

From Classical Dynamics to Continuous Time Random Walks

Robert Zwanzig¹

The migration of a classical dynamical system between regions of configuration space can be treated as a continuous time random walk between these regions. Derivation of a classical analog of the quantum mechanical generalized master equation provides expressions for the waiting time distribution in terms of transition memory functions. A short memory approximation to these memory functions is equivalent to the well-known transition state method. An example is discussed for which this approximation seems reasonable but is entirely wrong.

KEY WORDS: Classical dynamics; continuous time; random walks.

1. INTRODUCTION

A theory of the migration of a dynamical system between regions of configuration space may be of value in understanding the metastability of supercooled liquids. Under certain reasonable conditions, this migration is described by a generalized master equation, or equivalently, a continuous time random walk. The generalized master equation contains transition memory kernels, which are related to waiting time distributions. As usual, these kernels are given by formal expressions containing projected Liouville operators, and are not likely to be easily calculated. However, a short memory approximation to the transition memory kernels is easy to obtain, and is the classical analog of Eyring's "theory of absolute reaction rates," well known to physical chemists.

Much of the relevant theoretical work has already been done, in somewhat different form, in connection with chemical kinetics.⁽¹⁻⁴⁾ The

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¹ Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742.

connection between generalized master equations and continuous time random walks is well known.⁽⁵⁾ A recent review by Montroll and West⁽⁶⁾ describes in detail the general ideas of continuous time random walks, and gives many references.

Of particular interest is the short memory approximation to transition memory kernels, since this is likely to be all that one can calculate explicitly in most cases. Moreover, ad hoc attempts to model complex dynamical processes are usually based on a short memory approximation. This, however, may not always be safe: at the end of this article, an example is given in which the short memory approximation leads to quite erroneous results.

The first part of the article deals with the generalized master equation describing transitions between regions of configuration space. This is followed by a brief discussion of the corresponding continuous time random walk. Then the short memory approximation is presented. In the final section, a special dynamical model is discussed.

2. GENERALIZED MASTER EQUATION

The standard derivation of the quantum mechanical master equation is based on a projection of the quantum mechanical Liouville equation onto the subspace of the probabilities of occupation of quantum states. The classical counterpart is a projection onto cells in phase space; the classical master equation determines the time evolution of the probability of finding a system in a certain cell in phase space.

In this article, we restrict attention to cells in configuration space rather than in the complete phase space.

The state of the system, i.e., a point in phase space, is denoted by X . The position in configuration space is Q . The motion of the system is governed by the Liouville operator L . The state at time t is given by $X(t) = \exp(tL)X$. Cells in configuration space are denoted by

$$\begin{aligned} S_\alpha(Q) &= 1 && \text{if } Q \text{ is in cell } \alpha \\ &= 0 && \text{otherwise} \end{aligned} \quad (1)$$

The cells do not overlap, and they span the complete configuration space,

$$\begin{aligned} S_\alpha(Q)S_\beta(Q) &= S_\alpha(Q)\delta_{\alpha\beta} \\ \sum_\alpha S_\alpha(Q) &= 1 && \text{for all } Q. \end{aligned} \quad (2)$$

Averages are taken with the phase space distribution function $f(X, t)$. The initial distribution is $f(X, 0)$, and the equilibrium distribution is $f_{\text{eq}}(X)$.

Time-dependent averages are denoted by

$$\langle A; t \rangle = \int dX A(X) f(X, t) \tag{3}$$

and equilibrium averages are denoted by $\langle A \rangle$, without any time variable. The average of the cell characteristic function $S_\alpha(Q)$ is the probability $P_\alpha(t)$ that the system is in cell α at time t ,

$$\langle S_\alpha(Q); t \rangle = P_\alpha(t) \tag{4}$$

These are the quantities of interest here. The equilibrium average and second moment are needed:

$$\langle S_\alpha(Q) \rangle = w_\alpha, \quad \langle S_\alpha(Q) S_\beta(Q) \rangle = w_\alpha \delta_{\alpha\beta} \tag{5}$$

Now we use the well-known Mori algorithm to find Langevin equations of motion for the set of observables $\{S_\alpha(Q)\}$. Since the application of this algorithm is straightforward, details are omitted. A compressed notation is used, and subscripts are left out. We need the inner product

$$(A, B) = \langle AB \rangle \tag{6}$$

and the projector

$$PB = (B, S) \cdot w^{-1} \cdot S \tag{7}$$

onto the subspace of linear combinations of the S 's. The systematic frequency $i\Omega = (LS, S) \cdot (S, S)^{-1}$ vanishes, because S depends on coordinates only, and LS is linear in momentum. The "random force" is

$$F_\alpha^\dagger(t) = \exp[t(1 - P)L](1 - P)LS_\alpha(Q) \tag{8}$$

Because $PLS = 0$, the terminal $(1 - P)$ may be replaced by 1. The transition memory kernel is

$$K_{\alpha\beta}(t) = (F_\alpha^\dagger(t), F_\beta^\dagger(0))/w_\beta = (\exp[t(1 - P)L]LS_\alpha, LS_\beta)/w_\beta \tag{9}$$

