# MEAN-SQUARE DISPLACEMENT OF TRACER DIFFUSION ON DEFORMABLE LATTICES

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**Abstract :**

*We study theoretically, tracer diffusion in a lattice-gas model that has been proposed to explain the anomalous diffusion anisotropy of hydrogen (H) adatoms on a W (110). We use the Green's function method to develop an analytic mean-field theory for the tracer diffusion . We then present a derivation of an improved solution to second order in the Green's function expansion for the tracer-diffusion coefficients and the mean-square displacement.*

## 1. Introduction :

Perhaps the simplest example of a diffusive process consists of particles executing isotropic random walks on an inert lattice. In the case of only one particle, the corresponding diffusion constant can trivially be written down as $l\,a^2/z$, where z is the coordination number of the lattice, l is the jump rate, and a is the lattice constant (i.e., the length of each jump)[1] . However, in the presence of other particles, the diffusion process becomes correlated and nontrivial[2]. Additionally, a distinction has to be made between single particle or tracer and collective - or chemical - diffusion processes. The interparticle correlations play a particularly important role in two-dimensional systems. A substantial amount of analytic work and numerical simulations have been done in simple lattice-gas systems in order to study these correlation effects as a function of the coverage $c(0<c<1)$[1,2] . So far, complete analytic solutions for all coverages exist only in cases where interactions between particles can be neglected, except for the double-occupancy or site exclusion hard-core interaction[2]. Most of

the current work has concentrated on tracer diffusion, since with only on one-site hard-core interaction present the collective-diffusion tensor is independent of coverage[3], while tracer diffusion shows complicated dependence on c.

Surface diffusion of adatoms on a substrate provides an important realization of classical diffusion in two dimensions, which has frequently been modeled by lattice-gas systems[2, 5 to 7]. However, in reality, the adsorption of an adatom is often accompanied by a local substrate relaxation or distortion[4 to 9]. Recently, it has been proposed that this local distortion can have significant effect on the surface-diffusion tensor[5 to 8]. A novel lattice-gas model was introduced which incorporates the essence of such a distortion with respect to diffusion[6]. This model has been proposed to explain the observed diffusion anisotropy of H adatoms on a W (110) surface[7].

## 2. The Model :

The essence of the model is to recognize that the binding energy of a H adatom can be lowered if it is displaced locally from the original adsorption site along the $[1\ \bar{1}\ 0]$ direction and accompanied by the shift of surrounding substrate atoms in the same direction (see Fig. 1). Obviously, the same is ture if the displacements of both the adatom and surrounding substrate atoms are reversed. This results in a "dynamical" double-well-type adsorption potential, which is imposed on the surface unit cell by each diffusing particle. When these distortions start to correlate mutually for higher coverages, a global surface reconstruction may occur, such as has been observed for H on W (110) around[9] c ~0.5.

An important feature of the model is that, even without direct adatom interactions, double occupation of an adsorption site is not favorable. This happens because of the opposing substrate distortions of two adatoms within the same cell that leads to a large local increase in the energy. Since the time scale for the adatom motion is much longer than a typical time scale for the substrate response, the effect just described can be approximately modeled by splitting the original single adsorption site into two symmetric sites. When this is done, an energy barrier exists for the motion from one subsite to another. Moreover, a simultaneous occupation of the two subsites is then forbiden; i.e., the hard-core repulsion applies within each cell. In the context of a simple

random-walk theory, the diffusive motion of the adatoms then be considered to consist of two separate steps on a static lattice. The first is an intracell jump across the barrier orginating from the local distortion, while the second is an intercell jump across the barrier due to the usual periodic arrangement of the substrate atoms. The competition between these two processes can be parameterized by a branching ratio r, which is the ratio of the intracell-to-intercell difusion rates. In realistic adsorption systems additional direct or indirect interactions exist between adatoms on different adsorption sites, as evidenced by the appearance of many distinct ordered phases of the adlayer[9]. However, even without these interactions, the presence of both intracell and intercell jumps as well as the exclusion of double occupancy within a cell already leads to a very complicated coverage dependence and causes strong correlation effects to appear for both tracer and collective diffusion in the model . Having said this, a note of caution must also be added. The assumption of a static substrate renders the model physically applicable for H/W (110) only in the regime where no global reconstruction of the substrate occurs.

