1.2: Master Equations

Motivation and Derivation

The techniques developed in the basic theory of Markov processes are widely applicable, but there are of course many instances in which the discretization of time is either inconvenient or completely unphysical. In such instances, a master equation (more humbly referred to as a rate equation) may provide a continuous-time description of the system that is in keeping with all of our results about stochastic processes.

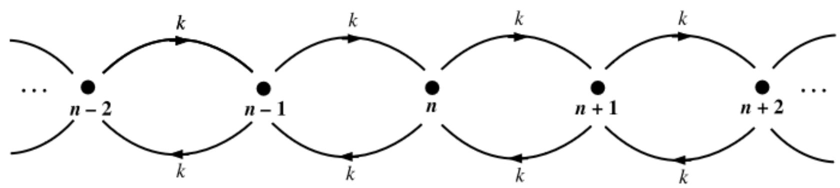

Figure 1.4: Infinite lattice with transition rate *[Math Processing Error]* between all contiguous states

Eq. *[Math Processing Error]* is a master equation. As the derivation suggests, *[Math Processing Error]* plays the role of a transition probability matrix in this formulation. You may notice that the master equation looks structurally very similar to rate equations in elementary kinetics; in fact, the master equation is a generalization of such rate equations, and the derivation above provides some formal justification for the rules we learn in kinetics for writing them down. The matrix *[Math Processing Error]* is analogous to the set of rate constants indicating the relative rates of reaction between species in the system, and the probabilities *[Math Processing Error]* are analogous to the relative concentrations of these species.

Example: Consider a random walk on a one-dimensional infinite lattice (see Figure 1.4). As indicated in the figure, the transition probability between a lattice point and either adjacent lattice point is *[Math Processing Error]*, and all other transition probabilities are zero (in other words, the system cannot "hop" over a lattice point without first occupying it). We can write down a master equation to describe the flow of probability among the lattice sites in a manner analogous to writing down a rate law. For any given site *[Math Processing Error]* on the lattice, probability can flow into *[Math Processing Error]* from either site *[Math Processing Error]* or site *[Math Processing Error]*, and both of these occur at rate *[Math Processing Error]*; likewise, probability can flow out of state *[Math Processing Error]* to either site *[Math Processing Error]* or site *[Math Processing Error]*, both of which also happen at rate *[Math Processing Error]*. Hence, the master equation for all sites *[Math Processing Error]* on the lattice is

[Math Processing Error]

Now we define the average site of occupation as a sum over all sites, weighted by the probability of occupation at each site,

[Math Processing Error]

Then we can compute, for example, how this average site evolves with time,

[Math Processing Error]

Hence the average site of occupation does not change over time in this model, so if we choose the initial distribution to satisfy *[Math Processing Error]*, then this will always be the average site of occupation.

However, the mean square displacement *[Math Processing Error]* is not constant; in keeping with our physical interpretation of the model, the mean square displacement increases with time. In particular,

[Math Processing Error]

If the initial probability distribution is a delta function on site *[Math Processing Error]*, then it turns out that Fourier analysis provides a route towards a closed-form expression for the long-time limit of *[Math Processing Error]* :

[Math Processing Error]

[Math Processing Error]

In the above manipulations, we have replaced *[Math Processing Error]* with the diffusion constant *[Math Processing Error]*, the long-time limit of the rate constant (in this case, the two are identical). Thus the probability distribution for occupying the various sites becomes Gaussian at long times.

Mean First Passage Time

One of the most useful quantities we can determine from the master equation for a random walk is the average time it takes for the random walk to reach a particular site *[Math Processing Error]* for the first time. This quantity, called the mean first passage time, can be determined via the following trick: we place an absorbing boundary condition at *[Math Processing Error]*. Whenever the walk reaches site *[Math Processing Error]*, it stays there for all later times. One then calculates the survival probability *[Math Processing Error]*, that is, the probability that the walker has not yet visited *[Math Processing Error]* at time *[Math Processing Error]*,

[Math Processing Error]

The mean first passage time *[Math Processing Error]* then corresponds to the time-averaged survival probability,

[Math Processing Error]

Sometimes it is more convenient to write the mean first passage time in terms of the probability density of reaching site *[Math Processing Error]* at time *[Math Processing Error]*. This quantity is denoted by *[Math Processing Error]* and satisfies

[Math Processing Error]

In terms of *[Math Processing Error]*, the mean first passage time is given by

[Math Processing Error]

The mean first passage time is a quantity of interest in a number of current research applications. Rates of fluorescence quenching, electron transfer, and exciton quenching can all be formulated in terms of the mean first passage time of a stochastic process.

Example: Let's calculate the mean first passage time of the three-site model introduced in Figure *[Math Processing Error]*, with all transition rates having the same value *[Math Processing Error]*. Suppose the system is prepared in state 1 , and we're interested in knowing the mean first passage time for site 3 . Applying the absorbing boundary condition at site 3 , we derive the following master equations:

[Math Processing Error]

The transition matrix *[Math Processing Error]* corresponding to this system would have a zero column since *[Math Processing Error]* does not occur on the right hand side of any of these equations; hence the sink leads to a zero eigenvalue that we can ignore. The relevant submatrix

[Math Processing Error]

has eigenvalues *[Math Processing Error]*. Using the spectral decomposition formula, we find that the survival probability is

[Math Processing Error]

Hence, the previously defined probability density *[Math Processing Error]* is given by *[Math Processing Error]*, and the mean first passage time for site 3 is

[Math Processing Error]
