Random walk on a lattice: Basic formulas

Andriy Zhugayevych (http://zhugayevych.me)

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Notations

References to procedures from LatticeTools package (`https://zhugayevych.me/maple/LatticeTools/`) are marked as [`procedure_name`]. Calculation of velocity and diffusion tensor can be cited as Ref.[Zhugayevych13].

§1. Introduction

By lattice we mean any subset $X \subset \mathbb{Z}^d$ immersed in $\mathbb{R}^d$, so that for any point $x \in X$ the vector $\boldsymbol{r}_x \in \mathbb{R}^d$ is defined. We consider a random walk problem whose sojourn probability $p_x(t)$ is governed by the equation

$$\dot{p}_x = -p_x(\nu_x + w_x) + \sum_z p_z w_{zx}, \tag{1.1}$$

where w_{zx} is the transition rate from z to x and

$$w_x = \sum_z w_{xz}, \tag{1.2}$$

here and throughout the text a sum without limits means the sum over all possible values of the indicated variable. The transition probability $p_{yx}(t)$ is the solution of Eq. (1.1) with the initial condition $p_{yx}(0) = \delta_{yx}$. The Laplace transform of $p_{yx}(t)$ is the Green's function $G_{yx}(s)$ satisfying the equation

$$(s + \nu_x + w_x)G_{yx} - \delta_{yx} = \sum_z G_{yz} w_{zx}. \tag{1.3}$$

To find a large-time asymptotics, the Tauberian theorem is useful:

$$sG_{yx}(s) \sim s^{-\mu}\varphi(1/s),\ s \to +0 \iff p_{yx}(t) \sim \frac{t^\mu}{\Gamma(\mu+1)}\boldsymbol{\varphi}(t),\ t \to \infty, \tag{1.4}$$

where $\boldsymbol{\varphi}$ is a slow varying function. In particular,

$$p_{yx}(\infty) = \lim_{s\to 0} sG_{yx}(s) \tag{1.5}$$

if the limit exists. Next,

$$\sum_x p_{yx}(t)\boldsymbol{r}_x \sim \boldsymbol{v}t + \boldsymbol{a}(t),\ t \to \infty \iff s\sum_x G_{yx}(s)\boldsymbol{r}_x \sim \boldsymbol{v}/s + \boldsymbol{a}_y(1/s),\ s \to +0 \tag{1.6}$$

here $\boldsymbol{v}$ is the stationary velocity and for $\boldsymbol{v} = 0$ the vector $\boldsymbol{a}$ gives the mean stationary position (both may depend on y). Finally, if $\boldsymbol{v} = 0$ then the positively definite diffusion tensor is defined by

$$\sum_x p_{yx}(t)\ \boldsymbol{r}_x \otimes \boldsymbol{r}_x \sim 2\mathbf{D}t,\ t \to \infty \tag{1.7}$$

so that

$$\mathbf{D} = \lim_{s\to 0} \frac{s^2}{2} \sum_x G_{yx}(s)\ \boldsymbol{r}_x \otimes \boldsymbol{r}_x. \tag{1.8}$$

The diffusion coefficient is $\operatorname{tr}\mathbf{D}/d$. In the ergodic case both $\boldsymbol{v}$ and $\mathbf{D}$ do not depend on y.

The integral

$$p_{yx}^{\text{abs}}(t) = \nu_x \int_0^t p_{yx}(\tau)\,\mathrm{d}\tau \tag{1.9}$$

gives the absorption probability at the site x. Using Tauberian theorems

$$p_{yx}^{\text{abs}}(\infty) = G_{yx}(0)\nu_x \tag{1.10}$$

(if the limit exists). If $\mathbf{D} = 0$ then the absorption area tensor is defined by

$$\mathbf{\Lambda}_y = \frac{1}{2} \sum_x p_{yx}^{\text{abs}}(\infty)\ \boldsymbol{r}_x \otimes \boldsymbol{r}_x. \tag{1.11}$$

