

Random degenerate transitions and the master equation

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We explore the consequences of making the following assumptions for transitions in isolated, degenerate systems, where we describe the state of the system by a vector in a linear vector space: changes in the state are due to a series of random events where each event is given by a unitary operator that is equal to an exponential function of a random Hermitian matrix; the principle of superposition applied to all possible paths gives the path taken; the statistical properties of the random variable are a system property. For systems where the elements of the random Hermitian matrix are i.i.d. and uncorrelated, we find that on using the central limit theorem the above leads to a unitary time evolution operator that is a function of time increments to the half power. On applying this operator to an isolated thermodynamic system we show it leads to an equation consisting of two terms. The time derivative of the first term is the master equation; the second term is shown to represent fluctuations. The transition probabilities in the master equation satisfy the principle of detailed balance. The two terms taken together describe a system that evolves to a final state in which the system fluctuates about equilibrium. A single set of assumptions lead to the master equation, the principle of detailed balance and fluctuations.

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I. INTRODUCTION

In this paper we present a new quantum mechanical based approach to the origin of the master equation.

First we assume that a stochastic process can describe the evolution of a thermodynamic system. Stochastic processes have been used to model the time evolution of thermodynamic systems [1]. As there, we assume that changes in the state of a system can be described as a series of events. In the present case we assume that for a single event the change in the state $|\Phi\rangle$ is given by

$$|\Phi(i+1)\rangle = \exp(-iA)|\Phi(i)\rangle, \quad (1)$$

where the elements a_{ij} of the Hermitian matrix A are random variables. We call this the random matrix hypothesis. We are unaware of prior work where the random variables have been cast in the above functional form.

Second we assume that the nature of the random variables is a system property. In this paper we consider systems with particularly simple statistical properties. We assume that the elements of the matrix A are iid and uncorrelated. Stochastic systems can evolve along many different paths. We assume that the number of events along a path is a linear

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function of time and that the constant of proportionality between number of events and time is the same for all possible paths.

We apply the principal of superposition: When a system can be in two or more states it can be in a state that is a linear combination of those states [2]. This requires that given the numerous paths the system can take, one should combine all possible outcomes. This prescription is indefinite for the present case. For example, two paths can arrive at a given state after a significantly different number of events and they can arrive at significantly different states after undergoing the same number of events. We make the simplifying assumption that we need only combine all outcomes that have undergone the same number of events.

The above assumptions are formally presented in Sec. II.

We show in Sec. III that for an isolated M fold degenerate system the assumptions lead to the state of the system $|\Psi(t)\rangle$ evolving according to

$$|\Psi(t)\rangle = \exp(-iGt^{1/2})|\Psi(0)\rangle, \quad (2)$$

where G is a Hermitian matrix.

We explore the consequences when Eq. (2) is used to describe changes in the state of a single, isolated, M fold degenerate system, such as a thermodynamic system. It leads to an equation consisting of two terms as shown in Sec. IV. After deriving the principle of detailed balance in Sec. V, we show in Sec. VI that the time derivative of the first of the aforementioned terms is the master equation. The second term represents fluctuations as covered in Sec. VII.

Pauli was the first to derive the master equation

$$\frac{dp_i}{dt} = \sum_j w_{ij} p_j - \sum_j w_{ji} p_i \quad (3)$$

from standard quantum theory using a perturbation approach. Here, p_i is the occupation probability of the system being in state $|i\rangle$ and w_{ij} is the transition probability between states $|j\rangle$ and $|i\rangle$. An outline of Pauli's derivation along with his approximations and assumptions can be found in Ref. [3].

Since Pauli's original paper, considerable effort has been expended on deriving the master equation under less restrictive conditions, particularly as part of a larger effort to place statistical mechanics on a firmer foundation. Many of the various directions taken along with their difficulties are summarized in reviews of the foundations of statistical mechanics by ter Haar [4], Penrose [5], Sklar [6], and Uffink [7].

