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Random walk with a hop-over site: a novel approach to tagged diffusion and its applications

R K P Zia and Z Toroczkai

Physics Department and Center for Stochastic Processes in Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0435, USA

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Abstract. We study, on a d-dimensional hypercubic lattice, a random walk which is homogeneous except for one site. Instead of visiting this site, the walker hops over it with arbitrary rates. The probability distribution of this walk and the statistics associated with the hop-overs are found exactly. This analysis provides a simple approach to the problem of tagged diffusion, i.e. the movements of a tracer particle due to the diffusion of a vacancy. Applications to vacancy mediated disordering are given through two examples.

1. Introduction

The venerable problem of a random walk on a regular d-dimensional hypercubic, infinite lattice continues to generate considerable interest [1–3], from both novel quantities associated with the simple walk and new variations of the walk itself. In the simplest case (which is called Pólya walk [4]), the walker moves to one of the nearest-neighbour sites with probability $1/2d$ at each timestep. One of the variations involves a 'taboo' site, to which the walker may never visit. The question that is usually asked refers to the probability [5, 1] ('taboo probability') of the walker visiting a certain site on the nth step without having visited the taboo site on any of the erlier steps $1, 2, \ldots, n-1$. An alternative way to think about the taboo site is to consider it as an irreversible trap, so that the above question translates into a question on the survival probability. A slightly different situation is when the walker arriving at a neighbouring site of the taboo, is allowed to remain stationary, with probability $1/2d$, instead of moving into the forbidden site. All these variations belong to the chapter of lattice walks with 'defective' sites in the theory of lattice walks [1]. In this paper, we investigate a further case of walks with a defective site, namely, the walker *hopping over* this special site. Since it is no longer 'taboo' (in the above sense), it will be referred to as the 'hop-over' site. We write the Master equation for such a walk, with $2d$ arbitrary hop-over rates. Thanks to translational invariance, we may choose to locate the hop-over site at the origin. In Fourier space, we obtain a closed expression, in terms of the inverse of a matrix, for the probability distribution generating function, given a particular initial position $\boldsymbol{s}_0$.

Similar to the derivation of 'taboo probabilities', the straightforward way to find the hop-over probabilities would rely on a study of return probabilities and first passage times. In this approach, probabilities of returning to the neighbourhood of the origin *without* hopping over it are exploited in infinite sums over individual hop-over attempts. A similar method was used for solving the related problem of tagged diffusion [6, 7]. Our present approach is different, considerably simpler and more compact in terms of formulae. Instead of infinite sums, only the inverse of a certain $2d \times 2d$ matrix needs to be computed. In $d = 2$, where this walk displays the most interesting characteristics, the inversion is quite simple.

We are also able to keep track of both the direction and the frequency of the hop-over attempts. As a result, an interesting application is the diffusive behaviour of a tagged particle [6, 7]. Such a tag may also be thought of as a 'passive walker', namely, a particle which remains inert until it is forced to exchange places with a normal, 'active' random walker. In metals or alloys, an impurity atom can play the role of a tag, while a vacancy diffuses as a typical walker [8–15]. We will discuss how to map the hop-over problem to the tagged walk. Finally, from the frequency of hop-over attempts, we can compute the distribution of 'hits' received by the tag. We present two related applications: the first studies the rate of disordering of the surface of an A-B alloy, with a certain type of interactions, due to the wandering of a surface vacancy, while the second investigates the asymptotic time evolution of the disorder caused by a single Brownian vacancy in an initially completely phase seggregated, two-species system.

This paper is organized as follows. In the next section, the model and the Master equation are carefully defined (sections 2.1 and 2.2) and the explicit solution is presented allowing for the extraction of the statistics on the hop-over events (section 2.3). Section 3 presents the relationship to the tagged diffusion problem with its complete solution through the techniques of section 2, along with two associated applications presented in sections 3.2 and 3.3. The last section is devoted to a summary and possible generalizations.

2. Random walk with a hop-over site

For completeness, we devote section 2.1 to definitions, notations, and some well known properties of a random walk on a lattice.

2.1. The simple random walk

On an infinite d-dimensional hypercubic lattice, the sites are labelled by $\boldsymbol{s}$ while the set of $2d$ lattice vectors is denoted by $\{\boldsymbol{a}\}$. A walker, performing a pure random walk of Pólya type [1, 4] moves from a site to one of the $2d$ nearest neighbour sites at each timestep (i.e. from $\boldsymbol{s}$ to $\boldsymbol{s}+\boldsymbol{a}$) with probability p. If $2dp < 1$, the walker remains stationary with probability $1 - 2dp$. Given an initial position $\boldsymbol{s}_0$ we are interested in the probability distribution of finding the walker after n steps at site $\boldsymbol{s}$: $P_n^F(\boldsymbol{s}|\boldsymbol{s}_0)$. Here, the superscript F reminds us that this is the distribution for 'free' diffusion. The equation governing this walk is

$$P_{n+1}^F(\boldsymbol{s}|\boldsymbol{s}_0) - P_n^F(\boldsymbol{s}|\boldsymbol{s}_0) = p\sum_{\{\boldsymbol{a}\}}[P_n^F(\boldsymbol{s}+\boldsymbol{a}|\boldsymbol{s}_0) - P_n^F(\boldsymbol{s}|\boldsymbol{s}_0)] \tag{1}$$

with the initial condition:

$$P_0^F(\boldsymbol{s}|\boldsymbol{s}_0) = \delta_{\boldsymbol{s},\boldsymbol{s}_0}. \tag{2}$$

Due to translational invariance, the solution can be obtained simply in terms of the generating function in Fourier space:

$$P(\boldsymbol{s}|\boldsymbol{s}_0;\xi) \equiv \sum_{n=0}^{\infty} P_n(\boldsymbol{s}|\boldsymbol{s}_0)\xi^n \qquad |\xi| < 1 \tag{3}$$

$$\tilde{P}(\boldsymbol{k};\xi) \equiv \sum_{\boldsymbol{s}} P(\boldsymbol{s}|\boldsymbol{s}_0;\xi)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{s}}. \tag{4}$$

Applying (3) to $s = 0$ in (1), we obtain a useful identity

$$\xi p \sum_{\{a\}} P^F(\boldsymbol{a}|\boldsymbol{s}_0;\xi) = [P^F(\boldsymbol{0}|\boldsymbol{s}_0;\xi) - \delta_{\boldsymbol{0},\boldsymbol{s}_0}] + \xi(2dp-1)P^F(\boldsymbol{0}|\boldsymbol{s}_0;\xi). \tag{5}$$

Continuing, we substitute (1) into (3) and (4) to arrive at

$$\frac{1}{\xi}[\tilde{P}^F(\boldsymbol{k};\xi) - \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{s}_0}] - \tilde{P}^F(\boldsymbol{k};\xi) = -p\sum_{\{a\}}[1-\cos(\boldsymbol{k}\cdot\boldsymbol{a})]\tilde{P}^F(\boldsymbol{k};\xi).$$

The solution is trivial:

$$\tilde{P}^F(\boldsymbol{k};\xi) = G(\boldsymbol{k},\xi)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{s}_0} \tag{6}$$

where

$$G(\boldsymbol{k},\xi) \equiv \left\{1 - \xi + \xi p \sum_{\{a\}}[1-\cos(\boldsymbol{k}\cdot\boldsymbol{a})]\right\}^{-1} \tag{7}$$

is the well known propagator for free diffusion.

