

Effective transport properties of lattices

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Abstract

The method of multiple scales is used to calculate the effective macroscopic transport properties of a random walk on a periodic lattice with arbitrary, spatially-dependent transition rates. In contrast to the standard multiple-scales approach for continuous media, the fast scale here is discrete, and only the slow scale is continuous. The solution is found as the discrete probability distribution of finding the particle at a particular node in the unit cell, modulated by a continuous slow function of the position of the unit cell in the macroscopic material. This last function represents the macroscopic drift-diffusion of the particle, with drift and diffusion coefficients calculated in terms of the individual transition probabilities.

Keywords Homogenisation, random walk, diffusion, multiple scales, discrete.

AMS subject classifications 41A60, 60J27

1 Introduction

Many physically important problems in biology, fluid mechanics and solid-state physics involve transport in heterogeneous materials. Despite advances in computational efficiency, direct simulations of systems of composite materials that vary rapidly on the microscopic scale are often not feasible. In such cases, it is useful to approximate the composite medium with a homogeneous, effective medium that takes into account the variations on the micro-scale.

This idea is generally known as homogenization, and several techniques exist for determining these effective properties. All these approaches depend on a separation of scale, where the heterogeneities are fine relative to the global dimensions of the medium.

In a continuum description, a variety of perturbation methods may be used. A common approach is that of multi-scale homogenization via asymptotic expansions, as presented in the classical texts of Bensoussan et al. (1978); Sanchez-Palencia (1986). Writing the system as a function of both the microscopic and macroscopic length-scales, the governing equations are expanded asymptotically in powers of the ratio of these scales, denoted by ϵ . Making use of the periodicity of the microstructure, the leading-order behaviour of the system can be expressed in terms of an integral over the microscopic unit cell, which describes the geometry of the system. The approach may be

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thought of as a second-order perturbation theory (in contrast to averaging, which is a first-order theory) and is a form (or consequence) of the central limit theorem (Pavliotis and Stuart, 2008).

Most solids are crystalline, and what is often referred to as diffusion in such structures actually occurs by atomic hops in a lattice. There is a separation of time-scales between the elementary jump process of particles moving between neighbouring lattice sites and the succession of steps that lead to macroscopic diffusion (Mehrer, 2007). In fact, many properties of these two formulations (the jump process and diffusion) are equivalent on macroscopic length-scales or in the slow-time limit. However, this correspondence does not always hold, particularly when the quantities of interest depend on distances comparable to the lattice constant (Blumen and Zumofen, 1981). The asymptotic homogenization described above for continuum models is not directly applicable when the period of the microscopic variations is of the same order of magnitude as the lattice spacing, and other techniques must be used.

These limitations are often seen in solid state physics (Haus and Kehr, 1987) and lattice gas dynamics (Kutner, 1981). To overcome the continuum limitation, it is common to consider jump-diffusion processes of single particles on the microscopic scale as probabilistic random walks on an ordered lattice, or, in the case of a one-dimensional random walk, a periodic potential well (Zwenger and Kehr, 1980). In statistical mechanics, the Brownian motion of particles in a periodic potential well is described by Langevin equations. Using linear response theory, it is possible to derive the Kubo-Green relation relating the diffusion coefficient to the velocity autocorrelation, or an ensemble average of the second moment. Typically, this approach only allows for the calculation of the effective diffusion coefficient in the over-damped limit, as this is the limit in which only single jumps occur. It has also been noted that the Kubo-Green formula is invalid when the probe size is of the order of the applicable scale length for the lattice gas (Uebing et al., 1996).

Effective medium approximations of continuous time random walks on a lattice have also been treated using a generating function approach by Montroll and Weiss (1965). These approaches make use of Lattice Green functions, constructed from discrete Fourier transforms of single-step transition probabilities, expressing the effective diffusion coefficient in terms of the zeroth and second moment of the hopping probability (Scher and Lax, 1973). A thorough description of this method, as well as related techniques, can be found in reviews by Bouchaud and Georges (1990); Havlin and Ben-Avraham (1987); Kehr et al. (1998). The Montroll-Weiss method was used by Kehr and Haus (1978) to determine the effective transport in a material with traps, such as charge transport in semiconductors and diffusion of particles in metals with defects, confirming an existing result of frequency-independent effective conductivity in an n -state trapping model originally proposed by Tunaley (1974). Later Braun and Sholl (1998), building on the work of Kutner and Sosnowska (1977); Kehr et al. (1978), developed method of determining effective diffusion coefficient, D , in arbitrary periodic lattice systems satisfying the detailed balance condition.

The general procedure, summarised in Braun and Sholl (1998); Koza (1999) is to split the single parameter indexing position in the lattice into two lattice parameters, one indexing position in the periodic cell, and one indexing which unit cell the particle is in. Since the transition probabilities do not vary from one unit cell to another it is possible to take a discrete Fourier transform with respect to the second index. The drift and diffusion coefficients are then related to the first and second derivatives of this Fourier Transform with respect to wavenumber k . Expanding in powers of k reduces the infinite system to single elementary cell with periodic boundary conditions, for which steady state occupancy probabilities can be calculated.

In this paper we use an extension of the method of multiple scales to calculate the effective macroscopic transport properties of a random walk on periodic lattices with arbitrary, spatially-

dependent transition rates. The results we find are in some sense equivalent to those described above, but the calculations and physical interpretations are somewhat more straightforward. We do not make use of Laplace or discrete Fourier transforms, but work directly with the master equation. We will find simple conditions determining whether drift or diffusion is the dominant behaviour on the long time-scale. We present an exact analytic form of the partial differential equation governing the evolution of the system on the macro-scale, and then illustrate closed-form solutions for the special cases of source- and destination-dependent transition rates of a Markov process. Our approach is able to recover the effective diffusion coefficient of Kehr et al. (1978). In addition, we do not lose the microscopic information in the continuum limit, since the solution we derive is a discrete probability density function on the periodic cell modulated by the continuum effective diffusion.

2 A simple example

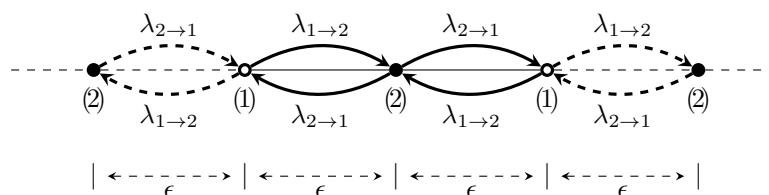


Figure 1: One-step transition for a one-dimensional, periodic Markov chain consisting of two distinct node types, separated by distance ϵ .

To illustrate the general approach, we start by considering the simplest possible case. Consider a one-dimensional Markov chain, consisting of two distinct types of node each separated by a distance ϵ , arranged in a periodic, alternating manner (see Fig. 1). A particle at a node of type 1 has a transition rate $\lambda_{1 \rightarrow 2}$ to each neighbouring node (of type 2), while a particle at a node of type 2 has a transition rate $\lambda_{2 \rightarrow 1}$ to each neighbouring node (of type 1). Let $p_n(t)$ be the probability of finding a particle at node n at time t . The continuous-time master equation for $p_n(t)$ is

$$\frac{\partial p_n}{\partial t} = \lambda_{(n-1) \rightarrow n} p_{n-1} + \lambda_{(n+1) \rightarrow n} p_{n+1} - (\lambda_{n \rightarrow (n+1)} + \lambda_{n \rightarrow (n-1)}) p_n \quad (1)$$

where $\lambda_{n \rightarrow (n+1)}$ is the hopping rate from node n to node $n+1$, so that

$$\lambda_{n \rightarrow (n+1)} = \begin{cases} \lambda_{1 \rightarrow 2} & \text{if } n \text{ is odd,} \\ \lambda_{2 \rightarrow 1} & \text{if } n \text{ is even,} \end{cases}$$

We define the spatial coordinate $x = n\epsilon$. We aim to perform a multiple scales analysis in the limit $\epsilon \rightarrow 0$. In the standard multiple scales technique, the fast scale X and the slow scale $x = \epsilon X$ are supposed independent. The extra freedom this gives is used to impose periodicity on the fast scale, so that the deviation of the actual solution from being periodic results in a modulation or drift on the slow scale.

Here, in contrast to the standard approach, our fast scale will be discrete, and only the slow scale will be continuous. We write $p_n(t) = P_n(x, t)$, so that the probability of finding a particle at

a particular node is a function of both the fast index n and the slow scale x . As is standard in multiple scales analyses, we then treat these as independent variables. The resulting degeneracy is removed by imposing exact periodicity in n , leading to a modulation on the slow scale. Thus n can be thought of as indexing position within the unit cell, and x can be thought of as determining which unit cell the particle is in.

Writing (1) in terms of $P_n(x, t)$ gives

$$\frac{\partial P_n}{\partial t}(x, t) = \lambda_{(n-1) \rightarrow n} P_{n-1}(x - \epsilon, t) + \lambda_{(n+1) \rightarrow n} P_{n+1}(x + \epsilon, t) - (\lambda_{n \rightarrow (n+1)} + \lambda_{n \rightarrow (n-1)}) P_n(x, t).$$

Since there are only two nodes in the unit cell in our simple example, $P_n(x, t)$ is periodic in n with period 2, and this reduces to the pair of equations

$$\begin{aligned} \frac{\partial P_1}{\partial t}(x, t) &= \lambda_{2 \rightarrow 1} P_2(x - \epsilon, t) + \lambda_{2 \rightarrow 1} P_2(x + \epsilon, t) - 2\lambda_{1 \rightarrow 2} P_1(x, t), \\ \frac{\partial P_2}{\partial t}(x, t) &= \lambda_{1 \rightarrow 2} P_1(x - \epsilon, t) + \lambda_{1 \rightarrow 2} P_1(x + \epsilon, t) - 2\lambda_{2 \rightarrow 1} P_2(x, t), \end{aligned}$$

where $P_1(x, t)$ (respectively $P_2(x, t)$) is the probability of being in a node of type 1 (respectively type 2) at position x and time t .

