

Physical applications of multiplicative stochastic processes

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The theory of multiplicative stochastic processes has been shown to lead to a density matrix description of nonequilibrium quantum mechanical phenomena. In the present paper a detailed treatment of the approach to the uniform, microcanonical, and canonical equilibrium density matrices is presented. The canonical equilibrium density matrix is approached by the density matrix which represents a subsystem in contact with a constant temperature heat reservoir.

INTRODUCTION

In a recent paper the theory of multiplicative stochastic processes was explained, and it was shown how such a theory potentially leads to a description of nonequilibrium phenomena.¹ In the present paper the density matrix formulation of nonequilibrium quantum mechanical phenomena will be presented with a detailed account of the approach to the uniform, microcanonical, and canonical equilibrium density matrices. The circumstances in which the canonical equilibrium density is approached are of particular interest since they correspond to a subsystem which is in contact with a constant temperature heat reservoir.

RECAPITULATION

The Schrödinger equation for nonrelativistic quantum mechanics may be written in matrix form as²

$$i \frac{d}{dt} C_{\alpha}(t) = \sum_{\alpha'} M_{\alpha\alpha'} C_{\alpha'}(t), \quad (1)$$

where $M_{\alpha\alpha'} = M_{\alpha\alpha'}^*$, which is the condition of Hermiticity, and where $\sum_{\alpha} C_{\alpha}^*(t) C_{\alpha}(t) = 1$ for all t , which is the condition of conservation of total probability. The Hermiticity of $M_{\alpha\alpha'}$ in (1) is a necessary and sufficient condition for the conservation of total probability. Suppose that a fluctuating contribution to the Hamiltonian is considered. Then (1) becomes

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

where $\tilde{M}_{\alpha\alpha'}(t) = \tilde{M}_{\alpha\alpha'}^*(t)$, and the following properties hold for the averaged moments of $\tilde{M}_{\alpha\alpha'}(t)$ ¹:

$$\langle \tilde{M}_{\alpha\alpha'}(t) \rangle = 0, \quad (3)$$

$$\langle \tilde{M}_{\alpha\alpha'}(t) \tilde{M}_{\beta\beta'}(s) \rangle = 2Q_{\alpha\alpha'\beta\beta'} \delta(t-s), \quad (4)$$

$$\langle \tilde{M}_{\mu_1\nu_1}(t_1) \cdots \tilde{M}_{\mu_{2n-1}\nu_{2n-1}}(t_{2n-1}) \rangle = 0 \quad \text{for } n = 1, 2, \dots, \quad (5)$$

$$\begin{aligned} & \langle \tilde{M}_{\mu_1\nu_1}(t_1) \cdots \tilde{M}_{\mu_{2n}\nu_{2n}}(t_{2n}) \rangle \\ &= \frac{1}{2^n n!} \sum_{p \in S_{2n}} \prod_{j=1}^n \langle \tilde{M}_{\mu_{p(2j-1)}\nu_{p(2j-1)}}(t_{p(2j-1)}) \\ & \quad \times \tilde{M}_{\mu_{p(2j)}\nu_{p(2j)}}(t_{p(2j)}) \rangle \\ &= \frac{1}{2^n n!} \sum_{p \in S_{2n}} \prod_{j=1}^n 2Q_{\mu_{p(2j-1)}\nu_{p(2j-1)}\mu_{p(2j)}\nu_{p(2j)}} \\ & \quad \times \delta(t_{p(2j-1)} - t_{p(2j)}), \end{aligned} \quad (6)$$

where S_{2n} is the symmetric group of order $(2n)!$ The properties given by (3), (4), (5), and (6) are those appropriate for a purely random, Gaussian, stochastic, matrix process. Such stochastic processes are the only type of stochastic process to be considered in this paper.

A density matrix representation for the Schrödinger equation is obtained in terms of the density matrix $\rho_{\alpha\beta}(t)$, which is defined by³

$$\rho_{\alpha\beta}(t) \equiv C_{\alpha}^*(t) C_{\beta}(t). \quad (7)$$

With the definitions

$$L_{\alpha\beta\alpha'\beta'} \equiv \delta_{\alpha\alpha'} M_{\beta\beta'} - \delta_{\beta\beta'} M_{\alpha\alpha'}^* \quad (8)$$

$$\tilde{L}_{\alpha\beta\alpha'\beta'} \equiv \delta_{\alpha\alpha'} \tilde{M}_{\beta\beta'}(t) - \delta_{\beta\beta'} \tilde{M}_{\alpha\alpha'}^*(t), \quad (9)$$

Eq. (2) may be used to directly verify

$$i \frac{d}{dt} \rho_{\alpha\beta}(t) = \sum_{\alpha'} \sum_{\beta'} [L_{\alpha\beta\alpha'\beta'} + \tilde{L}_{\alpha\beta\alpha'\beta'}(t)] \rho_{\alpha'\beta'}(t). \quad (10)$$

This is the fluctuating density matrix equation. Using (3)–(6) to average over the stochastic contribution to (10), an equation for the averaged density matrix $\langle \rho_{\alpha\beta}(t) \rangle$ may be obtained, although only after considerable computation¹

$$\begin{aligned} \frac{d}{dt} \langle \rho_{\alpha\beta}(t) \rangle &= -i \sum_{\alpha'} \sum_{\beta'} L_{\alpha\beta\alpha'\beta'} \langle \rho_{\alpha'\beta'}(t) \rangle \\ & \quad - \sum_{\alpha'} \sum_{\beta'} R_{\alpha\beta\alpha'\beta'} \langle \rho_{\alpha'\beta'}(t) \rangle. \end{aligned} \quad (11)$$