The inverses to (4), (3) are given by

$$P(\boldsymbol{s}|\boldsymbol{s}_0;\xi) = \int_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{s}}\tilde{P}(\boldsymbol{k};\xi) \tag{8}$$

and

$$P_n(\boldsymbol{s}|\boldsymbol{s}_0) = \oint_{\xi} \xi^{-n} P(\boldsymbol{s}|\boldsymbol{s}_0;\xi) \tag{9}$$

where

$$\int_{\boldsymbol{k}} \equiv \int_{-\pi}^{\pi} \frac{\mathrm{d}^d k}{(2\pi)^d} \qquad \text{and} \qquad \oint_{\xi} \equiv \frac{1}{2\pi\mathrm{i}}\oint_{\mathcal{C}} \frac{\mathrm{d}\xi}{\xi}$$

and $\mathcal{C}$ is a suitable (counterclockwise) contour around $\xi = 0$. Thus, the solution to the simple random walk can be written as

$$P^F(\boldsymbol{s}|\boldsymbol{s}_0;\xi) = \int_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{s}-\boldsymbol{s}_0)} G(\boldsymbol{k},\xi) \tag{10}$$

and

$$P_n^F(\boldsymbol{s}|\boldsymbol{s}_0) = \int_{\boldsymbol{k}}\oint_{\xi} \xi^{-n}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{s}-\boldsymbol{s}_0)} G(\boldsymbol{k},\xi). \tag{11}$$

In subsequent sections, several probability distributions will occur frequently. For convenience, we summarize their properties here. Define

$$t \equiv P^F(\boldsymbol{0}|\boldsymbol{0};\xi) \tag{12}$$
$$u \equiv P^F(\boldsymbol{a}|\boldsymbol{0};\xi) \tag{13}$$
$$h \equiv P^F(\boldsymbol{a}|-\boldsymbol{a};\xi) \tag{14}$$
$$v \equiv P^F(\boldsymbol{a}|\boldsymbol{b};\xi) \qquad \boldsymbol{b} \neq \pm\boldsymbol{a} \qquad \text{(only for } d \geqslant 2) \tag{15}$$

all of which are known functions of ξ. In particular, $t(\xi)$ is just the generating function for the return probability of a pure random walk. The definitions (12), (14) and (15) allow us to write

$$P^F(\boldsymbol{a}|\boldsymbol{b};\xi) = v + (t-v)\delta_{\boldsymbol{a},\boldsymbol{b}} + (h-v)\delta_{\boldsymbol{a},-\boldsymbol{b}} \tag{16}$$

where both $\boldsymbol{a}$ and $\boldsymbol{b}$ are lattice vectors (nearest neighbours of the origin). Applying (5) to the simplest random walk ($p = 1/2d$), we find relations between t, u, h, and v [6], e.g. by choosing $\boldsymbol{s}_0 \equiv 0$ in (5)

$$t = 1 + \xi u \tag{17}$$

and (for $d \geqslant 2$) by choosing $\boldsymbol{s}_0 \equiv \boldsymbol{b}$

$$\xi p[t + 2(d-1)v + h] = u. \tag{18}$$

Finally, since we will be interested in late times ($n \to \infty$) corresponding to the limit $\xi \to 1^-$, we note the following well known asymptotic behaviour of t [1]:

$$t \to \begin{cases} 1/\sqrt{2(1-\xi)} & \text{for } d = 1 \\ \dfrac{1}{\pi} \ln\left(\dfrac{8}{1-\xi}\right) & \text{for } d = 2 \\ \text{constant} & \text{for } d > 2. \end{cases} \tag{19}$$

From (17), we conclude that u behaves the same way.

2.2. Walks with a hop-over site

Without loss of generality, let us place the hop-over site at the origin. The probability for the walker to hop from $-\boldsymbol{a}$ to $\boldsymbol{a}$ will be denoted by $p_{\boldsymbol{a}}$. By keeping this rate different from p, we will be able to log the different hop-over attempts. Clearly, $P_n^H(\boldsymbol{s}|\boldsymbol{s}_0)$, the distribution with such a site, will be a polynomial in the various $p_{\boldsymbol{a}}$'s. Meanwhile, the coefficient of $p_{\boldsymbol{a}}^{\nu_a}$ will be associated with the subset of those walks which have hopped over the origin (from $-\boldsymbol{a}$ to $\boldsymbol{a}$) $\nu_{\boldsymbol{a}}$ times. We will return to these considerations in more detail below.

Again, we let the walker start at $\boldsymbol{s}_0$, which is not the origin, i.e.

$$P_0^H(\boldsymbol{s}|\boldsymbol{s}_0) = \delta_{\boldsymbol{s},\boldsymbol{s}_0} \qquad \text{and} \qquad \boldsymbol{s}_0 \neq \mathbf{0}. \tag{20}$$

The subsequent evolution of P^H is governed by the following Master equation:

$$\begin{aligned} P_{n+1}^H(\boldsymbol{s}|\boldsymbol{s}_0) - P_n^H(\boldsymbol{s}|\boldsymbol{s}_0) &= p(1-\delta_{\boldsymbol{s},\mathbf{0}}) \sum_{\{a\}} [P_n^H(\boldsymbol{s}+\boldsymbol{a}|\boldsymbol{s}_0) - P_n^H(\boldsymbol{s}|\boldsymbol{s}_0)] \\ &\quad + \sum_{\{a\}} \delta_{\boldsymbol{s},\boldsymbol{a}} [p_{\boldsymbol{a}} P_n^H(-\boldsymbol{a}|\boldsymbol{s}_0) - (p_{-\boldsymbol{a}} - p) P_n^H(\boldsymbol{a}|\boldsymbol{s}_0)] \end{aligned} \tag{21}$$

the first term on the right shows that the walker never visits the forbidden site ($\mathbf{0}$) and that, away from the neighbourhood of the origin, it performs a simple Pólya walk (a 'free walk'). The latter term describes the possibility of hop-over, when the walker finds itself on a nearest-neighbour site of $\mathbf{0}$ (see figure 1).

Going over to $(\boldsymbol{k}, \xi)$ space by (4), (3), this equation becomes

$$\begin{aligned} G^{-1}(\boldsymbol{k};\xi)\tilde{P}^H(\boldsymbol{k};\xi) - \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{s}_0} &= -\xi p \sum_{\{a\}} P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi) \\ &\quad + \xi \sum_{\{a\}} [p_{\boldsymbol{a}} P^H(-\boldsymbol{a}|\boldsymbol{s}_0;\xi) - (p_{-\boldsymbol{a}} - p) P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi)] \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}. \end{aligned}$$

This representation clearly displays the effects of the 'defect' (associated with the hop-over site), since the left-hand side consists of the terms for the pure random walk, only. A more elegant form would be

$$G^{-1}(\boldsymbol{k};\xi)\tilde{P}^H(\boldsymbol{k};\xi) - \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{s}_0} = \xi \sum_{\{a\}} \Gamma(\boldsymbol{k},\boldsymbol{a}) P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi) \tag{22}$$

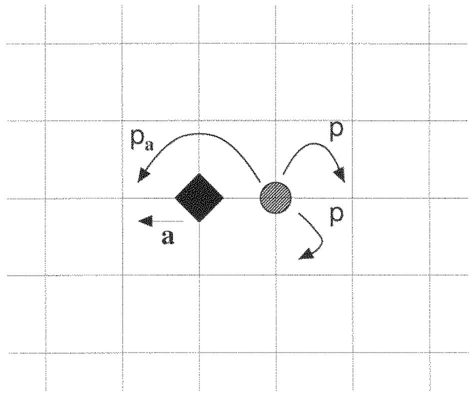

Figure 1. Random walk with a single hop-over site. The diamond symbolizes the hop-over site located in the origin and the circle represents the vacancy.

where

$$\Gamma(\boldsymbol{k},\boldsymbol{a}) \equiv p(\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}-1)+p_{-\boldsymbol{a}}(\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}-\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}). \tag{23}$$

Now, the right-hand side of (22) can be regarded as an extra inhomogeneity for the solution:

$$\tilde{P}^H(\boldsymbol{k};\xi) = G(\boldsymbol{k};\xi)\left[\mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{s}_0}+\xi\sum_{\{\boldsymbol{a}\}}\Gamma(\boldsymbol{k},\boldsymbol{a})P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi)\right]. \tag{24}$$

To find the solution explicitly, we must determine the $2d$ quantities $P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi)$. This can be done by exploiting (8) and (24)

$$\begin{aligned}P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi) &= \int_{\boldsymbol{k}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}\tilde{P}^H(\boldsymbol{k};\xi)\\ &= \int_{\boldsymbol{k}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}G(\boldsymbol{k};\xi)\left[\mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{s}_0}+\xi\sum_{\{\boldsymbol{b}\}}\Gamma(\boldsymbol{k},\boldsymbol{b})P^H(\boldsymbol{b}|\boldsymbol{s}_0;\xi)\right]\\ &= P^F(\boldsymbol{a}|\boldsymbol{s}_0;\xi)+\sum_{\{\boldsymbol{b}\}}\xi\int_{\boldsymbol{k}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}G(\boldsymbol{k};\xi)\Gamma(\boldsymbol{k},\boldsymbol{b})P^H(\boldsymbol{b}|\boldsymbol{s}_0;\xi).\end{aligned} \tag{25}$$