The generalized Langevin equation is

$$\frac{d}{dt} S_\alpha(t) = - \int_0^t dt' \sum_\beta K_{\alpha\beta}(t') S_\beta(t - t') + F_\alpha^\dagger(t) \tag{10}$$

This is still a formally exact result.

As is always so, this result is useful only when the "random force" term can be neglected. The usual argument is as follows: If the initial distribution deviates linearly from equilibrium in the dynamical variables of interest, the average of $F_\alpha^\dagger(t)$ is second order in deviations from equilibrium. Then the resulting averaged equation is valid for linear transport processes. In the present instance, we can be somewhat more general. Any function $G(S)$ of the S 's can be written as a linear combination of the S 's because

$S_\alpha S_\beta = S_\alpha \delta_{\alpha\beta}$. If the initial distribution has the form

$$f(X, 0) = f_{\text{eq}}(X)G(S) \quad (11)$$

then the average of the random force vanishes identically, and the generalized master equation for the occupation probabilities $P_\alpha(t)$ is simply

$$\frac{d}{dt} P_\alpha(t) = - \int_0^t dt' \sum_\beta K_{\alpha\beta}(t') P_\beta(t-t') \quad (12)$$

This choice of initial ensemble is a classical analog to the quantum mechanical choice of an initially diagonal density matrix.

3. THE WAITING TIME DISTRIBUTION

Since the main ideas of the theory of continuous time random walks were reviewed recently by Montroll and West,⁽⁶⁾ this section will contain only some necessary definitions and a statement of results.

Instead of talking about a random walker making sudden jumps between lattice sites, we speak of a dynamical system moving between cells in configuration space. The system remains in cell β for some length of time, and then suddenly leaves it for another cell α . The waiting time distribution for this transition is denoted by $\psi_{\alpha\beta}(t)$, so that $\psi_{\alpha\beta}(t) dt$ is the probability that the system makes its first move from cell β to cell α in the time interval $(t, t + dt)$. This is the fundamental quantity of CTRW theory. [This differs slightly in notation from the Montroll–West review. They use the same waiting time distribution $\psi(t)$ for each lattice site, and combine it with the transition rate $p_{\alpha\beta}$ for jumps between the sites β and α . Their quantity $\psi(t)p_{\alpha\beta}$ corresponds to our $\psi_{\alpha\beta}(t)$. It is easy to reconstruct their arguments using the more general $\psi_{\alpha\beta}(t)$].

When the waiting time distribution is given for all pairs of cells, and the initial probabilities $P_\alpha(0)$ are specified, then the distribution $P_\alpha(t)$ is fully determined at any later time. The result is given most simply using Laplace transforms. The transform variable is ϵ , and the transform of any function $f(t)$ is $\hat{f}(\epsilon)$. The result, in a compressed notation, is

$$\hat{P}_\alpha = \frac{1}{\epsilon} \left[1 - \sum_\gamma \hat{\psi}_{\gamma\alpha} \right] \sum_\beta \left(\frac{1}{\epsilon - \hat{\psi}} \right)_{\alpha\beta} P_\beta(0) \quad (13)$$

But the generalized master equation provides another exact expression for the same quantity,

$$\hat{P}_\alpha = \sum_\beta \left(\frac{1}{\epsilon + \hat{K}} \right)_{\alpha\beta} P_\beta(0) \quad (14)$$

On comparing these two formulas, it is easy to extract a relation between

the waiting time distribution and the transition memory kernels,

$$\begin{aligned} \hat{\psi}_{\alpha\beta} &= \hat{K}_{\alpha\beta} / (\epsilon - \hat{K}_{\beta\beta}) \quad (\alpha \neq \beta) \\ \hat{\psi}_{\alpha\alpha} &= 0 \end{aligned} \tag{15}$$

A simple and well-known consequence is that if the transition memory kernels are independent of ϵ (the ‘‘Markoffian’’ approximation), then the waiting time distributions are exponentially damped in time, and vice versa.

In the present treatment of movement between cells in configuration space, just as in lattice random walks, there is no technical advantage in the CTRW language (although there is often a pictorial advantage). All correct statements are fully equivalent to correct statements in the GME language. The advantage of the GME approach is that it provides expressions for the transition memory kernels.