To explore fully the effects of a local lattice distortion on diffusion, we have undertaken a comprehensive study of the collective-diffusion prcoess within our lattice-gas model. In this paper we shall concentrate on the case of a hard-core repulsion which applies to both sites in a given cell. This implies a strict exclusion of a dobule occupany in each cell.

**3. Green's-Function :**

To calculate the effect of correlations for the case of tracer diffusion, an equation-of-motion based on Green's-function formalism has been developed by Tahir-Kheli and Elliott[11] (TKE) and further refined by Tahir-Kheli and El-Meshad[10, 12] . The TKE method has been applied with very good results to a variety of lattice-gas systems, where only the one-site blocking interaction is present. This method can be generalized to treat the case of collective diffusion as well as we use it below to derive an analytic solution of D for our lattice-gas model.

Let us consider diffusion on the somewhat more general alttice-gas model of Fig. 2 with two distinct sublattices A and B in a given unit cell. In addition to the single-site hard-core exclusion, we shall impose the condition that only one of these sublattice sites can be simultaneously occupied. Each cell of this generalized model then correspnods to the hourglass adsorption sites of our surface model . Let

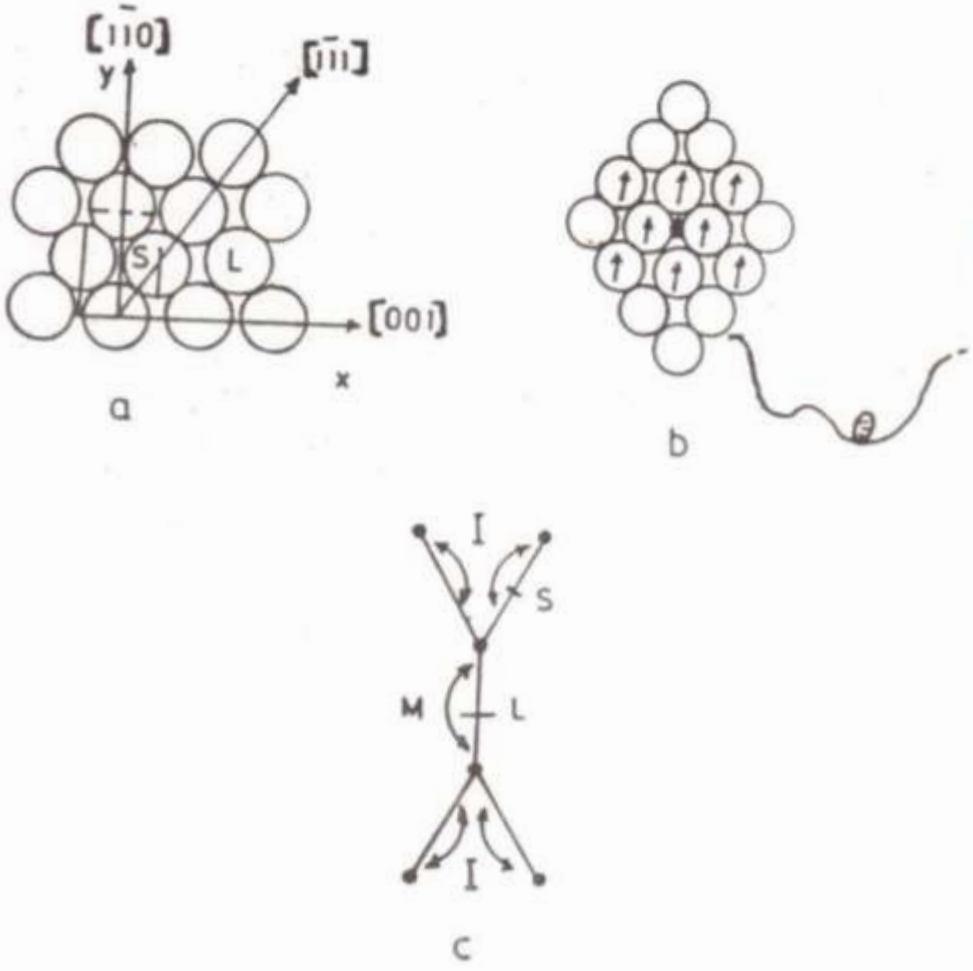


Fig. 1.