Taylor expanding about the position x gives

$$\frac{\partial \mathbf{P}}{\partial t} = A\mathbf{P} + \epsilon^2 C \frac{\partial^2 \mathbf{P}}{\partial x^2} + O(\epsilon^3), \quad (2)$$

where

$$\mathbf{P} = \begin{bmatrix} P_1(x, t) \\ P_2(x, t) \end{bmatrix}, \quad A = \begin{bmatrix} -2\lambda_{1 \rightarrow 2} & 2\lambda_{2 \rightarrow 1} \\ 2\lambda_{1 \rightarrow 2} & -2\lambda_{2 \rightarrow 1} \end{bmatrix}, \quad C = \begin{bmatrix} 0 & \lambda_{2 \rightarrow 1} \\ \lambda_{1 \rightarrow 2} & 0 \end{bmatrix}.$$

Now we expand \mathbf{P} in powers of ϵ as

$$\mathbf{P}(x, t) = \mathbf{P}^{(0)}(x, t) + \epsilon \mathbf{P}^{(1)}(x, t) + \epsilon^2 \mathbf{P}^{(2)}(x, t) + \dots \quad (3)$$

(where in fact we expect $\mathbf{P}^{(1)}$ to be zero since there are no terms proportional to ϵ in (2)). At leading order this gives

$$\frac{\partial \mathbf{P}^{(0)}}{\partial t} = A\mathbf{P}^{(0)},$$

with solution

$$\mathbf{P}^{(0)} = a_1 e^{\mu_1 t} \mathbf{u}_1 + a_2 e^{\mu_2 t} \mathbf{u}_2,$$

where μ_1 and μ_2 are the eigenvalues of A with corresponding eigenvectors \mathbf{u}_1 and \mathbf{u}_2 , and a_1, a_2 are constant in time but may depend on the slow space scale x . In our example

$$\mu_1 = 0, \quad \mathbf{u}_1 = \begin{bmatrix} \frac{1}{\lambda_{1 \rightarrow 2}} \\ \frac{1}{\lambda_{2 \rightarrow 1}} \end{bmatrix}, \quad \mu_2 = -2(\lambda_{1 \rightarrow 2} + \lambda_{2 \rightarrow 1}), \quad \mathbf{u}_2 = \begin{bmatrix} 1 \\ -1 \end{bmatrix}.$$

We see that there is a zero eigenvalue, and that $\mathbf{P}^{(0)}$ evolves until it lies parallel to the corresponding eigenvector, which is the stationary distribution. Since A is a transition matrix this will always be the case.

We have described the evolution of \mathbf{P} on a short timescale. More interesting is the long time dynamics in which the diffusion becomes apparent. To investigate this we switch now to a long timescale by rescaling time as $t = \epsilon^{-2}\hat{t}$ to give

$$\epsilon^2 \frac{\partial \mathbf{P}}{\partial \hat{t}} = A\mathbf{P} + \epsilon^2 C \frac{\partial^2 \mathbf{P}}{\partial x^2} + O(\epsilon^3). \quad (4)$$

Again expanding \mathbf{P} in powers of ϵ we find now at leading order that

$$A\mathbf{P}^{(0)} = \mathbf{0}. \quad (5)$$

Thus

$$\mathbf{P}^{(0)}(x, \hat{t}) = f(x, \hat{t})\mathbf{u}_1, \quad (6)$$

where \mathbf{u}_1 is as before, and the coefficient f may now depend on both the slow time \hat{t} and the slow space scale x .

Equating coefficients of ϵ^2 in (4) gives

$$A\mathbf{P}^{(2)} = \frac{\partial \mathbf{P}^{(0)}}{\partial \hat{t}} - C \frac{\partial^2 \mathbf{P}^{(0)}}{\partial x^2}. \quad (7)$$

Since A is singular, by the Fredholm Alternative there is a solution to (7) if and only if the right-hand side is orthogonal to the null space of A^T . This is spanned by

$$\mathbf{v} = \begin{bmatrix} 1 \\ 1 \end{bmatrix},$$

giving the solvability condition

$$\mathbf{v}^T \frac{\partial f}{\partial \hat{t}} \mathbf{u}_1 = \mathbf{v}^T C \frac{\partial^2}{\partial x^2} (f \mathbf{u}_1). \quad (8)$$

Evaluating gives the governing equation for the slowly varying amplitude $f(x, \hat{t})$ as

$$\frac{\partial f}{\partial \hat{t}} = D \frac{\partial^2 f}{\partial x^2}, \quad (9)$$

where the diffusion coefficient

$$D = \frac{2}{\frac{1}{\lambda_{1 \rightarrow 2}} + \frac{1}{\lambda_{2 \rightarrow 1}}}, \quad \text{i.e.} \quad \frac{1}{D} = \frac{1}{2} \left(\frac{1}{\lambda_{1 \rightarrow 2}} + \frac{1}{\lambda_{2 \rightarrow 1}} \right). \quad (10)$$

3 Generalisations

3.1 N -node case in one dimension

We now consider the general case of a one-dimensional Markov chain consisting of an N -node unit period (Figure 2), of which the illustrative example from Section 2 is a special case. For $N > 2$, the transition rates left and right are not necessarily equal, allowing for drift-dominant behaviour on the macroscopic scale.

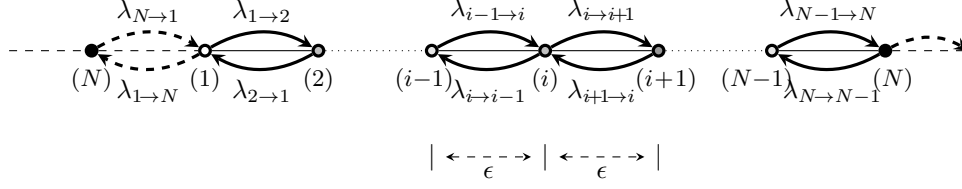


Figure 2: One-step transition for a one-dimensional, periodic Markov chain consisting of N distinct node types, separated by distance ϵ .

Introducing circular indexing notation $\overline{i \pm 1} \equiv (i \pm 1 - 1 \bmod N) + 1$ to denote nodes adjacent to index $i \in [1, N]$, the probability of being in state i at position x and time t satisfies the master equation

$$\frac{\partial P_i}{\partial t}(x, t) = \lambda_{\overline{i-1} \rightarrow i} P_{\overline{i-1}}(x - \epsilon, t) + \lambda_{i+1 \rightarrow i} P_{i+1}(x + \epsilon, t) - (\lambda_{i \rightarrow \overline{i-1}} + \lambda_{i \rightarrow i+1}) P_i(x, t). \quad (11)$$

Taylor expanding about x we find

$$\frac{\partial \mathbf{P}}{\partial t} = \mathbf{A} \mathbf{P} + \epsilon \mathbf{B} \frac{\partial \mathbf{P}}{\partial x} + \epsilon^2 \mathbf{C} \frac{\partial^2 \mathbf{P}}{\partial x^2} + O(\epsilon^3), \quad (12)$$

where $\mathbf{P} = [P_1 \ \cdots \ P_N]^T$ and the matrices \mathbf{A} , \mathbf{B} and \mathbf{C} are $N \times N$ tridiagonal matrices with corners, and can be written as

$$\begin{aligned} \mathbf{A} &= M_N \text{diag}(\lambda_{i \rightarrow \overline{i+1}}) - \text{diag}(\lambda_{i \rightarrow \overline{i-1}} + \lambda_{i \rightarrow i+1}) + M_N^T \text{diag}(\lambda_{i \rightarrow \overline{i-1}}), \\ \mathbf{B} &= -M_N \text{diag}(\lambda_{i \rightarrow \overline{i+1}}) + M_N^T \text{diag}(\lambda_{i \rightarrow \overline{i-1}}), \\ \mathbf{C} &= \frac{1}{2} (M_N \text{diag}(\lambda_{i \rightarrow \overline{i+1}}) + M_N^T \text{diag}(\lambda_{i \rightarrow \overline{i-1}})), \end{aligned} \quad (13)$$

where

$$M_N = \left[\begin{array}{c|c} 0 & 1 \\ \hline \mathbf{I}_{N-1} & 0 \end{array} \right]$$

is the $N \times N$ cyclic permutation matrix.

As in Section 2, the transition matrix \mathbf{A} is singular, as conservation of probability implies that each column sums to zero for any choice of $\lambda_{j \rightarrow i}$. From this, we see that the left-eigenvector associated to the zero eigenvalue is $\mathbf{v}^T = \mathbf{1}_{1 \times N}$. We assume that the dimension of the null space is 1 (that is, that the continuous time Markov chain corresponding to the transition matrix \mathbf{A} is irreducible), so that \mathbf{v} is the generator of the null space of \mathbf{A}^T . This will be the case whenever the λ are such that there is a path of nonzero transition rates from any node to any other node.

As in Section 2, there is a fast timescale on which \mathbf{P} becomes aligned with the stationary distribution associated with \mathbf{A} . We are interested in the behaviour on a longer timescale. However, in contrast to the simple example in Section 2, the drift matrix \mathbf{B} is not zero in general. Thus we have a choice of slow timescales: the drift timescale $t = O(\epsilon^{-1})$, and the diffusion timescale $t = O(\epsilon^{-2})$. We begin by assuming that the drift terms are nonzero, thereby rescaling time as $t = \epsilon^{-1} \tilde{t}$. If it turns out that the drift is zero, we will then rescale onto the diffusion time.

Expanding \mathbf{P} in terms of the small parameter ϵ as

$$\mathbf{P} = \mathbf{P}^{(0)} + \epsilon \mathbf{P}^{(1)} + \epsilon^2 \mathbf{P}^{(2)} + O(\epsilon^3), \quad (14)$$

and equating coefficients of powers of ϵ we find at leading order that

$$A\mathbf{P}^{(0)} = 0. \quad (15)$$

Thus

$$\mathbf{P}^{(0)}(x, \tilde{t}) = f(x, \tilde{t})\mathbf{u}, \quad (16)$$

where \mathbf{u} is the zero eigenvector of A , representing the stationary distribution on the fast-scale, and the coefficient $f(x, \tilde{t})$ varies slowly in space and time.

At $O(\epsilon)$ we find

$$A\mathbf{P}^{(1)} = \frac{\partial f}{\partial t}\mathbf{u} - B\frac{\partial}{\partial x}(f\mathbf{u}). \quad (17)$$

Since the matrix A is singular, by the Fredholm Alternative there is a solution only if the right-hand side is orthogonal to $\mathbf{v} = \mathbf{1}_{1 \times N}^T$, which spans the null space of A^T . This gives the solvability condition

$$\frac{\partial f}{\partial \tilde{t}} = \nu \frac{\partial f}{\partial x}, \quad (18)$$

where the drift coefficient, ν , is given by

$$\nu = \frac{\mathbf{v}^T B \mathbf{u}}{\mathbf{v}^T \mathbf{u}}. \quad (19)$$

If it happens that $\mathbf{v}^T B \mathbf{u} = 0$, so that $\nu = 0$, then there is no drift at this order and we should rescale onto the diffusion time by setting $t = \epsilon^{-2}\tilde{t}$. In that case we find at $O(\epsilon)$ that

$$A\mathbf{P}^{(1)} = -\frac{\partial f}{\partial x}B\mathbf{u}. \quad (20)$$

Then

$$\mathbf{P}^{(1)} = \frac{\partial f}{\partial x}\mathbf{p} + g\mathbf{u},$$

where \mathbf{p} is any solution to

$$A\mathbf{p} = -B\mathbf{u}$$

and the coefficient $g(x, \hat{t})$ may depend on slow space and time.