The diffusion length is $\sqrt{\langle \operatorname{tr}\mathbf{\Lambda}_y\rangle_y}$. If ν_x does not depend on x then from (1.3) and (1.8) it follows that

$$\lim_{\nu\to 0} \nu\mathbf{\Lambda}_y(\nu) = \mathbf{D}(\nu = 0). \tag{1.12}$$

Let the random walk be quasisymmetric, that is

$$\frac{w_{xy}}{w_{yx}} = \mathrm{e}^{\frac{\varepsilon_x - \varepsilon_y}{T}} \tag{1.13}$$

with some on-site energies ε and positive temperature T. Then if ε and w are bounded, and the immersion in $\mathbb{R}^d$ is regular (the ratio $w_{xy}/|\boldsymbol{r}_x - \boldsymbol{r}_y|$ is bounded), it can be shown (*show!*) that $\boldsymbol{v} = 0$. Next, if we substitute $\varepsilon_x \to \varepsilon_x - \boldsymbol{r}_x\boldsymbol{E}$, then in the limit of vanishing external field $\boldsymbol{E}$ we obtain the Einstein relation (*prove!*):

$$\boldsymbol{v} \sim T^{-1}\mathbf{D}\boldsymbol{E}. \tag{1.14}$$

§2. Periodic lattice

Let X have a translational invariance so that each point $x \in X$ can be presented as $x = (\xi, \alpha)$, where ξ runs $\mathbb{Z}^d$ or a torus L^d (L means $L_1, \dots, L_d$ and $\xi_i = \overline{0, L_i - 1}$), α runs the unit cell, and

$$\nu_{(\xi,\alpha)} = \nu^\alpha, \qquad w_{(\eta,\beta)(\xi,\alpha)} = w_{\xi-\eta}^{\beta\alpha}. \tag{2.1}$$

The Eq. (1.3) can be simplified by Fourier transformation with respect to the variable ξ, which for a function f_ξ is defined as

$$\hat{f}^\alpha(k) = \sum_\xi f_\xi \mathrm{e}^{\mathrm{i}k\xi},$$

where $k\xi = \sum_{i=1}^d k_i\xi_i$. The inverse transformation for an infinite lattice is given by

$$f_\xi = \frac{1}{(2\pi)^d} \int_{[-\pi,\pi]^d} \hat{f}(k)\mathrm{e}^{-\mathrm{i}k\xi}\,\mathrm{d}k$$

and in case of torus

$$f_\xi = \frac{1}{L_1 \dots L_d} \sum_k \hat{f}(k)\mathrm{e}^{-\mathrm{i}k\xi}, \quad k_i = \frac{2\pi l_i}{L_i},\ l_i = \overline{0, L_i - 1}.$$

In the Fourier domain, Eq. (1.3) reads

$$(s+\nu^\alpha+w^\alpha)\hat{G}^{\beta\alpha}-\delta^{\beta\alpha}=\sum_\gamma \hat{G}^{\beta\gamma}\hat{w}^{\gamma\alpha}, \tag{2.2}$$

where

$$\hat{G}^{\beta\alpha}(k)=\sum_\xi G_\xi^{\beta\alpha}\mathrm{e}^{\mathrm{i}k\xi} \tag{2.3}$$

and

$$\hat{w}^{\beta\alpha}(k)=\sum_\xi w_\xi^{\beta\alpha}\mathrm{e}^{\mathrm{i}k\xi} \tag{2.4}$$

with the essentially nonzero diagonal elements which can be neglected only for $k=0$ when they reduce in (2.2) because of the identity

$$w^\alpha\equiv\sum_\gamma \hat{w}^{\alpha\gamma}(0). \tag{2.5}$$

Often we need to calculate derivatives with respect to k, this can be easily done using the fact that $\hat{G}$ is the Green's function of Eq. (2.2) yielding

$$\frac{\partial\hat{G}}{\partial k}=\hat{G}\frac{\partial\hat{w}}{\partial k}\hat{G} \tag{2.6}$$

in matrix notations.