Linear in $P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi)$, equation (25) can be solved:

$$P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi) = \sum_{\{\boldsymbol{b}\}}\boldsymbol{L}_{a,b}(\xi)P^F(\boldsymbol{b}|\boldsymbol{s}_0;\xi) \tag{26}$$

where $\boldsymbol{L}$ is the inverse of the $2d\times 2d$ matrix with elements:

$$(\boldsymbol{L}^{-1})_{a,b} = \delta_{a,b}-\xi\int_{\boldsymbol{k}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}G(\boldsymbol{k};\xi)\Gamma(\boldsymbol{k},\boldsymbol{b}). \tag{27}$$

Once $P^H(\boldsymbol{a}|\boldsymbol{s}_0;\xi)$ are known, they can be substituted back into (24) and the explicit solution can be obtained:

$$\tilde{P}^H(\boldsymbol{k};\xi) = \tilde{P}^F(\boldsymbol{k};\xi)+\sum_{\{\boldsymbol{a},\boldsymbol{b}\}}\xi G(\boldsymbol{k};\xi)\Gamma(\boldsymbol{k},\boldsymbol{a})\boldsymbol{L}_{a,b}(\xi)P^F(\boldsymbol{b}|\boldsymbol{s}_0;\xi). \tag{28}$$

Using (8), we may return to the lattice:

$$P^H(\boldsymbol{s}|\boldsymbol{s}_0;\xi) = P^F(\boldsymbol{s}|\boldsymbol{s}_0;\xi)+\sum_{\{\boldsymbol{a},\boldsymbol{b}\}}\left[\xi\int_{\boldsymbol{k}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{s}}G(\boldsymbol{k};\xi)\Gamma(\boldsymbol{k},\boldsymbol{a})\right]\boldsymbol{L}_{a,b}(\xi)P^F(\boldsymbol{b}|\boldsymbol{s}_0;\xi). \tag{29}$$

Making use of equation (23) the elements of $\boldsymbol{L}^{-1}$ become expressed solely in free walk terms:

$$(\boldsymbol{L}^{-1})_{\boldsymbol{a},\boldsymbol{b}} = \delta_{\boldsymbol{a},\boldsymbol{b}} - \xi\{p_{-\boldsymbol{b}}P^F(\boldsymbol{a}|-\boldsymbol{b};\xi) + (p - p_{-\boldsymbol{b}})P^F(\boldsymbol{a}|\boldsymbol{b};\xi) - pP^F(\boldsymbol{a}|\boldsymbol{0};\xi)\}. \tag{30}$$

The integral in the square bracket of equation (29) is computed similarly:

$$\begin{aligned}\xi\int_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\boldsymbol{s}}G(\boldsymbol{k};\xi)\Gamma(\boldsymbol{k},\boldsymbol{a}) &= \xi p_{-\boldsymbol{a}}P^F(\boldsymbol{s}|-\boldsymbol{a};\xi)\\ &\quad+\xi(p-p_{-\boldsymbol{a}})P^F(\boldsymbol{s}|\boldsymbol{a};\xi) - \xi pP^F(\boldsymbol{s}|\boldsymbol{0};\xi).\end{aligned} \tag{31}$$

Equations (29)–(31) express the generating function of the hop-over walk in terms of the hop-over rates $\{p_{\boldsymbol{a}}\}$ and the generating function characterizing the free walk. It may be worthwhile to interpret the second term in (29) physically. From (27) $\boldsymbol{L}$ can be expanded as a power series in $\boldsymbol{\Gamma}$, which accounts for the difference between a free passage through the origin and an hop-over. Thus, the nth term in this $\boldsymbol{\Gamma}$ series in (29) can be thought of as paths which have n encounters with the hop-over site. This connection will be explored further in the next section.

Here, we end with a closer look into the case with *isotropic* hop-over rates, i.e.

$$p_{\boldsymbol{a}} = p'$$

but with p' not necessarily being equal to p. Then, equations (29)–(31) reduce to

$$\begin{aligned}P^H(\boldsymbol{s}|\boldsymbol{s}_0;\xi) &= P^F(\boldsymbol{s}|\boldsymbol{s}_0;\xi) + \xi\sum_{\{\boldsymbol{a},\boldsymbol{b}\}}[p'P^F(\boldsymbol{s}|-\boldsymbol{a};\xi) + (p-p')P^F(\boldsymbol{s}|\boldsymbol{a};\xi)\\ &\quad-pP^F(\boldsymbol{s}|\boldsymbol{0};\xi)]\boldsymbol{L}_{\boldsymbol{a},\boldsymbol{b}}(\xi)P^F(\boldsymbol{b}|\boldsymbol{s}_0;\xi)\end{aligned} \tag{32}$$

while our task is to invert,

$$(\boldsymbol{L}^{-1})_{\boldsymbol{a},\boldsymbol{b}} = \delta_{\boldsymbol{a},\boldsymbol{b}} - \xi[p'P^F(\boldsymbol{a}|-\boldsymbol{b};\xi) + (p-p')P^F(\boldsymbol{a}|\boldsymbol{b};\xi) - pP^F(\boldsymbol{a}|\boldsymbol{0};\xi)] \tag{33}$$

where $\boldsymbol{a}$ and $\boldsymbol{b}$ are nearest neighbours of the origin. Due to isotropy and homogeneity, this matrix reduces considerably. The last term in the [...] brackets above is seen to be a constant (13), $-pu$, for *all* matrix elements. Using (16), we write (33) as

$$\begin{aligned}(\boldsymbol{L}^{-1})_{\boldsymbol{a},\boldsymbol{b}} &= \xi p(u-v) + \delta_{\boldsymbol{a},\boldsymbol{b}}[1 - \xi(p'(h-t) + p(t-v))]\\ &\quad-\delta_{\boldsymbol{a},-\boldsymbol{b}}\xi[p'(t-h) + p(h-v)].\end{aligned} \tag{34}$$

Since this matrix is of the form

$$A + B\delta_{\boldsymbol{a},\boldsymbol{b}} + C\delta_{\boldsymbol{a},-\boldsymbol{b}} \tag{35}$$

it is easy to check that its inverse is also of this form, namely,

$$\boldsymbol{L}_{\boldsymbol{a},\boldsymbol{b}} = A' + B'\delta_{\boldsymbol{a},\boldsymbol{b}} + C'\delta_{\boldsymbol{a},-\boldsymbol{b}} \tag{36}$$

$$= \frac{1}{B^2 - C^2}\left[\left(\frac{A(C-B)}{2dA + B + C}\right) + B\delta_{\boldsymbol{a},\boldsymbol{b}} - C\delta_{\boldsymbol{a},-\boldsymbol{b}}\right]. \tag{37}$$

With the help of (34)–(37), we can carry out the matrix multiplication in (32). Note that a quite a few sums over $\{\boldsymbol{a},\boldsymbol{b}\}$ decouple. For example, using (5) and $P^F(\boldsymbol{s}|\boldsymbol{s}';\xi) = P^F(\boldsymbol{s}'|\boldsymbol{s};\xi)$, we have

$$\xi\sum_{\{\boldsymbol{a}\}}[p'P^F(\boldsymbol{s}|-\boldsymbol{a};\xi) + (p-p')P^F(\boldsymbol{s}|\boldsymbol{a};\xi) - pP^F(\boldsymbol{s}|\boldsymbol{0};\xi)] = (1-\xi)P^F(\boldsymbol{s}|\boldsymbol{0};\xi).$$