Then equating coefficients of ϵ^2 gives

$$\begin{aligned} A\mathbf{P}^{(2)} &= -B\frac{\partial \mathbf{P}^{(1)}}{\partial x} + \frac{\partial \mathbf{P}^{(0)}}{\partial \hat{t}} - C\frac{\partial^2 \mathbf{P}^{(0)}}{\partial x^2} \\ &= -B\frac{\partial^2 f}{\partial x^2}\mathbf{p} - B\frac{\partial g}{\partial x}\mathbf{u} + \frac{\partial f}{\partial \hat{t}}\mathbf{u} - C\frac{\partial^2 f}{\partial x^2}\mathbf{u}. \end{aligned}$$

Applying the Fredholm Alternative as usual gives the solvability condition

$$\mathbf{v}^T \frac{\partial f}{\partial \hat{t}} \mathbf{u} = \mathbf{v}^T B \frac{\partial^2 f}{\partial x^2} \mathbf{p} + \mathbf{v}^T C \frac{\partial^2 f}{\partial x^2} \mathbf{u}, \quad (21)$$

where we have used the fact that $\mathbf{v}^T B \mathbf{u} = 0$. Thus the amplitude f again satisfies the diffusion equation

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}, \quad (22)$$

with diffusion coefficient D given by

$$D = \frac{\mathbf{v}^T B \mathbf{p} + \mathbf{v}^T C \mathbf{u}}{\mathbf{v}^T \mathbf{u}}. \quad (23)$$

Looking at (12), it seems we can identify the first term in (23) with dispersion, and the second term with diffusion. However, we will see that the first term is in fact negative.

We note that with transition rates which are independent of ϵ we either have a drift-dominated problem or a drift-free problem. If the rates depend on ϵ it is of course possible to choose them in such a way that drift and diffusion balance each other in the continuum limit. The analysis is straightforward, so we do not present it.

3.2 Examples

3.2.1 Symmetric transition rates

Although we have an explicit formula for A in terms of $\lambda_{i \rightarrow j}$ in (13), the general solution for \mathbf{u} is too unwieldy to be useful. However, in the particular case in which the transitions are symmetric, so that $\lambda_{i \rightarrow j} = \lambda_{j \rightarrow i}$, we find A is symmetric and $\mathbf{u} = \mathbf{v} = \mathbf{1}_{N \times 1}$. Then $B \mathbf{u} = 0$ so that

$$D = \frac{\mathbf{v}^T C \mathbf{v}}{\mathbf{v}^T \mathbf{v}} = \frac{1}{n} \sum_{i=1}^n \lambda_{i \rightarrow i+1}.$$

Note that this is in agreement with (10) when $\lambda_{1 \rightarrow 2} = \lambda_{2 \rightarrow 1}$.

3.2.2 Nonsymmetric transition rates

We illustrate the importance of the first term in (23) with the following example. We choose a Markov chain with period 3, and transition rates

$$\lambda_{1 \rightarrow 2} = \frac{1}{4}, \quad \lambda_{2 \rightarrow 3} = 1, \quad \lambda_{3 \rightarrow 1} = 4, \quad \lambda_{1 \rightarrow 3} = 16, \quad \lambda_{2 \rightarrow 1} = \frac{1}{4}, \quad \lambda_{3 \rightarrow 2} = \frac{1}{4}. \quad (24)$$

Then

$$A = \begin{pmatrix} -\frac{65}{4} & \frac{1}{4} & 4 \\ \frac{1}{4} & -\frac{5}{4} & \frac{1}{4} \\ 16 & 1 & -\frac{17}{4} \end{pmatrix}, \quad B = \begin{pmatrix} 0 & \frac{1}{4} & -4 \\ -\frac{1}{4} & 0 & \frac{1}{4} \\ 16 & -1 & 0 \end{pmatrix}, \quad C = \begin{pmatrix} 0 & \frac{1}{8} & 2 \\ \frac{1}{8} & 0 & \frac{1}{8} \\ 8 & \frac{1}{2} & 0 \end{pmatrix}.$$

The stationary distribution is

$$\mathbf{u} = (1/6, 1/6, 2/3)^T$$

which is such that $\mathbf{v}^T B \mathbf{u} = 0$ so that there is no drift. However, $B \mathbf{u} = (-21/8, 1/8, 5/2)$ so that there is dispersion. The auxilliary vector $\mathbf{p} = (0, 37/162, 52/81)$ so that

$$\mathbf{v}^T B \mathbf{p} = -\frac{557}{216}, \quad \mathbf{v}^T C \mathbf{u} = \frac{23}{8}, \quad \mathbf{v}^T \mathbf{u} = 1.$$

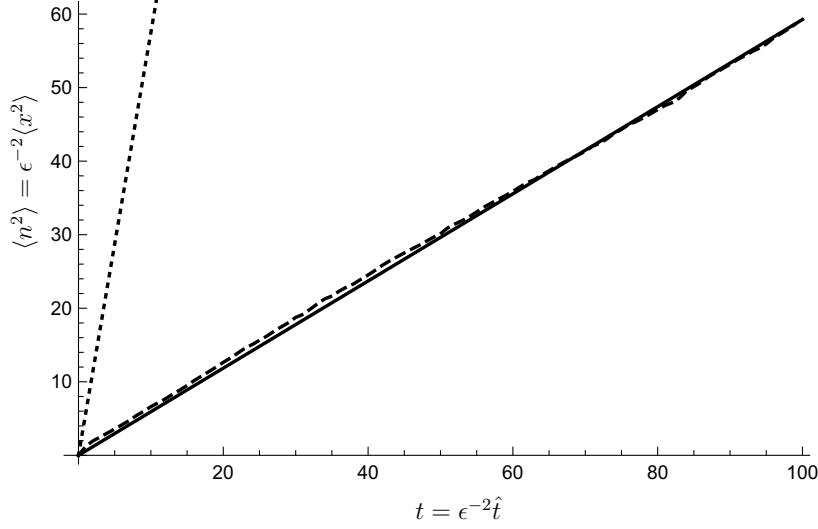


Figure 3: Mean square displacement as a function of time, averaged over 10,000 realisations of the continuous-time Markov chain with transition rates given by (24) (dashed). For a simple continuous diffusion process $\langle x^2 \rangle = 2D\hat{t}$. The solid line shows this with homogenised result (25); the dotted line shows the effect of ignoring the term $\mathbf{v}^T B \mathbf{p}$ and including only $\mathbf{v}^T C \mathbf{u}$.

and

$$D = 8/27. \quad (25)$$

In Figure 3 we show the mean square displacement of a particle as a function of time, averaged over 10,000 realisations, along with the continuum approximation $\langle x^2 \rangle = 2D\hat{t}$.

3.3 A rectangular lattice with $N \times N$ -periodicity in two-dimensions

In this section we generalise the approach outlined in Section 3.1 to a two-dimensional rectangular lattice with $N \times N$ periodicity. This extension allows us to represent a structured domain with obstacles (via a zero transition rate), while retaining non-zero macroscopic drift or diffusion in the system.

Introducing notation $\lambda_{(i,j) \rightarrow (k,l)}$ to denote the transition rate from node (i,j) to (k,l) , we consider a network in which each node is connected only to its four nearest neighbours, that is, the only nonzero transition rates are $\lambda_{(i,j) \rightarrow (i,j \pm 1)}$ and $\lambda_{(i,j) \rightarrow (\pm 1, j)}$, as shown in Figure 4.

The master equation is

$$\begin{aligned} \frac{\partial}{\partial t} P_{i,j}(x, y, t) = & \lambda_{(\overline{i-1}, j) \rightarrow (i, j)} P_{\overline{i-1}, j}(x - \epsilon, y, t) + \lambda_{(\overline{i+1}, j) \rightarrow (i, j)} P_{\overline{i+1}, j}(x + \epsilon, y, t) \\ & + \lambda_{(i, \overline{j-1}) \rightarrow (i, j)} P_{i, \overline{j-1}}(x, y - \epsilon, t) + \lambda_{(i, \overline{j+1}) \rightarrow (i, j)} P_{i, \overline{j+1}}(x, y + \epsilon, t) \\ & - \left(\lambda_{(i, j) \rightarrow (\overline{i-1}, j)} + \lambda_{(i, j) \rightarrow (\overline{i+1}, j)} + \lambda_{(i, j) \rightarrow (i, \overline{j-1})} + \lambda_{(i, j) \rightarrow (i, \overline{j+1})} \right) P_{i,j}(x, y, t). \end{aligned}$$

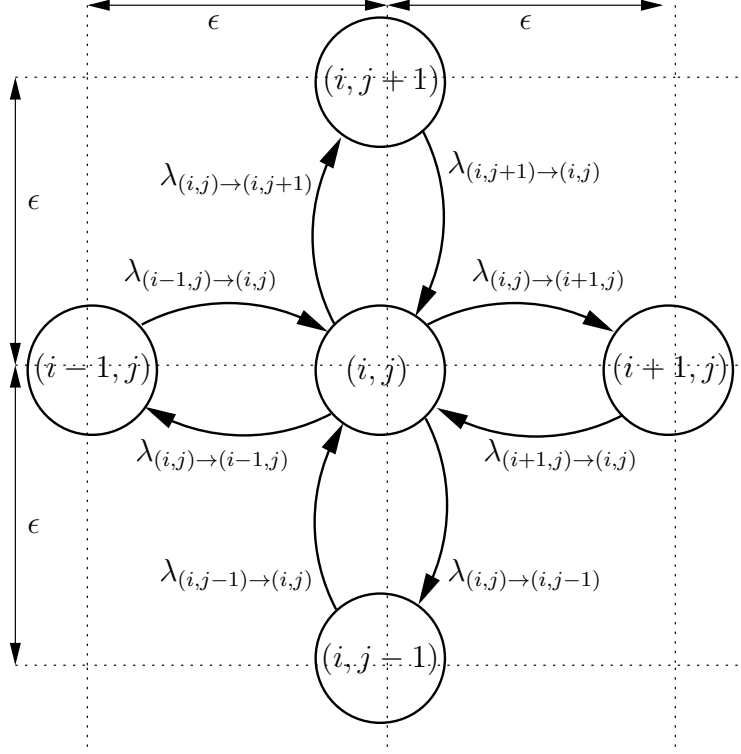


Figure 4: One-step transition for a two-dimensional, periodic Markov chain consisting of $N \times N$ distinct node types, each separated by distance ϵ .

