

Monte Carlo Studies of Particle Diffusion on a Patchwise Bivariate Surface

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Abstract—The diffusion of particles adsorbed on a patchwise surface with two non equivalent sites is investigated in the framework of a lattice-gas model. We derived the analytical expressions for the diffusion coefficients. Using the kinetic Monte Carlo simulations we calculate the coverage dependencies of the diffusion coefficients in the wide region of the lateral interaction between the particles. The theoretical dependencies are compared with the numerical data. The good coincidence of the data obtained by the two different methods corroborates the validity of the approach developed for the description of the particle migration over such complex heterogeneous lattices.

Index Terms—surface diffusion; kinetic Monte Carlo simulations; patchwise lattice.

I. INTRODUCTION

The diffusive mass transfer controls the rates of a multitude of physical, chemical, and biological processes. The theoretical investigations of these processes attract much attention, but the complexity of the real systems also makes their study extremely difficult. The majority of the widely used systems are strongly heterogeneous. Crystals and thin films consist of small nanocrystals, domains, and other heterogeneities. The surfaces have random potential reliefs with broad distributions of energetic parameters like adsorption energies and potential barriers.

A theoretical model has been developed by Ross and Olivier to describe the particle (atoms, molecules) adsorption on such heterogeneous surfaces [1]. In this model the surface is composed of a number of randomly distributed or ordered patches with different adsorption sites. The model is widely used in experimental and theoretical investigations of effects of the heterogeneity on a variety of surface processes like adsorption, desorption, diffusion and catalysis [2]. Due to the great versatility and complexities of the patchy surfaces, it seems impossible to do some definitive conclusions about the transport of particles over such surfaces. Nevertheless, it occurs that in some simple cases one can obtain a rather satisfactory description of the particle diffusion over the heterogeneous surfaces.

We study the influence of the heterogeneity on the surface diffusion of adsorbed particles in the framework of the lattice-gas formalism. In particular, we consider a special case of the surface with only two different types of the adsorption sites, grouped into small square clusters of a given size, and given energy of adsorption. This simple model includes

the most important features that are expected to influence the transport over such surfaces. The general and universal approach developed for the investigation of the migration of particles adsorbed on the strongly heterogeneous lattices is applied here for the description of the particle migration on the patchwise bivariate lattices [3].

We rederive the analytical expressions for the diffusion coefficients for the patchwise lattice. The coefficients are also evaluated by the kinetic Monte Carlo (kMC) simulations [4] of the particle migration over the patchwise lattice mentioned above. The theoretical dependencies are compared with the numerical data. It occurs that the coincidence between the data, obtained by the two independent qualitatively different methods, is rather good.

The paper is organized as follows. In Section II, we describe the model and give the definitions of the diffusion coefficients and other necessary quantities. In Section III, we analyze the peculiarities of the particle migration over the lattice. Some details of the kMC method are presented in Section IV. The results are discussed in Section V. Finally, we present the summary of our results and conclusions in Section VI.

II. THE LATTICE-GAS MODEL AND DIFFUSION COEFFICIENTS

We consider the migration of particles adsorbed on a square lattice of N adsorption sites with a regular and periodic heterogeneity. The lattice is composed of the deep, d , and

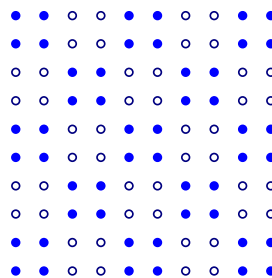


Fig. 1. Schematic view of the square patchwise bivariate lattice. The open and filled circles denote the shallow and deep adsorption sites.

shallow, s , sites arranged in the square 2×2 patches, as shown in Figure 1. The corresponding adsorption energies, ε_d and ε_s , are large relative to the thermal energy, $k_B T$. The N_a particles populate the sites, jumping occasionally to the nearest neighbor (NN) empty adsorption sites. When the duration of the jumps is much shorter than the particle sojourn in the sites, the state of the particle system is completely described by a set of the occupation numbers n_i with

$$n_i = \begin{cases} 1, & \text{if the } i\text{th site is occupied,} \\ 0, & \text{if the } i\text{th site is empty.} \end{cases} \quad (1)$$

The double occupancy is forbidden. The particle concentration, or surface coverage θ , equals to N_a/N . There is also a lateral interaction φ between the NN particles.