The explicit expression for our walker to move from $\boldsymbol{s_0}$ to $\boldsymbol{s}$, with isotropic hop-over rate p', is

$$\begin{aligned}P^H(\boldsymbol{s}|\boldsymbol{s}_0;\xi) = P^F(\boldsymbol{s}|\boldsymbol{s}_0;\xi) - [B' + C' - A'(1-\xi)/\xi p] \\ \times[1-\xi+2d\xi p]P^F(\boldsymbol{s}|\boldsymbol{0};\xi)P^F(\boldsymbol{0}|\boldsymbol{s_0};\xi) \\ +\xi[B'p + (C'-B')p']\sum_{\{a\}} P^F(\boldsymbol{s}|\boldsymbol{a};\xi)P^F(\boldsymbol{a}|\boldsymbol{s}_0;\xi) \\ +\xi[C'p + (B'-C')p']\sum_{\{a\}} P^F(\boldsymbol{s}|-\boldsymbol{a};\xi)P^F(\boldsymbol{a}|\boldsymbol{s}_0;\xi)\end{aligned} \tag{38}$$

where A', B', and C' are to be read off from (34)–(37). Except for the first term (which stands for the 'free' case), this expression shows the non-trivial effect of a single hop-over site on the random walk explicitly . The various terms can be easily interpreted: the second term removes the (free) walks which pass through the origin, while the last two takes into account walks which land on a neighbour. If we take the usual continuum limit (the lattice spacing $a \to 0$, unit timestep $\tau \to 0$, such that $a^2/\tau = 2d$) of this expression, the effect becomes vanishingly small. This result is perhaps not surprising, since a single site cannot affect the properties of the random walker in the large distance, long time limit. However, buried in this approach is a non-trivial question, namely, the statistics associated with the hop-overs (how often and in which direction does the walker hops over the origin). That is the subject of the next section.

2.3. *Statistics of hop-overs*

Next, we turn to a study of the statistics of the hop-overs. Note that, due to the longer jumps (across the origin), the walker suffers an *extra* displacement when compared with the simple free walk. We define the variable $\boldsymbol{\rho}$ as the *negative* of this extra displacement, for reasons that will become obvious later. We will also be interested in the number of times a hop-over jump has occurred. Thus, we define $\phi_n^\nu(\boldsymbol{s},\boldsymbol{\rho}|\boldsymbol{s}_0)$ as the probability that, starting from $\boldsymbol{s}_0$, the walker arrives at site $\boldsymbol{s}$ after n steps,

- having performed ν hops over the origin and
- suffering a total 'extra' displacement equal to $-\boldsymbol{\rho}$.

As usual, it is more convenient to work with generating functions in Fourier space. Accordingly, we trade the variables $(\boldsymbol{s},\boldsymbol{\rho})$ and (n,ν) for their conjugates: $(\boldsymbol{k},\boldsymbol{\kappa})$ and (ξ,ζ). We can write

$$\tilde{\Phi}(\boldsymbol{k},\boldsymbol{\kappa};\xi,\zeta) = \sum_{n,\nu=0}^{\infty}\sum_{\boldsymbol{s},\boldsymbol{\rho}} \xi^n\zeta^\nu \mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{s}+\boldsymbol{\kappa}\cdot\boldsymbol{\rho})}\phi_n^\nu(\boldsymbol{s},\boldsymbol{\rho}|\boldsymbol{s}_0). \tag{39}$$

Once $\tilde{\Phi}(\boldsymbol{k},\boldsymbol{\kappa};\xi,\zeta)$ is known, the inverse transforms will lead us to the distribution itself:

$$\phi_n^\nu(\boldsymbol{s},\boldsymbol{\rho}|\boldsymbol{s}_0) = \oint_{\xi,\zeta}\int_{\boldsymbol{k},\boldsymbol{\kappa}} \xi^{-n}\zeta^{-\nu}\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{s}+\boldsymbol{\kappa}\cdot\boldsymbol{\rho})}\tilde{\Phi}(\boldsymbol{k},\boldsymbol{\kappa};\xi,\zeta). \tag{40}$$

To arrive at an expression for $\tilde{\Phi}(\boldsymbol{k},\boldsymbol{\kappa};\xi,\zeta)$, we first study a more detailed distribution: $\phi_n^{\{\nu_a\}}(\boldsymbol{s}|\boldsymbol{s}_0)$, i.e. the probability of the walker makes exactly $\nu_{\boldsymbol{a}}$ hops from $-\boldsymbol{a}$ to $\boldsymbol{a}$ (for each $\boldsymbol{a}$). Here $\{\nu_{\boldsymbol{a}}\}$ denotes the set of $2d$ numbers associated with the different directions of hop-over. Since each hop-over may occur only with probability $p_{\boldsymbol{a}}$, and the events are independent, we conclude that $\phi_n^{\{\nu_a\}}(\boldsymbol{s}|\boldsymbol{s}_0)$ must contain the factor $\prod_{\{a\}} p_{\boldsymbol{a}}^{\nu_a}$, where $\Pi_{\{a\}}$ is product over all the $2d$ nearest neighbours.

Meanwhile, the extra displacement is just $-\boldsymbol{\rho} = \sum_{\{a\}} \boldsymbol{a}\nu_{\boldsymbol{a}}$, so that

$$\phi_n^{\nu}(\boldsymbol{s}, \boldsymbol{\rho}|\boldsymbol{s}_0) = \sum_{\{\nu_a\}} \phi_n^{\{\nu_a\}}(\boldsymbol{s}|\boldsymbol{s}_0)\ \delta_{\nu, \sum_{\{a\}} \nu_a}\ \delta_{-\boldsymbol{\rho}, \sum_{\{a\}} \boldsymbol{a}\nu_a}. \tag{41}$$

In terms of generating functions, this expression becomes:

$$\tilde{\Phi}(\boldsymbol{k}, \boldsymbol{\kappa}; \xi, \zeta) = \sum_{\{\nu_a\}} \tilde{\Phi}^{\{\nu_a\}}(\boldsymbol{k}; \xi) \prod_{\{a\}} \zeta^{\nu_a} \mathrm{e}^{-\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{a}\nu_a} \tag{42}$$

where $\tilde{\Phi}^{\{\nu_a\}}(\boldsymbol{k}; \xi)$ is the generating function and Fourier transform of $\phi_n^{\{\nu_a\}}(\boldsymbol{s}|\boldsymbol{s}_0)$.

Armed with these considerations, we interpret the expression (28) physically. Expanding $\boldsymbol{L}$ in a power series in the $p_{\boldsymbol{a}}$'s, we see that P^H itself is a power series in these rates. Naively, it is tempting to identify these coefficients with $\phi_n^{\{\nu_a\}}(\boldsymbol{s})$. However, there is an *implicit* probability for the walker to *remain* at the site $-\boldsymbol{a}$:

$$(1 - p_{\boldsymbol{a}} - (2d - 1)p)$$

so that the coefficient of $p_{\boldsymbol{a}}$ also includes paths that avoid the origin. Another way to see this difficulty is through the original Master equation (21), in which a particular $p_{\boldsymbol{a}}$ appears twice, once in the 'gain' of $P^H(\boldsymbol{a})$ and once in the 'loss' of $P^H(-\boldsymbol{a})$. Of course, both of these terms represent the *same* jump. Therefore, to avoid double counting, we can label one of them by $q_{\boldsymbol{a}}$ and, only at the end, set $q_{\boldsymbol{a}} = p_{\boldsymbol{a}}$. Let us emphasize that, with $q_{\boldsymbol{a}} \neq p_{\boldsymbol{a}}$, total probability will not be conserved. But this is precisely the trick for distinguishing making a hop-over jump from *not* making one.

For definiteness, let us choose to label the 'gain' term by $q_{\boldsymbol{a}}$. A little care leads us to a modified version of (23):

$$\begin{aligned}\overline{\Gamma}(\boldsymbol{k}, \boldsymbol{a}) &\equiv p(\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} - 1) + q_{-\boldsymbol{a}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} - p_{-\boldsymbol{a}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} \\ &= q_{-\boldsymbol{a}}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} + (p - p_{-\boldsymbol{a}})\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} - p\end{aligned} \tag{43}$$

from which we can find

$$\overline{\tilde{P}}^H(\boldsymbol{k}; \xi) = \tilde{P}^F(\boldsymbol{k}; \xi) + \sum_{\{\boldsymbol{a},\boldsymbol{b}\}} \xi G(\boldsymbol{k}; \xi)\overline{\Gamma}(\boldsymbol{k}, \boldsymbol{a})\overline{L}_{\boldsymbol{a},\boldsymbol{b}}(\xi) P^F(\boldsymbol{b}; \xi). \tag{44}$$

Note that the overline over a quantity symbolizes the dependence on both sets of rates: $\{q_{\boldsymbol{a}}\}$ and $\{p_{\boldsymbol{a}}\}$.