If $\boldsymbol{T}$ is a set of translation vectors then $\boldsymbol{r}=\xi\boldsymbol{T}\equiv\sum_{i=1}^d\xi_i\boldsymbol{T}_i$ is a vector of Cartesian coordinates corresponding to lattice coordinates ξ. If T is the matrix whose columns are the translation vectors then the above transformation can be written as $r_p=\sum_{i=1}^d T_{pi}\xi_i,\ p=\overline{1,d}$. The transformation rule for wave-vectors is reverse: $k_i=\sum_{p=1}^d\kappa_pT_{pi}$.

2.1. Mean linear displacement and velocity

To find the mean linear displacement, we apply the Tauberian theorem (1.6). First, using (2.6) we derive the identity

$$\sum_\xi G_\xi^{\beta\alpha}\xi\equiv\left.\frac{\partial\hat{G}^{\beta\alpha}(k)}{\mathrm{i}\partial k}\right|_{k=0}\equiv\sum_{\gamma\delta\xi}\hat{G}^{\beta\gamma}(0)\ w_\xi^{\gamma\delta}\xi\ \hat{G}^{\delta\alpha}(0). \tag{2.7}$$

Now by expanding

$$\boldsymbol{r}_{(\xi,\alpha)}=\boldsymbol{r}^\alpha+\xi\boldsymbol{T} \tag{2.8}$$

we obtain

$$\sum_x G_{yx}\boldsymbol{r}_x=\sum_{\alpha\gamma\delta\xi}\hat{G}^{\beta\gamma}(0)\ w_\xi^{\gamma\delta}\xi\boldsymbol{T}\ \hat{G}^{\delta\alpha}(0)+\sum_\alpha\hat{G}^{\beta\alpha}(0)\boldsymbol{r}^\alpha. \tag{2.9}$$

For $\nu=0$ the sum $\sum_\alpha\hat{G}^{\beta\alpha}(0)=1/s$. Because the unit cell is finite

$$\hat{G}^{\beta\alpha}(s,0)=s^{-1}p^{\beta\alpha}(\infty)+R^{\beta\alpha}+o(1),\ s\to+0, \tag{2.10}$$

where p is the transition probability for the unit cell with the transition rates $\hat{w}^{\beta\alpha}(0)$ and periodic boundary conditions and R is some matrix. Now by taking the limit in Eq. (1.6) we obtain [Velocity]

$$\boldsymbol{v}=\sum_\gamma p^{\beta\gamma}(\infty)\left(\sum_{\delta\xi}w_\xi^{\gamma\delta}\xi\right)\boldsymbol{T}. \tag{2.11}$$

2.2. Mean square displacement and diffusion tensor

Let find the mean square displacement assuming that $\boldsymbol{v}=0$. In the same way as we do it in the previous subsection we derive the identity

$$\sum_{\xi} G_{\xi}^{\beta\alpha}\xi_i\xi_j \equiv -\left.\frac{\partial \hat{G}^{\beta\alpha}(k)}{\partial k_i \partial k_j}\right|_{k=0} \equiv \sum_{\gamma\delta\xi} \hat{G}^{\beta\gamma}(0)\; w_{\xi}^{\gamma\delta}\xi_i\xi_j\; \hat{G}^{\delta\alpha}(0) + \sum_{\gamma\delta\lambda\mu\xi\eta} \hat{G}^{\beta\gamma}(0)\, w_{\xi}^{\gamma\delta}\hat{G}^{\delta\lambda}(0)\, w_{\eta}^{\lambda\mu}\hat{G}^{\mu\alpha}(0)\; (\xi_i\eta_j+\eta_i\xi_j) \tag{2.12}$$

