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Diffusion of particles on the patchwise bivariate surfaces

Alexander Tarasenko *, Lubomir Jastrabik

Institute of Physics, v.v.i., AS CR, Na Slovance 2, 18221 Prague 8, Czech Republic

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ABSTRACT

The diffusion of particles adsorbed on patchwise surfaces is investigated in the framework of a lattice-gas model. We propose the analytical expressions for the center-of-mass and Fickian diffusion coefficients. The theoretical dependencies are compared with the numerical data obtained by the kinetic Monte Carlo simulations for three different patchwise lattices. The good coincidence of the theoretical dependencies and the numerical data corroborates the validity of the approach developed to describe the particle migration on such lattices.

1. 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. Usually, the real surfaces are heterogeneous. They have random potential reliefs with the broad distributions of the energetic parameters like adsorption energies and potential barriers. This fact significantly affects the behavior of the adsorbed atoms on the surfaces with complex topographies. To include all these aspects in the theoretical investigations it is most convenient to employ the lattice gas (LG) models. Lattice models are also ideal for study by the methods of computational physics. In these models the particles perform stochastic jumps among the sites of a discrete lattice.

A patchwise LG model has been developed by Ross and Olivier to describe the monolayer adsorption on heterogeneous surfaces [1]. In this model the surface is composed of a number of randomly distributed or ordered homotattic patches (i.e. sub-microscopic uniform and homogeneous regions of the surface) and variations in the adsorption energy on different patches are taken into account. Although this model is far too simple to make any quantitative predictions about the behavior of real adsorption systems, it includes the most important components that are expected to influence their properties, particularly the transport on such surfaces. This model is very popular in the experimental and theoretical investigations of the effects of the heterogeneity on a variety of the surface processes like adsorption, desorption and catalysis [2,3]. A few Monte Carlo studies of the diffusion of non-interacting particles adsorbed on the one-dimensional and two-dimensional patchwise lattices [4–6] also exist.

To develop a self-consistent theory of the particle diffusion on the patchwise surfaces, which would give the values of the diffusion coefficients in terms of easily accessible system properties, is a hard problem. The theory capable of accounting for the coverage dependencies of the diffusion coefficients would represent a significant advance. Due to the great versatility and complexity of these systems it seems impossible to do some definitive conclusions about the transport of particles on such surfaces.

Nevertheless, it occurs that in a simple case we have obtained a rather satisfactory description of the particle diffusion on the patchy lattice. We studied the influence of the patchwise heterogeneity on the surface diffusion in the framework of the LG formalism. In particular, we considered a special case of the lattice with only two different types of the adsorption sites, deep and shallow, grouped into square 2×2 patches. The interesting and surprising result of this investigation was the following: the migration of particles in the patchwise lattice is fairly well described by the diffusion coefficients derived for the other class of the heterogeneous lattices (these lattices may be regarded as composed of two interpenetrating sublattices which contain only deep or shallow sites, and the sites of each sublattice have the nearest neighbors entirely on the other sublattice) [7,8].

The behavior of the diffusion coefficients can be explained by the specific mode of the particle diffusion on the patchwise lattices. The particles perform sequences of strongly correlated jumps analogous to the heterogeneous case. The main objection, which can be put forward to this explanation, is that it is related only with the small size of the patches and the characteristic peculiarities of the behavior of the diffusion coefficients will be smoothed

* Corresponding author. Tel.: +420 266052165; fax: +420 286581448.
E-mail address: taras@fzu.cz (A. Tarasenko).

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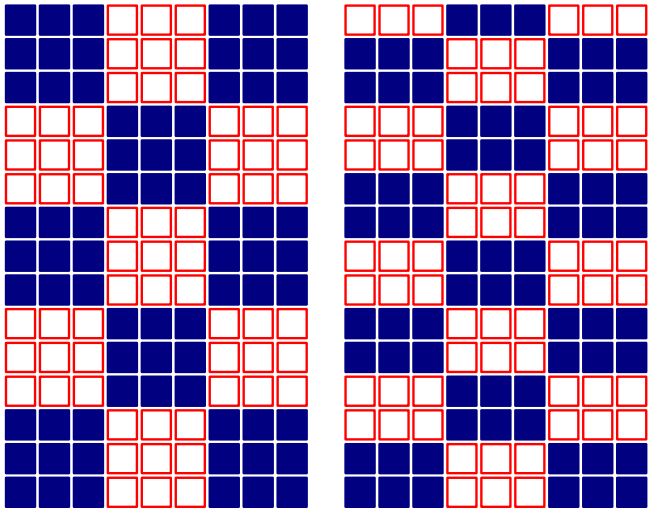

Fig. 1. A schematic view of the 3×3 and 3×2 patchwise lattices. The open and filled squares denote the shallow and deep adsorption sites, respectively.

out with the growth of the size of the patches or changing their form.

It is interesting to investigate the particle diffusion on a variety of the patchwise lattices. The tendency to perform jump sequences should survive in the bigger patches and the dependencies of the diffusion coefficients should be similar, at least qualitatively, to the heterogeneous case.