With this trick, we can associate the coefficient of $(q_{\boldsymbol{a}})^{\nu_a}$, in a power series expansion of $\overline{\tilde{P}}^H$, with walks that include $\nu_{\boldsymbol{a}}$ hop-overs (jumps from $-\boldsymbol{a}$ to $\boldsymbol{a}$). Now, we must pick out these coefficients and then multiply them with the correct weight: $(p_{\boldsymbol{a}})^{\nu_a}$. This is accomplished by applying $p_{\boldsymbol{a}}^{\nu_a} \oint_{q_a} q_{\boldsymbol{a}}^{-\nu_a}$ for each $\boldsymbol{a}$, so that

$$\tilde{\Phi}^{\{\nu_a\}}(\boldsymbol{k}; \xi) = \prod_{\{a\}} \oint_{q_a} (p_a/q_a)^{\nu_a} \overline{\tilde{P}}^H(\boldsymbol{k}; \xi). \tag{45}$$

Substituting equation (45) back into (42), we see that the dependence on the variables $\nu_{\boldsymbol{a}}$ factorizes. Performing the sums over each $\nu_{\boldsymbol{a}}$, we arrive at

$$\tilde{\Phi}(\boldsymbol{k}, \boldsymbol{\kappa}; \xi, \zeta) = \prod_{\{a\}} \frac{1}{2\pi\mathrm{i}} \oint \frac{\mathrm{d}q_{\boldsymbol{a}}}{q_{\boldsymbol{a}} - p_{\boldsymbol{a}}\zeta\,\mathrm{e}^{-\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{a}}} \overline{\tilde{P}}^H(\boldsymbol{k}; \xi) \tag{46}$$

i.e.

$$\tilde{\Phi}(\boldsymbol{k}, \boldsymbol{\kappa}; \xi, \zeta) = \overline{\tilde{P}}^H(\boldsymbol{k}; \xi)|_{q_a = p_a\zeta\,\mathrm{e}^{-\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{a}}}. \tag{47}$$

In other words, $\tilde{\Phi}(\boldsymbol{k}, \boldsymbol{\kappa}; \xi, \zeta)$ is nothing but $\tilde{\overline{P}}^H(\boldsymbol{k}; \xi)$ with all the $q_{\boldsymbol{a}}$'s simply replaced by $p_{\boldsymbol{a}}\zeta\,\mathrm{e}^{-\mathrm{i}\boldsymbol{\kappa a}}$.

From expression (44) for $\tilde{\overline{P}}^H$, we write explicitly:

$$\tilde{\Phi}(\boldsymbol{k}, \boldsymbol{\kappa}; \xi, \zeta) = \tilde{P}^F(\boldsymbol{k}; \xi) + \sum_{\{\boldsymbol{a},\boldsymbol{b}\}} \xi G(\boldsymbol{k}; \xi)\overline{\Gamma}(\boldsymbol{k}, \boldsymbol{\kappa}, \boldsymbol{a}; \zeta)\overline{\boldsymbol{L}}_{\boldsymbol{a},\boldsymbol{b}}(\boldsymbol{\kappa}; \xi, \zeta)P^F(\boldsymbol{b}|\boldsymbol{s}_0; \xi) \tag{48}$$

where

$$\overline{\Gamma}(\boldsymbol{k}, \boldsymbol{\kappa}, \boldsymbol{a}; \zeta) = p_{-\boldsymbol{a}}[\zeta\,\mathrm{e}^{-\mathrm{i}(\boldsymbol{k}-\boldsymbol{\kappa})\cdot\boldsymbol{a}} - \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}}] + p(\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} - 1) \tag{49}$$

and

$$(\overline{\boldsymbol{L}}^{-1}(\boldsymbol{\kappa}; \xi, \zeta))_{\boldsymbol{a},\boldsymbol{b}} = \delta_{\boldsymbol{a},\boldsymbol{b}} - \xi\{p_{-\boldsymbol{b}}\zeta\mathrm{e}^{\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{b}}P^F(\boldsymbol{a}| - \boldsymbol{b}; \xi) + (p - p_{-\boldsymbol{b}})P^F(\boldsymbol{a}|\boldsymbol{b}; \xi) - pu\}. \tag{50}$$

Due to the extra factor $\zeta\mathrm{e}^{\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{b}}$, it is difficult, even for the isotropic hop-over walk, to invert $\overline{\boldsymbol{L}}$ in arbitrary d. However, since most of the interesting effects occur in $d = 2$ (where the return probability approaches unity for large times), the 4×4 matrix can always be inverted.

2.4. A hidden pure random walk

Finally, if we are interested in the simple hop-over problem in which all the rates are identical, then we simply set all $p_{\boldsymbol{a}}$'s to p. In this case, we should also retrieve the pure random walk if we *subtract* the extra displacements due to the hop-overs. In other words, let us consider the probability of finding the walker at $\boldsymbol{s} - (-\boldsymbol{\rho})$, regardless of how many hop-overs occurred or their directions. Thus, we study

$$P_n(\boldsymbol{r}|\boldsymbol{s}_0) \equiv \sum_{\boldsymbol{s}}\sum_{\boldsymbol{\rho}} \delta_{\boldsymbol{r},\boldsymbol{s}+\boldsymbol{\rho}} \sum_{\nu=0}^{\infty} \phi_n^{\nu}(\boldsymbol{s}, \boldsymbol{\rho}|\boldsymbol{s}_0).$$

Again, it is easier to study the generating function in Fourier space: Using $\boldsymbol{k}$ as the variable conjugate to $\boldsymbol{r}$, we see that the above sums result in

$$\begin{aligned}\tilde{P}(\boldsymbol{k}; \xi) &= \sum_{n,\boldsymbol{r}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\xi^n P_n(\boldsymbol{r}|\boldsymbol{s}_0) \\ &= \tilde{\Phi}(\boldsymbol{k}, \boldsymbol{\kappa} = \boldsymbol{k}; \xi, \zeta = 1).\end{aligned}$$

Setting in (49) $p_{-\boldsymbol{a}} = p$ for each $\boldsymbol{a}$, $\boldsymbol{\kappa} = \boldsymbol{k}$ and $\zeta = 1$ we see that $\overline{\Gamma}(\boldsymbol{k}, \boldsymbol{\kappa} = \boldsymbol{k}, \boldsymbol{a}; \zeta = 1) = 0$. Thus, from (44), we obtain

$$\tilde{P}(\boldsymbol{k}; \xi) = \tilde{P}^F(\boldsymbol{k}; \xi) \tag{51}$$

justifying our expectation that, if we *subtract* the displacements due to hop-overs, the simple random walk re-emerges.

3. Relation to tagged diffusion and some applications

The problem of tagged diffusion has been solved previously [7] (in two dimensions), [6] (in d dimensions), using a 'direct' approach, i.e. by keeping track of all the possible ways for the tag to be displaced by a random walker. In this section, we will first show that the above analysis can be applied to provide a new approach to this venerable problem. As examples of applications of our results, we devote the latter subsections to the dynamics of two particular physical systems.

3.1. The passive walk or tagged diffusion

For completeness, let us describe tagged diffusion in terms of a 'passive' random walker. Returning to our infinite d-dimensional hypercubic lattice, we place two walkers, one active and one passive. Respectively, we label them B (for Brownian) and T (for tagged, or tracer, particle). The former performs the simplest random walk, as in section 1.1 with $p = 1/2d$. When B attempts to move to the site occupied by T, the two simply exchange places. Thus, T does not move except when it is 'kicked' by B. In this sense, the motion of T could be called 'passive' and will be referred to as a '*Brownian driven walk*'. The mathematical properties of this pair of walkers are contained in the joint probability

$$\Phi_n^\nu(\boldsymbol{r}, \boldsymbol{\rho}|\boldsymbol{r}_0, 0) \tag{52}$$

for finding B at site $\boldsymbol{r}$ and T at site $\boldsymbol{\rho}$, on the nth step of B and the νth step of T. Note that, ν just represents the number of 'kicks' T received from B. The last arguments refer to the initial condition, i.e. T being at the origin $\mathbf{0}$ and B at site $\boldsymbol{r}_0 \neq \mathbf{0}$.

