Physica E 74 (2015) 556–560

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Migration of particles on heterogeneous bivariate lattices: The universal analytical expressions for the diffusion coefficients

Alexander Tarasenko*, Petr Boháč, Lubomír Jastrabík

Institute of Physics, v.v.i., Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic

HIGHLIGHTS

- The analytical expressions for the diffusion coefficients are derived.
- The expressions have the universal character: they describe diffusion on different heterogeneous lattices.
- The universality is explained by the specific mode of the particle migration over the lattices.
- The expressions can be used for the effective estimations of the diffusion coefficients.

ARTICLE INFO

Article history:
Received 26 June 2015
Received in revised form
12 August 2015
Accepted 13 August 2015
Available online 14 August 2015

Keywords:
Surface diffusion
Heterogeneous lattices
Lattice-gas models
Kinetic Monte Carlo simulation

ABSTRACT

We have derived the analytical expressions for the diffusion coefficients describing the particle diffusion on different heterogeneous lattices. It occurs that these expressions can be used for description of the particle diffusion on the patchwise lattices. The coverage dependencies of the center-of-mass and Fickian diffusion coefficients obtained for some patchwise lattices by the Monte Carlo simulation can be perfectly fitted by these expressions. The good coincidence of the numerical data with the theoretical results demonstrates the applicability of the analytical expressions for the wide class of heterogeneous lattices.

1. Introduction

The diffusive mass transfer controls the rates of a multitude of physical, chemical, and biological processes. For the theoretical investigations of these processes it is most convenient to employ the lattice gas (LG) models. In these models particles perform stochastic jumps among the sites of a discrete lattice. During migration acts, affected by a thermal activation, the particles have to surmount barriers separating the sites. This is certainly an accurate description at sufficiently low temperatures where the thermal energy is comparable to, or lesser than, the energy barrier to jumping. The lateral interactions between particles play an important role considerably changing the rates of jumps. Although these models are far too simple to make any quantitative predictions about the behavior of real adsorption systems, they include the most important components influencing their properties, particularly the transport over such surfaces.

We studied the influence of the heterogeneity on the surface diffusion in the framework of the LG formalism. In particular, we considered the bivariate surfaces with only two different types of the sites, deep and shallow. We derived the analytical expressions for the diffusion coefficients for this case. They describe the particle diffusion on a number of heterogeneous bivariate lattices very well. It occurs that these expressions are rather universal. They can be applied for the description of the diffusion in another class of the heterogeneous lattices, the so-called patchwise lattices.

The paper is organized as follows. In Section 2 we describe the LG model and give the definitions of the diffusion coefficients. In Sections 3 and 4 we analyze the peculiarities of the particle migration in the heterogeneous lattices. The results are discussed in Section 5. Finally, we present the summary of our results and conclusions in Section 6.

2. The bivariate lattice-gas model of the surface

In the following we consider the heterogeneous lattices with only two different types of sites: deep d and shallow s with

* Corresponding author.
E-mail addresses: taras@fzu.cz (A. Tarasenko), bohac@fzu.cz (P. Boháč), jastrab@fzu.cz (L. Jastrabík).

http://dx.doi.org/10.1016/j.physe.2015.08.027
1386-9477/

adsorption energies ε_d and ε_s ($\varepsilon_d > \varepsilon_s$). The deep and shallow sites can be arranged in an ordered structure or randomly distributed over the lattice. Some ordered heterogeneous square lattices are shown in Fig. 1. If the adsorption energies ε_d, ε_s sites are large relative to the thermal energy k_BT the particles will populate the lattice sites, jumping occasionally to the nearest neighbor (NN) sites. There is a pairwise lateral interaction φ between the NN particles.

The particle migration is described by some diffusion coefficients. The center-of-mass (CM) diffusion coefficient D_{cm} describes the asymptotic behavior of the center of mass of the particle system:

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

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

The Fickian diffusion coefficient D, describing the mass transfer over 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 the particle coverage, $\theta(\vec{r}, t)$:

$$\vec{J}(\vec{r}, t) = -D\vec{\nabla}\theta(\vec{r}, t). \tag{2}$$

The Fickian and CM diffusion coefficients are related by the Kubo–Green equation $D = \theta D_{cm}/\chi_T$, where χ_T is the isothermal susceptibility of the system.

3. Migration of particles on the heterogeneous lattices

There are a number of heterogeneous lattices which have the d and s sites arranged in an alternating order: every d site has only s NN sites and vice versa, every s site is surrounded by the d sites.