The "matrix" $R_{\alpha\beta\alpha'\beta'}$ which appears in (11) is defined by¹

$$\begin{aligned} R_{\alpha\beta\alpha'\beta'} &\equiv \delta_{\alpha\alpha'} \sum_{\theta} Q_{\beta\theta\theta\beta'} + \delta_{\beta\beta'} \sum_{\theta} Q_{\theta\alpha\alpha'\theta} \\ & \quad - Q_{\beta\beta'\alpha'\alpha} - Q_{\alpha'\alpha\beta\beta'}, \end{aligned} \quad (12)$$

where $Q_{\alpha\beta\mu\nu}$ is the "matrix" which appears in (4) and (6).

From (12) it also follows that for arbitrary complex matrices $X_{\alpha\beta}^1$,

$$\sum_{\alpha} \sum_{\beta} \sum_{\alpha'} \sum_{\beta'} X_{\alpha\beta}^* R_{\alpha\beta\alpha'\beta'} X_{\alpha'\beta'} \geq 0 \quad (13)$$

and for arbitrary μ and ν ¹,

$$\sum_{\alpha} R_{\mu\nu\alpha\alpha} = 0. \quad (14)$$

APPROACH TO THE UNIFORM EQUILIBRIUM DENSITY MATRIX

Equations (13) and (14) lead to a proof that (11) describes the approach of $\langle \rho_{\alpha\beta}(t) \rangle$ to an equilibrium density matrix which is uniform¹:

$$\langle \rho_{\alpha\beta}(t) \rangle \xrightarrow{t \rightarrow \infty} \rho_0 \delta_{\alpha\beta}. \tag{15}$$

If there are N eigenstates involved, then conservation of total probability implies $\rho_0 = 1/N$. The equilibrium density matrix given by (15) has been discussed by Tolman.⁴ If the different eigenstates also have different energy eigenvalues, then the uniform equilibrium density matrix nevertheless gives equal weight to each eigenstate independently of its energy eigenvalue. Physically, the uniform equilibrium density matrix has found almost no applications, and only possesses theoretical interest. The reason that the uniform equilibrium density matrix asymptotically occurs is that in (2) no restrictions with respect to eigenstate-eigenstate couplings have been imposed upon $\tilde{M}_{\alpha\alpha'}(t)$. Unrestricted, $\tilde{M}_{\alpha\alpha'}(t)$ may couple any two eigenstates, even if their energy eigenvalues are greatly different. It is this feature of $\tilde{M}_{\alpha\alpha'}(t)$ which leads to the uniform equilibrium density matrix.

APPROACH TO THE MICROCANONICAL EQUILIBRIUM DENSITY MATRIX

Consider Eq. (2). Because both $M_{\alpha\alpha'}$ and $\tilde{M}_{\alpha\alpha'}(t)$ are Hermitian matrices, there exists a unitary transformation which diagonalizes $M_{\alpha\alpha'}$ while transforming $\tilde{M}_{\alpha\alpha'}(t)$ into another Hermitian matrix $\tilde{M}_{\alpha\alpha'}^T(t)$. This transformation may be schematized by

$$M_{\alpha\alpha'} \rightarrow d_\alpha \delta_{\alpha\alpha'}, \tag{16}$$

$$\tilde{M}_{\alpha\alpha'}(t) \rightarrow \tilde{M}_{\alpha\alpha'}^T(t). \tag{17}$$

In the following, the superscript T will be dropped. Therefore, by unitary transformation, Eq. (2) may always be written in the form

$$i \frac{d}{dt} C_\alpha(t) = d_\alpha C_\alpha(t) + \sum_{\alpha'} \tilde{M}_{\alpha\alpha'}(t) C_{\alpha'}(t), \tag{18}$$

where the d_α are real numbers and correspond to the energy eigenvalues.² Equation (18) is as general as (2).

In order to obtain the approach to the microcanonical equilibrium density matrix instead of the uniform equilibrium density matrix, it will be required that the $\tilde{M}_{\alpha\alpha'}(t)$ in (18) be restricted by the condition that it does not generate couplings between eigenstates α and β , for which $d_\alpha \neq d_\beta$. In this way the fluctuating contribution to the Hamiltonian only couples eigenstates corresponding to the same degenerate energy eigenvalue. Formally, this situation is achieved by the replacement of $\tilde{M}_{\alpha\alpha'}(t)$ with $\tilde{M}_{\alpha\alpha'}(t) \delta(d_\alpha - d_{\alpha'})$, where $\delta(d_\alpha - d_{\alpha'})$ is the Kronecker delta symbol in the two arguments d_α and $d_{\alpha'}$. Equation (18) then becomes

$$i \frac{d}{dt} C_\alpha(t) = d_\alpha C_\alpha(t) + \sum_{\alpha'} \tilde{M}_{\alpha\alpha'}(t) \delta(d_\alpha - d_{\alpha'}) C_{\alpha'}(t), \tag{19}$$

which clearly separates into an equation for each distinct degenerate energy eigenvalue manifold of eigenstates.