The master equation is frequently recast in the form

$$\frac{dp_i}{dt} = \sum_j w_{ij} (p_j - p_i) \quad (4)$$

by utilizing the principle of detailed balance, $w_{ij} = w_{ji}$. This principle is sometimes called the principle of microscopic reversibility. The relation $w_{ij} = w_{ji}$ is derived separately from the master equation. Examples of that derivation can be found in Ref. [8, 9]. The derivations are based on the classical or quantum equations of motion augmented with assumptions.

The methodologies used to justify the existence of fluctuations are different again from those used to derive the master equation and the principle of detailed balance. Examples can be found in Ref. [10, 11].

In this paper a single set of assumptions leads to the master equation, the principle of detailed balance and fluctuations.

The penultimate section is devoted to a brief discussion of some of the assumptions.

Fractional time evolution operators with time taken to a different fractional exponent than given in Eq. (2) are considered in the Appendix.

II. FUNDAMENTAL ASSUMPTIONS AND RELATIONS

Consider an isolated, M fold degenerate system. The state of the system $|\Phi\rangle$ is given by a vector in a M dimensional linear vector space. Isolated thermodynamic systems fit this description [Schrödinger].

ASSUMPTION 1 (DEGENERATE TRANSITIONS): The state of the system $|\Phi\rangle$ changes due to a series of events, each event being a degenerate transition.

ASSUMPTION 2 (RANDOM MATRIX HYPOTHESIS): For each event the change in the state $|\Phi(i)\rangle$ is given by

$$|\Phi(i+1)\rangle = \exp(-i A_i) |\Phi(i)\rangle, \quad (5)$$

where A_i is a random $M \times M$ Hermitian matrix, $|\Phi(i)\rangle$ is the state of the system before event i and $|\Phi(i+1)\rangle$ is its state after the event. Further, the matrices A_i and A_j commute for all i and j .

Because A_i is a random matrix a system can evolve along many different paths.

The change in state along a single path j due to n consecutive events is given by

$$|\Phi_j(n)\rangle = \prod_{i=1}^n \exp(-i A_i^j) |\Phi(0)\rangle. \quad (6)$$

Rearranging gives

$$|\Phi_j(n)\rangle = \exp[-i \Omega_j(n)] |\Phi(0)\rangle, \quad (7)$$

where

$$\Omega_j(n) = \sum_{i=1}^n A_i^j. \quad (8)$$

ASSUMPTION 3 (SYSTEM PROPERTY): The statistical nature of the random matrix A_i and the relation between the number of events and the time is a system property.

MODEL SYSTEM: In this paper we only consider a system with the following simple statistical properties. This system is particularly important because we believe its dynamical behavior is a reasonable model for most real systems.

In the following we drop the index j used to denote a specific path unless needed for clarity.

MODEL SYSTEM ASSUMPTIONS:

- 1: The expected values for A_i and all its elements a_{kl} are zero.
- 2: The matrix A_i and all its elements are i.i.d.
- 3: All of the elements of A_i are uncorrelated.

A system can evolve along different paths due to the outcome of each event being given by a random variable.

- 4: The number of events along each path is approximately proportional to the time and the proportionality constant is approximately the same for all paths,

$$n_i \approx kt. \tag{9}$$

In the following for convenience we initially describe the state of the system at any time as a function of n , the number of events, where we have dropped the subscript as for any time the number of events is approximately the same for all paths.

ASSUMPTION 4 (PRINCIPLE OF SUPERPOSITION): For a model system the state of the system after n events $|\Psi(n)\rangle$ is given by taking the sum of the outcomes $|\Phi_j(n)\rangle$ over all possible paths,

$$|\Psi(n)\rangle = \sum_j |\Phi_j(n)\rangle. \tag{10}$$

III. FRACTIONAL TIME EVOLUTION OPERATOR

In this section we derive the operator that gives the change in the state of a model system as a function of time.