Taylor expanding for small ϵ gives

$$\begin{aligned}
\frac{\partial}{\partial t} P_{i,j} &= \lambda_{(\bar{i}-1,j) \rightarrow (i,j)} P_{\bar{i}-1,j} + \lambda_{(\bar{i}+1,j) \rightarrow (i,j)} P_{\bar{i}+1,j} \\
&\quad + \lambda_{(i,\bar{j}-1) \rightarrow (i,j)} P_{i,\bar{j}-1} + \lambda_{(i,\bar{j}+1) \rightarrow (i,j)} P_{i,\bar{j}+1} \\
&\quad - \left(\lambda_{(i,j) \rightarrow (\bar{i}-1,j)} + \lambda_{(i,j) \rightarrow (\bar{i}+1,j)} + \lambda_{(i,j) \rightarrow (i,\bar{j}-1)} + \lambda_{(i,j) \rightarrow (i,\bar{j}+1)} \right) P_{i,j} \\
&\quad - \epsilon \lambda_{(\bar{i}-1,j) \rightarrow (i,j)} \frac{\partial P_{\bar{i}-1,j}}{\partial x} + \epsilon \lambda_{(\bar{i}+1,j) \rightarrow (i,j)} \frac{\partial P_{\bar{i}+1,j}}{\partial x} \\
&\quad - \epsilon \lambda_{(i,\bar{j}-1) \rightarrow (i,j)} \frac{\partial P_{i,\bar{j}-1}}{\partial y}(x, y, t) + \epsilon \lambda_{(i,\bar{j}+1) \rightarrow (i,j)} \frac{\partial P_{i,\bar{j}+1}}{\partial y} \\
&\quad + \frac{\epsilon^2}{2} \lambda_{(\bar{i}-1,j) \rightarrow (i,j)} \frac{\partial^2 P_{\bar{i}-1,j}}{\partial x^2} + \frac{\epsilon^2}{2} \lambda_{(\bar{i}+1,j) \rightarrow (i,j)} \frac{\partial^2 P_{\bar{i}+1,j}}{\partial x^2} \\
&\quad + \frac{\epsilon^2}{2} \lambda_{(i,\bar{j}-1) \rightarrow (i,j)} \frac{\partial^2 P_{i,\bar{j}-1}}{\partial y^2} + \frac{\epsilon^2}{2} \lambda_{(i,\bar{j}+1) \rightarrow (i,j)} \frac{\partial^2 P_{i,\bar{j}+1}}{\partial y^2} + \dots,
\end{aligned}$$

which we may write using index notation and Einstein's summation convention as

$$\frac{\partial P_{i,j}}{\partial t} = a_{ijkl} P_{k,l} + \epsilon b_{ijkl}^x \frac{\partial P_{k,l}}{\partial x} + \epsilon b_{ijkl}^y \frac{\partial P_{k,l}}{\partial y} + \epsilon^2 c_{ijkl}^x \frac{\partial^2 P_{k,l}}{\partial x^2} + \epsilon^2 c_{ijkl}^y \frac{\partial^2 P_{k,l}}{\partial y^2} + \dots,$$

where

$$\begin{aligned} a_{ijkl} &= \lambda_{(\bar{i}-1,j) \rightarrow (i,j)} \delta_{k,\bar{i}-1} \delta_{l,j} + \lambda_{(\bar{i}+1,j) \rightarrow (i,j)} \delta_{k,\bar{i}+1} \delta_{l,j} + \lambda_{(i,\bar{j}-1) \rightarrow (i,j)} \delta_{k,i} \delta_{l,\bar{j}-1} + \lambda_{(i,\bar{j}+1) \rightarrow (i,j)} \delta_{k,i} \delta_{l,\bar{j}+1} \\ &\quad - \left(\lambda_{(i,j) \rightarrow (\bar{i}-1,j)} + \lambda_{(i,j) \rightarrow (\bar{i}+1,j)} + \lambda_{(i,j) \rightarrow (i,\bar{j}-1)} + \lambda_{(i,j) \rightarrow (i,\bar{j}+1)} \right) \delta_{k,i} \delta_{l,j} \\ b_{ijkl}^x &= -\lambda_{(\bar{i}-1,j) \rightarrow (i,j)} \delta_{k,\bar{i}-1} \delta_{l,j} + \lambda_{(\bar{i}+1,j) \rightarrow (i,j)} \delta_{k,\bar{i}+1} \delta_{l,j}, \\ b_{ijkl}^y &= -\lambda_{(i,\bar{j}-1) \rightarrow (i,j)} \delta_{k,i} \delta_{l,\bar{j}-1} + \lambda_{(i,\bar{j}+1) \rightarrow (i,j)} \delta_{k,i} \delta_{l,\bar{j}+1}, \\ c_{ijkl}^x &= \frac{1}{2} \lambda_{(\bar{i}-1,j) \rightarrow (i,j)} \delta_{k,\bar{i}-1} \delta_{l,j} + \frac{1}{2} \lambda_{(\bar{i}+1,j) \rightarrow (i,j)} \delta_{k,\bar{i}+1} \delta_{l,j}, \\ c_{ijkl}^y &= \frac{1}{2} \lambda_{(i,\bar{j}-1) \rightarrow (i,j)} \delta_{k,i} \delta_{l,\bar{j}-1} + \frac{1}{2} \lambda_{(i,\bar{j}+1) \rightarrow (i,j)} \delta_{k,i} \delta_{l,\bar{j}+1}, \end{aligned}$$

and $\delta_{i,j}$ is the Kronecker δ . We may write this in vectorized form by defining

$$\mathbf{P} = (P_{1,1}, \dots, P_{1,N}, P_{2,1}, \dots, P_{2,N}, \dots, P_{N,1}, \dots, P_{N,N})^T.$$

We find

$$\frac{\partial \mathbf{P}}{\partial t} = A\mathbf{P} + \epsilon B_x \frac{\partial \mathbf{P}}{\partial x} + \epsilon B_y \frac{\partial \mathbf{P}}{\partial y} + \epsilon^2 C_x \frac{\partial^2 \mathbf{P}}{\partial x^2} + \epsilon^2 C_y \frac{\partial^2 \mathbf{P}}{\partial y^2} + \dots,$$

where the matrices A , B_x , B_y , C_x and C_y are block matrices, each consisting of an $N \times N$ array of $N \times N$ matrices, in which the (i,j) th block A^{ij} has entries

$$A_{kl}^{ij} = a_{ikjl},$$

etc.

As expected, transition matrix A conserves mass, and the left null vector is given by $\mathbf{v}^T = \mathbf{1}^T$. As before, we have a choice of slow timescales: the drift timescale $t = O(\epsilon^{-1})$, and the diffusion timescale $t = O(\epsilon^{-2})$. We begin by assuming that the drift terms are nonzero, thereby rescaling time as $t = \epsilon^{-1} \tilde{t}$. If it turns out that the drift is zero, we will then rescale onto the diffusion time. Expanding \mathbf{P} as usual in terms of the small parameter ϵ as

$$\mathbf{P} = \mathbf{P}^{(0)} + \epsilon \mathbf{P}^{(1)} + \epsilon^2 \mathbf{P}^{(2)} + O(\epsilon^3), \quad (26)$$

and equating coefficients of powers of ϵ we find at leading order that

$$A\mathbf{P}^{(0)} = 0. \quad (27)$$

Thus

$$\mathbf{P}^{(0)}(x, y, \tilde{t}) = f(x, y, \tilde{t}) \mathbf{u}, \quad (28)$$

where \mathbf{u} is the null vector of A , representing the stationary distribution on the fast-scale, and the coefficient $f(x, y, \tilde{t})$ varies slowly in space and time.

At $O(\epsilon)$ we find

$$A\mathbf{P}^{(1)} = \frac{\partial f}{\partial t} \mathbf{u} - B_x \frac{\partial}{\partial x} (f\mathbf{u}) - B_y \frac{\partial}{\partial y} (f\mathbf{u}). \quad (29)$$

Since the matrix A is singular, by the Fredholm Alternative there is a solution only if the right-hand side is orthogonal to $\mathbf{1}$, which spans the null space of A^T . This gives the solvability condition

$$\frac{\partial f}{\partial t} = \nu_x \frac{\partial f}{\partial x} + \nu_y \frac{\partial f}{\partial y}, \quad (30)$$

where the drift, (ν_x, ν_y) , is given by

$$\nu_x = \frac{\mathbf{v}^T B_x \mathbf{u}}{\mathbf{v}^T \mathbf{u}}, \quad \nu_y = \frac{\mathbf{v}^T B_y \mathbf{u}}{\mathbf{v}^T \mathbf{u}}. \quad (31)$$

If it happens that $\mathbf{v}^T B_x \mathbf{u} = \mathbf{v}^T B_y \mathbf{u} = 0$, then there is no drift at this order and we should rescale onto the diffusion time by setting $t = \epsilon^{-2} \hat{t}$. In that case we find at $O(\epsilon)$ that

$$A\mathbf{P}^{(1)} = -\frac{\partial f}{\partial x} B_x \mathbf{u} - \frac{\partial f}{\partial y} B_y \mathbf{u}. \quad (32)$$

Then

$$\mathbf{P}^{(1)} = \frac{\partial f}{\partial x} \mathbf{p}_x + \frac{\partial f}{\partial y} \mathbf{p}_y + g\mathbf{u},$$

where $\mathbf{p}_x, \mathbf{p}_y$ are any solutions of

$$A\mathbf{p}_x = -B_x \mathbf{u}, \quad A\mathbf{p}_y = -B_y \mathbf{u} \quad (33)$$

and the coefficient $g(x, y, \hat{t})$ may depend on slow space and time.

