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Abstract
We investigate diffusion of particles adsorbed on a heterogeneous honeycomb lattice with two kinds of non-equivalent sites. General analytical expressions for the chemical and jump diffusion coefficients have been derived in the case of strong inhomogeneity. It is shown that the character of the particle migration depends crucially on the relative jump frequencies of particles occupying deep and shallow sites. In the case of widely differing jump frequencies, particles perform pairs of strongly correlated jumps. We have calculated coverage dependencies of the diffusion coefficients and some thermodynamic quantities for attractive and repulsive lateral pairwise interactions and compared them with the results of the kinetic Monte Carlo simulations of the particle diffusion. Almost perfect agreement between the respective results has been found.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Diffusive mass transfer controls the rates of a multitude of physical, chemical, and biological processes. Theory primarily aims at understanding the details of migration processes in these application areas. The theoretical description of various kinetic phenomena observed in experimental studies presents a considerable challenge. Appropriate models must reflect the elementary microscopic migration acts of particles which depend on the structure and mutual particle–particle interaction. Therefore, it is not surprising that a great deal of effort has been devoted to developing the simplest possible models, which offer the advantage of exact treatment, despite oversimplifying the real phenomena. To take all these aspects into account it is most convenient to employ the lattice gas models. In these models particles perform stochastic jumps among the sites of a discrete lattice. During migration, affected by thermal activation, the particles have to surmount barriers separating the sites. The effective barrier height depends on the specific atomic environment and also, as a consequence of the lateral interaction, on the number and configuration of the neighbor particles.

In general the determination of the diffusion coefficients requires the solution of a kinetic equation for a many-particle system. However, under simplifying assumptions, the problem can be reduced to the calculation of purely thermodynamic quantities: free energy and its derivatives over chemical potential and interaction parameters [1–3]. The task of computing thermodynamic quantities is substantially simpler and computationally less expensive by orders of magnitude than kinetic Monte Carlo (kMC) simulations of migration which suffer from the statistical uncertainty of the results. The analytical expressions for the diffusion coefficients are quite simple and valid over wide regions of the particle coverage and temperature down to the subcritical values. These expressions work perfectly in homogeneous lattices with different dimensions and symmetries.

Diffusion on inhomogeneous honeycomb lattice has been studied theoretically in some previous investigations [4, 5]. The derived analytical expressions for the diffusion coefficients failed to give even qualitatively correct results. The discrepancies between the theoretical results and the kMC data were considerable. The surface inhomogeneity changes the particle migration substantially. The coverage dependencies for tracer, jump, and chemical diffusion coefficients differ

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qualitatively from those obtained for the homogeneous lattice. The striking disagreement between the analytical and kMC results demonstrates clearly that the description of the diffusion based on the single-particle jumps is inapplicable in the inhomogeneous systems. Despite the fact that particles really perform single jumps over the lattice and the kMC algorithms simulate these elementary migration acts correctly, the analytical treatment of the diffusion should take into account a rather specific pair jump correlation arising due to the lattice inhomogeneity.

In the present work we have revisited the honeycomb inhomogeneous lattice with two non-equivalent sites, the so-called bivariate trap model. The purpose of the investigation is to present the derivation of the expressions for the jump and chemical diffusion coefficients. These expressions are quite accurate and give a correct description of the particle migration. Using kMC simulations we check these expressions comparing the numerical and analytical results. The new expressions derived in this work fit perfectly the MC data in the whole coverage region for attractive and repulsive lateral interaction between the particles.

The paper is structured as follows. In section 2 we formulate the model, derivation of the diffusion equation, and the expressions for the diffusion coefficients. Sections 3 and 4 respectively present some details of the RSRG approach and MC technique employed in this work. Our results are presented and discussed in section 5. Finally, we conclude with a brief summary of our results in section 6.

2. Diffusion of particles on inhomogeneous lattices

In the following we consider an array of adsorption sites which form a regular honeycomb lattice of spacing a and coordination number $z = 3$. There are two kinds of sites: deep (d) with a depth ε_d and shallow (s) with a depth ε_s, arranged in alternate order. Hence, the lattice may be regarded as being composed of two equivalent interleaved sublattices comprised of d and s sites only. Surfaces of such type really exist. There are (111) planes of crystals having the fcc structure. Every surface atom on these planes is surrounded by six hollow sites. One half of the hollow sites has atoms from the second layer at the bottom and the other half has atoms from the third layer. Therefore, it seems quite natural to suppose that for most adsorbates the adsorption energies will be different in these sites.

