau)}{\sqrt{\mu}} \tag{19}$$

the form

$$\frac{\partial\,\bar{p}(\xi;\tau)}{\partial\tau} - \frac{\partial\bar{p}}{\partial\xi}\,\frac{w'(\tau)}{\sqrt{\mu}} = \left(\frac{1+\mu}{2\mu}\right)^2 \int_{-\infty}^{\infty}\Big[\bar{p}(\zeta;\tau)\,\phi_0\left(\frac{1+\mu}{2\sqrt{\mu}}\,\xi-\frac{1-\mu}{2\sqrt{\mu}}\,\zeta+w(\tau)\right)-\bar{p}(\xi;\tau)\,\phi_0\left(\frac{1+\mu}{2\sqrt{\mu}}\,\zeta-\frac{1-\mu}{2\sqrt{\mu}}\,\xi+w(\tau)\right)\Big]\,|\xi-\zeta|\,d\zeta \tag{20}$$

We introduce now an "arbitrary" smooth function $g(\xi)$ which vanishes sufficiently fast at $\pm\infty$ and after multiplying both sides of (20) by g we integrate on ξ from $-\infty$ to $+\infty$.

Introducing on the right hand side the new varriable η by the linear substitution

$$\xi = \zeta + \eta \frac{2\sqrt{\mu}}{1+\mu} \tag{21}$$

we recast (20) in the form

$$\int_{-\infty}^{\infty} g(\xi) \frac{\partial \bar{p}}{\partial \tau} d\xi - \frac{w'(\tau)}{\sqrt{\mu}} \int_{-\infty}^{\infty} g(\xi) \frac{\partial \bar{p}}{\partial \xi} d\xi$$

$$= \frac{1}{\mu} \int_{-\infty}^{\infty} \bar{p}(\zeta;\tau) \int_{-\infty}^{\infty} \left[g(\zeta + \eta \frac{2\sqrt{\mu}}{1+\mu}) - g(\zeta) \right] |\eta| \, \phi_o(\eta + w(\tau) + \zeta\sqrt{\mu}) d\eta \, d\zeta \tag{22}$$

Expanding in powers of $\sqrt{\mu}$, up to and including $(\sqrt{\mu})^2$, we obtain after a few transformations.

$$\int_{-\infty}^{\infty} g(\xi) \frac{\partial \bar{p}}{\partial \tau} d\xi - \frac{w'(\tau)}{\sqrt{\mu}} \int_{-\infty}^{\infty} g(\xi) \frac{\partial \bar{p}}{\partial \xi} d\xi =$$

$$\frac{2}{\sqrt{\mu}} \int_{-\infty}^{\infty} \bar{p}(\zeta;\tau) g'(\zeta) d\zeta \, K_1(w(\tau)) + 2 \int_{-\infty}^{\infty} \bar{p}(\zeta;\tau) g'(\zeta) \zeta d\zeta \int_{-\infty}^{\infty} \phi_o'(\eta + w(\tau)) \eta |\eta| d\eta + 2 \int_{-\infty}^{\infty} \bar{p}(\xi;\tau) g''(\zeta) d\zeta \, K_2(w(\tau)) +$$

terms of order $(\sqrt{\mu})^3$ and higher

where

$$K_n(w) = \int_{-\infty}^{\infty} \phi_o(\eta + w) \eta^n |\eta| d\eta \tag{23}$$

It is clear that in order for the two terms of order $1/\sqrt{\mu}$ to cancel we must have

$$w'(\tau) = 2K_1(w(\tau)) \tag{24}$$

and this is the dimensionless version of (8). Thus $w(\tau)/\sqrt{\mu}$ with $w(\tau)$ obeying (24) is the deterministic law of decay of velocity in dimensionless terms.