Therefore, in the following, consideration will be confined to one particular, but otherwise arbitrary, degenerate manifold of eigenstates for which the energy eigenvalue will be denoted by d .² Therefore, (19) becomes

$$i \frac{d}{dt} C_\alpha(t) = d C_\alpha(t) + \sum_{\alpha'} \tilde{M}_{\alpha\alpha'}(t) C_{\alpha'}(t), \tag{20}$$

where it is understood that all the eigenstates coupled by $\tilde{M}_{\alpha\alpha'}(t)$ have energy eigenvalue d . With this in mind,

properties (3)-(6) characterize the various averaged moments of $\tilde{M}_{\alpha\alpha'}(t)$.

The averaged density matrix equation corresponding with (20) is given by

$$\frac{d}{dt} \langle \rho_{\alpha\beta}(t) \rangle = - \sum_{\alpha'} \sum_{\beta'} R_{\alpha\beta\alpha'\beta'} \langle \rho_{\alpha'\beta'}(t) \rangle. \tag{21}$$

The analog to the first term in the right-hand side of (11) is zero in (21) because

$$\begin{aligned} L_{\alpha\beta\alpha'\beta'} &\equiv \delta_{\alpha\alpha'} M_{\beta\beta'} - \delta_{\beta\beta'} M_{\alpha\alpha'}^* \rightarrow d \delta_{\alpha\alpha'} \delta_{\beta\beta'} - d \delta_{\alpha\alpha'} \delta_{\beta\beta'} \\ &= 0. \end{aligned} \tag{22}$$

The equilibrium state follows from conditions (13) and (14) and is given by

$$\langle \rho_{\alpha\beta}(t) \rangle \xrightarrow{t \rightarrow \infty} \rho_0 \delta_{\alpha\beta}, \tag{23}$$

where $\rho_0 = 1/N$ if the degeneracy is equal to N . Therefore, each eigenstate in the degenerate manifold becomes equally probably in equilibrium.

It is of particular interest to consider how the total energy behaves during the approach to the microcanonical equilibrium density matrix. The total energy is given by³

$$\begin{aligned} E_{\text{total}}(t) &\equiv \sum_{\alpha} \sum_{\beta} [d \delta_{\alpha\beta} + \tilde{M}_{\alpha\beta}(t)] \rho_{\alpha\beta}(t) \\ &= d + \sum_{\alpha} \sum_{\beta} \tilde{M}_{\alpha\beta}(t) \rho_{\alpha\beta}(t). \end{aligned} \tag{24}$$

The first term in the second expression follows from conservation of total probability. In the Appendix it is proved that

$$\left\langle \sum_{\alpha} \sum_{\beta} \tilde{M}_{\alpha\beta}(t) \rho_{\alpha\beta}(t) \right\rangle = 0. \tag{25}$$

Therefore, the total energy, on the average, is d for all times t , while $\sum_{\alpha} \sum_{\beta} \tilde{M}_{\alpha\beta}(t) \rho_{\alpha\beta}(t)$ represents the fluctuations of the total energy around the average value d . These energy considerations complete the treatment of the approach to the microcanonical equilibrium density matrix.

APPROACH TO THE CANONICAL EQUILIBRIUM DENSITY MATRIX

Consider a subsystem in contact with a constant temperature heat reservoir. The complete system will have an equilibrium state characterized by a microcanonical density matrix. However, the equilibrium state of the subsystem will be characterized by a canonical equilibrium density matrix if the heat reservoir is very large. Of interest here is the situation in which the heat reservoir remains in its equilibrium state throughout time while the subsystem relaxes into equilibrium with the reservoir from an initial nonequilibrium state. The problem will be to determine the dynamical equations for the relaxation of the subsystem into its canonical equilibrium density matrix.

Denote the Hamiltonians for the subsystem and the heat reservoir by H_S and H_R , respectively. It is assumed that the state of reservoir is given, on the average, by its equilibrium state throughout time. Therefore, the in-

teraction between the reservoir and the subsystem is represented by a stationary, purely random, Gaussian Hamiltonian $\tilde{H}(t)$.

Latin indices will be used to denote eigenstates of the subsystem

$$\mathbf{H}_S|i\rangle = E_i|i\rangle. \quad (26)$$

Greek indices will be used to denote reservoir eigenstates

$$\mathbf{H}_R|\alpha\rangle = E_\alpha|\alpha\rangle. \quad (27)$$

Generally, $\tilde{H}(t)$ will have nonzero matrix elements in the direct product manifold of the two eigenstate manifolds of \mathbf{H}_S and \mathbf{H}_R . Denoting the identity matrices for the subsystem eigenstate manifold and for the reservoir eigenstate manifold by $\mathbf{1}_S$ and $\mathbf{1}_R$, respectively, the total Hamiltonian for the complete system may be written as

$$\mathbf{H}_{\text{total}} = \mathbf{H}_S \otimes \mathbf{1}_R + \mathbf{1}_S \otimes \mathbf{H}_R + \tilde{H}(t), \quad (28)$$

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

$$\psi(t) = \sum_i \sum_\alpha C_{i\alpha}(t)|i\rangle|\alpha\rangle. \quad (29)$$

With the Hamiltonian given by (28), (29) leads to²

$$i \frac{d}{dt} C_{i\alpha}(t) = (E_i + E_\alpha)C_{i\alpha}(t) + \tilde{H}_{i\alpha j\beta}(t)C_{j\beta}(t), \quad (30)$$

where $\tilde{H}_{i\alpha j\beta}(t)$ is defined by

$$\tilde{H}_{i\alpha j\beta}(t) \equiv \langle \alpha | \langle i | \tilde{H}(t) | j \rangle | \beta \rangle. \quad (31)$$

In (30) and throughout the remainder of this section the repeated index summation convention is used.