4. THE SHORT MEMORY APPROXIMATION

The short memory approximation to the transition memory kernels is easy to work out. We start by eliminating the projection from K , using a familiar procedure.^(7,8) The unprojected memory kernel is defined by

$$\lambda_{\alpha\beta}(t) = (\exp(tL)LS_{\alpha}, LS_{\beta}) / w_{\beta} \tag{16}$$

Then the Laplace transforms of K and λ are related by the matrix equation

$$\hat{K} = \epsilon \hat{\lambda} / (\epsilon - \hat{\lambda}) \tag{17}$$

In the short memory approximation, the complete memory kernel \hat{K} is replaced by its large ϵ limit, $\hat{K}(\infty)$. This is equivalent to approximating the time dependence of $K(t)$ by a delta function of time. In the large ϵ limit, Eq. (17) provides the relationship

$$\hat{K}(\infty) = \hat{\lambda}(\infty) \tag{18}$$

where $\hat{\lambda}(\infty)$ is the large ϵ limit of $\hat{\lambda}(\epsilon)$. Thus the short-time behavior of $K(t)$ is approximated by the short-time behavior of $\lambda(t)$. At long times, of course, the two functions may be quite different. In particular, the limit $\epsilon \rightarrow 0$ of $\hat{\lambda}$ must vanish, while the corresponding limit of \hat{K} need not vanish. In effect, the short-time behavior of $\lambda(t)$ is used to guess at the complete time behavior of $K(t)$.

The short-time behavior of $\lambda(t)$ can be found by a procedure that is essentially the same as in Ref. 1. First, we get an explicit expression for $LS_{\alpha}(Q) = (LQ) \cdot \Delta_Q S_{\alpha}(Q)$. The first factor, LQ , is the velocity J in configuration space. The second factor, $\nabla_Q S_{\alpha}(Q)$, vanishes everywhere except on the boundary B_{α} of the region α , where it has delta function

behavior. We define the outward normal to the surface B_α as $n(B_\alpha)$: then

$$\nabla_Q S_\alpha = -\oint dB_\alpha n(B_\alpha) \delta(Q - B_\alpha) \quad (19)$$

where the integral is taken over the whole surface of region α , and $\delta(Q - B)$ is a delta function in the full configuration space. The quantity $n(B_\alpha) \cdot J = J_n(B_\alpha)$ is the normal flux outward from the region. Thus we have

$$LS_\alpha = -\oint dB_\alpha J_n(B_\alpha) \delta(Q - B_\alpha) \quad (20)$$

Now the memory kernel can be written as

$$\begin{aligned} \lambda_{\alpha\beta}(t)w_\beta &= \langle LS_\beta \exp(tL) LS_\alpha \rangle \\ &= \left\langle \oint dB_\beta J_n(B_\beta) \oint dB_\alpha J_n(B_\alpha) \delta(Q - B_\beta) \delta(Q(t) - B_\alpha) \right\rangle \quad (21) \end{aligned}$$

For small t , we can expand $Q(t) = Q + tLQ + \dots = Q + tJ + \dots$. We put this into the second delta function and combine it with the first to get $\delta(Q - B_\beta) \delta(B_\beta - B_\alpha + tJ(B_\beta) + \dots)$. These are still delta functions in the full configuration space. We want to separate off a one-dimensional delta function in the direction normal to the boundary, leaving a $(N - 1)$ -dimensional delta function δ_\perp along the boundary. For small t , the important configurations are those for which $B_\alpha \cong B_\beta$. Let $(\alpha\beta)$ denote the common boundary of the region α and β . If B_α is close to B_β , the difference vector $\Delta B = B_\alpha - B_\beta$ is tangent to the common boundary $(\alpha\beta)$. Next, we separate J into its normal part $J \cdot n(B)$ and its tangential part ΔJ . Now we can separate the delta function,

$$\delta(B_\beta - B_\alpha + tJ) = \delta(tJ_n) \delta_\perp(t\Delta J - \Delta B) \quad (22)$$

The integration over B_β is restricted to the common boundary $(\alpha\beta)$ and the integration over B_α is replaced by integration over the small difference ΔB . The latter integration removes the $(N - 1)$ -dimensional delta function, leaving the short memory approximation

$$\lambda_{\alpha\beta}(t)w_\beta \cong \delta(t) \left\langle \oint_{(\alpha\beta)} dB |J_n(B)| \delta(Q - B) \right\rangle \quad (23)$$

Taking the Laplace transform removes $\delta(t)$ and introduces a factor $1/2$. In the short memory approximation for the transition memory kernel K , we use $\hat{K} \cong \hat{\lambda}$, so that (for $\alpha \neq \beta$)

$$\hat{K}_{\alpha\beta} \cong \frac{1}{2} \left\langle \oint_{(\alpha\beta)} dB |J_n(B)| \delta(Q - B) \right\rangle / w_\beta \quad (24)$$

This is the classical analog of Eyring's well-known transition state formula for the rate of passage from region β to region α . Note that it has the form of a probability of finding the system on the common boundary, times the normal flux across the boundary.

