Physica A 391 (2012) 1048–1061

Contents lists available at SciVerse ScienceDirect

Physica A

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

Diffusion of particles over anisotropic heterogeneous lattices

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ARTICLE INFO

Article history:
Received 20 June 2011
Received in revised form 21 September 2011
Available online 13 November 2011

Keywords:
Lattice-gas models
Diffusion
kMC simulations

ABSTRACT

The diffusion of particles adsorbed on an anisotropic heterogeneous surface with two non-equivalent sites arranged in the alternated rows is investigated in the framework of the lattice-gas model. Analysis of the particle migration reveals rather interesting non-trivial peculiarities of this process. The particle diffusion has a qualitatively different character depending on the direction of migration and particle concentration. Using an approach describing the migration by sequences of strongly correlated particle jumps we derived the analytical expressions for the diffusion coefficients. The calculated coverage dependencies of the jump and chemical diffusion coefficients have been compared with the numerical data obtained by kinetic Monte Carlo simulations. Very good coincidence between the data obtained by two independent methods corroborates strongly the correctness of the approach for description of the particle diffusion in such heterogeneous lattices.

1. Introduction

Diffusive mass transfer controls a multitude of processes such as melting, roughening, crystal and film growth, to name but a few. The understanding of mechanisms of the particle migration is of fundamental importance in many branches of material sciences. The theoretical description of various kinetic phenomena observed in experimental studies presents a considerable challenge. To include different aspects of the particle diffusion is the most convenient to employ lattice–gas models. In these models particles perform random walks among sites of a discrete lattice. The appropriate models must reflect the elementary microscopic migration of particles which depends on the specific atomic environment and also on the number and configuration of the neighbor particles as a consequence of the lateral interaction. Typically, there are different binding sites in contrast to the majority of the lattice–gas models which ignore this aspect by assuming the equivalent lattice sites. Such heterogeneous systems are rather complex for the exact theoretical treatment. A lot of models have been proposed and investigated, e.g. Ref. [1]. Due to the diversity of these models it is not surprising that despite great attempts the understanding of the diffusion in such systems is far from complete.

We have investigated the particle diffusion over the inhomogeneous lattices composed of deep and shallow sites arranged in the alternating order that every deep site has the nearest neighbor (NN) shallow sites only, and vice versa, every shallow site has, exclusively, the deep NN sites (see, for example Ref. [2]). Such ordered inhomogeneity produces a specific correlation in the particle jumps. The particle migration is quite different from the homogeneous case. The diffusion is correctly described by the pairs of correlated jumps, not by the ordinary single jumps. Using such jump pairs as the elementary acts of migration we have derived the analytical expressions for the chemical diffusion coefficient and check them by kinetic Monte Carlo (kMC) simulations. The theoretical dependencies coincide with the numerical data amazingly well.

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doi:10.1016/j.physa.2011.11.006

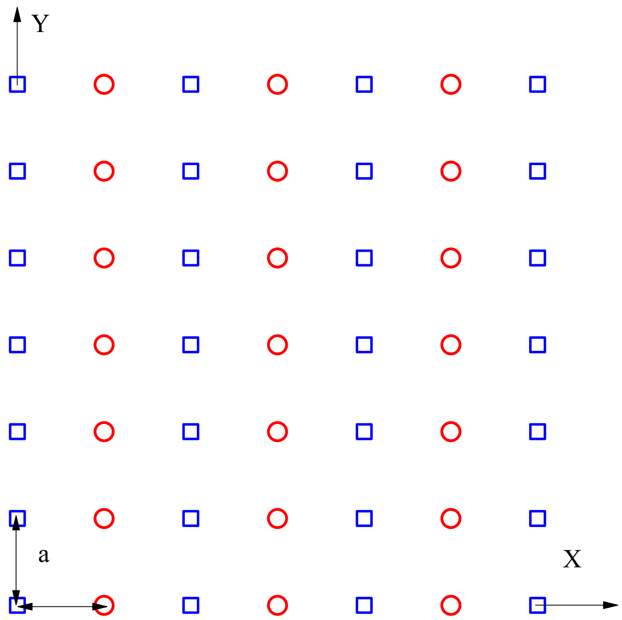

Fig. 1. Schematic view of the anisotropic heterogeneous lattice. The circles and squares denote shallow and deep sites, respectively.

The complex heterogeneous lattices like the disordered heterogeneous square lattice with an arbitrary ratio of deep and shallow sites [3] or triangular heterogeneous lattices [4] has some new specific peculiarities. The diffusion in these lattices is described by long successions of correlated jumps.

The case of the anisotropic lattice with the alternating rows of deep and shallow sites, shown in Fig. 1, is the most interesting. There are four different jump sequences which control the particle diffusion in the four different combinations (direction/particle coverage). It occurs that the particles migrate over the lattice using all possible modes of jumps: single jumps, jump pairs and long successions of correlated jumps. In the low coverage region (concentration less than half monolayer) diffusion along the rows proceeds by long successions of jumps and across the rows—by pairs of jumps. In the high coverage region diffusion along the rows is described by the ordinary single jumps, and across the rows particles migrate using another pair of correlated jumps.

The diffusion coefficients differ not only by the absolute value (fast diffusion along the rows and slow diffusion across the rows), but their coverage dependencies are qualitatively different due to the different character of the particle migration.

We study the diffusion of particles over this lattice in the framework of the lattice–gas formalism. Using simple ideas about the particle migration over the lattice we derived analytical expressions for the diffusion coefficients. These expressions work perfectly well in the whole coverage region and in a wide region of the lateral interactions.

The paper is organized as follows. In Section 2 we describe the lattice used for investigations and give some necessary definitions. We analyze the peculiarities of the particle migration along and across the rows of the lattice in Section 3. A short description of the kMC simulations is presented in Section 4. The results are discussed in Section 5. Finally, in Section 6 we present the summary of our results and conclusions.

2. The lattice–gas model and diffusion coefficients

We consider a square lattice of N adsorption sites. The lattice is anisotropic and heterogeneous: there are rows of deep d and shallow s sites arranged in an alternative order. The d and s sites have adsorption energies ε_d and ε_s, respectively. If the energies are large relative to the thermal energy k_BT, the particles will almost exclusively populate the sites jumping occasionally to the empty NN sites (henceforth we use the system of units with $k_BT = 1$). The system of N_a adsorbed particles is described by a set of occupation numbers $\{n_i\}$, with $n_i = 1/0$ if the ith site is occupied/empty. There is a lateral interaction between the NN particles. The interaction energy of the pair NN particles is equal φ ($\varphi > 0$ and $\varphi < 0$ correspond to the repulsive and attractive interaction, respectively).

The particle migration is described by diffusion coefficients. Conceptually, the simplest diffusion coefficient is the tracer diffusion coefficient $\hat{D}_t$. It addresses the random walks of the individual tagged particles. The jump diffusion coefficient $\hat{D}_j$ describes the asymptotic behavior of the particle system center of mass. The coefficients are expressed via the particle displacements as follows