and obtain

$$\sum_x G_{yx}\, \boldsymbol{r}_x\otimes\boldsymbol{r}_x = \sum_{\alpha\gamma\delta\xi} \hat{G}^{\beta\gamma}(0)\; w_{\xi}^{\gamma\delta}\hat{G}^{\delta\alpha}(0)\,[\xi\boldsymbol{T}\otimes\xi\boldsymbol{T}] + \sum_{\alpha\gamma\delta\lambda\mu\xi\eta} \hat{G}^{\beta\gamma}(0)\; w_{\xi}^{\gamma\delta}\hat{G}^{\delta\lambda}(0)\; w_{\eta}^{\lambda\mu}\hat{G}^{\mu\alpha}(0)\,[\xi\boldsymbol{T}\otimes\eta\boldsymbol{T}+\eta\boldsymbol{T}\otimes\xi\boldsymbol{T}]$$
$$+\sum_{\alpha\gamma\delta\xi} \hat{G}^{\beta\gamma}(0)\, w_{\xi}^{\gamma\delta}\hat{G}^{\delta\alpha}(0)\,[\xi\boldsymbol{T}\otimes\boldsymbol{r}^{\alpha}+\boldsymbol{r}^{\alpha}\otimes\xi\boldsymbol{T}] + \sum_{\alpha}\hat{G}^{\beta\alpha}(0)\;\boldsymbol{r}^{\alpha}\otimes\boldsymbol{r}^{\alpha}. \tag{2.13}$$

Now using (2.10) and the condition $\boldsymbol{v}=0$ we obtain [DiffusionTensor]

$$\mathbf{D} = \frac{1}{2}\sum_{ij}\sum_{\gamma} p^{\beta\gamma}(\infty)\left(\sum_{\delta\xi} w_{\xi}^{\gamma\delta}\xi_i\xi_j + \sum_{\delta\lambda\mu\xi\eta} w_{\xi}^{\gamma\delta}R^{\delta\lambda}w_{\eta}^{\lambda\mu}(\xi_i\eta_j+\eta_i\xi_j)\right)\boldsymbol{T}_i\otimes\boldsymbol{T}_j. \tag{2.14}$$

2.3. Diffusion length

By substituting (2.13) into (1.12) and using the identity $\sum_x G_{yx}(0)\nu_x = 1$ we obtain [DiffusionLength]

$$\boldsymbol{\Lambda}_{\beta} = \frac{1}{2}\sum_{ij}\Bigg[\sum_{\gamma}\hat{G}^{\beta\gamma}(0)\left(\sum_{\delta\xi} w_{\xi}^{\gamma\delta}\xi_i\xi_j + \sum_{\delta\lambda\mu\xi\eta} w_{\xi}^{\gamma\delta}\hat{G}^{\delta\lambda}(0)\; w_{\eta}^{\lambda\mu}(\xi_i\eta_j+\eta_i\xi_j)\right)\boldsymbol{T}_i\otimes\boldsymbol{T}_j$$
$$+\sum_{\gamma\delta\xi}\hat{G}^{\beta\gamma}(0)\; w_{\xi}^{\gamma\delta}\hat{G}^{\delta\alpha}(0)\;\nu^{\alpha}\left(\xi_i\;\boldsymbol{T}_i\otimes\boldsymbol{r}_j^{\alpha}+\xi_j\;\boldsymbol{r}_i^{\alpha}\otimes\boldsymbol{T}_j\right)+\sum_{\alpha}\hat{G}^{\beta\alpha}(0)\;\nu^{\alpha}\left(\boldsymbol{r}_i^{\alpha}\otimes\boldsymbol{r}_j^{\alpha}\right)\Bigg]. \tag{2.15}$$

2.4. One-dimensional example

Let consider one-dimensional lattice with two sites (1 and 2) per unit cell and nearest neighbor transitions so that all the nonequivalent rates are w_{12}, w_{21} (intracell), w_{10}, w_{01} (intercell, here 0 denotes replica of site 2). Equation (2.2) reads

$$\hat{G}\begin{pmatrix} s+w_{12}+w_{10} & -w_{12}-w_{10}\mathrm{e}^{-\mathrm{i}k} \\ -w_{21}-w_{01}\mathrm{e}^{\mathrm{i}k} & s+w_{21}+w_{01}\end{pmatrix}=1. \tag{2.16}$$