By Eq. (8) an element of $\Omega(n)$, $\omega_{kl}(n)$, is

$$\omega_{kl}(n) = \sum_{i=1}^n a_{kl}(i). \tag{11}$$

Let

$$\sigma_{kl} = \text{Var}(a_{kl}). \tag{12}$$

By the central limit theorem and using model system Assumptions 1 through 3, we obtain the distribution

$$\sqrt{n} \left(\frac{\omega_{kl}(n)}{n} \right) \stackrel{d}{=} \sigma_{kl} N(0,1) \quad n \rightarrow \infty, \tag{13}$$

where $N(0,1)$ is the normal distribution. In practice Eq. (13) holds for relatively small values of n . Taking it to hold for all but the smallest values of n , and rearranging gives the distribution

$$\omega_{kl}(n) \stackrel{d}{=} n^{1/2} \sigma_{kl} N(0,1), \tag{14}$$

which has an expectation value of

$$\mathbf{E}(\omega_{kl}(n)) = n^{1/2} \sigma_{kl}. \tag{15}$$

As A_i is a Hermitian matrix, the distribution of ω_{kl} equals ω_{lk}^* , and $\Omega(n)$ is a random Hermitian matrix.

Let Σ be a $M \times M$ matrix whose elements are σ_{kl} and $\Upsilon(0, \Sigma)$ be a $M \times M$ matrix whose elements are $\sigma_{kl} N(0, 1)$. From the definition of $\Omega(n)$ and Eqs. (14) and (15) we obtain

$$\Omega(n) \stackrel{d}{=} n^{1/2} \Upsilon(0, \Sigma), \quad (16)$$

and

$$\mathbf{E}(\Omega(n)) = n^{1/2} \Sigma. \quad (17)$$

Combining Eqs. (7) and (16) yields the distribution

$$|\Phi(n)\rangle \stackrel{d}{=} \exp(-i n^{1/2} \Upsilon(0, \Sigma)) |\Phi(0)\rangle, \quad (18)$$

and combining Eqs. (7) and Eq. (17) yields the expectation vector

$$\mathbf{E}|\Phi(n)\rangle = \exp(-i n^{1/2} \Sigma) |\Phi(0)\rangle. \quad (19)$$

The final state for each path $|\Phi^j(n)\rangle$ is a vector in a M dimensional linear vector space. The matrix A_i determines the rotation of the state vector for an event and $\Omega_i(n)$ determines the rotation along a single path after n events. The distribution of the sum $\Omega(n)$ represents the distribution of rotations after n events.

We add the contribution from all possible paths: because the normal distribution is symmetric, the unit vectors for all paths are distributed symmetrically about the expectation vector $\mathbf{E}|\Phi(n)\rangle$. As such they can be divided into pairs, each pair consisting of a vector and its mirror image taken about the expectation vector.

We add the two vectors in a pair. The components perpendicular to the expectation vector cancel. The components parallel to the expectation vector add to form a vector coincident with the expectation vector. Doing this for all pairs, and adding the resulting vectors yields a vector coincident with the expectation vector. As the state of the system is determined by the direction and not the length of a vector, the expectation vector can be taken as the vector representing the state of the system.

Using Eqs. (10) and (19) we can write for the state of the system $|\Psi(n)\rangle$,

$$|\Psi(n)\rangle = \exp(-i n^{1/2} \Sigma) |\Psi(0)\rangle, \quad (20)$$

where we have also used the identity $|\Psi(0)\rangle = |\Phi(0)\rangle$.

Using the relation between events and time [Eq. (9)] we obtain

$$|\Psi(t)\rangle = \exp(-i G t^{1/2}) |\Psi(0)\rangle, \quad (21)$$

where G is a Hermitian matrix proportional to Σ and scaled so as to make Eq. (21) an equality. This can be rewritten as

$$|\Psi(t)\rangle = V(t, 0) |\Psi(0)\rangle \quad (22)$$

where

$$V = \exp(-i G(t - t_0)^{1/2}). \quad (23)$$

We call V the fractional time evolution operator. As covered below, it leads to the principle of detailed balance, the master equation, and fluctuations.