In order to insure that this description leads to a microcanonical equilibrium density matrix for the complete system, it is necessary to restrict $\tilde{H}_{i\alpha j\beta}(t)$ to be zero unless $E_i + E_\alpha = E_j + E_\beta$. This restriction is schematized in Fig. 1. With this restriction, (3) is a special case of (20) if the substitutions

$$d \rightarrow (E_i + E_\alpha) \equiv E_{\text{total}} \quad \text{and} \quad \tilde{M}_{\alpha\alpha'}(t) \rightarrow \tilde{H}_{i\alpha j\beta}(t) \quad (32)$$

are made, and if (30) is restricted to a single degenerate manifold of eigenstates for the complete system with total energy E_{total} . Because of a result analogous with (25), the energy eigenstates of the complete Hamiltonian are, on the average, direct products of the energy eigenstates of the subsystem and reservoir Hamiltonians.

The density matrix is defined by³

$$\rho_{i\alpha j\beta}(t) \equiv C_{i\alpha}^*(t)C_{j\beta}(t). \quad (33)$$

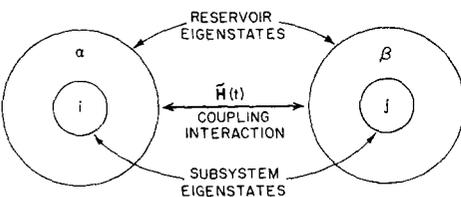


FIG. 1. $\tilde{H}_{i\alpha j\beta} = 0$ unless $E_i + E_\alpha = E_j + E_\beta$.

The stochastically averaged density matrix satisfies the equation²

$$\frac{d}{dt} \langle \rho_{i\alpha j\beta}(t) \rangle = -i L_{i\alpha j\beta i'\alpha'j'\beta'} \langle \rho_{i'\alpha'j'\beta'}(t) \rangle - R_{i\alpha j\beta i'\alpha'j'\beta'} \langle \rho_{i'\alpha'j'\beta'}(t) \rangle, \quad (34)$$

where

$$L_{i\alpha j\beta i'\alpha'j'\beta'} = \delta_{ii'} \delta_{\alpha\alpha'} (E_j + E_\beta) \delta_{jj'} \delta_{\beta\beta'} - \delta_{jj'} \delta_{\beta\beta'} \times (E_i + E_\alpha) \delta_{ii'} \delta_{\alpha\alpha'}. \quad (35)$$

The expression in (35) is actually equal to zero since the direct product eigenstates are restricted to the manifold satisfying

$$E_i + E_\alpha = E_{\text{total}} = E_j + E_\beta, \quad (36)$$

as is implied by (32). This corresponds to the absence of an L term in (21). However, an L term is explicitly indicated in (34) since it will actually manifest itself later. The $R_{i\alpha j\beta i'\alpha'j'\beta'}$ in (34) is defined by

$$R_{i\alpha j\beta i'\alpha'j'\beta'} \equiv \delta_{ii'} \delta_{\alpha\alpha'} Q_{j\beta\theta\theta'\theta\theta'j'\beta'} \quad (37)$$

$$+ \delta_{jj'} \delta_{\beta\beta'} Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'} - Q_{j\beta j'\beta' i'\alpha' i\alpha} - Q_{i'\alpha' i\alpha j\beta j'\beta'},$$

where

$$\langle \tilde{H}_{i\alpha j\beta}(t) \tilde{H}_{i'\alpha'j'\beta'}(s) \rangle = 2Q_{i\alpha j\beta i'\alpha'j'\beta'} \delta(t-s). \quad (38)$$

The condition that the reservoir state remain the equilibrium state throughout time is imposed by assuming that the averaged density matrix $\langle \rho_{i\alpha j\beta}(t) \rangle$ factors into a direct product of the subsystem density matrix, and the reservoir density matrix in which the reservoir density matrix is given, for all times, by its equilibrium density matrix. The reservoir equilibrium density matrix must be the canonical density matrix because of: (36), the condition that the complete system has a microcanonical equilibrium density matrix, and the condition that the subsystem has a canonical equilibrium density matrix. Formally, the factorization is given by

$$\langle \rho_{i\alpha j\beta}(t) \rangle \rightarrow \langle \rho_{ij}(t) \rangle \langle \rho_{\alpha\beta} \rangle, \quad (39)$$

where

$$\langle \rho_{\alpha\beta} \rangle = (1/Q_R) \exp[-(E_\alpha/K_B T)] \delta_{\alpha\beta}, \quad (40)$$

where $Q_R = \sum_\alpha \exp[-(E_\alpha/K_B T)]$, K_B is Boltzmann's constant, and T is the temperature of the reservoir.

Putting (39) and (40) into (34), followed by taking the trace over reservoir eigenstates, produces the following equation for the averaged subsystem density matrix:

$$\frac{d}{dt} \langle \rho_{ij}(t) \rangle = -i(E_j - E_i) \langle \rho_{ij}(t) \rangle - R_{i\alpha j\alpha i'\alpha'j'\alpha'} \frac{1}{Q_R} \exp\left(-\frac{E_{\alpha'}}{K_B T}\right) \langle \rho_{i'j'}(t) \rangle. \quad (41)$$

Note that the L term of (34) does contribute to (41).