The state of the particle system is described by a set of occupation numbers $\{n_i\}$:

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

In thermodynamic equilibrium the system behavior is described by the grand partition function,

$$Q = \sum_{\{n_i\}} \exp\left(\mu N_a - H_a\right), \tag{2}$$

or its corresponding potential, $F = N^{-1} \ln Q$, termed the free energy. Here μ, H_a, N_a, and N denote the chemical potential, Hamiltonian of the system, and number of particles and lattice

sites, respectively; the summation is carried out over all particle configurations (here and henceforth we use the system of units with $k_B T = 1$). The Hamiltonian and number of particles are given by

$$H_a = -\varepsilon_d \sum_{i \in d} n_i - \varepsilon_s \sum_{i \in s} n_i + \varphi \sum_{\langle NN \rangle} n_i n_j, \qquad N_a = \sum_i n_i. \tag{3}$$

Here φ is the pair interaction energy of the nearest neighbor (NN) particles and symbols $i \in d$, $i \in s$, $\langle NN \rangle$ denote summation over all d and s sites, and lattice bonds, respectively. We introduce surface coverage, θ, as follows: $\theta = N_a/N$.

The migration of particles over the lattice is described by some diffusion coefficients. Conceptually the simplest diffusion coefficient is a single particle or tracer diffusion coefficient, D_t, which addresses the random walks of individual tagged particles. Another useful quantity is the jump diffusion coefficient, D_j, related to the asymptotic behavior of the center of mass of the system. The coefficients are well-suited for the kMC simulations as they are expressed in terms of directly accessible quantities, i.e.

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

$$D_j = \lim_{t \to \infty} \frac{1}{4 N_a t} \left\langle \left[\sum_{k=0}^{N_a} \Delta \vec{r}_k(t)\right]^2 \right\rangle. \tag{4}$$

Here $\Delta \vec{r}_k(t)$ denotes the displacement of the kth particle after time t; the brackets $\langle \cdots \rangle$ denote the canonical ensemble average.

The chemical diffusion coefficient D_c is determined by Fick's first law, which constitutes the relationship between the flux of particles, $\vec{J}$, and the gradient of the surface coverage: $\vec{J} = -D_c \vec{\nabla} \theta$. The jump and the chemical diffusion coefficients are simply related by the Kubo–Green equation [6]

$$D_c = D_j \theta / \chi_T, \tag{5}$$

where χ_T is the isothermal susceptibility of the system.

To describe particle diffusion, the whole process must be resolved into its elementary components. It is quite natural to consider the evolution of the occupation numbers in terms of the particle jumps. A particle being in a site can jump to any empty NN site. This process is constrained by the hard-core repulsion preventing multiple occupancy of the sites. The jumping particle must surmount a potential barrier E_{if} separating the initial and final sites. In the simplest case of the Langmuir lattice gas ($\varphi = 0$) the barrier is a constant ε_d or ε_s depending on the type of initial site. For interacting particles the activation energy depends on the number of adjacent particles. We assume that the interactions affect the minima of the potential landscape and neglect their influence on an activated particle at the saddle point of the potential barrier. Then, the jump frequency from the ith to the fth site

has the following form

$$v_{if} = v \exp \left\{ -\varepsilon_i + \varphi \sum_{k=1}^{z} n_k \right\}, \qquad (6)$$

where summation runs over all NNs of the ith site.

The expression for the jump frequency is quite simple and has been used widely. It was obtained in the transition state theory [7]. It is the escape rate of particles from a deep potential well. All details of the particle motion are hidden in the pre-exponential factor v, which (weakly) depends on the temperature and the parameters of the potential relief. The leading exponential factor determines the main features of the particle migration. The jump frequency depends on the energy of the initial state only and is the same for jumps to all NN sites. And really it is very suitable for the kMC simulations. It is certainly important to note that equation (6) represents a mathematical recipe or transition algorithm describing how particles move over the lattice. Different algorithms are conceivable and have been used in the diffusion theory and kMC simulations, some of them are described in [8].