a) Geometry of an undistorted W (110) surface (from [ 6 ]). The hourglass adsorption sites of adatoms (cells) are denoted by L, While S denotes the saddle points of the surface potential. b) A schematic figure of a local distortion caused by an adsorped H adatoms (shaded circle). The arrows represent the displacements of the out most atomic layer. c) Each hourglass now contains two equivalent sites, denoted by dots . Diffusion consists of two steps namely, intracell jumps with rate M and intercell jumps with rate I.

n (t) denotes a stochastic occupancy variable of the diffusing particles, which are all assumed to be identical. If at a time t a particle is on sublattice A in cell (i.e., the hourglass) labelled g, then $n_g^A$ (t) = 1 ; otherwise, $n_g^A$ (t) = 0 .

Taking into account that a background particle can be blocked by the tracer as well as an other background particle, we can write an exact rate equation for a particle occupying sublattice A in cell g :

$$\frac{d}{dt} n_g^A (t) = - M^A n_g^A (t) + M^B n_g^B (t)$$

$$- \sum_f l^A (gf) n_g^A (t) \left[1 - n_f^A (t) - n_f^A (t) - p_f^A (t) - p_f^B (t)\right] \quad (3.1)$$

$$+ \sum_f l^B (fg) n_f^B (t) \left[1 - n_g^A (t) - n_g^B (t) - p_g^A (t) - p_g^B (t)\right].$$

The diffusing particles jump between neighboring lattice cells, which have sublattices A and B. Double occupation of a cell by either the tracer and a background particle, or two background particles, is forbidden. Let p (t) be the stochastic occupancy variable of the tracer particle. Thus, the rate equation for the tracer particle occupying sublattice A at cell g is :

$$\frac{d}{dt} p_g^A(t) = - M^{Ao} p_g^A(t) + M^{Bo} p_g^B(t)$$

$$- \sum_f p_g^A (t) l^{Ao} (gf) \left[1 - n_f^B(t) - n_f^A(t)\right] \quad (3.2)$$

$$+ \sum_f p_f^B (t) l^{Bo} (fg) \left[1 - n_g^A(t) - n_g^B(t)\right]$$

The corresponding equation for sublattice B follows by interchanging labels for A and B. Here $M^A$ is the intracell jump rate associated with the particle hopping form sublattice A to sublattice B within the hourglass, while $M^B$ is the rate for a jump in the opposite direction. In the same way $M^{Ao}$ and $M^{Bo}$ are defined as a jump rates assocaited with the tracer. $l^A$ (gf) and $l^B$ (fg) are hopping rates of particles jump in an intercell jump from cell g to cell f originating from either A or B sublattice, respectively. The same is for $l^{Ao}$ and $l^{Bo}$ , but the lattter are associated with the tracer jump. We restrict ourselves to the case where

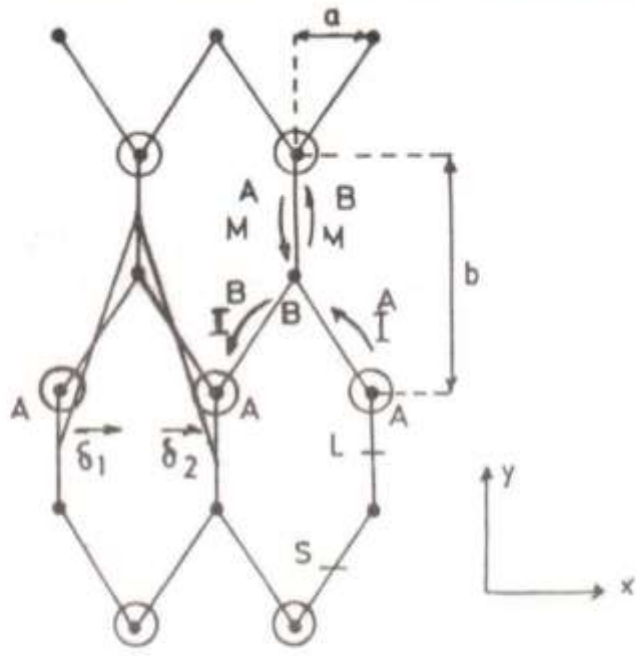


Fig. 2.