Then equating coefficients of ϵ^2 gives

$$\begin{aligned} A\mathbf{P}^{(2)} &= -B_x \frac{\partial \mathbf{P}^{(1)}}{\partial x} - B_y \frac{\partial \mathbf{P}^{(1)}}{\partial y} + \frac{\partial \mathbf{P}^{(0)}}{\partial \hat{t}} - C_x \frac{\partial^2 \mathbf{P}^{(0)}}{\partial x^2} - C_y \frac{\partial^2 \mathbf{P}^{(0)}}{\partial y^2} \\ &= -B_x \frac{\partial^2 f}{\partial x^2} \mathbf{p}_x - B_x \frac{\partial^2 f}{\partial x \partial y} \mathbf{p}_y - B_x \frac{\partial g}{\partial x} \mathbf{u} - B_y \frac{\partial^2 f}{\partial x \partial y} \mathbf{p}_x - B_y \frac{\partial^2 f}{\partial y^2} \mathbf{p}_y - B_y \frac{\partial g}{\partial y} \mathbf{u} \\ &\quad + \frac{\partial f}{\partial \hat{t}} \mathbf{u} - C_x \frac{\partial^2 f}{\partial x^2} \mathbf{u} - C_y \frac{\partial^2 f}{\partial y^2} \mathbf{u}. \end{aligned}$$

Applying the Fredholm Alternative as usual gives the solvability condition

$$\begin{aligned} \mathbf{v}^T \frac{\partial f}{\partial \hat{t}} \mathbf{u} &= \mathbf{v}^T B_x \frac{\partial^2 f}{\partial x^2} \mathbf{p}_x + \mathbf{v}^T B_x \frac{\partial^2 f}{\partial x \partial y} \mathbf{p}_y + \mathbf{v}^T B_y \frac{\partial^2 f}{\partial x \partial y} \mathbf{p}_x + \mathbf{v}^T B_y \frac{\partial^2 f}{\partial y^2} \mathbf{p}_y \\ &\quad + \mathbf{v}^T C_x \frac{\partial^2 f}{\partial x^2} \mathbf{u} + \mathbf{v}^T C_y \frac{\partial^2 f}{\partial y^2} \mathbf{u}, \end{aligned}$$

where we have used the fact that $\mathbf{v}^T B \mathbf{u} = 0$. Thus the amplitude f satisfies the diffusion equation

$$\frac{\partial f}{\partial \hat{t}} = D_{xx} \frac{\partial^2 f}{\partial x^2} + D_{xy} \frac{\partial^2 f}{\partial x \partial y} + D_{yy} \frac{\partial^2 f}{\partial y^2}, \quad (34)$$

with diffusion maxtrix given by

$$D_{xx} = \frac{\mathbf{v}^T B_x \mathbf{p}_x + \mathbf{v}^T C_x \mathbf{u}}{\mathbf{v}^T \mathbf{u}}, \quad D_{xy} = \frac{\mathbf{v}^T B_x \mathbf{p}_y + \mathbf{v}^T B_y \mathbf{p}_x}{\mathbf{v}^T \mathbf{u}}, \quad D_{yy} = \frac{\mathbf{v}^T B_y \mathbf{p}_y + \mathbf{v}^T C_y \mathbf{u}}{\mathbf{v}^T \mathbf{u}}. \quad (35)$$

3.4 Examples

3.4.1 Symmetric transition rates

If $\lambda_{(i,j) \rightarrow (k,l)} = \lambda_{(k,l) \rightarrow (i,j)}$ the A is symmetric and, as in the one-dimensional case, the stationary distribution is uniform, so that $u_{ij} = 1/N^2$. Then

$$B_x \mathbf{u} = B_y \mathbf{u} = \mathbf{0},$$

so that, as expected, there is no drift. Since

$$\begin{aligned} c_{ijkl}^x &= \frac{1}{2} \lambda_{(\overline{i-1}, j) \rightarrow (i, j)} \delta_{k, \overline{i-1}} \delta_{l, j} + \frac{1}{2} \lambda_{(\overline{i+1}, j) \rightarrow (i, j)} \delta_{k, \overline{i+1}} \delta_{l, j}, \\ c_{ijkl}^y &= \frac{1}{2} \lambda_{(i, \overline{j-1}) \rightarrow (i, j)} \delta_{k, i} \delta_{l, \overline{j-1}} + \frac{1}{2} \lambda_{(i, \overline{j+1}) \rightarrow (i, j)} \delta_{k, i} \delta_{l, \overline{j+1}}, \end{aligned}$$

$$\begin{aligned} \mathbf{v}^T C_x \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{2} \lambda_{\overline{i-1}, j} u_{\overline{i-1}, j} + \frac{1}{2} \lambda_{\overline{i+1}, j} u_{\overline{i+1}, j} = N^2, \\ \mathbf{v}^T C_y \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{2} \lambda_{i, \overline{j-1}} u_{i, \overline{j-1}} + \frac{1}{2} \lambda_{i, \overline{j+1}} u_{i, \overline{j+1}} = N^2, \\ \mathbf{v}^T \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{\lambda_{ij}}. \end{aligned}$$

Thus we obtain the isotropic effective diffusion equation

$$\frac{\partial f}{\partial t} = D \nabla^2 f, \quad (36)$$

where

$$D = \frac{N^2}{\sum_{i,j=1}^N 1/\lambda_{ij}}. \quad (37)$$

3.4.2 Source-dependent transition rates

We consider now a source-driven jump process, that is, one in which the transition rate depends only on the current node and not on the destination node. In this case we may write

$$\lambda_{(i,j) \rightarrow (i, \overline{j \pm 1})} = \lambda_{(i,j) \rightarrow (\overline{i \pm 1}, j)} = \lambda_{ij},$$

say. Such a restriction is typical for particles trapped in a potential well, such as in the effective diffusion calculations for crystalline structures with impurities in solid-state physics. In this formulation, transition rates (which are typically of temperature-dependent, Arrhenius type) relate to the energy required to overcome the trapping potential, and may be thought of as the inverse mean time to escape from a given well. Once this energy is overcome, the particle is free to move isotropically to any neighbouring well, resulting in purely diffusive macroscopic behaviour. Variations of this, such as the tilted washboard potentials found in Josephson junctions and molecular ratchets,

result in asymmetric potentials where the transition probabilities depend on the jump direction. This introduces a bias in the system, which results in a macroscopic drift.

The stationary distribution satisfies

$$A\mathbf{u} = a_{ijkl}u_{kl} = 0,$$

which can be written out as

$$\lambda_{i-1,j}u_{i-1,j} + \lambda_{i+1,j}u_{i+1,j} + \lambda_{i,j-1}u_{i,j-1} + \lambda_{i,j+1}u_{i,j+1} - 4\lambda_{ij}u_{ij} = 0.$$

Thus we have simply

$$u_{ij} = \frac{1}{\lambda_{ij}}. \quad (38)$$

We find that

$$\begin{aligned} B_x \mathbf{u} &= -\lambda_{i-1,j}u_{i-1,j} + \lambda_{i+1,j}u_{i+1,j} = 0, \\ B_y \mathbf{u} &= -\lambda_{i,j-1}u_{i,j-1} + \lambda_{i,j+1}u_{i,j+1} = 0, \end{aligned}$$

so that, as expected, there is no drift. This also gives $\mathbf{p}_x = \mathbf{p}_y = \mathbf{0}$, so that there is no dispersion. Finally

$$\begin{aligned} \mathbf{v}^T C_x \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{2} \lambda_{i-1,j}u_{i-1,j} + \frac{1}{2} \lambda_{i+1,j}u_{i+1,j} = N^2, \\ \mathbf{v}^T C_y \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{2} \lambda_{i,j-1}u_{i,j-1} + \frac{1}{2} \lambda_{i,j+1}u_{i,j+1} = N^2, \\ \mathbf{v}^T \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{\lambda_{ij}}. \end{aligned}$$

Thus we obtain the isotropic effective diffusion equation

$$\frac{\partial f}{\partial t} = D \nabla^2 f, \quad (39)$$

where

$$D = \frac{N^2}{\sum_{i,j=1}^N 1/\lambda_{ij}}. \quad (40)$$

The application of source-dependent transition rates to trapping states in heterogeneous (non-Bravais) lattices has been studied extensively by Haus and Kehr (1987); Kutner (1981); Dieterich et al. (1980) in solid-state conductors and charge transport in semiconductors. Using Lattice Greens functions, Kehr et al. (1978) derive the effective diffusion coefficient

$$D_{\text{eff}} = \frac{n}{2d} \frac{a^2}{\langle \tau \rangle}, \quad (41)$$

where $\langle \tau \rangle$ is the residence time averaged over all sites, n is the number of nearest neighbour sites and a is the lattice constant. In our case $a = 1$, $d = 2$, $n = 4$. Since $\tau_{ij} = 1/\lambda_{ij}$, (41) is equivalent to (40).

To illustrate this example we consider the case of a 2×2 -node periodic unit cell with purely source-dependent transitions, placed in a checkerboard such that $\lambda_{11} = \lambda_{22} = \lambda$ and $\lambda_{12} = \lambda_{21} = \mu$. Figure 5 shows the predicted diffusion coefficient as a function of λ for the two cases $\mu = 1/2$ and $\mu = 1/\lambda$. Also shown are the empirical estimates given by the mean square x and y displacements at time $T = 100$ averaged over 100,000 realisations of the stochastic hopping process, divided by $2T$.

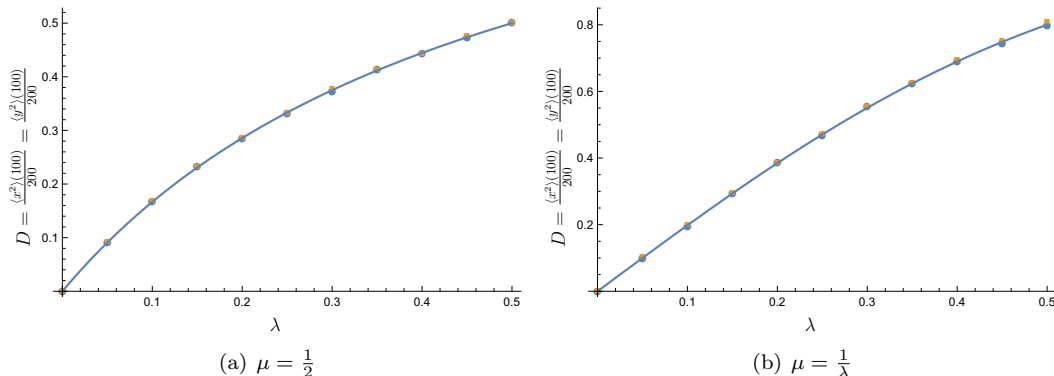


Figure 5: Effective diffusion coefficient as a function of λ for 2×2 source-driven transition with $\lambda_{11} = \lambda_{22} = \lambda$ and $\lambda_{12} = \lambda_{21} = \mu$. The solid curve is the predicted homogenised value, while the points are empirical estimates given by the mean square x (circles) and y (squares) displacements at time $T = 100$ averaged over 100,000 realisations of the stochastic hopping process, divided by $2T$.

3.4.3 Destination-dependent transition rates

Another important type of periodic unit Markov process is one where the transition rate depends purely on the destination node, so that

$$\lambda_{(i,j\pm 1) \rightarrow (i,j)} = \lambda_{(\overline{i\pm 1},j) \rightarrow (i,j)} = \lambda_{ij},$$

say. In contrast to the source-dependent case, where the transition rates represented an energy trap binding the particle to its current node, the destination-dependent case represents a barrier to overcome on arriving to a new node. This has important physical application in biology, where spatial heterogeneities such as layered media can be modelled by varying λ . The limiting case in which $\lambda_{ij} = 0$ for some (i, j) represents nodes which are effectively removed from the lattice, and so can be used to model diffusion through porous media (Ölveczky and Verkman, 1998; Posnansky and Shah, 2008; Aliev and Tikhonov, 2004; Saxton and Jacobson, 1997). There are also applications in solid-state physics, where diffusion process across a step edge is known to differ from diffusion on a terrace. Such interlayer diffusion processes are usually characterized by an additional barrier, the Ehrlich-Schwobel (ES) barrier, added to the activation energy for diffusion on a terrace (Rabbering et al., 2009).