The particle migration is described by some diffusion coefficients. Conceptually, the simplest diffusion coefficient is a single particle, or tracer diffusion coefficient, D_t . It addresses the random walks of the individual tagged particles

$$D_t = \lim_{t \rightarrow \infty} \frac{1}{4tN_a} \left\langle \sum_{k=1}^{N_a} \vec{r}_k^2(t) \right\rangle. \quad (2)$$

The jump, or center-of-mass diffusion coefficient, D_j , describes the asymptotic behavior of the center of mass of the system of adsorbed particles

$$D_j = \lim_{t \rightarrow \infty} \frac{1}{4tN_a} \left\langle \left[\sum_{k=1}^{N_a} \vec{r}_k(t) \right]^2 \right\rangle. \quad (3)$$

Here $\vec{r}_k(t)$ is the displacement of the k th particle after the time t ; the brackets $\langle \dots \rangle$ denote the average over the particle configurations. The coefficients are well-suited for the kMC simulations, as they are expressed in terms of the directly accessible quantities $\vec{r}_k(t)$.

The Fickian (also chemical, collective, transport) diffusion coefficient D_c , describing the mass transfer over the lattice, is determined by the Fick's first law which constitutes the relationship between the flux of the particles, $\vec{J}(\vec{r}, t)$, and the gradient of their concentration, $\theta(\vec{r}, t)$

$$\vec{J}(\vec{r}, t) = -D_c \vec{\nabla} \theta(\vec{r}, t). \quad (4)$$

III. DIFFUSION OF PARTICLES OVER THE PATCHWISE LATTICE

In the following we consider the case of a strongly heterogeneous lattice, i.e., $\exp(\varepsilon_d) \gg \exp(\varepsilon_s)$. The heterogeneity results in the striking difference between the s and d sites. The particles tend to occupy the deep sites. Therefore, in the low coverage region, $\theta < 1/2$, almost all s sites are empty, and the overwhelming majority of the particles occupy the d sites. In the high coverage region, $\theta > 1/2$, almost all d sites are filled and the rest $N_a - N/2$ particles occupy the shallow sites.

Also, the inhomogeneity implies the much higher jump rate ν_s for the fast $s \rightarrow d$ and $s \rightarrow s$ jumps than for the slow $d \rightarrow s$ and $d \rightarrow d$ jumps with the jump rate ν_d . We call them fast and slow jumps, that means not the duration of a jump itself, but

the fact that the averaged time of a particle sojourn in the d sites, ν_d^{-1} , is considerably longer than the corresponding time for the s sites, ν_s^{-1} . There is an important difference between fast and slow jumps. The slow and fast jumps take place on the largely different time scale as $\nu_s \gg \nu_d$. The particles do not stay long in the s sites. Any jump to a shallow site gives rise to the fast jump, which occurs almost immediately after the previous slow jump. In the time scale determined by the slow jumps the fast jump cannot be separated from the precedent slow jump. They should be considered together like a single elementary act of the particle migration. The characteristic coverage, $\theta = 1/2$, separates concentration regions where the particle migration has qualitatively different behavior. In the following Subsections, we consider the specific properties of the diffusion in these regions.

A. Low coverage region

At low coverages, the d patches are partially filled and the s patches are empty. Any migration act starts with a slow jump from an initial d site. There are two possibilities for the activated particle. It can jump to some d or s empty NN site. The $d \rightarrow d$ jumps correspond to the ordinary diffusion over the homogeneous lattice of d sites. But the jumps to the shallow sites are more effective. In this case, the particle can perform $1, 2, \dots$ fast jumps until it finds an empty d site. The particle migrates performing sequence of jumps: the first slow jump and some fast jumps. The final fast jump to the d site finishes the succession. These jump successions, performed by single particles, give the main contribution to the total particle displacement in the low coverage region.