Geometry of the generalized two-step model. Sublattices A (circled dots) and sublattices B (dots). The vectors $\delta_1$ and $\delta_2$ connecting periodic cells. L and S refer to the original surface model of Fig. 1.

only nearest-neighbor jumps are allowed, i.e. $l^A(gf) = l^A$, where $f-g = \delta_1$ or $\delta_2$, $l^{Bo}(fg) = l^{Bo}$ for $f-g = -\delta_1$ or $-\delta_2$, and both are zero otherwise. Here $\delta_1 = (a, b)$ and $\delta_2 = (-a, b)$ connect adjacent cells, as shown in Fig. 2.

The background occupancy variables can be written in terms of fluctuations $u_g^s(t) = n_g^s(t) - c^s$ on sublattice s= A or B. the components of the tracer-diffusion tensor can be extracted from the pole of the retarded Green's-function for the tracer, this pole occurs at $\omega = -ik.D.k$. in the limit $k \to 0$, $\omega \to 0$. The result is:

$$G^s_{gg'}(t) = -2\pi i \Theta(t) < p^s_g(t)\ p^A_{g'}(0) > \quad . \qquad (3.3)$$

Where $\Theta(t)$ is a step function. The corresponding four next-higher-order Green's functions are given by :

$$G^{ss'}_{gig'} = << p^s_g(t)\ u^{s'}_i(t);\ p^A_{g'}(0) >> \quad . \qquad (3.4)$$

for s, s' = A or B. To obtain an equatin of motion for $G^{S}_{gg'}(t)$ , we use the rate equation (3.2). This gives :

$$\frac{d}{dt} G^{S}_{gg'}(t) = -2\pi i \delta(t) < p^{S}_{g}(t)\ p^{A}_{g'}(0) >$$

$$= -2\pi i \delta(t) < p^{A}_{g}(0) > \delta_{gg'} . \delta_{S,A}$$

$$= -2\pi i \delta(t) \frac{1}{N} \delta_{gg'} . \delta_{S,A} \qquad (3.5)$$

where N is the total number of lattice sites. Defining the Fourier transforms of the Green's-functins in frequency and reciprocal space:

$$G^{S}_{gg'}(t) = \frac{1}{N} \int_{-\infty}^{\infty} d\omega \sum_{k} G^{S}_{k}(\omega)\ e^{-i\omega t}\ e^{ik.(g-g')} \qquad (3.6)$$

and

$$G^{ss'}_{gg'}(t) = \frac{1}{N^2} \int_{-\infty}^{\infty} d\omega G^{ss'}_{gg'}(t) = \frac{1}{N^2} \int_{-\infty}^{\infty} d\omega \sum_{k1\ k2} G^{ss'}_{k1,k2}(\omega)\ e^{-i\omega t}\ e^{ik_1.(g-g') + ik2(1-g)} \qquad (3.7)$$

The corresponding Fourier transforms for the jump rates are :

$$J^{S}(q) = \sum_{g-f} I^{S}(gf)\ e^{iq.(g-f)} . \qquad (3.8)$$

Now, we can write the corresponding equations of motion for $G^{A}_{k}(\omega)$ and $G^{B}_{k}(\omega)$ as :

$$\left[-i\omega + M^{A0} + vJ^{A0}(0)\right] G^{A}_{k}(\omega) - \left[M^{Bo} + v J^{Bo}(-k)\right] G^{B}_{k}(\omega)$$

$$= -\frac{i}{N} + I^{A0} \sum_{\delta} \frac{1}{N} \sum_{\mu} \left[ e^{i\mu.\delta} G^{AA}_{k-\mu,\mu}(\omega) + e^{i\mu.\delta} G^{AB}_{k-\mu,\mu}(\omega) \right] \qquad (3.9)$$

$$- I^{Bo} \Sigma_{\delta}\, e \frac{1}{n} \Sigma\mu\ e^{ik.\delta} \left[ e^{-i\mu.\delta} G^{BB}_{k-\mu,\mu}(\omega) + e^{i\mu.\delta} G^{BA}_{k-\mu,\mu}(\omega) \right]$$