In this paper we have investigated the diffusion of adsorbed particles in three lattices with patches of different forms, sizes and ordering. We have considered the lattices with square 3×3 and rectangular 3×2 patches arranged in a strictly ordered chessboard structure, and a random patchwise lattice with the rectangular $m\times n$ patches arranged in the chessboard-like structure. The lattices are shown in Figs. 1 and 2.

The paper is organized as follows. In Section 2 we describe the model and give the definitions of the diffusion coefficients and other necessary quantities. The specific features of the particle diffusion on the heterogeneous lattices are discussed in Section 3. The details of the kinetic Monte Carlo (kMC) simulations and generation of the random patchwise lattices are described in Section 4. The results are discussed in Section 5. Finally, we present the summary of our results and conclusions in Section 6. The readers interested in the details of the derivation of the diffusion coefficients can follow a rather simple math text presented in the Appendix.

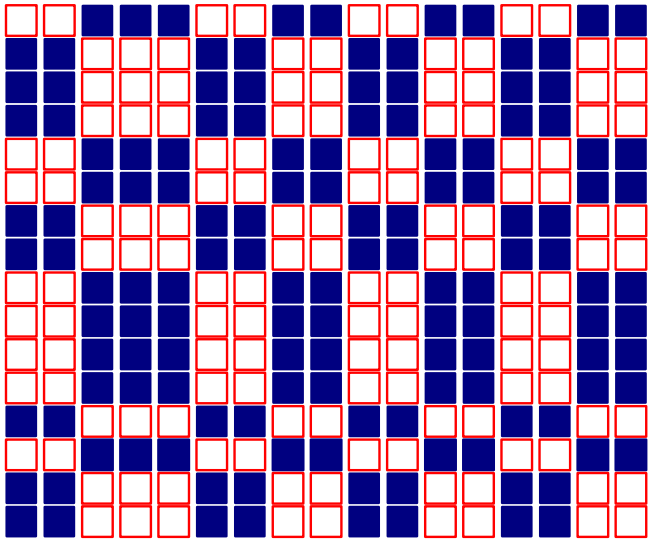

Fig. 2. A schematic view of the random patchwise lattice with the rectangular patches. The open and filled squares denote the shallow and deep adsorption sites, respectively.

2. The lattice-gas model of the surface

Let us consider the patchwise lattices composed of deep (d) and shallow (s) adsorption sites with adsorption energies ε_d and ε_s, respectively. If the energies are large relative to the temperature ($\exp \varepsilon_{d,s}/k_BT \gg 1$), the particles will stay almost exclusively within the potential minima, jumping occasionally to the empty nearest neighbor (NN) sites.

During migration acts, affected by the thermal activation, the particles have to surmount barriers separating the adsorption sites. This is certainly an accurate description of the migration at sufficiently low temperatures where the thermal energies are comparable to, or lesser than, the energy barrier to jumping. The lateral interactions between the particles play an important role considerably changing the rates of jumps.

The system of N_a particles is described by a set of occupation numbers n_i with

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

and the double occupancy is forbidden.

Let us introduce the concentration of the particles (surface coverage) $\theta = N_a/N$, the occupancies of the d sites $n_d = N_{ad}/N_d$, and s sites $n_s = N_{as}/N_s$, where N_{ad} and N_{ad} are the numbers of particles adsorbed in the d and s sites, respectively; N_d and N_s are the numbers of the d and s sites, respectively. There are simple relations between these quantities:

$$\theta = (N_d n_d + N_s n_s)/N, \quad N = N_d + N_s, \quad N_a = N_{ad} + N_{as}, \tag{2}$$

There is also a lateral interaction φ between the NN particles. The positive and negative values of the parameter φ correspond to the repulsive and attractive interactions between the particles.

The particle migration is described by some diffusion coefficients. It should be noted that there are no well-established terms for these quantities. There are many diffusion coefficients, diffusivities, diffusion constants with different names.

Conceptually, the simplest diffusion coefficient is a single particle (tracer or self-) diffusion coefficient D_{tr}. It addresses the random walks of individual tagged particles. Another kinetic coefficient D_{cm} describes the asymptotic behavior of the center of mass of the particle system, hence the name - the center-of-mass (CM) diffusion coefficient (also the jump, limiting, activity-corrected). The coefficients can be determined via the easily accessible quantities generated by the kMC simulations as

$$D_{tr} = \lim_{t\to\infty} \frac{1}{4tN_a} \sum_{k=1}^{N_a} \left\langle \vec{r}_k^{\,2}(t) \right\rangle,$$
$$D_{cm} = \lim_{t\to\infty} \frac{1}{4tN_a} \left\langle \left[\sum_{k=1}^{N_a} \vec{r}_k(t) \right]^2 \right\rangle. \tag{3}$$

Here $\vec{r}_k(t)$ is the displacement of the kth particle after time t; the brackets $\langle\cdots\rangle$ denote the average over the initial particle configurations.

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