The probability to find an empty final d site decreases as $\theta \rightarrow 1/2$. At the stoichiometric coverage $\theta = 1/2$ the system of particles is strongly ordered: almost all d sites are occupied and almost all s sites are empty. Many activated particles cannot find the empty d sites and return to their initial sites. The tracer and jump diffusion coefficients have minimum at this coverage. An interesting consequence of the fact that the particle migration proceeds by the jump sequences performed by single particles is the similar behavior of the tracer and jump diffusion coefficients: they are practically equal in the wide coverage region $0 \leq \theta < 1/2$.

The probabilities of the jump successions are determined by the particle configurations on the perimeter d sites surrounding the s patch. There are $z = 4l$ sites surrounding the $l \times l$ patch, which we label by the index $i = 1, 2, \dots, z$. The particle configuration on the perimeter sites is determined by the occupation numbers of these sites: for particles n_i and for vacancies $h_i \equiv 1 - n_i$. For example, $h_1 n_2 \dots h_z$ denotes the configuration when the 1st site is empty, the second is filled, ..., the z th is empty. The probabilities of the particle configurations are the average values of the product $\langle h_1 n_2 \dots h_z \rangle$.

Let us suppose that the probability to occupy an empty perimeter d site is the same for all these sites. It is a rather simple approximation. The sites located closer to the initial site have higher probabilities to be occupied than the

further located ones. To obtain the correct probabilities one should calculate, in principle, the infinite series of jumps for every configuration. But, our aim is to demonstrate only the applicability of the approach to the description of the particle diffusion over the patchwise lattice. This approximation permits to derive the analytical expressions for the diffusion coefficients, which are rather simple, but, nevertheless, give quite satisfactory results.

B. High coverage region

At high coverages all d sites are occupied. The $N/2$ particles are trapped in the deep patches and the rest $N_a - N/2$ particles occupy the s sites. The weakly adsorbed particles perform a lot of the fast jumps in the s patches. But it is easy to see that these fast jumps do not give noticeable contribution to the total displacement. The particles are confined in the s patches and cannot migrate over the surface jumping between the s sites only.

It is a specific feature of the patchwise lattices, that there is no infinite connected cluster of the s sites spanning over the whole lattice. The migration over the whole lattice should include slow jumps. The non-zero contribution to the diffusion is produced by successions of slow and fast jumps. But these successions are different from the previous low coverage case.

Again, the first jump of the succession is a slow one. A particle jumps from a d site to some empty s site. And the vacancy in the d patch is filled very fast by the other mobile particle. If the fast jump is performed by a particle from another s patch, these succession of the slow and fast jumps performed by different particles transfers particle between the s patches (over the occupied d patch). Such jump successions, performed by different particles, give the main contribution to the diffusion in the high coverage region $\theta > 1/2$. These jump successions considerably reduce the tracer diffusion coefficient as compared with the jump diffusion coefficient: $D_j \gg D_t$, if $1/2 < \theta < 1$.

The probabilities of the jump successions are determined by the particle configurations in the two s patches (denoted as 1st and 2nd), which are the NNs of the initial d site. There are $z' = 2l^2$ s sites, which we label by the index $i = 1, 2, \dots, z'$. The particle configurations in the patches are determined by the occupation numbers of the s sites. After the slow jump from the initial d site to the 2nd patch, the particles from the 1st and the 2nd patches try to occupy the vacancy in the initial site. The jump succession ends when some particle fills the vacancy. If the particle jumps from the 1st patch, the total particle displacement changes. The jump succession transfers one particle from the 1st patch to the 2nd patch. This concerted jumps of different particles are equivalent to a single jump of a particle between the NN s patches. In the case, when the vacancy is filled by a particle from the 2nd patch, the total particle displacement remains the same. There is no particle transfer between the s patches.