From the description above, it is clear that, *relative to* T, B is performing a random walk with a hop-over site. Thus,

$$\Phi_n^\nu(\boldsymbol{r}, \boldsymbol{\rho}|\boldsymbol{r}_0, \mathbf{0}) = \phi_n^\nu(\boldsymbol{s}, \boldsymbol{\rho}|\boldsymbol{s}_0) \tag{53}$$

of the previous section, provided $\boldsymbol{r}_0 \equiv \boldsymbol{s}_0$, and

$$\boldsymbol{s} = \boldsymbol{r} - \boldsymbol{\rho} \tag{54}$$

which is just the position of B relative to T. Of course, we expect the results following this approach to be identical to those from the more 'direct' approaches in [6, 7]. To be brief, here we will present only a certain projection of the distribution $\Phi_n^\nu(\boldsymbol{r}, \boldsymbol{\rho}|\boldsymbol{r}_0, \mathbf{0})$, and compare the results with those in [6].

Let us focus on the probability that T received ν 'kicks' during n steps of B, regardless of the final locations of the two walkers. Denoting this quantity by $\phi_n^\nu(\boldsymbol{r}_0)$, it is

$$\phi_n^\nu(\boldsymbol{r}_0) = \sum_{\boldsymbol{r},\boldsymbol{\rho}} \Phi_n^\nu(\boldsymbol{r}, \boldsymbol{\rho}|\boldsymbol{r}_0, \mathbf{0}) = \sum_{\boldsymbol{s},\boldsymbol{\rho}} \phi_n^\nu(\boldsymbol{s}, \boldsymbol{\rho}|\boldsymbol{s}_0). \tag{55}$$

From (39) and (47), we see that the generating function

$$\phi(\xi, \zeta) \equiv \sum_{n,\nu} \phi_n^\nu \xi^n \zeta^\nu$$

is given by

$$\phi(\xi, \zeta) = \tilde{\Phi}(\mathbf{0}, \mathbf{0}; \xi, \zeta) = \overline{\tilde{P}}^H(\mathbf{0}, \mathbf{0}; \xi, \zeta). \tag{56}$$

Since B performs a random walk, we set $p_{\boldsymbol{a}} = p$ everywhere. Thus, from equation (48), we have

$$\phi(\xi, \zeta) = \frac{1}{1-\xi}\left[1 + \xi \sum_{\{\boldsymbol{a},\boldsymbol{b}\}} \overline{\Gamma}(\mathbf{0}, \mathbf{0}, \boldsymbol{a}; \zeta)\overline{L}_{\boldsymbol{a},\boldsymbol{b}}(\mathbf{0}; \xi, \zeta) P^F(\boldsymbol{b}|\boldsymbol{s}_0; \xi)\right]. \tag{57}$$

Using (49), (50) and (16), we find

$$\overline{\Gamma}(\mathbf{0}, \mathbf{0}, \boldsymbol{a}; \zeta) = -p(1-\zeta) \tag{58}$$

and

$$(\overline{\boldsymbol{L}}^{-1}(\mathbf{0}; \xi, \zeta))_{\boldsymbol{a},\boldsymbol{b}} = \xi p(u - \zeta v) + [1 - \xi\zeta p(h - v)]\delta_{\boldsymbol{a},\boldsymbol{b}} - \xi\zeta p(t - v)\delta_{\boldsymbol{a},-\boldsymbol{b}}. \tag{59}$$

Following (35)–(37), we write $\bar{\boldsymbol{L}}_{\boldsymbol{a},\boldsymbol{b}}$ in the form

$$\bar{\boldsymbol{L}}_{\boldsymbol{a},\boldsymbol{b}} = A' + B'\delta_{\boldsymbol{a},\boldsymbol{b}} + C'\delta_{\boldsymbol{a},-\boldsymbol{b}} \tag{60}$$

so that

$$\phi(\xi,\zeta) = \frac{1}{1-\xi}\left[1 - \xi p(1-\zeta)(2dA' + B' + C')\sum_{\{b\}} P^F(\boldsymbol{b}|\boldsymbol{s}_0;\xi)\right]. \tag{61}$$

Now, to simplify this some more, we make use of (5) and carry out the algebra for A', A, etc:

$$\frac{1}{1-\xi}\left[1 - \frac{(1-\zeta)}{1+\xi u + \zeta\xi p((2-2d)v - h - t)} P^F(\mathbf{0}|\boldsymbol{s}_0;\xi)\right]. \tag{62}$$

Finally, exploiting (17), (18), we write a compact form for the generating function:

$$\phi(\xi,\zeta) = \frac{1}{1-\xi}\left[1 - \frac{\xi(1-\zeta)}{\xi t - \zeta t + \zeta} P^F(\mathbf{0}|\boldsymbol{s}_0;\xi)\right]. \tag{63}$$

Before inverting this result to obtain ϕ_n^ν, let us explore the scaling properties of $\phi(\xi,\zeta)$, in the limit $\xi,\zeta \to 1^-$. For $d \leqslant 2$, t diverges according to (19), but $(1-\xi)t \to 0$. So does $P^F(\mathbf{0}|\boldsymbol{s}_0;\xi)$ for any $\boldsymbol{s}_0$, with the result that $P^F(\mathbf{0}|\boldsymbol{s}_0;\xi)/t \to 1$. Keeping the leading non-trivial orders, a simple scaling function emerges

$$(1-\xi)\phi(\xi,\zeta) \to \frac{1}{1+x} \tag{64}$$

where

$$x \equiv (1-\zeta)t \tag{65}$$

is the scaling variable. If we trace the origins of (19), we can use an explicit and more general form: $x = (1-\zeta)(1-\xi)^{(d-2)/2}$.

Returning to the inverse transforms, the one with respect to ζ is trivial. Keeping in mind (17), we find that $\oint_\zeta \zeta^{-\nu}\phi(\xi,\zeta)$ is identical to equations (34) and (35) of [6] obtained via a completely different method. Since t is a non-trivial function of ξ, the transform with respect to ξ cannot be carried out explicitly. Thus, we leave the final result in the form of an inverse transform:

$\nu \geqslant 1$:

$$\phi_n^\nu(\boldsymbol{r}_\mathbf{0}) = \oint_\xi \frac{\xi^{-n-\nu}}{(1-\xi)t}(1+\xi t - t)(1-1/t)^{\nu-1} P^F(\mathbf{0}|\boldsymbol{r}_0;\xi) \tag{66}$$

$\nu = 0$:

$$\phi_n^0(\boldsymbol{r}_\mathbf{0}) = \oint_\xi \frac{\xi^{-n}}{(1-\xi)t}[t - P^F(\mathbf{0}|\boldsymbol{r}_\mathbf{0};\xi)]. \tag{67}$$

These are the explicit formulae, in any d, for the probability that the tag particle (passive walker) moves ν steps while the vacancy (active walker) takes n steps, starting at $\boldsymbol{r}_\mathbf{0}$ from the tag. Of course, for $\nu, n \to \infty$, the scaling analysis above implies that

$$\nu \sim \sqrt{n} \qquad \text{and} \qquad \sqrt{\ln n}$$

in $d = 1$ and 2, respectively. Above two dimensions, the return probability of the random walker remains less than unity as $n \to \infty$, so that ϕ_n^ν decays exponentially in ν.