By defining $T_{ij i'j'}$ by

$$T_{ij i'j'} \equiv R_{i\alpha j\alpha i'\alpha'j'\alpha'} (1/Q_R) \exp[-(E_{\alpha'}/K_B T)], \quad (42)$$

Eq. (41) becomes

$$\frac{d}{dt} \langle \rho_{ij}(t) \rangle = -i(E_j - E_i) \langle \rho_{ij}(t) \rangle - T_{ijj'j'} \langle \rho_{i'j'}(t) \rangle. \tag{43}$$

It is of interest to consider the relationship between $T_{ijj'j'}$ and $T_{i'j'ij}$. The use of (37), (38), and Fig. 1 is required.

Figure 1 and (38) imply that

$$Q_{i\alpha j\beta i'\alpha'j'\beta'} = 0 \quad \text{unless} \quad E_i + E_\alpha = E_j + E_\beta$$

and $E_{i'} + E_{\alpha'} = E_{j'} + E_{\beta'}$. (44)

This may be written with Kronecker deltas as

$$Q_{i\alpha j\beta i'\alpha'j'\beta'} \delta(E_i + E_\alpha - E_j - E_\beta) \delta(E_{i'} + E_{\alpha'} - E_{j'} - E_{\beta'}). \tag{45}$$

Using expressions similar to (45) in (37) leads to

$$R_{i\alpha j\beta i'\alpha'j'\beta'} = [\delta_{ii'} \delta_{\alpha\alpha'} Q_{j\beta\theta\theta'\theta\theta'j'\beta'} \delta(E_j + E_\beta - E_\theta - E_{\theta'})$$

$$\times \delta(E_\theta + E_{\theta'} - E_{j'} - E_{\beta'})$$

$$+ \delta_{jj'} \delta_{\beta\beta'} Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'} \delta(E_\theta + E_{\theta'} - E_i - E_\alpha)$$

$$\times \delta(E_{i'} + E_{\alpha'} - E_\theta - E_{\theta'}) - 2Q_{j\beta j'\beta' i'\alpha i\alpha'}]$$

$$\times \delta(E_j + E_\beta - E_{j'} - E_{\beta'}) \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha). \tag{46}$$

Using (46), along with appropriate index changes, in (42) gives

$$T_{ijj'j'} = [\delta_{ii'} \delta_{\alpha\alpha'} Q_{j\alpha\theta\theta'\theta\theta'j'\alpha'} \delta(E_j + E_\alpha - E_\theta - E_{\theta'})$$

$$\times \delta(E_\theta + E_{\theta'} - E_{j'} - E_{\alpha'}) + \delta_{jj'} \delta_{\alpha\alpha'} Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'}$$

$$\times \delta(E_\theta + E_{\theta'} - E_i - E_\alpha) \delta(E_{i'} + E_{\alpha'} - E_\theta - E_{\theta'})$$

$$- 2Q_{j\alpha j'\alpha' i'\alpha i\alpha'}] \delta(E_j + E_\alpha - E_{j'} - E_{\alpha'})$$

$$\times \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha) (1/Q_R) \exp[-(E_{\alpha'}/K_B T)]$$

$$= [\delta_{ii'} \delta_{\alpha\alpha'} Q_{j'\alpha'\theta\theta'\theta\theta'j\alpha} \delta(E_j + E_\alpha - E_\theta - E_{\theta'})$$

$$\times \delta(E_\theta + E_{\theta'} - E_{j'} - E_{\alpha'}) + \delta_{jj'} \delta_{\alpha\alpha'} Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'}$$

$$\times \delta(E_\theta + E_{\theta'} - E_i - E_\alpha) \delta(E_{i'} + E_{\alpha'} - E_\theta - E_{\theta'})$$

$$- 2Q_{j'\alpha'j\alpha i'\alpha i\alpha'}] \delta(E_j + E_\alpha - E_{j'} - E_{\alpha'})$$

$$\times \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha)$$

$$\times (1/Q_R) \exp[-(E_{\alpha'}/K_B T)]$$

$$= [\delta_{ii'} \delta_{\alpha\alpha'} Q_{j'\alpha'\theta\theta'\theta\theta'j\alpha} \delta(E_j + E_\alpha - E_\theta - E_{\theta'})$$

$$\times \delta(E_\theta + E_{\theta'} - E_{j'} - E_{\alpha'}) + \delta_{jj'} \delta_{\alpha\alpha'} Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'}$$

$$\times \delta(E_\theta + E_{\theta'} - E_i - E_\alpha) \delta(E_{i'} + E_{\alpha'} - E_\theta - E_{\theta'})$$

$$- 2Q_{j'\alpha'j\alpha i'\alpha i\alpha'}] \delta(E_j + E_\alpha - E_{j'} - E_{\alpha'})$$

$$\times \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha)$$

$$\times (1/Q_R) \exp[-(E_{\alpha'}/K_B T)]. \tag{47}$$

The second equality in (47) follows from the Hermiticity of $\tilde{H}(t)$ in (38), while the third equality follows from re-

naming the indices α and α' according to the interchange $\alpha \leftrightarrow \alpha'$. In the last expression for $T_{ijj'j'}$ in (47), the factors $\delta(E_j + E_\alpha - E_{j'} - E_{\alpha'}) \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha)$ require that $E_\alpha = E_{\alpha'} + E_j - E_{j'} = E_{\alpha'} + E_i - E_{i'}$, which may be combined to give