The stationary distribution satisfies

$$\lambda_{ij}u_{\overline{i-1},j} + \lambda_{ij}u_{\overline{i+1},j} + \lambda_{ij}u_{i,\overline{j-1}} + \lambda_{ij}u_{i,\overline{j+1}} - \left(\lambda_{\overline{i-1},j} + \lambda_{\overline{i+1},j} + \lambda_{i,\overline{j-1}} + \lambda_{i,\overline{j+1}} \right) u_{ij} = 0,$$

with solution

$$u_{ij} = \lambda_{ij}. \quad (42)$$

We find that

$$\begin{aligned} B_x \mathbf{u} &= -\lambda_{ij} u_{i-1,j} + \lambda_{ij} u_{i+1,j}, \\ B_y \mathbf{u} &= -\lambda_{ij} u_{i,j-1} + \lambda_{ij} u_{i,j+1}. \end{aligned}$$

Thus

$$\mathbf{v}^T B_x \mathbf{u} = \sum_{i,j=1}^N \lambda_{ij} (\lambda_{i+1,j} - \lambda_{i-1,j}) = 0, \quad (43)$$

$$\mathbf{v}^T B_y \mathbf{u} = \sum_{i,j=1}^N \lambda_{ij} (\lambda_{i,j+1} - \lambda_{i,j-1}) = 0. \quad (44)$$

Thus in this case also there is no drift. In contrast to the previous example though, $B_x \mathbf{u}$ and $B_y \mathbf{u}$ need not be zero, so there may be dispersion. The equations for \mathbf{p}_x and \mathbf{p}_y are

$$\begin{aligned} a_{ijkl} p_{kl}^x &= -b_{ijkl}^x \lambda_{kl}, \\ a_{ijkl} p_{kl}^y &= -b_{ijkl}^y \lambda_{kl}, \end{aligned}$$

i.e.

$$\begin{aligned} \lambda_{ij} p_{i-1,j}^x + \lambda_{ij} p_{i+1,j}^x + \lambda_{ij} p_{i,j-1}^x + \lambda_{ij} p_{i,j+1}^x \\ - \left(\lambda_{i-1,j} + \lambda_{i+1,j} + \lambda_{i,j-1} + \lambda_{i,j+1} \right) p_{ij}^x &= \lambda_{ij} (\lambda_{i-1,j} - \lambda_{i+1,j}), \end{aligned} \quad (45)$$

$$\begin{aligned} \lambda_{ij} p_{i-1,j}^y + \lambda_{ij} p_{i+1,j}^y + \lambda_{ij} p_{i,j-1}^y + \lambda_{ij} p_{i,j+1}^y \\ - \left(\lambda_{i-1,j} + \lambda_{i+1,j} + \lambda_{i,j-1} + \lambda_{i,j+1} \right) p_{ij}^y &= \lambda_{ij} (\lambda_{i,j-1} - \lambda_{i,j+1}), \end{aligned} \quad (46)$$

Unfortunately there is no simple solution to this set of equations in general. Thus we have no general closed for expression for the dispersive component of the effective diffusion equation. For the diffusive part, we find that

$$\begin{aligned} \mathbf{v}^T C_x \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{2} \lambda_{ij} u_{i-1,j} + \frac{1}{2} \lambda_{ij} u_{i+1,j} = \sum_{i,j=1}^N \lambda_{ij} \lambda_{i-1,j}, \\ \mathbf{v}^T C_y \mathbf{u} &= \sum_{i,j=1}^N \frac{1}{2} \lambda_{ij} u_{i,j-1} + \frac{1}{2} \lambda_{ij} u_{i,j+1} = \sum_{i,j=1}^N \lambda_{ij} \lambda_{i,j-1}, \\ \mathbf{v}^T \mathbf{u} &= \sum_{i,j=1}^N \lambda_{ij}. \end{aligned}$$

In contrast to the source-dependent jump rates, diffusion in the destination-dependent case is not necessarily isotropic.

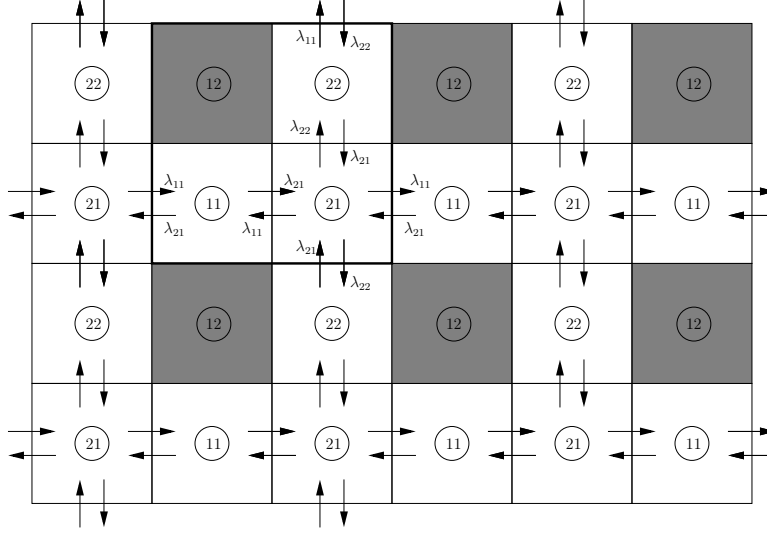


Figure 6: A 2×2 -node periodic position jump process with destination-dependent transition rates. The unit cell is highlighted. Jumping rates to position $(1, 2)$ are zero, so that this node represents an obstacle.

Example We consider the simple case of a 2×2 -node periodic Markov chain with an obstacle at position $(1, 2)$, so that $\lambda_{12} = 0$ (see Figure 6). In this case (and indeed, for any 2×2 -periodic unit cell) the right-hand sides of (45) and (46) are zero, so that $\mathbf{p}_x = \mathbf{p}_y = \mathbf{0}$ and there is no dispersion. The effective diffusion equation is then

$$\frac{\partial f}{\partial t} = D_{xx} \frac{\partial^2 f}{\partial x^2} + D_{yy} \frac{\partial^2 f}{\partial y^2},$$

where

$$D_{xx} = \frac{2\lambda_{11}\lambda_{21}}{\lambda_{11} + \lambda_{21} + \lambda_{22}}, \quad (47)$$

$$D_{yy} = \frac{2\lambda_{21}\lambda_{22}}{\lambda_{11} + \lambda_{21} + \lambda_{22}}. \quad (48)$$

Comparing this result to the mean squared displacement in x and y for 1000 Monte-Carlo simulations of a destination-dependent checkerboard with $\lambda_{11} = 1/8$, $\lambda_{21} = 1/4$ and $\lambda_{22} = 1/2$ in Figure 7(a), we see excellent agreement between our predicted effective properties and the numerical results.

3.4.4 General transition rates

For general transition rates that depend on both the source and destination node, the form of eigenvector \mathbf{u} is non-trivial. However, it is possible to write in closed-form for certain special cases.

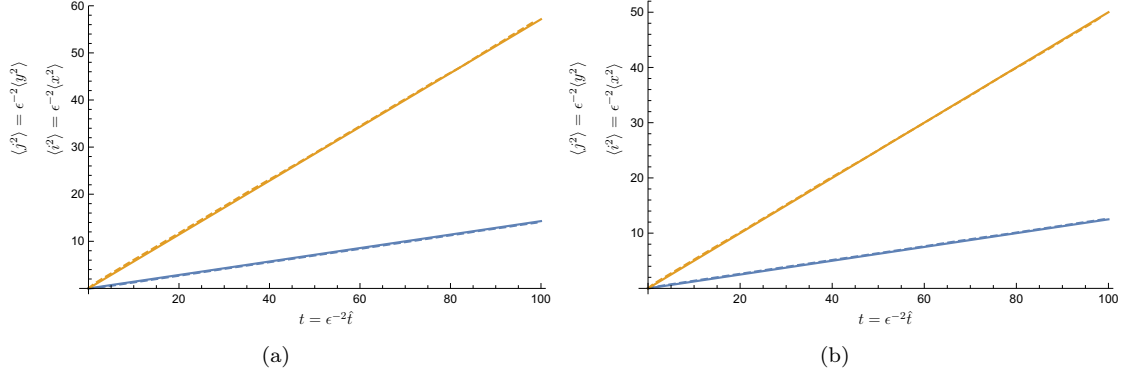


Figure 7: (a) Mean Squared Displacement for 2×2 -node destination-driven Markov chain with obstacle at $(1, 2)$ shown in Fig. 6, averaged over 100,000 realisations (dashed). Transition rates are $\lambda_{12} = 0$, $\lambda_{11} = 1/8$, $\lambda_{21} = 1/4$ and $\lambda_{22} = 1/2$. Also shown are the predicted homogenised values $2D_{xx}t$ and $2D_{yy}t$ with diffusion coefficients given by (47), (48). (b) Mean Squared Displacement for a general 2×2 -node Markov chain with obstacle at $(1, 2)$ averaged over 100,000 realisations (dashed). Nonzero transition rates are $\lambda_{(1,1) \rightarrow (2,1)} = 1/8$, $\lambda_{(2,1) \rightarrow (1,1)} = 1/16$, $\lambda_{(2,1) \rightarrow (2,2)} = 1/4$ and $\lambda_{(2,2) \rightarrow (2,1)} = 1/2$. Also shown are the predicted homogenised values $2D_{xx}t$ and $2D_{yy}t$ with diffusion coefficients given by (50), (51).