On the inhomogeneous lattice all particles tend to occupy d sites which results in either an almost empty s sublattice and partially filled d sublattice ($\theta < \frac{1}{2}$) or an almost completely filled d sublattice and partially filled s sublattice ($\theta > \frac{1}{2}$). The inhomogeneity implies a higher jump probability for $s \to d$, fast jumps, than for $d \to s$, slow jumps. The characteristic times of particle sojourn in the d and s sites, $\tau_d \sim \exp(\varepsilon_d)$ and $\tau_s \sim \exp(\varepsilon_s)$ differ considerably, $\tau_d \gg \tau_s$. And a rather specific correlation between the particle jumps arises in this case. Any $d \to s$ jump transfers a particle to the s sublattice and creates an unstable local non-equilibrium configuration consisting of a pair of NN sites with the occupied s and empty d sites. There are two possible ways for the fast decay of this configuration: either the particle jumps to an empty d site or the vacancy left by the particle is filled by another particle from a filled s site.

As the fast jump takes place almost immediately after the slow jump their combination ought to be considered as the central entity of the diffusion process. The particle jumps collect into pairs: any slow jump is followed by a fast jump. Such jump pairs govern the particle migration. The frequency of these events is determined by the slowest component, $d \to s$ jump frequency. Despite the fact that the individual jumps are statistically uncorrelated, the lattice inhomogeneity imposes a strong pairwise correlation between slow and fast jumps. Correlation between jump pairs is absent.

The characteristic coverage $\theta = \frac{1}{2}$ separates two regions with distinctly different types of jump pairs dominating in the particle migration. For $\theta < \frac{1}{2}$, the s sublattice is empty and any act of migration starts by a slow jump from an initial d site to an intermediate empty s site. Shortly after, the particle leaves the intermediate site and moves to a final d site. The fast jump probability depends on the total number of the occupied NN d sites, n_{occ} at the intermediate d site, i.e. $(z - n_{occ})^{-1}$. The migration of the particles proceeds by pairs of slow and fast jumps. The probability of the jump pair depends not only on the occupation numbers of the initial and final sites, but on the occupation numbers of the NN intermediate site.

For $\theta > \frac{1}{2}$ the d sublattice is filled and the s sublattice is partially occupied. Any act of migration starts by a slow jump from an intermediate d site to a final s site. The jump creates a vacancy in the completely filled d sublattice and initiates a fast jump from an initial s site to the intermediate site. The fast jump probability depends on the number of occupied NN sites, n_{occ}, at the intermediate d site, i.e. n_{occ}^{-1}. The pairs of successive slow and fast jumps performed by different particles transfer particles over the s sublattice using occupied d sites as intermediate steps.

The temporal evolution of the occupation numbers is described by the balance equation

$$n_i(t + \Delta t) - n_i(t) = \sum_{f=1}^{6} \left[J_{fi}(\Delta t) - J_{if}(\Delta t) \right] \qquad (7)$$

where $J_{if}(\Delta t)$ denotes the number of particle jumps from the ith to the fth site after time Δt. There are two contributions to J_{if} arising due to possible local particle configurations. Let us consider a cluster of four sites with the central s site (0th) and its three d NNs (1st, 2nd and 3rd). The sequence of slow and fast jumps (1st $\to$ 0th $\to$ 2nd) transfers particles from the 1st to the 2nd site if the 1st site is occupied and 0th and 2nd sites are empty ($n_1 = 1, n_0 = n_2 = 0$). The occupation of the 3rd site influences the probability of the fast jump. For $n_3 = 0$ there are three possible ways for the particle to leave the 0th site, otherwise there are only two

$$J_{12} \propto v_{10} n_1 h_0 h_2 (h_3/3 + n_3/2), \qquad 0 \in s, \qquad (8)$$

where $h_i \equiv 1 - n_i$.

The second type of jump sequence has a slightly different combination of multipliers. Again we consider a cluster of four sites with the central d site and its three s NNs. The sequence of slow and fast jumps (0th $\to$ 2nd and 1st $\to$ 0th) transfers particles from the 1st to the 2nd site if the 1st and 0th sites are occupied and the 2nd site is empty ($n_1 = n_0 = 1, n_2 = 0$). The occupation of the 3rd site influences the probability of the fast jump. For $n_3 = 0$ there are two particles which can occupy the vacancy, otherwise three particles could possibly fill the 0th site

$$J_{12} \propto v_{02} n_0 h_2 n_1 (n_3/3 + h_3/2), \qquad 0 \in d. \qquad (9)$$

Invoking the local equilibrium approximation and neglecting memory effects, the balance equation is easily reduced to the ordinary diffusion equation. The analytical expression for D_c can be derived quite easily (for details see, e.g. [1, 3, 9])

$$D_c = D_0 \exp(\mu) \chi_T^{-1} P_3, \qquad (10)$$

where $D_0 = \frac{3}{8} v a^2$; the correlation function P_3 depends on the occupation numbers of four sites

$$\begin{aligned} P_3 &= \langle h_1 h_0 h_2 (3 - h_3) \rangle, & 0 \in s, & \quad \theta < 1/2, \\ P_3 &= \langle h_1 h_0 n_2 (3 - n_3) \rangle, & 0 \in d, & \quad \theta > 1/2. \end{aligned} \qquad (11)$$