Let denote $w_{\mathrm{sum}} = w_{12}+w_{21}+w_{10}+w_{01}$. The stationary solution for $k=0$ is

$$\pi = w_{\mathrm{sum}}^{-1}\begin{pmatrix}(w_{21}+w_{01}) & (w_{12}+w_{10})\end{pmatrix} \quad \text{and} \quad R = w_{\mathrm{sum}}^{-2}\begin{pmatrix}(w_{12}+w_{10}) & -(w_{12}+w_{10}) \\ -(w_{21}+w_{01}) & (w_{21}+w_{01})\end{pmatrix}. \tag{2.17}$$

Hence the velocity

$$v = \frac{w_{01}w_{12}-w_{21}w_{10}}{w_{\mathrm{sum}}}a, \tag{2.18}$$

and the diffusion coefficient for the case $v=0$ (this condition is essential)

$$D = \frac{1}{2}\frac{w_{01}w_{12}+w_{21}w_{10}}{w_{\mathrm{sum}}}a^2, \tag{2.19}$$

where a is the unit cell length.

For quasisymmetric random walk in zero external field

$$D = \frac{\left((w_{01}w_{10})^{-1/2}+(w_{12}w_{21})^{-1/2}\right)^{-1}}{2\cosh\frac{\varepsilon_{12}}{2T}}a^2. \tag{2.20}$$

For a lattice with one site per unit cell, $v=(w_{01}-w_{10})\,a$. For $v=0$ the diffusion coefficient $D=w_{01}a^2$.

Importantly, when merging sites by taking an infinite rate limit one has to rescale the rest of rates appropriately to obtain a model with lower number of sites. For example, to derive the 1-site model from the 2-site one described above, one need to take a limit $w_{12}=w_{21}\to\infty$ and then rescale rates as follows: $w_{01,01}^{\text{1-site}} = w_{01,01}^{\text{2-site}}/2$.

2.5. Primitive lattices

For a primitive lattice there is only one site per unit cell. Therefore $\hat{G}^{\beta\alpha}(s,0)=s^{-1}$ and

$$\mathbf{D}=\frac{1}{2}\sum_x w_{0x}\boldsymbol{r}_x\otimes\boldsymbol{r}_x. \tag{2.21}$$

In particular, for nearest neighbor hopping on hypercubic, fcc, and bcc lattices $\mathbf{D}=wa^2\mathbf{1}$, where a is the length of the side of the cubic unit cell. For triangular lattice there is a prefactor 3/2 in this formula.

§3. Symmetric spectral problem

Let the transition rates be symmetric and

$$H_{xy}=-(\nu_x+w_x)\delta_{xy}+w_{xy}, \tag{3.1}$$

so that H is the symmetric matrix. Let consider the following eigenvalue problem

$$\sum_y H_{xy}\psi_y=E\psi_x. \tag{3.2}$$

For a periodic lattice

$$H_{(\xi,\alpha)(\eta,\beta)}=H^{\alpha\beta}_{\eta-\xi}=H^{\beta\alpha}_{\xi-\eta}, \tag{3.3}$$

and the normalized eigenvectors of (3.2) are given by

$$\psi_{(\xi,\alpha)}=\frac{1}{\sqrt{V}}u^\alpha \mathrm{e}^{\mathrm{i}k\xi},\quad k_i=\frac{2\pi l_i}{L_i},\ l_i=\overline{0,L_i-1},\ i=\overline{1,d},\ V=\prod_{i=1}^d L_i, \tag{3.4}$$

where u is the solution of the reduced to the unit cell eigenvalue problem

$$\sum_\beta \hat{H}^{\alpha\beta}u^\beta=Eu^\alpha \tag{3.5}$$

with

$$\hat{H}^{\alpha\beta}(k)=\sum_\xi H^{\alpha\beta}_\xi \mathrm{e}^{\mathrm{i}k\xi}. \tag{3.6}$$