As in the previous case, we supposed that the probability for any particle in the 1st and 2nd s patches to occupy the vacancy in the initial site is the same. To justify this approximation it

may be useful to consider the ideas developed in the method of the real-space renormalization group [5]. Analogously with this approach, the patches should be considered as the block sites, deep or shallow, depending on the type of lattice sites composing the block site. The lattice is transformed to the ordinary heterogeneous square lattice of d and s block sites arranged in the alternating order. The particle diffusion is a sequence of jumps between the NN sites. As the migration path for any particle includes many jumps between the block sites, the details of the particle migration inside the blocks (patches) should be smoothed out in some sense, averaged. The migration proceeds by the jump pairs between the blocks. And the jumps will be characterized by some renormalized jump rates and the jump length only. The similar character of the particle migration results in the similar expressions for the diffusion coefficients. The analytical expressions derived for the case of the patchwise lattice are the modified expressions obtained for the heterogeneous square lattice [3]. These expressions relate the kinetic quantities D_j and D_c with the equilibrium thermodynamic quantities as follows:

$$\begin{aligned} D_j &= \nu_d L_z^2 P_{00} P_z^< e^\mu / \theta, \\ D_c &= \nu_d L_z^2 P_{00} P_z^< e^\mu / \chi_T, \quad \theta < 1/2, \end{aligned}$$

and

$$\begin{aligned} D_j &= \nu_d L_{z'}^2 P_{00} P_{z'}^> e^\mu / \theta, \\ D_c &= \nu_d L_{z'}^2 P_{00} P_{z'}^> e^\mu / \chi_T, \quad \theta > 1/2. \end{aligned} \quad (5)$$

Here

$$\begin{aligned} P_z^< &= \frac{1}{z-1} (z-1 - n_d - n_d^2 - n_d^3 - \dots - n_d^{z-1}) \\ P_{z'}^> &= \frac{1}{z'-1} (z'-1 - h_s - h_s^2 - h_s^3 - \dots - h_s^{z'-1}) \end{aligned}$$

$P_{00} = \langle h_i h_j \rangle$ is the probability to find a pair of empty s and d NN sites; $z = 4l = 8$ is the number of d sites surrounding an s patch, and $z' = 2l^2 = 8$ is the number of s sites in two s patches; n_d, n_s are the average occupancies of the d and s sites; L_z^2 and $L_{z'}^2$ stand for the mean square displacements and $h_d = 1 - n_d, h_s = 1 - n_s$.

It should be noted the following. The analytical expressions derived for the inhomogeneous lattices work perfectly because all NN sites for the d and s sites are equivalent. The jumping particles occupy them with equal probabilities. In the patchwise lattice, the NN sites are not equivalent, and particles occupy these sites with different probabilities. The probabilities depend on the distance between the initial and final sites. The more distant sites give smaller contribution to the total displacement. Really, the quantities $L_z, L_{z'}, z,$ and z' should be considered as the fitting parameters of the approach.

IV. MONTE CARLO SIMULATIONS

For the kMC simulations, we used a 2D square arrangement of $M = 4096$ sites with periodic boundary conditions. The initial particle configurations are generated by placing $M\theta$ particles on the randomly chosen sites. The initial configurations $\{n_i\}$ are equilibrated by the first idle kMC run.

To simulate the particle diffusion one should define the rate of particle jumps, the so-called transition algorithm. We assume that the particles perform thermally activated jumps to their NN empty adsorption sites. A particle should surmount the potential barrier separating the initial and final sites. The activation energy is given by the difference between the saddle point energy $\varepsilon_{sp}(=0)$ and the initial state energy ε_i . Usually, the interaction between the activated particle at the saddle point and its NNs is neglected. We select the well established expression for the jump rate derived in the transition state theory [6], [7]

$$\nu_{if} = \nu_0 \exp\left(-\varepsilon_i + \varphi \sum_{k=1}^4 n_k\right). \quad (6)$$

Here ν_{if} is the jump rate from the initial i th site to the NN final f th site; the summation is carried out over the NNs of the initial site and $\varepsilon_i = \varepsilon_{d,s}$ depending on the type of the initial site. Here and henceforth we use the system of units with $k_B T = 1$.