IV. PROBABILITY-EVOLUTION EQUATION

A. Expansion coefficients

Consider an isolated system. For present purposes, the elements making up the system can be gas molecules, atoms in a crystal, modes of vibration, or any other collection of objects or elements that are normally the subject of thermodynamic analysis. For clarity, note we are considering only a single system and not an ensemble.

The allowed energies for an isolated system are quantized. The state ket $|\Psi\rangle$ of a single system whose energy is E can be expanded in terms of energy eigenkets $|i\rangle$ to give

$$|\Psi\rangle = \sum_i C_i |i\rangle \quad (i=1, M), \quad (24)$$

where M is the degree of degeneracy and $C_i = \langle i|\Psi\rangle$ is an expansion coefficient. Eigenkets $|i\rangle$ that have eigenvalues other than E are not included in Eq. (24) as the values of their expansion coefficients C_i are zero. The system need not be at equilibrium.

Because of degeneracy, the expansion can be made using any one of an infinite number of sets of orthogonal energy eigenkets. In Sec. VI C we show that there is a unique set of kets that must be used as base kets in order to give the proper value for the equilibrium entropy. The base set must also be unique in order to give unique values for the time evolution of the probabilities that are defined below.

In the following all summations are taken from one to M for all indices unless otherwise indicated.

We will be interested in the following primarily with how the probabilities p_i change with time where

$$p_i = C_i^* C_i, \quad (25)$$

and

$$\sum p_i = 1. \quad (26)$$

B. Rate of change of the state of the system

The expansion coefficients evolve according to

$$C_i(t) = \sum_j V_{ij} C_j(t_0). \quad (27)$$

Substituting Eq. (27) into Eq. (25) yields

$$p_i(t) = p_i^m(t) + p_i^f(t), \quad (28)$$

where

$$p_i^m(t) = \sum_j V_{ij}^*(t, t_0) V_{ij}(t, t_0) p_j(t_0), \quad (29)$$

and

$$p_i^f(t) = \sum_j \sum_{\substack{k \\ k \neq j}} V_{ik}^*(t, t_0) V_{ij}(t, t_0) C_k^*(t_0) C_j(t_0). \quad (30)$$

[Eqs. (28) through (30) are given by Tolman [12] with V replaced by the standard time evolution operator.]

We call Eq. (28) the probability-evolution equation. Its first term, given by Eq. (29), leads to the master equation as we show in Sec. VI. We examine in Sec. VII its second term, given by Eq. (30), and show that it represents fluctuations.

V. TRANSITION PROBABILITIES AND PRINCIPLE OF DETAILED BALANCE

In this section, we examine properties of V and develop relations we will need later. One of those relations is the principle of detailed balance.

Starting with Eq. (23), expanding the exponential, retaining terms through the second order (terms in $\Delta t^{1/2}$ are first order), setting

$$F = G^2 \quad (31)$$

and

$$\Delta t = (t - t_0), \quad (32)$$

we obtain

$$V = 1 - iG\Delta t^{1/2} - \frac{F}{2}\Delta t, \quad (33)$$

and

$$V_{ij} = \delta_{ij} - iG_{ij}\Delta t^{1/2} - \frac{F_{ij}}{2}\Delta t. \quad (34)$$

Multiplying V_{ij} by its complex conjugate and retaining only terms through second order (first order terms cancel) gives

$$V_{ij}^*V_{ij} = \delta_{ij} + G_{ij}^*G_{ij}\Delta t - \delta_{ij} \left[(F_{ij}^* + F_{ij})/2 \right] \Delta t. \quad (35)$$