The short memory approximation completely ignores the possibility of a correlated later return to the same boundary. This is why it may fail in some cases. One hopes that the cells have been constructed “sensibly,” and that the dynamical behavior is “sufficiently complex,” so that once the system has entered a cell, it does not remember how it got there. If so, one then has a remarkably simple way to estimate the transition rates between cells.

5. A CAUTIONARY EXAMPLE

We conclude with a short discussion of a simple dynamical model for which the short memory approximation seems to be very reasonable but is wrong. A detailed analysis of the model will be presented elsewhere⁽⁹⁾; here, only one numerical result is described.

A single particle moves freely, except for elastic collisions, through a periodic linear array of rooms connected by windows; see Fig. 1. Each room has size 1×1 . The windows are symmetrically centered on the walls and have length W . The particle starts out with the vector velocity $v_x = 1$, $v_y = +V$. The basic time unit for motion in the x direction is $t = 1$. Whenever the particle collides with a wall, v_x changes sign and v_y stays constant. Whenever the particle arrives at a window, it moves into the adjoining room.

If the windows are fully closed, the particle rattles around in one room.

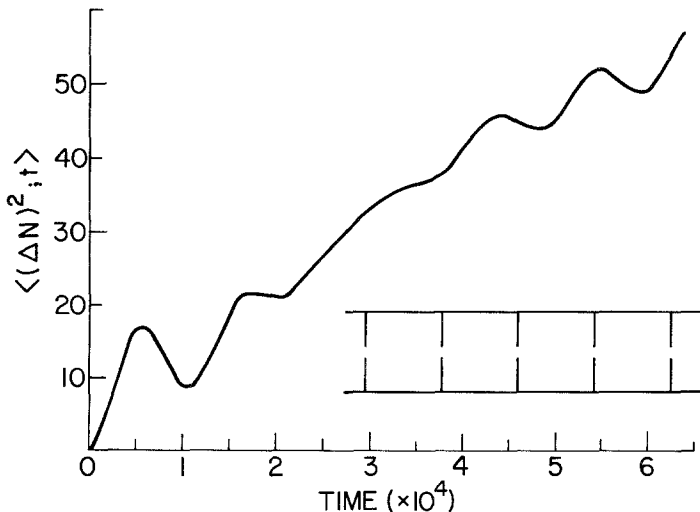


Fig. 1. The box model is illustrated. The curve is the mean squared displacement of the box number as a function of time, for $V = 0.397109$ and $W = 0.002$.

If V is a rational number, the orbit is periodic, but if V is irrational, the motion is ergodic; the trajectory ultimately fills the whole room.

Now suppose that the windows are open but that their size W is much smaller than 1. We expect, intuitively, that the particle makes very many randomizing bounces inside a room (if V is irrational) until it finds a window and moves to the next room, bounces again until another window is found, etc. This suggests that the motion between rooms is random or diffusive. In fact, the discussion just given of the short memory approximation to the transition rates between adjoining cells is very easy to apply to this model; the transition rate is $W/2$. Thus the mean squared displacement (in room numbers) should increase with time linearly as $\langle(\Delta N)^2\rangle = WT$.

But this is not what actually happens. Figure 1 shows a computer display of the mean squared displacement for the initial particle velocity $V = 0.397109$, and the window size $W = 0.002$. (The mean squared displacement is an average over the y component of the initial particle position. If the motion is ergodic, this is also a time average.) Because the computer does not recognize an irrational number, the motion is actually periodic. The computer run shown here extends to $t = 65000$, which is much shorter than the period. The initial slope of this curve is exactly what is predicted by the short memory approximation. Evidently this approximation is not valid here.

This peculiar behavior can be fully explained by a careful mathematical analysis of the model, which will be published elsewhere. It is associated with the Diophantine approximations to the irrational number V , $V_N = P_N/Q_N$ where P_N and Q_N are integers that increase very rapidly with the order of approximation N . In particular, the denominators play a central role in determining the dynamical behavior. At times $t = Q_N$, the particle "remembers" that V is almost rational.

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