Finally,

$$\int_{-\infty}^{\infty} \phi_o' (\eta+w(t))\eta|\eta|d\eta = K_1'(w(t)) \qquad (25)$$

and we are led (upon integration by parts) using the arbitrariness of g to the Fokker-Planck equation

$$\frac{\partial \bar{p}}{\partial \tau} = -2K_1' (w(\tau)) \frac{\partial}{\partial \xi} (\xi \bar{p}) + 2K_2(w(\tau)) \frac{\partial^2 \bar{p}}{\partial \xi^2} \qquad (26)$$

with $w(\tau)$ being a solution of (24).

The initial condition for $\bar{p}$ is (18) i.e.

$$\bar{p}(\xi;0)=\delta(\xi) \qquad (27)$$

and we must also prescribe the initial value of $w(\tau)$

$$w(0)=w_0 \qquad (28)$$

The solution of (26) with the initial conditions (27) and (28) is easily seen to be

$$\bar{p}(\xi;\tau) = \frac{1}{\sigma(\tau)\sqrt{2\pi}} \exp\left\{-\frac{\xi 2}{2\sigma^2(\tau)}\right\} \qquad (29)$$

where $\sigma^2(\tau)$ satisfies the ordinary differential equation

$$\frac{d\sigma^2}{d\tau} = 4K_1' (w(\tau))\sigma^2 + 4K_2(w(\tau)) \qquad (30)$$

and the initial condition

$$\sigma^2(0)=0.$$

The expression for $\sigma^2(\tau)$ will depend (functionally) on $w(\tau)$ and hence on w_o. The dependence on w_o is displayed by writing $\sigma^2(\tau;w_o)$.

If the initial distribution $p(u;0)$ is arbitrary one can write

$$p(u;0) = \frac{1}{\sqrt{\mu}} \int_{-\infty}^{\infty} p\left(\frac{w_o}{\sqrt{\mu}}\,;\,0\right) \delta\left(u - \frac{w_o}{\sqrt{\mu}}\right) dw_o \tag{31}$$

which easily leads to the solution

$$p(u;\tau) = \frac{1}{\sqrt{\mu}} \int_{-\infty}^{\infty} p\left(\frac{w_o}{\sqrt{\mu}}\,;\,0\right) \frac{1}{\sigma(\tau;w_o)\sqrt{2\pi}} \exp\left\{-\frac{(u-w(\tau)/\sqrt{\mu})^2}{2\sigma^2(\tau;w_o)}\right\} dw_o \tag{32}$$

This form is deceptively simple and the highly complex form of $\sigma^2(\tau;w_o)$ is determined by equation (30).

Commentary

The universality of Onsager's theory near equilibrium manifests itself in the thermodynamic character of the fluctuation-dissipation theorem.

In the simplest case of Brownian motion of a free particle which can be described by the Fokker-Planck equation.

$$\frac{P(u;\tau)}{\partial\tau} = \frac{\alpha}{M}\frac{\partial}{\partial u}(uP) + \frac{\lambda}{M^2}\frac{\partial^2 P}{\partial u^2} \tag{33}$$

it amounts to the universal proportionality of λ and α given by equation (4).

Away from equilibrium the situation is quite different. There the analogue of λ is $2K_2(w(t))$ and that of α, $2K_1'(w(t))$, and although they are related (since they both arise from the underlying microscpic mechanism) neither <u>determines</u> the other in the sense that λ determines α (or vice versa) as in equation (4), but instead they are related by equation (30).

Our example thus shows that away from equilibrium it is futile to expect the kind of "thermodynamic" universality as one finds near equilibrium. And yet a description of fluctuations far from equilibrium in terms of Fokker-Planck equations with time dependent coefficients (non-stationary) well be general.

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OFFICE OF
THE DIRECTOR OF
FINANCIAL AFFAIRS

January 26, 1977

Grants and Contracts Office
National Science Foundation
Washington, D. C. 20550

Gentlemen:

Enclosed is the original and two copies of the final fiscal report for grant number MPS73-08945 A01, formerly GP-39309.

If you have any questions or desire additional information, please let me know.