The jump rate is the same for all possible jumps from the i th site. The repulsive interaction increases and the attractive one decreases the particle energy and the jump rate.

For the kMC simulations we use the BKL algorithm [4]. The algorithm operates in a space of possible events. In contrast to the standard technique, where we consider fixed time intervals at which a jump may occur with a certain probability, the BKL algorithm randomly selects a jump out of all possible events and subsequently associates the number of clock ticks that must be passed for the event to take place. There are no rejected attempts, which results in a higher efficiency of the kMC simulations. We used the kMC simulations for the calculations of the tracer and jump diffusion coefficients, adsorption isotherms, the pair NN correlation function P_{00} , and the isothermal susceptibility

$$\chi_T = N^{-1} \sum_{ij} \langle (n_i - \theta)(n_j - \theta) \rangle. \quad (7)$$

The Fickian diffusion coefficient D_c is calculated via the Kubo–Green equation [8]

$$D_c = \theta D_j / \chi_T. \quad (8)$$

The values of the energetic parameters used for the kMC simulations are the same for all dependencies: $\varepsilon_d - \varepsilon_s = 6$, $\varphi = -2.5, -2, \dots, 2.5$. In order to obtain accurate values of the necessary quantities, runs of 10^6 kMC steps for up to 5×10^5 different initial configurations were performed.

V. RESULTS AND DISCUSSION

The coverage dependencies for the tracer diffusion coefficient $D_t(\theta)$ are plotted in Figures 2 and 3 for the repulsive and attractive lateral interaction, respectively. As it was mentioned above, the tracer diffusion coefficient describes the behavior of the tagged particles. For the homogeneous systems D_t is a monotone decreasing convex function of the surface coverage θ . In the heterogeneous lattices, the dependencies

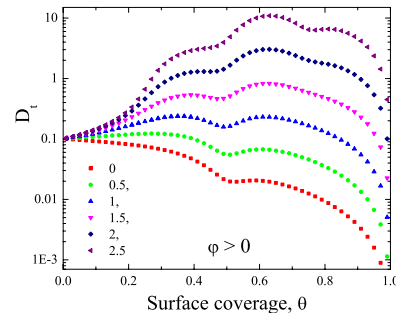


Fig. 2. The coverage dependencies of the tracer diffusion coefficient, D_t , for the repulsive interaction $0 \leq \varphi \leq 2.5$. Symbols denote the kMC data.

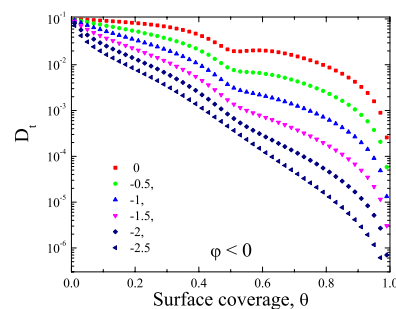


Fig. 3. The coverage dependencies of the tracer diffusion coefficient, D_t , for the attractive interaction $-2.5 \leq \varphi \leq 0$. The notations are the same as in the previous Figure 2.

$D_t(\theta)$ have minimum at the stoichiometric coverage $\theta = 1/2$. The nature of this minimum can be explained as follows. At this coverage, all d sites are filled and the overwhelming majority of the jump sequences are unsuccessful. Particles jump to the shallow sites and return back. The minimum is a characteristic feature for the tracer and jump diffusion coefficients for many heterogeneous lattices of different geometries and dimensions. We have two independent sets of data for the jump diffusion coefficient: the kMC data and the analytical dependencies 5. They are plotted as symbols and solid lines, respectively, in Figures 4 and 5. The coverage dependencies have qualitatively the same behavior as the corresponding dependencies for the tracer diffusion coefficient. As in the previous case, the dependencies $D_j(\theta)$ have minimum at the stoichiometric coverage $\theta = 1/2$.

There is a good coincidence of the kMC data with the analytical dependencies 5. The expressions give a qualitatively correct description of the coverage dependencies in the whole coverage region for the wide region of the lateral interaction.