$G^{B}_{k}(\omega)$ can be obtained by interchanging lables for A and B. Here $\mu$ is summed over the first Brillouin Zone, $\delta$ is summed over $\delta_1$ and $\delta_2$, and the vacancy factor $v = (1-c) = [1 - (c^{A} + c^{B})]$ . The quantity

$$J^{SO}(0) \equiv \sum_{f} I^{SO}(gf)$$

and $J^{Ao}(k) \equiv \sum_{g-f} I^{Ao}(gf)\ e^{-ik.(g-f)}$

$$= I^{Ao}(\ e^{-ik.\delta_1} + e^{-ik.\delta_2})$$

Similarly, $J^{Bo}(k) = I^{Bo}(\ e^{ik.\delta_1} + e^{ik.\delta_2})$

**4. Mean-field solution :**

Within the mean-field (MF) approximation, we neglect all second-order Green's functions in (3.9) , which, in addition to the tracer occupancy variable, also involve a density-fluctuation field for the background particles. This leads to the set of equations :

$$\begin{vmatrix} [-i\omega + M^{Ao} + v\,J^{Ao}\ (0)] & -[M^{Bo} + v\,J^{Bo}(-k)] \\ -[\,M^{Ao} + v\,J^{Ao}\ (-k)] & [-i\omega + M^{Bo} + v\,J^{Bo}(o)] \end{vmatrix} \begin{vmatrix} G_k^A\ (\omega) \\ G_k^B\ (\omega) \end{vmatrix}$$

$$= \begin{vmatrix} -i/N \\ 0 \end{vmatrix} \qquad (4.1)$$

We observe that the background particles enter only through the vacancy factor v in (4.1). We obtain the elements of the diffusion tensor from the pole of the Green's-function.

$$D_{xx} = \frac{2\,v\,I^{Bo}\,(M^{Ao} + 2\,v\,I^{Ao})}{M^{Ao} + M^{Bo} + 2\,v\,(I^{Ao} + I^{Bo})}\ a^2\ , \qquad (4.2)$$

and

$$D_{yy} = \frac{2\,v\,M^{Ao}\ I^{Bo}}{M^{Ao} + M^{Bo} + 2\,v\,(I^{Ao} + I^{Bo})}\ b^2\ . \qquad (4.3)$$

To make the connection to model of diffusin of identical particles, we set

$M^{Ao} = M^{Bo} = M^o$ , $I^{Ao} = I^{Bo} = I^o$ , and $c^A = c^B = c/2$, which gives

$$D_{xx} = vI^o\,a^2 \qquad (4.4)$$

and

$$D_{yy} = \frac{v\,I^o\,M^o}{(M^o + 2\,v\,I^o)}\ b^2 \qquad (4.5)$$

For the diffusion anisotropy we then obtain, in terms of the branching ratio , $r = M^0/l^0$ ,

$$\frac{D_{yy}}{D_{xx}} = \frac{r}{r+2v} \left|\frac{b}{a}\right|^2 . \qquad (4.6)$$

The corresponding mean-square displacements are :

$$< r_x^2(t) > = 2 v l^\circ a^2 t \qquad (4.7)$$

$$< r_y^2(t) > = \frac{2 v l^\circ M^\circ}{(M^\circ + 2 v l^\circ)} b^2 t . \qquad (4.8)$$

Interestingly enough, this latter result applies for the isotropic lattice cases as well, where collective diffusion is constant for all coverages $c < 1$ and is given simpley by $D_0 = D(c = 0)$[3] . It is also interesting to note that while the coverage dependence of $D_{XX}$ in(4.4) is identical to the usual isotropic MF result with $D_0 = l^0 a^2$ , $D_{yy}$ reduces to this simple functional form only in the limit $r \to \infty$ .

**5. Second-order solutin :**

To derive second-order correction, which is obtained from the equation of motion for the Green's-functins $G^{SS'}_{glg'}(t)$ . we get :

$$\frac{d}{dt} G^{SS'}_{glg'}(t) = -2\,\delta(t) < p^S_g(0)\; u^{S'}_l(0)\; p^A_{g'}(0) >$$
$$+ << \left[\frac{d}{dt} p^S_g(t)\right] u^{S'}_l(t) ; p^A_{g'}(0) >>$$
$$+ << p^S_g(t) \left[\frac{d}{dt} u^{S'}_l(t)\right] ; p^A_{g'}(0) >> \qquad (5.1)$$