Sincerely yours,

C. Evan Crosby
Associate Director of
Financial Affairs

CEC/bs
enclosures:

cc: Dr. R. F. Fox
Mr. E. E. Renfro
Mr. A. H. Becker
File G-41-627 / G-41-324

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA GEORGIA 30332

SCHOOL OF PHYSICS

Feb. 10 1977

Dear Dr. Isaacson,

Enclosed in my Final Technical Report and form 98A for NSF grant MPS73-08945 A01 (formerly GP39309).

Please note the inclusion of the preprints of current research which is not being sponsored by NSF but which is directly related to my presently pending proposal. I believe that this material strongly supports my previous claims regarding the superiority of my approach to non-equilibrium statistical physics.

Yours truly,

Ronald F. Fox

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

SUMMARY OF COMPLETED PROJECT

Form Approved
OMB No. 99R0013

Please read instructions on reverse carefully before completing this form.

1. INSTITUTION AND ADDRESS	2. NSF PROGRAM	3. GRANT PERIOD
Georgia Institute of Tech. Atlanta, Ga. 30332	Theoretical Physics	from 6/1/73 to 11/30/76

4. GRANT NUMBER	5. BUDGET DUR. (MOS)	6. PRINCIPAL INVESTIGATOR(S)	7. GRANTEE ACCOUNT NUMBER
MPS73-08945 A01	36	Ronald F. Fox	G-41-627

8. SUMMARY (Attach list of publications to form)

The methods of multiplicative stochastic processes as developed by the principal investigator have been used to solve problems in non-equilibrium statistical mechanics. Special emphasis has been given to relaxation phenomena. Stochastic methods, combinatorie methods, and operator calculus methods have been used. The generalized cumulant method has been analyzed and corrected so that it is now a powerful tool for non-equilibrium studies. Current researches, not supported by NSF show that these methods lead to a distinctly superior approach to non-equilibrium problems. A rival, projection operator – memory kernel approach has been completely transformed away by the methods used by the principal investigator, and numerous other treatments of relaxation phenomena are being subsummed and extended.

Reprints of NSF supported work during the period of this grant, MPS 73-08945 A01 (formerly GP 39309) are attached. Preprints of recent, related work which NSF should also support is also attached. Both attachments constitute my technical report and I have appended a list of all these manuscripts to the back of this form.

9. SIGNATURE OF PRINCIPAL INVESTIGATOR/ PROJECT DIRECTOR	TYPED OR PRINTED NAME	DATE
	RONALD F. FOX	Feb. 10, 1977

SF Form 98A (5-76)

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Published

1) Physical Applications of Multiplicative Stochastic Processes. II Derivation of the Bloch Equations for Magnetic Relaxation. J. Math. Phys. 15, 217, (1974)

2) Application of Cumulant Techniques to Multiplicative Stochastic Processes. J. Math. Phys. 15, 1479, (1974)

3) Multiplicative Stochastic Processes, Fokker-Planck Equations, and a Possible Dynamical Mechanism for Critical Behavior J. Math. Phys. 15, 1918, (1974)

4) Physical Applications of Multiplicative Stochastic Processes. III Nonequilibrium Entropy. J. Math. Phys. 16, 1214, (1975)

5) A Generalized Theory of Multiplicative Stochastic Processes Using Cumulant Techniques. J. Math. Phys. 16, 289, (1975)

6) Critique of the Generalized Cumulant Expansion Method. J. Math. Phys. 17, 1148, (1976)

7) Fluctuating Hydrodynamics Explanation of the Alder-Wainwright Velocity Autocorrelation Computer Experiments. J. Chem. Phys. 64, 5307, (1976)

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Accepted to appear

1) Analysis of Nonstationary, Gaussian and Non-Gaussian, Generalized Langevin Equations Using Methods of Multiplicative Stochastic Processes. J. Stat. Phys. 16, 259, (1977)

2) A Remark on the Theory of Fluctuations Far From Thermodynamic Equilibrium. BioSystems, Lars Onsager Memorial Issue (1977) (with Mark Kac)

Submitted for publication

1) Removal of the Memory Kernel in Generalized Langevin Equations. Submitted to J. Chem. Phys.

2) Fluctuation Theories and Nonstationary Markov Processes. Submitted to J. Chem. Phys.