Example Consider the four-phase checkerboard with an obstacle at position $(1, 2)$, but with otherwise general transition rates that may depend on both source and destination nodes. Then

$$\lambda_{(1,1) \rightarrow (1,2)} = \lambda_{(2,2) \rightarrow (1,2)} = \lambda_{(1,2) \rightarrow (1,1)} = \lambda_{(1,2) \rightarrow (2,2)} = 0,$$

so that

$$A = 2 \begin{pmatrix} -\lambda_{(1,1) \rightarrow (2,1)} & 0 & \lambda_{(2,1) \rightarrow (1,1)} & 0 \\ 0 & 0 & 0 & 0 \\ \lambda_{(1,1) \rightarrow (2,1)} & 0 & -\lambda_{(2,1) \rightarrow (1,1)} - \lambda_{(2,1) \rightarrow (2,2)} & \lambda_{(2,2) \rightarrow (2,1)} \\ 0 & 0 & \lambda_{(2,1) \rightarrow (2,2)} & -\lambda_{(2,2) \rightarrow (2,1)} \end{pmatrix}$$

The eigenvector, \mathbf{u} , is given by

$$\mathbf{u} = \begin{pmatrix} \lambda_{(2,1) \rightarrow (1,1)} \lambda_{(2,2) \rightarrow (2,1)} & 0 & \lambda_{(2,2) \rightarrow (2,1)} \lambda_{(1,1) \rightarrow (2,1)} & \lambda_{(1,1) \rightarrow (2,1)} \lambda_{(2,1) \rightarrow (2,2)} \end{pmatrix}^T.$$

We find

$$\begin{aligned} B_x \mathbf{u} &= -\lambda_{(k,l) \rightarrow (\overline{k+1}, l)} u_{\overline{k+1}, l} + \lambda_{(k,l) \rightarrow (\overline{k-1}, l)} u_{\overline{k-1}, l} = 0, \\ B_y \mathbf{u} &= -\lambda_{(k,l) \rightarrow (k, \overline{j+1})} u_{k, \overline{j+1}} + \lambda_{(k,l) \rightarrow (k, \overline{j-1})} u_{k, \overline{j-1}} = 0, \end{aligned}$$

so that there is no drift or dispersion. Since

$$\begin{aligned} \mathbf{v}^T C_x \mathbf{u} &= 2\lambda_{(1,1) \rightarrow (2,1)} \lambda_{(2,1) \rightarrow (1,1)} \lambda_{(2,2) \rightarrow (2,1)}, \\ \mathbf{v}^T C_y \mathbf{u} &= 2\lambda_{(1,1) \rightarrow (2,1)} \lambda_{(2,1) \rightarrow (2,2)} \lambda_{(2,2) \rightarrow (2,1)}, \\ \mathbf{v}^T \mathbf{u} &= \lambda_{(2,1) \rightarrow (1,1)} \lambda_{(2,2) \rightarrow (2,1)} + \lambda_{(2,2) \rightarrow (2,1)} \lambda_{(1,1) \rightarrow (2,1)} + \lambda_{(1,1) \rightarrow (2,1)} \lambda_{(2,1) \rightarrow (2,2)} \end{aligned}$$

the effective diffusion equation on the macroscale is

$$\frac{\partial f}{\partial t} = D_{xx} \frac{\partial^2 f}{\partial x^2} + D_{yy} \frac{\partial^2 f}{\partial y^2}, \quad (49)$$

with effective diffusion coefficients

$$D_{xx} = 2 \left(\frac{\lambda_{2,1 \rightarrow 2,2}}{\lambda_{2,1 \rightarrow 1,1} \lambda_{2,2 \rightarrow 2,1}} + \frac{1}{\lambda_{1,1 \rightarrow 2,1}} + \frac{1}{\lambda_{2,1 \rightarrow 1,1}} \right)^{-1}, \quad (50)$$

$$D_{yy} = 2 \left(\frac{\lambda_{2,1 \rightarrow 1,1}}{\lambda_{1,1 \rightarrow 2,1} \lambda_{2,1 \rightarrow 2,2}} + \frac{1}{\lambda_{2,1 \rightarrow 2,2}} + \frac{1}{\lambda_{2,2 \rightarrow 2,1}} \right)^{-1}. \quad (51)$$

In Figure 7(b) we show the mean squared displacement averaged over 1000 Monte-Carlo realizations with the transition rates $\lambda_{1,1 \rightarrow 2,1} = 1/8$, $\lambda_{2,1 \rightarrow 1,1} = 1/16$, $\lambda_{2,1 \rightarrow 2,2} = 1/4$ and $\lambda_{2,2 \rightarrow 2,1} = 1/2$. As in the previous cases, we see excellent agreement with the asymptotic results $D_{xx} = 1/16$ and $D_{yy} = 1/4$.

3.5 Non-rectangular unit cell lattices

Finally we consider periodic lattices in which the unit cell is not a rectangular lattice. Such a situation may model, for example, ion or electron hopping through a non-cubic crystalline material.

We suppose that the unit cell has period ϵL_x and ϵL_y and contains N nodes with positions $(\epsilon x_i, \epsilon y_i)$ ($i = 1, \dots, N$) relative to the cell corner (see Figure 8). Introducing the notation $\lambda_{i \rightarrow j}^{00}$ to denote the transition rate from node i to node j within the unit cell (with the convention that $\lambda_{i \rightarrow i} = 0$), and the notation the $\lambda_{i \rightarrow j}^{kl}$ to denote the transition rates from node i to node j in the neighbouring cell with relative position $(k\epsilon L_x, l\epsilon L_y)$ (see Figure 8) the master equation is

$$\begin{aligned} \frac{\partial}{\partial t} P_i(x, y, t) &= \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N \lambda_{j \rightarrow i}^{kl} P_j(x - \epsilon k L_x + \epsilon x_j - \epsilon x_i, y - \epsilon l L_y + \epsilon y_j - \epsilon y_i, t) \\ &\quad - \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N \lambda_{i \rightarrow j}^{kl} P_i(x, y, t). \end{aligned}$$

Taylor expanding for small ϵ gives

$$\begin{aligned} \frac{\partial}{\partial t} P_i &= \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N \lambda_{j \rightarrow i}^{kl} P_j - \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N \lambda_{i \rightarrow j}^{kl} P_i \\ &\quad + \epsilon \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N (-k L_x + x_j - x_i) \lambda_{j \rightarrow i}^{kl} \frac{\partial P_j}{\partial x} + \epsilon \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N (-l L_y + y_j - y_i) \lambda_{j \rightarrow i}^{kl} \frac{\partial P_j}{\partial y} \\ &\quad + \frac{\epsilon^2}{2} \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N (-k L_x + x_j - x_i)^2 \lambda_{j \rightarrow i}^{kl} \frac{\partial^2 P_j}{\partial x^2} + \frac{\epsilon^2}{2} \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N (-l L_y + y_j - y_i)^2 \lambda_{j \rightarrow i}^{kl} \frac{\partial^2 P_j}{\partial y^2} \\ &\quad + \epsilon^2 \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{j=1}^N (-k L_x + x_j - x_i)(-l L_y + y_j - y_i) \lambda_{j \rightarrow i}^{kl} \frac{\partial^2 P_j}{\partial x \partial y} + \dots, \end{aligned}$$

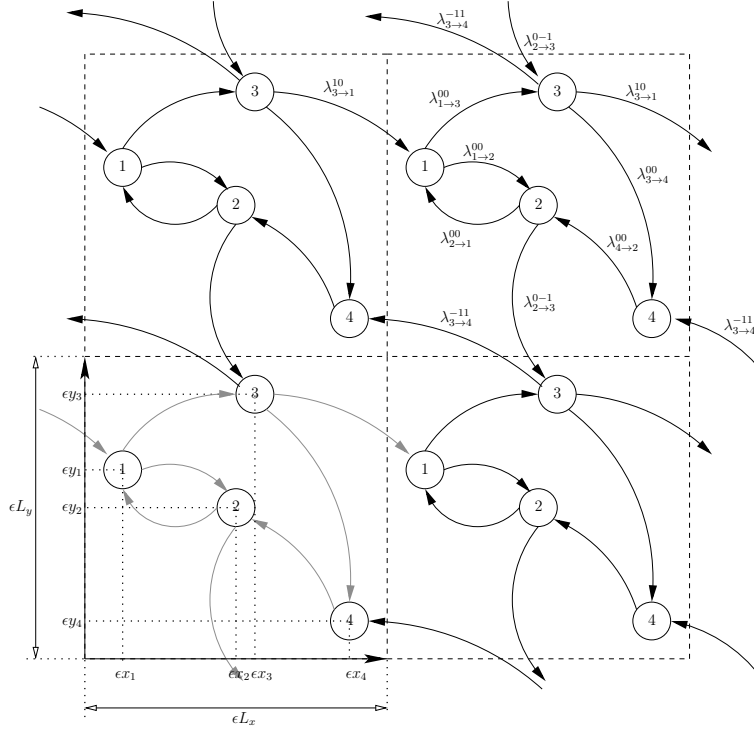


Figure 8: A general non-rectangular lattice unit cell

which we may write using vector notation as

$$\frac{\partial \mathbf{P}}{\partial t} = A\mathbf{P} + \epsilon B^x \frac{\partial \mathbf{P}}{\partial x} + \epsilon B^y \frac{\partial \mathbf{P}}{\partial y} + \epsilon^2 C^{xx} \frac{\partial^2 \mathbf{P}}{\partial x^2} + \epsilon^2 C^{xy} \frac{\partial^2 \mathbf{P}}{\partial x \partial y} + \epsilon^2 C^{yy} \frac{\partial^2 \mathbf{P}}{\partial y^2} + \dots,$$

where

$$\begin{aligned}
A_{ij} &= \sum_{k=-1}^1 \sum_{l=-1}^1 \lambda_{j \rightarrow i}^{kl} - \delta_{ij} \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{s=1}^N \lambda_{i \rightarrow s}^{kl}, \\
B_{ij}^x &= \sum_{k=-1}^1 \sum_{l=-1}^1 (-kL_x + x_j - x_i) \lambda_{j \rightarrow i}^{kl}, \\
B_{ij}^y &= \sum_{k=-1}^1 \sum_{l=-1}^1 (-lL_y + y_j - y_i) \lambda_{j \rightarrow i}^{kl}, \\
C_{ij}^{xx} &= \frac{1}{2} \sum_{k=-1}^1 \sum_{l=-1}^1 (-kL_x + x_j - x_i)^2 \lambda_{j \rightarrow i}^{kl}, \\
C_{ij}^{yy} &= \frac{1}{2} \sum_{k=-1}^1 \sum_{l=-1}^1 (-lL_y + y_j - y_i)^2 \lambda_{j \rightarrow i}^{kl}, \\
C_{ij}^{xy} &= \sum_{k=-1}^1 \sum_{l=-1}^1 (-kL_x + x_j - x_i)(-lL_y + y_j - y_i) \lambda_{j \rightarrow i}^{kl}.
\end{aligned}$$

As usual, we have a choice of slow timescales: the drift timescale $t = O(\epsilon^{-1})$, and the diffusion timescale $t = O(\epsilon^{-2})$. We begin by assuming that the drift terms are nonzero, thereby rescaling time as $t = \epsilon^{-1} \tilde{t}$. Expanding \mathbf{P} in terms of the small parameter ϵ we find at leading order that as before

$$\mathbf{P}^{(0)}(x, y, \tilde{t}) = f(x, y, \tilde{t}) \mathbf{u}, \quad (52)$$

where \mathbf{u} is the null vector of A , representing the stationary distribution on the fast-scale, and the coefficient $f(x, y, \tilde{t})$ varies slowly in space and time. The solvability condition at next order gives

$$\frac{\partial f}{\partial t} = \nu_x \frac{\partial f}{\partial x} + \nu_y \frac{\partial f}{\partial y}, \quad (53)$$

where

$$\nu_x = \frac{\mathbf{v}^T B^x \mathbf{u}}{\mathbf{v}^T \mathbf{u}}, \quad \nu_y = \frac{\mathbf{v}^T B^y \mathbf{u}}{\mathbf{v}^T \mathbf{u}}. \quad (54)$$

Note that since $A\mathbf{u} = \mathbf{0}$,

$$\sum_{i=1}^N \sum_{j=1}^N \sum_{k=-1}^1 \sum_{l=-1}^1 x_i \lambda_{j \rightarrow i}^{kl} u_j = \sum_{i=1}^N x_i \delta_{ij} \sum_{j=1}^N \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{s=1}^N \lambda_{i \rightarrow s}^{kl} u_j = \sum_{j=1}^N \sum_{k=-1}^1 \sum_{l=-1}^1 \sum_{s=1}^N x_j \lambda_{j \rightarrow s}^{kl} u_j,$$

so that

$$\mathbf{v}^T B^x \mathbf{u} = - \sum_{i=1}^N \sum_{j=1}^N \sum_{k=-1}^1 \sum_{l=-1}^1 kL_x \lambda_{j \rightarrow i}^{kl} u_j, \quad \mathbf{v}^T B^y \mathbf{u} = - \sum_{i=1}^N \sum_{j=1}^N \sum_{k=-1}^1 \sum_{l=-1}^1 lL_y \lambda_{j \rightarrow i}^{kl} u_j,$$

are independent of x_i and y_i as we would expect.