$$E_\alpha = E_{\alpha'} + \frac{1}{2}(E_j + E_i - E_{j'} - E_{i'}). \tag{48}$$

This means that

$$\delta(E_j + E_\alpha - E_{j'} - E_{\alpha'}) \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha)$$

$$\times (1/Q_R) \exp[-(E_\alpha/K_B T)]$$

$$= \delta(E_{j'} + E_{\alpha'} - E_j - E_\alpha) \delta(E_i + E_\alpha - E_{i'} - E_{\alpha'}) (1/Q_R)$$

$$\times \exp[-(E_{\alpha'}/K_B T)] \exp[-(E_j + E_i$$

$$- E_{j'} - E_{i'})/2K_B T]. \tag{49}$$

Putting (49) into the last expression for $T_{ijj'j'}$ in (47) gives

$$T_{ijj'j'} = [\delta_{ii'} \delta_{\alpha\alpha'} Q_{j'\alpha'\theta\theta'\theta\theta'j\alpha} \delta(E_j + E_\alpha - E_\theta - E_{\theta'})$$

$$\times \delta(E_\theta + E_{\theta'} - E_{j'} - E_{\alpha'}) + \delta_{jj'} \delta_{\alpha\alpha'}$$

$$\times Q_{\theta\theta'i\alpha i'\alpha'\theta\theta'} \delta(E_\theta + E_{\theta'} - E_i - E_\alpha)$$

$$\times \delta(E_{i'} + E_{\alpha'} + E_\theta - E_{\theta'}) - 2Q_{j'\alpha'j\alpha i'\alpha i\alpha'}]$$

$$\times \delta(E_j + E_\alpha - E_{j'} - E_{\alpha'}) \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha)$$

$$\times \frac{1}{Q_R} \exp\left(-\frac{E_{\alpha'}}{K_B T}\right)$$

$$\times \exp\left(-\frac{(E_j + E_i - E_{j'} - E_{i'})}{2K_B T}\right). \tag{50}$$

However, using (46) in (42) in order to calculate $T_{i'j'ij}$, directly verifies that (50) is simply

$$T_{ijj'j'} = T_{i'j'ij}^* \exp[-(E_j + E_i - E_{j'} - E_{i'})/2K_B T]. \tag{51}$$

Together, Eqs. (43) and (51) provide the dynamical description of the temporal approach to equilibrium of the averaged density matrix for the subsystem. Equation (51) is a generalized detailed balancing condition.

It can now be proved that the canonical equilibrium density matrix is obtained asymptotically:

$$\langle \rho_{ij}(t) \rangle \xrightarrow{t \rightarrow \infty} (1/Q_S) \exp[-(E_j/K_B T)] \delta_{ij}, \tag{52}$$

where $Q_S = \sum_j \exp[-(E_j/K_B T)]$. The proof of (52) uses the first equality given in (47) to show that

$$T_{ijj'j'} (1/Q_S) \exp[-(E_j/K_B T)] \delta_{i'j'} = 0. \tag{53}$$

Proof of (53):

From (47) it follows that

$$T_{ijj'j'} (1/Q_S) \exp[-(E_j/K_B T)] \delta_{i'j'}$$

$$= [\delta_{ii'} \delta_{\alpha\alpha'} Q_{j\alpha\theta\theta'\theta\theta'j'\alpha} \delta(E_j + E_\alpha - E_\theta - E_{\theta'})$$

$$\times \delta(E_\theta + E_{\theta'} - E_{j'} - E_{\alpha'}) + \delta_{jj'} \delta_{\alpha\alpha'}$$

$$\times \delta(E_\theta + E_{\theta'} - E_i - E_\alpha) \delta(E_{i'} + E_{\alpha'} - E_\theta - E_{\theta'})$$

$$- 2Q_{j\alpha j'\alpha' i'\alpha i\alpha'}] \delta(E_j + E_\alpha - E_{j'} - E_{\alpha'})$$

$$\times \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha)$$

$$\times (1/Q_S) \exp[-(E_\alpha/K_B T)].$$

$$\begin{aligned}
 & \times Q_{\theta\theta' i\alpha i'\alpha'\theta\theta'} \delta(E_\theta + E_{\theta'} - E_i - E_\alpha) \\
 & \times \delta(E_{i'} + E_{\alpha'} - E_\theta - E_{\theta'}) \\
 & - 2Q_{j\alpha j'\alpha' i'\alpha' i\alpha} \delta(E_j + E_\alpha - E_{j'} - E_{\alpha'}) \\
 & \times \delta(E_{i'} + E_{\alpha'} - E_i - E_\alpha) \\
 & \times \frac{1}{Q_R} \exp\left(-\frac{E_{\alpha'}}{K_B T}\right) \frac{1}{Q_S} \exp\left(-\frac{E_{j'}}{K_B T}\right) \delta_{i'j'} \\
 = & [\delta_{\alpha\alpha'} Q_{j\alpha\theta\theta'\theta\theta' i\alpha} \delta(E_j + E_\alpha - E_\theta - E_{\theta'}) \\
 & \times \delta(E_\theta + E_{\theta'} - E_i - E_{\alpha'}) + \delta_{\alpha\alpha'} Q_{\theta\theta' i\alpha j\alpha'\theta\theta'} \\
 & \times \delta(E_\theta + E_{\theta'} - E_i - E_{\alpha'}) \delta(E_j + E_{\alpha'} - E_\theta - E_{\theta'}) \\
 & - 2Q_{j\alpha\theta\alpha'\theta\alpha' i\alpha} \delta(E_j + E_\alpha - E_\theta - E_{\alpha'}) \delta(E_\theta + E_{\alpha'} \\
 & - E_i - E_{\alpha'}) (1/Q_R Q_S) \exp[-(E_{\text{total}}/K_B T)] \\
 = & (Q_{j\alpha\theta\theta'\theta\theta' i\alpha} + Q_{\theta\theta' i\alpha j\alpha'\theta\theta'} - 2Q_{j\alpha\theta\theta'\theta\theta' i\alpha}) \\
 & \times \delta(E_j + E_\alpha - E_\theta - E_{\theta'}) \delta(E_\theta + E_{\theta'} - E_i - E_{\alpha'}) \\
 & \times (1/Q_R Q_S) \exp[-(E_{\text{total}}/K_B T)] = 0. \tag{54}
 \end{aligned}$$