Defining

$$W_{ij} = G_{ij}^*G_{ij} - \delta_{ij} \left[(F_{ij}^* + F_{ij})/2 \right] \quad (36)$$

permits us to rewrite Eq. (35) as

$$V_{ij}^*V_{ij} = \delta_{ij} + W_{ij}\Delta t. \quad (37)$$

From the definition given in Eq. (31), $F_{ij} = \sum_k G_{ik}G_{kj}$. Taking its complex conjugate and noting that G is Hermitian, we obtain $F_{ji}^* = F_{ij}$. Using Eq. (36) and applying the Hermitian property of G again gives

$$W_{ij} = W_{ji}, \quad (38)$$

and $W_{ij} \geq 0$ for $i \neq j$.

Because V is unitary

$$\sum_j V_{kj}^*V_{ij} = \delta_{ki}. \quad (39)$$

Substituting Eq. (37) and rearranging yields for $k = i$

$$W_{ii} = -\sum_{j, j \neq i} W_{ij}. \quad (40)$$

We need to include the second order term $(F_{ij}/2)\Delta t$ in Eq. (34) for otherwise we would have had a contradiction. Without the second order term in Eq. (36) we would

have had $W_{ii} = G_{ii}^* G_{ii}$, a positive number. On the other hand, W_{ii} would be negative by Eq. (40) because all the W_{ij} 's on the right-hand side are greater than or equal to zero. This problem is eliminated by including the second order term in Eq. (34).

Unitary operators have the property that $AA^\dagger = 1$. Direct substitution of $G^\dagger = G$ into Eq. (31) gives $F^\dagger = F$. Using Eq. (33) yields on retaining only terms through second order (first order terms cancel)

$$V^\dagger V = 1 + G^\dagger G \Delta t - F \Delta t. \quad (41)$$

On using the Hermitian properties of G , the right-hand side of Eq. (41) reduces to unity even when Δt is not infinitesimal. Eq. (41) is an exact relation. Had we carried through higher order terms in Δt when performing this derivation we would have concluded that the higher order terms must sum to zero.

The relation $W_{ij} = W_{ji}$ [Eq. (38)] is the principle of detailed balance. (We will see this more clearly when we derive the master equation in Sec. VI A.) It flows here from the assumptions and the requirement that V is unitary and G Hermitian.

VI. MASTER EQUATION AND THE ENTROPY

A. Master equation

On substituting Eq. (37) into Eq. (29), taking the limit as set out below, and as any time can be taken as t_0 , we obtain the master equation

$$\frac{dp_i^m}{dt} = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} (p_i^m(t) - p_i^m(t_0)) = \sum_j W_{ij} p_j. \quad (42)$$

Using Eq. (40), Eq. (42) becomes on rearranging

$$\frac{dp_i^m}{dt} = \sum_j W_{ij} (p_j - p_i), \quad (43)$$

where we have dropped the requirement that $j \neq i$ as $W_{ii}(p_i - p_i) = 0$. Below we use the term ‘‘master equation’’ to refer to Eq. (43).

B. Equilibrium

We take

$$\frac{dp_i^m}{dt} = 0 \quad (44)$$

as the definition of equilibrium. Using Eq. (43), Eq. (44) has the obvious solution $p_i = p_j$ for all i and j ; all p_i 's are thus equal at equilibrium.

As all the p_i 's are equal at equilibrium, are M in number, and sum to unity,

$$p_i = \frac{1}{M}. \quad (45)$$

C. Entropy and choice of base kets

We take

$$S = -k \sum p_i \ln p_i \quad (46)$$

as the definition of the entropy.

At equilibrium the entropy is given by

$$S = k \ln M, \quad (47)$$

obtained by substituting Eq. (45) into Eq. (46). Schrödinger [13] gives this same equation for the entropy as a function of the degree of degeneracy M . He pointed out that the degree of degeneracy is the number of different configurations over which the energy E can be distributed within the system and that Eq. (47) thus corresponds to the usual definition of the entropy.