If it happens that $\mathbf{v}^T B^x \mathbf{u} = \mathbf{v}^T B^y \mathbf{u} = 0$, then there is no drift at this order and we should rescale onto the diffusion time by setting $t = \epsilon^{-2} \hat{t}$. In that case

$$\mathbf{P}^{(1)} = \frac{\partial f}{\partial x} \mathbf{p}_x + \frac{\partial f}{\partial y} \mathbf{p}_y + g \mathbf{u},$$

where $\mathbf{p}_x, \mathbf{p}_y$ are any solutions of

$$A \mathbf{p}_x = -B^x \mathbf{u}, \quad A \mathbf{p}_y = -B^y \mathbf{u} \quad (55)$$

and the coefficient $g(x, y, \hat{t})$ may depend on slow space and time. Applying the Fredholm Alternative at $O(\epsilon^2)$ gives

$$\begin{aligned} \mathbf{v}^T \frac{\partial f}{\partial \hat{t}} \mathbf{u} &= \mathbf{v}^T B^x \frac{\partial^2 f}{\partial x^2} \mathbf{p}_x + \mathbf{v}^T B^x \frac{\partial^2 f}{\partial x \partial y} \mathbf{p}_y + \mathbf{v}^T B^y \frac{\partial^2 f}{\partial x \partial y} \mathbf{p}_x + \mathbf{v}^T B^y \frac{\partial^2 f}{\partial y^2} \mathbf{p}_y \\ &\quad + \mathbf{v}^T C^{xx} \frac{\partial^2 f}{\partial x^2} \mathbf{u} + \mathbf{v}^T C^{xy} \frac{\partial^2 f}{\partial x \partial y} \mathbf{u} + \mathbf{v}^T C^{yy} \frac{\partial^2 f}{\partial y^2} \mathbf{u}, \end{aligned}$$

where we have used the fact that $\mathbf{v}^T B \mathbf{u} = 0$. Thus the amplitude f satisfies the diffusion equation

$$\frac{\partial f}{\partial \hat{t}} = D_{xx} \frac{\partial^2 f}{\partial x^2} + D_{xy} \frac{\partial^2 f}{\partial x \partial y} + D_{yy} \frac{\partial^2 f}{\partial y^2}, \quad (56)$$

with diffusion maxtrix given by

$$D_{xx} = \frac{\mathbf{v}^T B^x \mathbf{p}_x + \mathbf{v}^T C^{xx} \mathbf{u}}{\mathbf{v}^T \mathbf{u}}, \quad D_{xy} = \frac{\mathbf{v}^T B^x \mathbf{p}_y + \mathbf{v}^T B^y \mathbf{p}_x + \mathbf{v}^T C^{xy} \mathbf{u}}{\mathbf{v}^T \mathbf{u}}, \quad D_{yy} = \frac{\mathbf{v}^T B^y \mathbf{p}_y + \mathbf{v}^T C^{yy} \mathbf{u}}{\mathbf{v}^T \mathbf{u}}. \quad (57)$$

The coefficients D_{xx} , D_{xy} and D_{yy} are also independent of x_i and y_i : only the topology of the network in the unit cell matters, not the actual position of nodes.

3.5.1 Example

As an example we consider the network shown in Figure 8, with four nodes in the unit cell. We choose $L_x = L_y = 1$, and take the only non-zero transition rates to be $\lambda_{1 \rightarrow 2}^{00} = 8/3$, $\lambda_{1 \rightarrow 3}^{00} = 2$, $\lambda_{2 \rightarrow 1}^{00} = 6$, $\lambda_{2 \rightarrow 3}^{0-1} = 1$, $\lambda_{3 \rightarrow 1}^{10} = 2$, $\lambda_{3 \rightarrow 4}^{-11} = 2$, $\lambda_{3 \rightarrow 4}^{00} = 4$, $\lambda_{4 \rightarrow 2}^{00} = 3$. These are chosen so that there is no drift and the macroscale motion is diffusive. The predicted diffusion coefficients are $D_{xx} = 1/4$, $D_{xy} = -11/50$, $D_{yy} = 9/50$. Sample results are shown in Figure 9.

4 Summary

We have used the method of multiple scales to calculate the effective macroscopic transport properties of a random walk on periodic lattices with arbitrary, spatially-dependent transition rates.

In contrast to the standard multiple-scales approach for continuous media, our fast scale is discrete, and only the slow scale is continuous. The solution is found as the discrete probability distribution of finding the particle at a particular node in the unit cell, modulated by a continuous slow function of position of the unit cell in the macroscopic material. This last function represents the macroscopic drift-diffusion of the particle, with drift and diffusion coefficients given in terms of

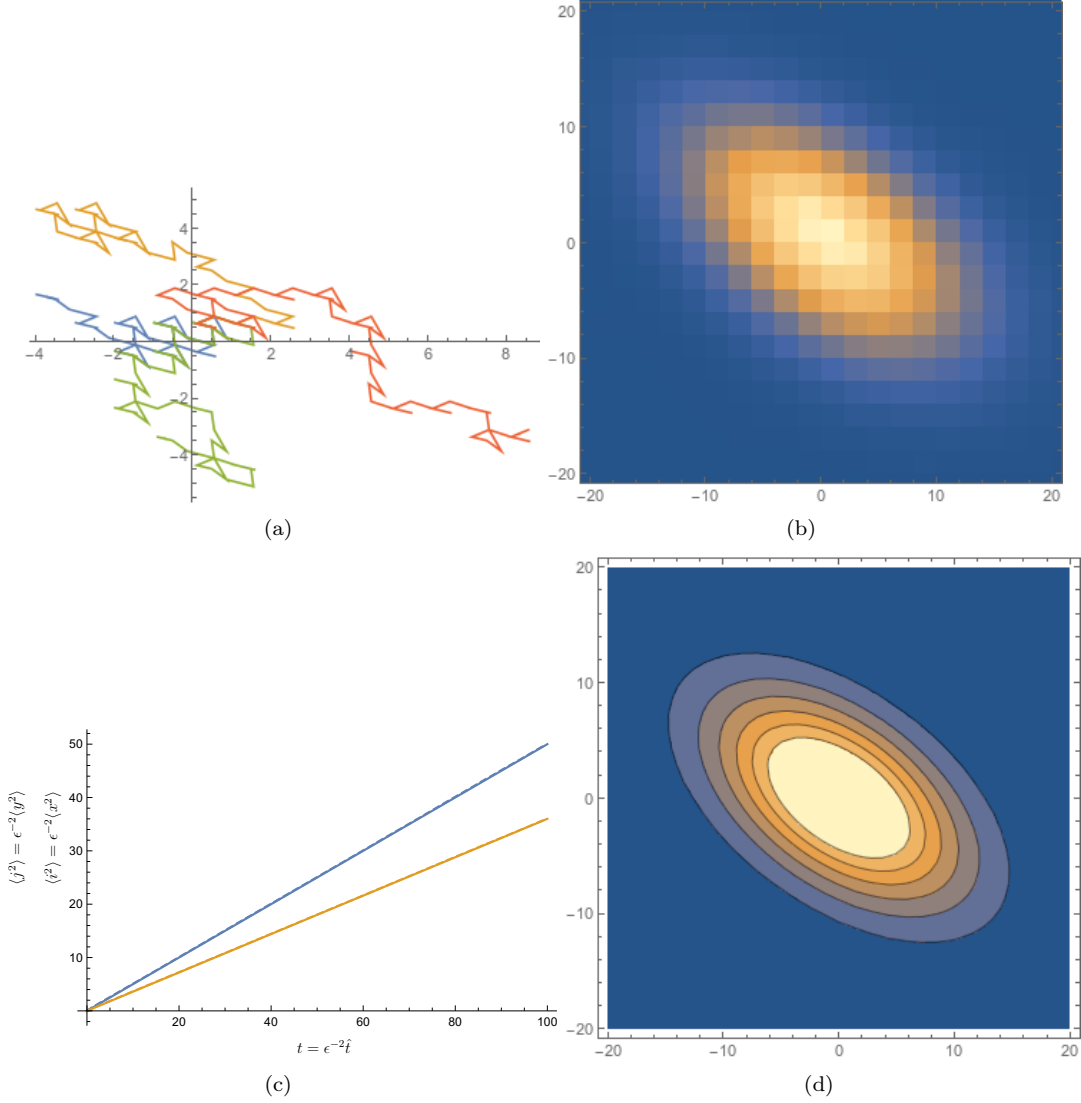


Figure 9: Results for the network shown in Figure 8, with $L_x = L_y = 1$, and non-zero transition rates $\lambda_{1 \rightarrow 2}^{00} = 8/3$, $\lambda_{1 \rightarrow 3}^{00} = 2$, $\lambda_{2 \rightarrow 1}^{00} = 6$, $\lambda_{2 \rightarrow 3}^{0-1} = 1$, $\lambda_{3 \rightarrow 1}^{10} = 2$, $\lambda_{3 \rightarrow 4}^{-11} = 2$, $\lambda_{3 \rightarrow 4}^{00} = 4$, $\lambda_{4 \rightarrow 2}^{00} = 3$. (a) Four sample paths for small times. (b) Histogram of the position at time $t = 100$ averaged over 10^6 monte carlo simulations. (c) Mean square x and y displacements averaged over 10^6 monte carlo simulations (dashed), with the predicted homogenised values $2D_{xx}t$ and $2D_{yy}t$ (solid). (d) Prediction of the distribution function at time $t = 100$ from the homogenisation.

the transition probabilities. For some special cases, such as transition rates which depend only on the source node and not the destination, we have been able to calculate simple explicit formulae

for these rates. In general, they require the solution of a pair of $n \times n$ linear systems of equations (55), where n is the number of nodes in the unit cell.

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