In Figures 6 and 7, we present the coverage dependencies for the Fickian diffusion coefficient $D_c(\theta)$. The dependencies have maximum at the half coverage $\theta = 1/2$ for the weak lateral interaction. The dependence $D_c(\theta)$ is symmetrical for the Langmuir lattice gas, i.e. $\varphi = 0$. But the lateral interaction spoils the symmetry. The limiting values of the

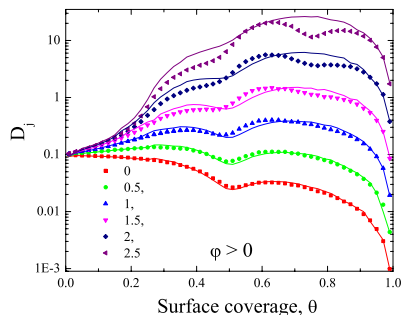


Fig. 4. The coverage dependencies of the jump diffusion coefficient, D_j , for the repulsive interaction $0 \leq \varphi \leq 2.5$ as indicated. Symbols denote the kMC data. The solid lines are analytical dependencies 5.

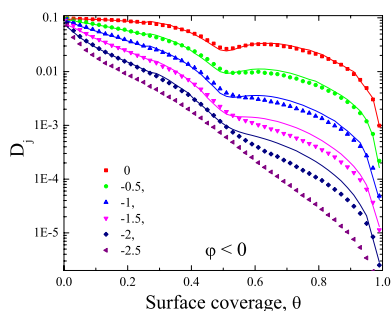


Fig. 5. The coverage dependencies of the jump diffusion coefficient, D_j , for the attractive interaction $-2.5 \leq \varphi \leq 0$. The notations are the same as in previous Figure 4.

Fickian diffusion coefficient for the empty and filled lattices are different. On the empty lattice jumping particles do not have NN particles. If $\theta \rightarrow 1$, every jumping particle has 3 NNs, which change its jump rate. The ordering in the particle system at the stoichiometric coverages $\theta = 1/4$ and $\theta = 3/4$ produces the additional fine structure and weak maxima on the coverage dependencies of the Fickian diffusion coefficient.

As it was mentioned above, the sites in the patches are located at different distances from the initial site. Then, their participation in the jump successions will be also different. The simplest way to account this difference is to fit the numerical data with the analytical dependencies calculated for the different z and z' . The dependencies D_j and D_c are smooth, slowly varying functions of z and z' . The best coincidence between the kMC and analytical data is achieved for $z = 5$ and $z' = 4$. One can consider them as the effective numbers of the NN sites participating in the particle migration. They are significantly reduced as compared with the exact geometrical values $z = z' = 8$.

VI. SUMMARY

We have investigated the diffusion of particles over the inhomogeneous patchwise lattice with two kinds of the adsorption sites. Such lattices have specific features qualitatively influencing the particle diffusion. The lattice inhomogeneity

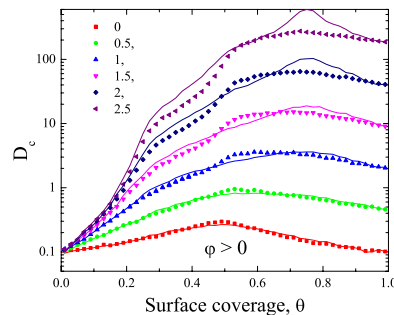


Fig. 6. The coverage dependencies of the Fickian diffusion coefficient, D_c , for the repulsive lateral interaction $0 \leq \varphi \leq 2.5$ as indicated. The notations are the same as in previous Figure 4.