As mentioned in Sec. IV A, any one of an infinite number of base ket sets can be used when expanding the state ket $|\Psi\rangle$. If we describe the state ket in terms of two different sets of base kets we would obtain two different sets of values for the probabilities p_i and thus the entropy. The rate of change of p_i , given by Eq. (43), would also be a function of the choice of base kets; no change would occur by Eq. (43), for example, if one chose a set of base kets such that all the p_i 's were equal. The value of the entropy and the rate of change in the state of the system must be independent of the choice of base kets. We conclude that there is only one set of base kets that is appropriate to use; it is the one that gives the right value for the entropy at equilibrium. At this point, though we know such a set of base kets exists, we do not have a prescription for how to choose it in advance.

D. Evolution of the entropy

Eq. (43) requires that the difference between p_i and p_j decreases with time. Following the usual treatment, if one takes the derivative of Eq. (46) with respect to p_i , subject to the constraint that probability is preserved, one finds that the entropy increases as $|p_i - p_j|$ decreases and that the system evolves to the equilibrium state. At equilibrium Eq. (45) is satisfied and the system has the maximum possible entropy. Once equilibrium is reached the probabilities p_i and thus the entropy do not change with time; the master equation taken alone predicts a fluctuation free final state.

VII. FLUCTUATIONS

In this section, we examine the properties and consequences of the fluctuation term $p_i^f(t)$ given by Eq. (30).

A. Fractional differential form

Substituting Eq.(34) into Eq. (30) and dropping higher order terms yields

$$p_i^f(t, t_0) = \sum_j \sum_{\substack{k \\ k \neq j}} i(\delta_{ij} G_{ik}^* - \delta_{ik} G_{ij}) C_k^*(t_0) C_j(t_0) \Delta t^{1/2}. \quad (48)$$

By grouping terms in Eq. (48) into pairs, it can be rewritten as

$$p_i^f = (i\Delta t^{1/2}) \sum_{l \neq i} B_{il}, \quad (49)$$

where

$$B_{il} = G_{il}^* C_l^* C_i - G_{il} C_i^* C_l. \quad (50)$$

Following Zaslavsky [14, 15], or Kolwankar and Gangal [16] in their derivations of the fractional Fokker-Plank-Kolmogorov equation, we can write

$$\frac{d^{1/2}}{dt^{1/2}} p_i^f(t_0) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t^{1/2}} [p_i^f(t) - p_i^f(t_0)]. \quad (51)$$

Using Eq. (49), the condition that $p_i^f(t_0) = 0$, and as any time can be taken as t_0 , we obtain the fractional differential equation

$$\frac{d^{1/2}}{dt^{1/2}} p_i^f(t) = i \sum_{l \neq i} B_{il}. \quad (52)$$

Fractional differential equations governing the time evolution of a variety of physical phenomena are known in physics Ref. [17, 18]. We are unaware of any equations exactly like Eq. (52). However, in general, fractional differential equations describe processes that are non-linear and non-differentiable. They are associated with fractals and continuous time random walks. The fractional differential form of Eq. (52) suggests that p_i^f represents processes that have the characteristics associated with fluctuations. We pursue this further below.

B. Kinetic equations and transition probabilities

There is a significant difference between Eq. (52) and kinetic type equations. We illustrate this difference by comparing it to the master equation.

Using Eq. (50), we can rewrite Eq. (52) as

$$\frac{d^{1/2}}{dt^{1/2}} p_i^f = i \sum_{l \neq i} (G_{il}^* C_l^* C_i - G_{il} C_i^* C_l). \quad (53)$$

The master equation, Eq.(43), can be rewritten using Eq. (25) as

$$\frac{dp_i^m}{dt} = \sum_j W_{ij} (C_j^* C_j - C_i^* C_i). \quad (54)$$

We first state the obvious. In Eq. (54), the time derivative of the probability is equal to a linear function of probabilities each given by a product of the form $C_j^* C_j$ where the indices in each pair are the same. In Eq. (53), on the other hand, the fractional time derivative is equal to a linear function of $C_l^* C_i$'s, where the indices in each pair are different. The terms on the right hand side of Eq. (53), representing the state of the system, are not probabilities; they are probabilities in Eq. (54).