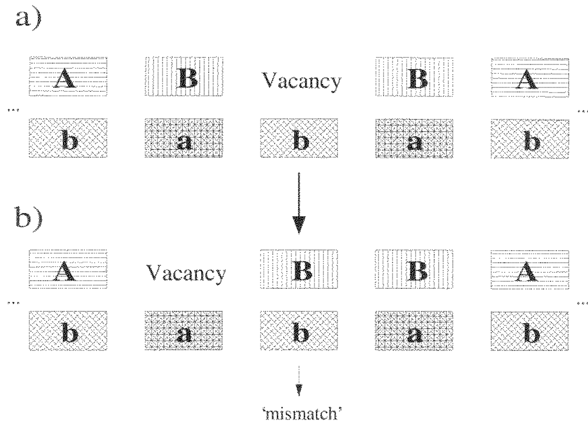

Figure 2. A binary alloy model with extreme anisotropy. The configuration (*a*) 'A on top of b' or 'B on top of a' is energetically favourable to, e.g. the configuration (*b*) 'B on top of b' which is considered as a mismatch.

3.2. Vacancy mediated disordering of an A-B alloy with extreme anisotropy

In some binary alloys, an ordered state consists of A and B atoms occupying alternate sites on a cubic lattice. Under appropriate conditions, an atom cannot move unless a vacancy comes in contact and exchanges places with it (also coined as the 'vacancy-mechanism') [8–15]. Therefore, each atom can be regarded as a passive walker, while the vacancy plays the role of an active walker. More precisely, consider a monolayer, composed of A and B atoms in a square lattice, adsorbed on a substrate which interacts strongly with these atoms in such a way that the ground state (of the monolayer) is a simple checkerboard configuration (antiferromagnetic state, in the spin language). To simplify the problem further, we suppose that the *intra*layer interactions are negligible. A similar arrangement may be realized by a binary alloy in a NaCl structure on a simple cubic lattice, with extreme anisotropic interactions. If the interactions are much stronger along the c-axis and we are focusing on a $(0, 0, 1)$ surface, the surface atoms will experience a much larger interaction with the bulk than with their neighbours on the surface. For clarity, we will distinguish the surface atoms from bulk ones, through labelling the former by A/B and the latter by a/b. The ground state, is shown in figure 2(*a*), with only Ab and Ba bonds (and, of course, AB and ab ones). Given our assumptions, Bb or Aa bonds, considered as 'mismatches', will be more costly. Thus the movement of the vacancy can cause such excitations (figure 2(*b*)). In a typical system, the vacancy will not perform a pure random walk, since its movements will be governed by these excitation (or de-excitation) energies. However, if subjected to sufficiently high temperatures, we could neglect this dependence and approximate the vacancy by a Brownian particle.

Focusing on such a vacancy wandering in our monolayer, we can investigate the evolution of the excitation energy through the creation of the mismatches. In particular, the analysis above can be applied to answer the following question: after a long time ($n \gg 1$) what is the expected excitation energy caused by this vacancy? Being proportional to the expected number of 'mismatches', this energy shift can be found readily. Note that, though the discussion above is clearly based on a $d = 2$ surface adsorbed on a $d = 3$ bulk, our considerations will be applicable in any d.

First, let the *vacancy* be located initially at the origin. Then we tag *each* atom simply by its initial location. Alternatively, using (54), we may use $\boldsymbol{s}_0$ (instead of $-\boldsymbol{s}_0$) to label the particle *uniquely*. After the vacancy has taken n steps, atom '$\boldsymbol{s}_0$' has suffered ν displacements with probability $\phi_n^\nu(\boldsymbol{s}_0)$, which is found in (55). If ν is odd, there is a 'mismatch' for that particle. The *expected* total number of mismatches is therefore expressed by

$$\langle Y_n \rangle = \sum_{\boldsymbol{s}_0}{}' \sum_{\nu=0}^{\infty} \tfrac{1}{2}[1-(-1)^\nu]\phi_n^\nu(\boldsymbol{s}_0) \tag{68}$$

where the prime on the summation symbol means that $\boldsymbol{s}_0 = \boldsymbol{0}$ is excluded. Such a sum for the quantities in equations (66) and (67) is trivial:

$$\sum_{\boldsymbol{s}_0}{}' P(\boldsymbol{0}|\boldsymbol{s}_0;\xi) = \sum_{\boldsymbol{s}_0} P(\boldsymbol{0}|\boldsymbol{s}_0;\xi) - P(\boldsymbol{0}|\boldsymbol{0};\xi) = \frac{1}{1-\xi} - t. \tag{69}$$

After summing over ν, we find the desired result:

$$\langle Y_n \rangle = \oint_\xi \frac{\xi^{1-n}}{(1-\xi)^2}\left[\frac{(\xi-1)t+1}{(\xi+1)t-1}\right]. \tag{70}$$

To proceed, let us consider the large n limit, corresponding to $\xi \to 1^-$. Since $(\xi-1)t \to 0$ even for cases when t diverges, the [.] bracket can be replaced by $1/(2t-1)$. The $n \to \infty$ behaviour can then be extracted by exploiting the discrete Tauberian theorem (see, e.g. [1, p 118]).

In $d = 1$, where we have a linear chain of atoms (adsorbed on a two-dimensional bulk), we find that the expected number of mismatches grows like

$$\langle Y_n \rangle \sim \sqrt{n}\sqrt{\frac{2}{\pi}}. \tag{71}$$

It is interesting to compare this result to the *expected number of distinct sites* visited in an n-step walk, which is a well known quantity [1]. In $d = 1$, it grows like

$$\langle S_n \rangle \sim \sqrt{n}\sqrt{\frac{8}{\pi}} \qquad \text{as } n \to \infty. \tag{72}$$

Thus, we find that

$$\frac{\langle Y_n \rangle}{\langle S_n \rangle} \to \frac{1}{2} \tag{73}$$

as $n \to \infty$, i.e. *half* of the visited sites will have mismatches. These results are hardly surprising, since, at any time, only the string of atoms between the walker and its initial position are 'mismatched'.

For $d = 2$, the physical case, the results are more interesting. With the help of the same theorem, we find

$$\langle Y_n \rangle \sim \frac{\pi}{2}\frac{n}{\ln(8n)} \qquad \text{as } n \to \infty \tag{74}$$

whereas [1]

$$\langle S_n \rangle \sim \frac{\pi n}{\ln(8n)} \qquad \text{as } n \to \infty \tag{75}$$

so that (73) proves to be valid in this case also.

Though bulk materials in four or higher dimensions are not physical, we may nevertheless consider the number of expected mismatches in $d \geqslant 3$. Here, $t(1)$ is finite, leading to

$$\langle Y_n \rangle \sim n \frac{1}{2t(1) - 1}. \tag{76}$$

Comparing it with

$$\langle S_n \rangle \sim n \frac{1}{t(1)} \tag{77}$$

we find, instead of (73), a more 'interesting' result:

$$\frac{\langle Y_n \rangle}{\langle S_n \rangle} \sim \frac{t(1)}{2t(1) - 1} = \frac{1}{1 + R(\mathbf{0})} \qquad \text{as } n \to \infty \tag{78}$$

where $R(\mathbf{0})$ is the probability that the walker ever returns to its starting site, another well known quantity in the theory of random walks. Actually, equation (78) is in fact valid for any $d \geqslant 1$. For $d \leqslant 2$, the walk is recurrent, i.e. $R(\mathbf{0}) = 1$, reducing (78) to $\frac{1}{2}$. Only for $d > 2$, is the walks transient, where $R(\mathbf{0}) < 1$. An alternative way to display (78) is to quote the ratio of particles performing an even number of exchanges with the hole to those 'visited' an odd number of times. Clearly, this ratio is simply $R(\mathbf{0})$. These remarks give an intuitive explanation for (78). Since the random walk is recurrent in $d = 1, 2$, every particle is sure to be *revisited.* Therefore, there should be as many particles visited an odd number of times as those visited an even number of times, on the average. However, for $d \geqslant 3$, a certain amount of the particles will be visited only *once*. Thus, the particles visited an odd number of times should be larger.