The second equality in (54) used (36), while the fourth equality used (38). This completes the proof of (53).

SUMMARY

It has been shown how the theory of multiplicative stochastic processes leads to a description of the approach to equilibrium of the density matrix for a quantum mechanical system. In the case of a system which maintains a constant average total energy, the approach to the microcanonical equilibrium density matrix is described. In the case of a subsystem in contact with a constant temperature heat reservoir, the approach to the canonical equilibrium density matrix is described. This last case provides a unified treatment of some aspects of the problems of magnetic resonance relaxation, spectral line shape when the line shape is Lorentzian, and molecular reaction relaxation phenomena.^{5,6} Detailed accounts of these and other problems from the perspective presented in this paper remains to be presented.

APPENDIX

Proof of (25): Using Eq. (20), $C_\beta(t)$ can be written as

$$\begin{aligned}
 C_\beta(t) = & e^{-idt} \sum_{\beta'} \sum_{k=0}^{\infty} (-i)^k \int_0^t \int_0^{S_k} \int_0^{S_{k-1}} \dots \int_0^{S_3} \int_0^{S_2} \sum_{\mu_{k-1}} \sum_{\mu_{k-2}} \\
 & \times \dots \sum_{\mu_2} \sum_{\mu_1} \tilde{M}_{\beta\mu_{k-1}}(S_k) \tilde{M}_{\mu_{k-1}\mu_{k-2}}(S_{k-1}) \dots \tilde{M}_{\mu_2\mu_1}(S_2) \\
 & \times \tilde{M}_{\mu_1\beta'}(S_1) dS_1 \dots dS_k C_{\beta'}(0). \tag{55}
 \end{aligned}$$

Similarly, $C_\alpha^*(t)$ can be written as

$$\begin{aligned}
 C_\alpha^*(t) = & e^{idt} \sum_{\alpha'} \sum_{l=0}^{\infty} (i)^l \int_0^t \int_0^{S_l} \int_0^{S_{l-1}} \dots \int_0^{S_3} \int_0^{S_2} \sum_{\nu_1} \sum_{\nu_2} \\
 & \times \dots \sum_{\nu_{l-2}} \sum_{\nu_{l-1}} \tilde{M}_{\alpha'\nu_1}(S_1) \tilde{M}_{\nu_1\nu_2}(S_2) \dots \tilde{M}_{\nu_{l-2}\nu_{l-1}}(S_{l-1}) \\
 & \times \tilde{M}_{\nu_{l-1}\alpha}(S_l) dS_1 \dots dS_l C_{\alpha'}^*(0). \tag{56}
 \end{aligned}$$

In (56) the Hermiticity of $\tilde{M}(t)$ has been used. In both (55) and (56) the multiple integrals are time ordered

with $t \geq S_k \geq S_{k-1} \geq \dots \geq S_2 \geq S_1 \geq 0$. Using (7), the quantity of interest in (25) may be written as

$$\begin{aligned}
 & \left\langle \sum_{\alpha} \sum_{\beta} \tilde{M}_{\alpha\beta}(t) \rho_{\alpha\beta}(t) \right\rangle \\
 = & \left\langle \sum_{\alpha} \sum_{\beta} C_\alpha^*(t) \tilde{M}_{\alpha\beta}(t) C_\beta(t) \right\rangle \\
 = & \sum_{\alpha} \sum_{\beta} \sum_{\alpha'} \sum_{\beta'} \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} (i)^l (-i)^k \int_0^t \int_0^{S_l} \dots \int_0^{S_2} \int_0^t \int_0^{S_k} \\
 & \times \dots \int_0^{S_2} \sum_{\nu_1} \dots \sum_{\nu_{l-1}} \sum_{\mu_{k-1}} \dots \sum_{\mu_1} \langle \tilde{M}_{\alpha'\nu_1}(S_1') \dots \tilde{M}_{\nu_{l-1}\alpha}(S_l') \\
 & \times \tilde{M}_{\alpha\beta}(t) \tilde{M}_{\beta\mu_{k-1}}(S_k) \dots \tilde{M}_{\mu_1\beta'}(S_1) \rangle C_{\alpha'}^*(0) C_{\beta'}(0) dS_1 \\
 & \times \dots dS_k dS_1' \dots dS_l' \\
 = & \sum_{l=0}^{\infty} \sum_{k=0}^{\infty} (i)^l (-i)^k \sum_{\alpha'} \sum_{\beta'} \int_0^t \int_0^{S_l} \dots \int_0^{S_2} \int_0^t \int_0^{S_k} \dots \int_0^{S_2} \\
 & \times \sum_{\alpha} \sum_{\beta} \sum_{\nu_1} \dots \sum_{\nu_{l-1}} \sum_{\mu_{k-1}} \dots \sum_{\mu_1} \langle \tilde{M}_{\alpha'\nu_1}(S_1') \\
 & \times \dots \tilde{M}_{\nu_{l-1}\alpha}(S_l') \tilde{M}_{\alpha\beta}(t) \tilde{M}_{\beta\mu_{k-1}}(S_k) \dots \tilde{M}_{\mu_1\beta'}(S_1) \rangle \\
 & \times C_{\alpha'}^*(0) C_{\beta'}(0) dS_1 \dots dS_k dS_1' \dots dS_l'. \tag{57}
 \end{aligned}$$