In kinetic type equations, such as the diffusion and master equations, changes in the variable representing the state of the system, such as p_i , are functions of variables of the same type. That is not so in the case of p_i^f .

The G_{il} 's are not transition probabilities. They are “transition amplitudes.” We cannot conceptually think of iB_{il} , given by Eq. (52), in terms of incoming and outgoing probability fluxes, in the same way that we can for the $W_{ij}(p_j - p_i)$ terms in the master equation.

C. Identification with fluctuations

We can write

$$iB_{il} = 2c_i c_l [-f_{il} \sin(\phi_i - \phi_l) + g_{il} \cos(\phi_i - \phi_l)], \quad (55)$$

where we have substituted

$$C_i = c_i \exp(i\phi_i) \quad (56)$$

and

$$G_{il} = f_{il} + ig_{il} \quad (57)$$

into Eq. (50). Using the above, Eq. (52) becomes

$$\frac{d^{1/2}}{dt^{1/2}} p_i^f = i \sum_{l \neq i} 2c_i c_l [-f_{il} \sin(\phi_i - \phi_l) + g_{il} \cos(\phi_i - \phi_l)]. \quad (58)$$

The processes described by Eq. (58) will cause a system at equilibrium to move away from equilibrium. Equilibrium is used here in the sense of that the system satisfies Eq. (45). For this to occur at least some of the terms $2c_i c_l [-f_{il} \sin(\phi_i - \phi_l) + g_{il} \cos(\phi_i - \phi_l)]$ given in Eq. (58) must be nonzero. At equilibrium, the probabilities given by Eq. (45) and hence the moduli of the C_i 's, and thus the c_i 's, are all equal and nonzero. Because the G_{il} 's are constants, the f_{il} 's and g_{il} 's are constants (most but not all may be zero, as some must be nonzero for the system to attain equilibrium). Irrespective of the value of $(\phi_i - \phi_l)$, the term in brackets in Eq. (58) will be non zero as long as either f_{il} or g_{il} or both are nonzero. (There is an exception, when $\tan(\phi_i - \phi_l) = g_{il}/f_{il}$, the term in brackets is zero. This is unlikely. Further, $(\phi_i - \phi_l)$ will change with time due to the operation of V on $|\Psi\rangle$.) As at least some of the terms in the sum in Eq. (58) are nonzero, p_i and all of the other probabilities will spontaneously change and the system will move away from equilibrium.

Any movement away from equilibrium will be counteracted by the processes described by the master equation, which bring the system back towards equilibrium. The rate at which the system is brought back towards equilibrium increases with the deviation from equilibrium. The net result is that the system will fluctuate about equilibrium.

The behavior represented by Eq. (58) is quite different from that given by kinetic equations. Kinetic equations take a system towards equilibrium; the fluctuation term p_i^f represents processes that take a system away from equilibrium.

We conclude that p_i^f causes fluctuations.

Though we have only considered the properties of p_i^f in the vicinity of the equilibrium state, we would expect that it also would cause fluctuations about the path a system takes towards its final state.

D. Final state

The picture presented above is that of an isolated system evolving to a final state wherein it fluctuates about equilibrium. The final state is thus one of constant motion where the system occupies a region centered on the equilibrium condition defined by Eq. (45). In this picture, the entropy of the system at any one time is close to, but rarely if ever attains, the value given by Eq. (47). This picture is in accord with how we view, say, the behavior of molecules confined to a box or more generally the behavior of any thermodynamic system.

The probability-evolution equation, Eq. (28), thus predicts the existence of a more realistic final state than the one predicted by the master equation alone.