The eigenelements can be enumerated by two indices: the wave-vector k and the branch index γ running the unit cell. Because H is symmetric, $\hat{H}$ is Hermitian and

$$\hat{H}^{\alpha\beta}(-k)\equiv\overline{\hat{H}^{\alpha\beta}(k)}\equiv\hat{H}^{\beta\alpha}(k). \tag{3.7}$$

The Green's function $G(s)\equiv(s-H)^{-1}$. Because for a symmetric matrix the spectrum is nondefective,

$$G_{xy}(s)=\sum_E\frac{\psi_x(E)\overline{\psi}_y(E)}{s-E}. \tag{3.8}$$

For a periodic lattice we obtain

$$G^{\alpha\beta}_{\xi 0}(s)=\frac{1}{V}\sum_{k,\gamma}\frac{u^\alpha_\gamma(k)\overline{u}^\beta_\gamma(k)}{s-E_\gamma(k)}\mathrm{e}^{\mathrm{i}k\xi}. \tag{3.9}$$

For a Hermitian operator the local density of states is defined:

$$\rho_x(s)=\sum_E|\psi_x(E)|^2\delta(s-E)\equiv\mp\frac{1}{\pi}\Im G_{xx}(s\pm\mathrm{i}0), \tag{3.10}$$

In practical calculations for finite configuration space δ-function is replaced by Gaussian or Lorentz lineshapes. The latter is obtained when the zero in the above formula is replaced by some finite value. The total density of states

$$\rho(s) = \sum_x \rho_x(s) = \sum_E \delta(s - E). \tag{3.11}$$

For a periodic lattice it is convenient to renormalize the density of states by the number of unit cells V, so that

$$\rho^\alpha(s) = \sum_{k,\gamma} |u_\gamma^\alpha(k)|^2 \delta(s - E_\gamma(k)). \tag{3.12}$$

In local minimums of $E_\gamma(k)$ function it can be expanded in k. The matrix with (p,q) elements

$$\frac{1}{\hbar^2} \sum_{i,j=1}^{d} T_{pi} \frac{\partial^2 E_\gamma(k)}{\partial k_i \partial k_j} T_{qj}, \qquad \frac{\hbar^2}{m_\mathrm{e}} \approx 7.6200\ \mathrm{eV\AA}^2, \tag{3.13}$$

is the *inverse mass tensor*, its eigenvalues give the inverse effective masses and the corresponding eigenvectors give the Euclidean directions for the quasiparticle moving with this mass.

3.1. Path expansion

Let

$$H = \begin{pmatrix} H_\mathrm{sys} & V^+ \\ V & H_\mathrm{env} \end{pmatrix} \text{ and } \tilde{H} = H_\mathrm{sys} + V^+ \left(E - H_\mathrm{env}\right)^{-1} V. \tag{3.14}$$

Then we can expand the renormalized matrix elements in series of transfer integrals as follows [PathExpansion]:

$$\tilde{t}_{ij} = t_{ij} + \sum_\alpha \frac{t_{i\alpha} t_{\alpha j}}{E - \varepsilon_\alpha} + \sum_{\alpha,\beta} \frac{t_{i\alpha} t_{\alpha\beta} t_{\beta j}}{(E - \varepsilon_\alpha)(E - \varepsilon_\beta)} + \cdots, \tag{3.15}$$

where $i, j, \dots \in$ ‘sys’ and $\alpha, \beta, \dots \in$ ‘env’, or in short notations:

$$\tilde{t} = \sum_{n=0}^{\infty} \tau^n t, \text{ where } \tau_{i\alpha} = \frac{t_{i\alpha}}{E - \varepsilon_\alpha} \text{ and } \tau_{\alpha\beta} = \frac{t_{\alpha\beta}}{E - \varepsilon_\beta}. \tag{3.16}$$

References

[Zhugayevych13] A Zhugayevych, O Postupna, R C Bakus II, G C Welch, G C Bazan, S Tretiak, Ab-initio study of a molecular crystal for photovoltaics: light absorption, exciton and charge carrier transport, J Phys Chem C 117, 4920 (2013)