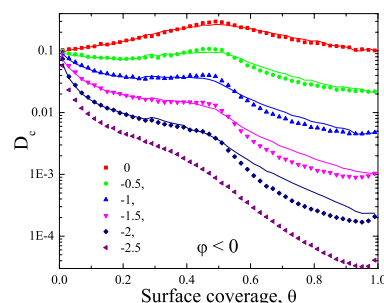


Fig. 7. The coverage dependencies of the Fickian diffusion coefficient, D_c , for the attractive lateral interaction $-2.5 \leq \varphi \leq 0$ as indicated. The notations are the same as in previous Figure 4.

governs the migration of particles. It imposes a very specific correlation on the particle jumps. The slow and fast jumps collect in the jump successions. The approach developed for the investigations of the particle diffusion in the heterogeneous lattices gives simple analytical expressions for the diffusion coefficients, which describe perfectly the particle migration in many heterogeneous lattices of different symmetry and dimensionality [3]. These expressions perfectly describe the particle diffusion in many heterogeneous lattices with two types of adsorption sites: 1D chain, square, honeycomb, dice, cubic, anisotropic, triangular (see, for example, [9]).

The successions of the correlated slow and fast jumps, performed by single particles, are the main migration acts in the low coverage region $\theta < 1/2$. The successions transfer particles between the d patches. They describe quite well the particle diffusion in this region.

Another type of the jump successions, performed by the two particles, dominates in the high coverage region $\theta > 1/2$. Such jump successions transfer particles between the s patches.

The coverage dependencies of the tracer, center-of-mass and Fickian diffusion coefficients are calculated using the kMC simulations of the particle migration and the theoretical approach based on the conception of jump successions. It should be noted the almost perfect coincidence between the analytical

dependencies and the kMC data in the rather wide region of the lateral interaction $-1.5 < \varphi < 1.5$. The noticeable discrepancies appear for the very strong lateral attractions $|\varphi| > 1.5$. The strong attraction results in the non-uniform distribution of the particles, i.e., the formation of islands of the dense phase with $\theta \rightarrow 1$ surrounded by a rarefied LG phase with $\theta \rightarrow 0$. The strong lateral repulsion tends to arrange particles in the ordered structures with alternating empty and filled sites. These correlations in the particle distribution should be accounted for the better coincidence of the theory with the kMC simulations.

The analytical expressions 5 can be used for the estimations of the diffusion coefficients for such lattices. The good coincidence demonstrates the correctness of the used approach based on the conception of the correlated jump successions.

The long jump successions control the particle diffusion over different heterogeneous lattices [11], [12]. But, it is salient to emphasize an important difference between the lattices mentioned above and the lattice considered here. The common feature of these quite different heterogeneous lattices (disordered square and triangular lattice) is the existence of an infinite connected cluster of shallow sites. The particles can migrate over the lattices jumping exclusively over the s sites. They perform long sequences of jumps and the diffusion is described by the simple law $D_t, D_j \sim (1 - n_d)^{-1}$. The percolation determines the character of the particle migration on these lattices. These lattices are equivalent for the particle diffusion, and the diffusion coefficients are the same. There is no such infinite connected cluster on the patchwise lattices. The particles perform long jump successions, but the effective length of these succession does not grow with the concentration of the particles trapped in the deep sites n_d . The coefficients D_t and D_j have a minimum at the stoichiometric coverage. The long jump successions transfer particles like ordinary pairs of slow and fast jumps. Only the first slow jump and the final fast jump are really effective. Many fast jumps over the s patches do not give any contribution to the migration. Therefore, the diffusion is described by the corresponding analytical expressions derived for the ordinary jump pairs [3]. It is rather interesting that almost the same expressions with some minor modifications describe the particle diffusion in the patchwise lattice, which looks very different from the above mentioned heterogeneous lattices.

It should be noted that the analysis and conclusions have a general character. One should expect that the results obtained for this lattice can be applied for a wide class of the patchwise surfaces. The specific character of the particle migration by the sequences of the jump pairs should not change considerably on the lattices with patches of the irregular forms and different sizes. The cardinal properties of the lattices, as the lattice symmetry and dimensionality, play a minor role when diffusion is determined by the long jump successions.

The main advantage of the proposed approach is the unified description of the particle diffusion in different heterogeneous lattices. The theoretical expressions for the diffusion coefficients give good description of the particle diffusion in the

different heterogeneous structures. The coincidence between the analytical and numerical data is really satisfactory despite the numerous approximations made during the derivation of the expressions.

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