The thermodynamic quantities occurring in the right-hand side (RHS) of equation (10) can be expressed via the first and

second derivatives of the free energy over its arguments as follows:

$$\theta = \frac{\partial F}{\partial \mu}, \qquad \chi_T = \frac{\partial^2 F}{\partial \mu^2},$$

$$P_{00} \equiv \langle h_0 h_1 \rangle = 1 - 2\theta - \frac{2}{z}\left(\frac{\partial F}{\partial \varphi}\right). \tag{12}$$

Note, that the kinetic coefficients D_c and D_j which describe, in principle, the non-equilibrium behavior of the lattice gas system, are related to the equilibrium thermodynamic quantities. They depend on the correlation functions of two, three, and four sites. These correlators can be approximately expressed via the pair correlation function P_{00} and mean values of the occupation numbers on the d and s sublattices.

3. Real-space renormalization group (RSRG) transformation

A variety of analytical methods can be used for the calculation of the thermodynamical quantities which enter the expressions for the diffusion coefficients. The RSRG approach is particular simple so that a rather modest effort suffices to compute data of good accuracy especially in the two-dimensional lattice gas systems. We outline briefly the RSRG method used for this purpose. It is well known that there is a one to one correspondence between the lattice gas model and spin model in an external magnetic field. Empty and occupied sites are equivalent to $s = -1$ and $s = 1$, respectively. Using the obvious relation between the spins and occupation numbers, $2n_i = 1 + s_i$, the equivalent reduced Hamiltonian $H_s = \mu N_a - H_a$ is

$$H_s = h_d \sum_{i \in d} s_i + h_s \sum_{i \in s} s_i + p \sum_{\langle nn \rangle} s_i s_j + Nc. \tag{13}$$

Here

$$\begin{aligned}
h_d &= (\mu + \varepsilon_d)/2 - z\varphi/4, \\
h_s &= (\mu + \varepsilon_s)/2 - z\varphi/4, \\
p &= -\varphi/4, \\
c &= \mu/2 + (\varepsilon_d + \varepsilon_s)/4 - z\varphi/8.
\end{aligned} \tag{14}$$

In the RSRG method the whole lattice is divided into blocks of L sites [10, 11]. A block spin S_α is assigned to each block. All blocks together must form a lattice of the same symmetry. The RSRG transformation of the spin system allows the reduction of the number of independent variables, i.e. the transition from the set of N site spins $\{s_i\}$ to N/L block spins $\{S_\alpha\}$. For blocks with an odd number of spins L the block spin S_α is usually determined by the so-called majority rule

$$S_\alpha = \text{sgn}\left(\sum_{i=1}^{L} s_i\right), \tag{15}$$

where $\text{sgn}(x) = \pm 1$ depending on the sign of its argument.

In the framework of the RSRG approach, one usually employs periodic boundary conditions. It is assumed that the whole lattice is given by the periodic continuation of a small cluster of blocks. In the present work we consider the cluster of two blocks only [12]. Due to the simplicity of this cluster, no additional interactions appear in the renormalized Hamiltonian. It is the same Hamiltonian of the honeycomb lattice with, however, renormalized values for the external magnetic fields H_d, H_s and interaction parameter P. The relations between the original and renormalized quantities are obtained via the equation

$$H_d S_1 + H_s S_2 + z P S_1 S_2 + 2Lg = \ln\left\{\sum_{\{s\}} \exp[H_s]\right\} = \Psi_{S_1, S_2}. \tag{16}$$

Here the summation is carried out over all possible configurations $\{s_i\}$ with fixed values of the block spins $S_{1,2} = \pm 1$. The system of the RG equations has simple form

$$\begin{aligned}
H_d(h_d, h_s, p) &= \left(\Psi_{1,1} - \Psi_{-1,-1} + \Psi_{1,-1} - \Psi_{-1,1}\right)/4, \\
H_s(h_d, h_s, p) &= \left(\Psi_{1,1} - \Psi_{-1,-1} - \Psi_{1,-1} + \Psi_{-1,1}\right)/4, \\
P(h_d, h_s, p) &= \left(\Psi_{1,1} + \Psi_{-1,-1} - \Psi_{1,-1} - \Psi_{-1,1}\right)/4z, \\
g(h_d, h_s, p) &= \left(\Psi_{1,1} + \Psi_{-1,-1} + \Psi_{1,-1} + \Psi_{-1,1}\right)/8L.
\end{aligned} \tag{17}$$