From (5.1), the scond order Green's-functions, as a matrix equation given by :

$$\underline{C}\, \underline{G}^{(2)}_{K-\mu,\,\mu} = \underline{E} \cdot \underline{G}^{(1)}_K + \underline{B} \cdot \underline{\rho}_K \qquad (5.2)$$

where the elements of the matrices $\underline{C}$, $\underline{E}$ and $\underline{B}$ are given in the appendix

$$\underline{G}^{(2)}_{K-\mu,\mu} = \begin{vmatrix} AA_{G_{K-\mu,\mu}} \\ BB_{G_{K-\mu,\mu}} \\ AB_{G_{K-\mu,\mu}} \\ BA_{G_{K-\mu,\mu}} \end{vmatrix} \tag{5.3}$$

and

$$\underline{G}^{(1)}_{K} = \begin{vmatrix} G^{A}_{\underline{K}} \\ G^{B}_{\underline{K}} \end{vmatrix} \tag{5.4}$$

The vector $\rho_K$ is given by

$$\rho_K = \begin{vmatrix} \rho_1 \\ \cdots\cdots \\ \cdots\cdots \\ \rho_{16} \end{vmatrix} \tag{5.5}$$

with component $\rho_1 - \rho_{16}$:

$$\begin{aligned}
\rho_1 &= \rho_K^{AB}(\delta_1) \quad . \quad \rho_2 = \rho_K^{AB}(\delta_2) \\
\rho_3 &= \rho_K^{BA}(-\delta_1) \quad . \quad \rho_4 = \rho_K^{BA}(-\delta_2) \\
\rho_5 &= \rho_K^{AA}(\delta_1) \quad . \quad \rho_6 = \rho_K^{AA}(\delta_2) \\
\rho_7 &= \rho_K^{BB}(-\delta_1) \quad . \quad \rho_8 = \rho_K^{BB}(-\delta_2) \\
\rho_9 &= \rho_K^{AA}(-\delta_1) \quad . \quad \rho_{10} = \rho_K^{AA}(-\delta_2) \\
\rho_{11} &= \rho_K^{BB}(\delta_1) \quad . \quad \rho_{12} = \rho_K^{BB}(\delta_2) \\
\rho_{13} &= \rho_K^{AB}(-\delta_1) \quad . \quad \rho_{14} = \rho_K^{AB}(-\delta_2) \\
\rho_{15} &= \rho_K^{BA}(\delta_1) \quad . \quad \rho_{16} = \rho_K^{BA}(\delta_2)
\end{aligned} \tag{5.6}$$

$$\rho_K^{SS'}(\delta) \equiv \frac{1}{N} \Sigma_\mu e^{i\mu.\delta} G_{k-\mu,\mu}^{SS'}(\omega) \qquad (5.7)$$

where the sum over $\mu$ goes over the first Brillouin zone, and $\delta$ is either $\delta_1$ or $\delta_2$ . In the fully symmetric case

$$I^{Ao} = I^{Bo} = I^o,\ M^{Ao} = M^{Bo} = M^o \text{ , and}$$

$$c^A = c^B = c/2 \text{ , we obtain}$$

$$D_{xx} = v\, I^o\, a^2\, f_x \qquad (5.8)$$

and

$$D_{yy} = \frac{v\, I^o\, M^o}{(M^o + 2\, v\, I^o)}\, b^2\, f_y \qquad (5.9)$$

where $f_x$ and $f_y$ represent the tracer correlation factors .

As a matter of fact equatios (5.8) and (5.9) are the two main equations of this paper. Consequently we can write the mean-square displacements of tracer diffuses anisotropically on a deformable lattices as :

$$< r_x^2(l) > = 2\, v\, I^o\, a^2\, f_x\, t \qquad (5.10)$$

$$< r_y^2(t) > = \frac{2\, v\, I^o\, M^o}{M^o + 2\, v\, I^o}\, b^2\, f_y\, t \qquad (5.11)$$

**6 - Conclusion :**

In this work we have presented a theoretical study of tracer diffusion in the two-step lattice-gas model with single-site and intracell hard-core interactions. To understand this model, we have used the Gren's function method of Tahir-Kheli and Elliott[11] to analytically compute the elments of the tracer-diffusion tensor for the model. We have derived an improved solution to second order in the Green's function expansion, which leads to an expression for D. We have also obtained an analytic solution for D within the mean field approximation. The second-order solution becomes less accurate for the tracer-diffusion process as r diminishes. The results presented in this anisotropy is a universal property of the underlying lattice for branching ratios $r \geq 1$ .

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