The diffusion coefficients for these heterogeneous lattices can be calculated using the analytical expressions derived in [1]:

$$D_{cm} = D_0 e^{\mu} P_{00}(P_z^{<} + P_{z'}^{>})\theta^{-1},$$
$$D = D_0 e^{\mu} P_{00}(P_z^{<} + P_{z'}^{>})\chi_T^{-1}, \tag{3}$$

where

$$P_z^{<} = \frac{1}{z-1}\left(z - \frac{1-n_d^z}{1-n_d} \right),$$
$$P_{z'}^{>} = \frac{1}{z'-1}\left(z' - \frac{1-h_s^{z'}}{1-h_s} \right). \tag{4}$$

In Eqs. (3) and (4) parameters z and z' denote the number of the NN sites surrounding the s and d sites, respectively; μ is the chemical potential of the particle system; P_{00} is the probability to find a pair of empty NN sites; $n_{d,s}$ denote the occupancies of the d and s sites, and $h_{d,s} \equiv 1 - n_{d,s}$. As all energetic parameters μ, ε_d, ε_s, φ enter the expressions divided by k_BT it is suitable to use the system of units with $k_BT = 1$. There is a simple relation between these occupancies and the coverage: $\theta = \theta_c n_d + (1-\theta_c)n_s$, where θ_c is the concentration of the deep sites in the heterogeneous lattice.

The inhomogeneity implies the much higher jump rate $\nu_s \propto e^{-\varepsilon_s}$ for the fast $s \to d$ and $s \to s$ jumps than the jump rate $\nu_d \propto e^{-\varepsilon_d}$ for the slow $d \to s$ and $d \to d$ jumps. The terms fast and slow 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}.

The slow and fast jumps take place on the different time scales as ν_s âª¢ ν_d. Any jump to a shallow site gives rise to fast jumps which occur immediately after the previous jump. The inhomogeneity imposes a strong correlation between the slow and the following fast jumps. They should be considered together as a single elementary migration act of the particle diffusion.

The characteristic concentration θ_c separates the whole coverage region into the low coverage region $0 < \theta < \theta_c$ and the high coverage region $1 > \theta > \theta_c$ where the particle diffusion proceeds by different modes of jumps.

In the low coverage region the migration of particles proceeds by the correlated pairs of jumps. Any migration act starts with a slow jump from an initial d site (as all s sites are empty) to an intermediate NN s site. Almost immediately the particle jumps from the intermediate to a final NN empty d site. The pairs of the correlated slow and fast jumps transfer particles between the d sites and give the dominant contribution to the total particle displacement.

In the high coverage region the other successions of the correlated slow and fast jumps, performed by the different particles, play important role in the particle migration. Any succession starts by a slow jump (as all d sites are occupied) from an intermediate d site to the final s site. Immediately, another particle from some NN (initial) s site fills the vacancy in the intermediate site. The net result of these jump successions is the transfer of particles between the s sites via the occupied d sites.

The approach describes perfectly the particle migration in many heterogeneous lattices [1–5]. It occurs that this approach based on the jump sequences gives a rather satisfactory description of the diffusion on the other class of the heterogeneous lattices, the so-called patchwise lattices. Eqs. (3) (derived for the heterogeneous lattices like the square heterogeneous lattice shown in Fig. 1a) can be also applied for the patchwise lattices like shown in Fig. 1b and c.

One can argue that the coincidence between the numerical data generated by the kinetic Monte Carlo (KMC) simulation and the theoretical results is fortuitous, obtained for some patchwise lattices only. In the next section we consider the particle migration over the patchwise lattice and reveal the close resemblance to the case of the heterogeneous lattices considered above. The similar mode of the particle jumping over these lattices means the similar behavior of the diffusion coefficients. Therefore the coincidence is not accidental and has real physical meaning.

4. Migration of particles on the patchwise lattices

The patchwise lattices have been introduced to describe the physical adsorption on the real surfaces [6]. The surfaces are composed of a number of randomly distributed or ordered homotattic patches of deep and shallow sites i.e. sub-microscopic uniform and homogeneous regions [7]. The patchwise lattices with square patches arranged in the regular order and randomly distributed rectangular patches of different sizes are plotted in Figs. 1 and 2.

The model is widely used in the experimental and theoretical investigations of the effects of heterogeneity on a variety of surface processes: adsorption, desorption, diffusion and catalysis [8]. Despite the great popularity of the patchwise model, there exists only a few KMC studies of the diffusion of particles adsorbed on a one-dimensional and two-dimensional patchwise lattices [9–11]. Due to the great versatility and complexities of these systems it seems impossible to do some definitive conclusions about the diffusion on such surfaces.

Let us consider the specific peculiarities of the particle migration on the patchwise lattices. The approach, considered in the