VIII. COMMENTS ON RANDOMNESS ASSUMPTION

An approach to non-equilibrium statistical mechanics is to start with the microscopic equations of motion, make a randomness assumption and from this derive the master equation, Ref. [19, 20]. Though making this type of assumption has a long and distinguished pedigree going back to Boltzmann, it is not justified by the equations of motion, either classical or quantum. We believe that there is a physical basis for making this assumption [21].

In Ref. [21] we used a conceptual experiment to show that under certain circumstances time reversal symmetry does not hold. This is ascribed to a system whose state is made up of multiple components randomly taking on one of those component states due to an interaction. The time evolution of this event can be represented by the change in the state of the system $|\Phi\rangle$ being given by an equation of the form

$$|\Phi_{i+1}\rangle = {}^R U |\Phi_i\rangle, \quad (59)$$

where ${}^R U$ is a random unitary matrix. That is under certain circumstances randomness is included in the basic quantum equations of motion.

In this paper we take Eq. (59) as our starting point and assume that it has the functional form given by Eq. (1) and in Sec. II make further assumptions as to its statistical properties.

IX. CONCLUDING REMARKS

We investigated the consequences of describing changes in isolated thermodynamic systems as a series of random events and then using the principle of superposition taking the change in the state of the system after many events as the sum of the outcomes over all possible paths. When making particularly simple assumptions as to the statistical nature of the random events, we found that the system evolves according to the master equation, upon which are superimposed fluctuations. In addition, the transition probabilities in the master equation satisfy the principle of detailed balance. We showed that the final state is one where the system fluctuates about equilibrium; this is a more realistic description of how thermodynamic systems behave than one based on the master equation alone. The sum over paths assumption was needed to ensure that the second law

of thermodynamics is not violated by a system whose evolution is governed by a series of random events. Our approach presents a level of compactness and parsimony not found in other treatments of this subject. There separate theories are used to develop the master equation, the principle of detailed balance and fluctuations, each with its own methodology, assumptions and approximations.

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APPENDIX

A simple generalization increases the range of dynamic behavior that can be described by fractional time evolution operators. We assume there exists a fractional time evolution operator of the more general form

$$V(t, t_0) = \exp(-iG(t-t_0)^{\beta/2}), \quad (\text{A1})$$

where β can have a value other than unity. The derivations given above remain unchanged other than as required by replacing $1/2$ with $\beta/2$. The probability evolution equation [Eq.(28)] remains unchanged. We obtain a fractional master equation,

$$\frac{d^\beta p_i^m}{dt^\beta} = \sum_j W_{ij} (p_j - p_i) \quad (\text{A2})$$

and the principle of detailed balance, $W_{ij} = W_{ji}$. The fractional master equation leads to the usual equilibrium entropy, $S = k \ln M$. Finally the fractional differential equations given in Sec. VII that are used to describe fluctuations are modified with

$$\frac{d^{\beta/2}}{dt^{\beta/2}} \text{ replacing } \frac{d^{1/2}}{dt^{1/2}}.$$

Eq. (53) becomes, for example,

$$\frac{d^{\beta/2}}{dt^{\beta/2}} p_i^f = i \sum_{l \neq i} (G_{il}^* C_l^* C_i - G_{il} C_i^* C_l). \quad (\text{A3})$$

A simplification occurs when the G operator and all the expansion coefficients C_i are real; then the fluctuation terms disappear, as can be seen on examining Eq. (A3). In this case some of the equations, such as Eq. (36), have a particularly simple form allowing one to calculate G_{ij} if W_{ij} is known.

Examples of systems whose dynamics are described by the fractional master equation and the related fractional Fokker-Plank equation can be found in Ref. [15, 22, 23]. As shown in the references, the fractional master equation and related equations lead to different dynamics than the conventional master equation. Care must be exercised in drawing conclusions from the similarity between Eq. (A2) and the functionally similar

equations found in the literature, particularly for thermodynamic systems; the method used to describe the state of a system there can differ from that used here.

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