3.3. Propagation of interfacial disorder

As another example of how our results can be applied in disordering dynamics, we investigate the asymptotic behaviour of the disorder induced by a single Brownian vacancy [16]. Since the most interesting case is $d = 2$, we will limit our study here. The initial configuration is a completely phase segregated system, i.e. an infinite square lattice, with the upper half-plane filled with one type of particles (white) and the lower half-plane with the other type (black). A single vacancy (the active random walker) is placed in the white region at the interface between the two half-planes (figure 3), and labelled as the origin of our coordinate system. As the vacancy wanders, particles will be drawn into the opposite phases, leading to disordering. In the following, we will show that, after n steps taken by the wanderer, the 'disorder-profile' parallel and perpendicular to the interface scales as $\sqrt{n}$ and $\sqrt{\ln n}$, respectively. The scaling functions are combinations of exponentials and a modified Bessel function.

Let us focus on the black particles. One definition of disorder is the density of black particles in the upper half-plane. Thus, we seek

$$\Phi_n^*(\boldsymbol{s})$$

the probability of finding a black particle at location $\boldsymbol{s}$, after n steps of the vacancy. Since each particle performs a 'passive' random walk independent of the others, we may simply track the movements of each black particle and sum over all those which reach $\boldsymbol{s}$. As in previous sections each black particle can be labelled uniquely by its initial position $\boldsymbol{s}_0$.

Since we are not interested in neither the location of the vacancy nor the frequency of a particle being kicked it is clear that we should sum over the vacancy's position and the

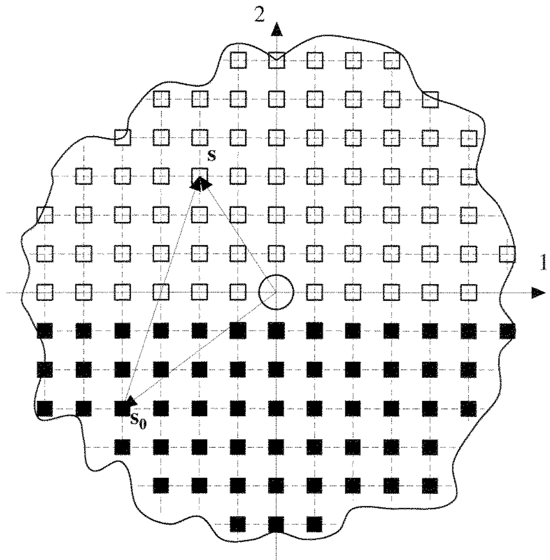

Figure 3. Initial configuration of a sharp interface between two different species (transparent and filled squares). The vacancy (large empty circle) is located initially at the origin of the coordinate system.

frequency of the hits the black particle receives. Summing over all the black particles, we see that

$$\Phi_n^*(s) = \sum_{s_0}^{(-)} \phi_n(s - s_0| - s_0) = \sum_{s_0}^{(-)} \sum_{r} \sum_{\nu=0}^{\infty} \phi_n^{\nu}(r, s - s_0| - s_0) \tag{79}$$

where $\sum^{(-)}$ denotes summation over the s_0's in the lower half-plane only, and r is the walker's position after n steps relative to the site s_0. In terms of the generating function (cf equations (39) and (40)), we have

$$\Phi^*(s;\xi) = \int_{\kappa} \sum_{s_0}^{(-)} \mathrm{e}^{-\mathrm{i}(s-s_0)\kappa} \tilde{\Phi}(\mathbf{0}, \kappa| - s_0; \xi, 1) \tag{80}$$

where the sums over ν and r have been carried out and the explicit dependence on s_0 restored. Referring to equations (48)–(50), we have

$$\tilde{\Phi}(\mathbf{0}, \kappa| - s_0; \xi, 1) = \frac{1}{1-\xi}\left\{1 + \xi \sum_{\{a,b\}} \overline{\Gamma}(\mathbf{0}, \kappa, a; 1)\overline{L}_{a,b}(\kappa; \xi, 1) P^F(b| - s_0; \xi)\right\} \tag{81}$$

$$\overline{\Gamma}(\mathbf{0}, \kappa, a; 1) = p(\mathrm{e}^{\mathrm{i}\kappa\cdot a} - 1) \tag{82}$$

and

$$(\overline{L}^{-1}(\kappa; \xi, 1))_{a,b} = \delta_{a,b} - \xi p\{\mathrm{e}^{\mathrm{i}\kappa\cdot b} P^F(a| - b; \xi) - u\}. \tag{83}$$

At this point, we will restrict our attention to $d = 2$ only. Clearly, there is no interesting behaviour in $d = 1$. On the other hand, the random walk being transient in $d > 2$, disorder will be confined in the large time limit.

In two dimensions, the matrix (83) is 4×4 and must be inverted laboriously. The calculations involved from (80) to (83) are reasonably straightforward, but extremely lengthy. We shall present only the final result obtained in the $n \gg 1$ limit.

For *fixed* $\boldsymbol{s} = (s_1, s_2)$, we obtain

$$\phi_n^*(\boldsymbol{s}) = \frac{1}{2} - \frac{1+2s_2}{2}\sqrt{\pi(\pi-1)}\frac{1}{\sqrt{\ln n}} - \frac{\ln\ln n}{\ln n} + \mathcal{O}\left(\frac{1}{\ln n}\right). \tag{84}$$

It is clear that the complete disorder is the final state, given by $\phi^* = \frac{1}{2}$, i.e. 'complete grey'. As expected, this value is approached from below if $s_2 > 0$, and from above if $s_2 < 0$. Since the frequency of 'kicks' scales as $\sqrt{\ln n}$, we see that the decay follows $1/\sqrt{\ln n}$ rather than the typical decay of a random walk, i.e. $1/\sqrt{n}$.

Instead of fixed $\boldsymbol{s}$, we seek a scaled distribution. For this we note first that disorder *along* the interface should arise relatively quickly, since it depends only on the presence of the random walker, which wanders as far as $\sqrt{n}$. On the other hand, disorder in the vertical direction (from the origin) relies entirely on the wandering of the passive walkers, so that it will occur at the $\sqrt{\ln n}$ timescale. The appropriate scaling variables turn out to be

$$x = 2s_1/\sqrt{n} \qquad \text{and} \qquad y = 2s_2\sqrt{\pi(\pi-1)/\ln n}$$

while the final result is

$$[\phi_n^*(x, y) - \Theta(-y)]\ln 8n = \mathrm{sgn}(y)K_0(|x|)\mathrm{e}^{-|y|} + \mathcal{O}\left(\frac{1}{\sqrt{\ln n}}\right) \tag{85}$$

where $\mathrm{sgn}(y)$ denotes the sign of y and K_0 is the modified Bessel function. Note that the square bracket on the left-hand side is a measure of the disorder, since Θ is the step function that represents the initial probability distribution for finding black particles. Finally, since $K_0(z) \to \sqrt{\pi/2z}\exp(-z)$ for large z, we see that the decay in both directions are dominated by exponentials (in the scaling variables x and y).

4. Summary and outlook

We have presented a study of a class of random walks on a d-dimensional hypercubic lattice in which the walker hops from site to nearest-neighbour site with one exception. It *hops over* a particular site. In case the hop-over rates are isotropic, the full probability distribution was found explicitly. We have also investigated the statistics associated with the hop-overs, so that we can find both how often and in which direction the hop-overs occur. The latter study can be readily applied to the behaviour of a tagged particle, which moves only if a mobile vacancy were to exchange places with it. All previously known results of tagged diffusion are easily recovered in this simpler, novel approach. Finally, we showed how this study can be applied to two physical examples of the vacancy mediated disordering process.

Though we have focussed only on infinite systems, our methods are readily generalizable to finite (periodic) lattices. In three or higher dimensions, such a generalization is crucial, since the random walk is transient, so that an infinitesimal density of vacancies cannot give rise to system-wide dynamics. One way to estimate the effects of finite density is to consider finite systems with periodic boundary conditions. Another interesting generalization is the *biased* random walk. With a bias, there would be little reason to study hop-over walks on an infinite lattice, since the walker never returns to the hop-over site. By contrast, on a *finite* lattice, the walker will 'run into' the special site periodically. In the steady state, i.e. for times large compared with the traverse time, we can expect an asymmetric distribution around the 'defect'. If the hop-over rates are also biased, say, in the opposite direction, it may be possible for an effective binding to occur. This problem can be mapped into a limiting version of the biased diffusion of two species introduced sometime ago [17]. It would be very interesting to examine the walker-defect distributions and check if long-range correlations [18] also appear.

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