Two cases need to be considered in evaluating the last expression (57). These two cases are (a) $k + l$ is even and (b) $k + l$ is odd.

Case (a): If $k + l$ is even, then there are $k + l + 1$ $\tilde{M}(t)$'s in the product, and the average will be zero because of condition (5).

Case (b): If $k + l$ is odd, then there are $k + l + 1$ $\tilde{M}(t)$'s in the product, and the average will not be zero because of condition (6). However, it will be shown below that these nonzero terms occur in pairs of opposite sign so that the sum of all such nonzero terms is zero.

Let $p + q$ be odd and consider the two terms: $k = p$ and $l = q$, and $k = q$ and $l = p$. In the first case the last expression in (57) contains the factor $(i)^q (-i)^p$, whereas in the second case it contains the factor $(i)^p (-i)^q$. However, $p + q$ is odd implies

$$(i)^q (-i)^p = (-1)^p (i)^{p+q} = -(-1)^q (i)^{q+p} = -(i)^p (-i)^q. \tag{58}$$

Therefore, if the remaining integral factors of these two terms are equal, then a pair of nonzero terms with opposite signs have been identified.

The remaining integral factor in the $k = p$ and $l = q$ case is

$$\begin{aligned}
 & \sum_{\alpha'} \sum_{\beta'} \int_0^t \int_0^{S_q'} \dots \int_0^{S_2'} \int_0^t \int_0^{S_p} \dots \int_0^{S_2} \sum_{\alpha} \sum_{\beta} \sum_{\nu_1} \dots \sum_{\nu_{q-1}} \sum_{\mu_{p-1}} \dots \\
 & \times \sum_{\mu_1} \langle \tilde{M}_{\alpha'\nu_1}(S_1') \dots \tilde{M}_{\nu_{q-1}\alpha}(S_q') \tilde{M}_{\alpha\beta}(t) \tilde{M}_{\beta\mu_{p-1}}(S_p) \\
 & \times \dots \tilde{M}_{\mu_1\beta'}(S_1) \rangle C_{\alpha'}^*(0) C_{\beta'}(0) dS_1 \dots dS_p dS_1' \dots dS_q' \tag{59}
 \end{aligned}$$

In the $k = q$ and $l = p$ case the remaining integral factor is

$$\begin{aligned} & \sum_{\alpha'} \sum_{\beta'} \int_0^t \int_0^{S_{\beta'}} \dots \int_0^{S_2'} \int_0^t \int_0^{S_q} \dots \int_0^{S_2} \sum_{\alpha} \sum_{\beta} \sum_{\nu_1} \dots \sum_{\nu_{p-1}} \sum_{\mu_{q-1}} \dots \\ & \times \sum_{\mu_1} \langle \tilde{M}_{\alpha' \nu_1}(S_1') \dots \tilde{M}_{\nu_{p-1} \alpha}(S_p') \tilde{M}_{\alpha \beta}(t) \tilde{M}_{\beta \mu_{q-1}}(S_q) \\ & \times \dots \tilde{M}_{\mu_1 \beta'}(S_1) \rangle C_{\alpha'}^*(0) C_{\beta'}(0) dS_1 \dots dS_q dS_1' \dots dS_p'. \end{aligned} \tag{60}$$

Therefore, the proof of (25) is reduced to proving that (59) and (60) are equal. That (59) and (60) are equal follows from the property that the trace of a product of matrices equals the trace of the transpose of the product of matrices. This is explicitly illustrated above by considering $C_{\alpha'}^*(0) C_{\beta'}(0)$ as a matrix, using the transpose property of the trace, renaming indices, and relabeling

the variables of integration. Thereby, the expression in (60) may be transformed into the expression in (59). This completes the proof of (25).

¹R. F. Fox, *J. Math. Phys.* **13**, 1196 (1972).

²Throughout this paper physical units are assumed in terms of which Planck's constant \hbar has the value 1 and, therefore, does not explicitly appear in any equation.

³This definition is to be contrasted with the definition given by R. C. Tolman, *The principles of statistical mechanics* (Oxford U.P., New York, 1962), Chap. IX. The expressions for density matrix averages of quantum mechanical operators are, therefore, also different.

⁴R. C. Tolman, Ref. 3, Chap. IX.

⁵R. Kubo and N. Hashitsume, *Prog. Theor. Phys. Suppl.* (46), 210 (1970).

⁶M. Blume, *Phys. Rev.* **174** (2), 351 (1968); M. Clauser and M. Blume, *Phys. Rev. B* **3** (3), 583 (1971).