The RSRG transformation functions $\Psi_{\pm 1, \pm 1}$ can be written in the general form as follows

$$\Psi_{\pm 1, \pm 1} = \ln\left[\sum_{i=1}^{N_{\pm\pm}} T_{i1}^{\pm\pm} \exp\left(T_{i2}^{\pm\pm} h_d + T_{i3}^{\pm\pm} h_s + T_{i4}^{\pm\pm} p\right)\right]. \tag{18}$$

The four matrices $\hat{T}^{\pm\pm}$ are determined by the blocks of the RSRG transformation. These matrices are used for fast calculations of the free energy, F, and its derivatives for any values of the magnetic fields and interaction in the process of sequential RSRG transformations of the original Hamiltonian [11]

$$F(h_d, h_s, p) = c + \sum_{m=0}^{\infty} L^{-m} g\left(H_d^{(m)}, H_s^{(m)}, P^{(m)}\right). \tag{19}$$

Here $H_d^{(m)}$, $H_s^{(m)}$, $P^{(m)}$ are the parameters of the renormalized Hamiltonian obtained after the mth RSRG transformation; $H_{d,s}^{(0)} = h_{d,s}$, $P^{(0)} = p$.

The accuracy of the RSRG data depends crucially on the size and symmetry of the blocks used in the RSRG transformation. Very good results have been obtained for the RSRG blocks with $L = 7$ and 13 investigated in [12].

4. Monte Carlo simulations

Here we give a brief overview of the kMC algorithm used for simulations. For application of the MC method in surface diffusion interested readers are referred to [13].

The system is realized by a two-dimensional array of $N = M \times M + 2$ sites ($M = 32, 64$) with the helical boundary conditions [14]. An initial configuration is generated by adsorbing N_a particles on the lattice at random. The main drawback of the ordinary kMC algorithm for inhomogeneous
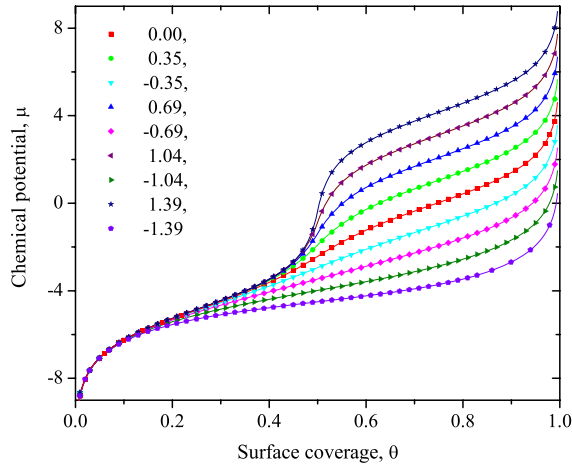
Figure 1. Adsorption isotherms θ versus μ for different values of the interaction parameter φ as indicated. Lines denote the RSRG results, symbols denote the kMC data.
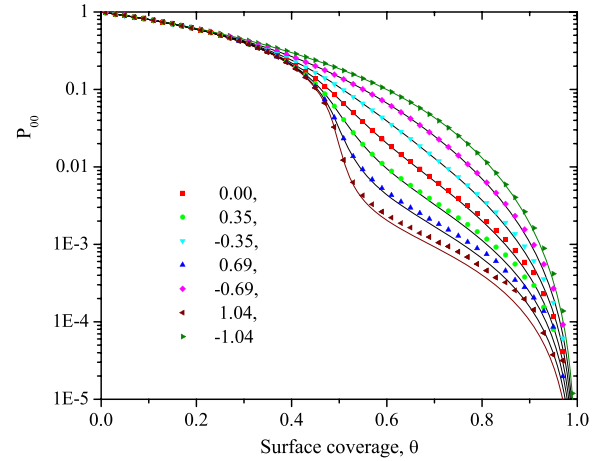

Figure 2. The pair correlation function P_{00} versus θ.

Figure 3. The isothermal susceptibility χ_T versus θ.

lattices is a very small transition probability for slow jumps. A large part of the computing time is spent in attempting jumps which are rejected. To overcome this difficulty we use the so-called Bortz, Kalos and Lebowitz (BKL) algorithm [15]. It operates in the space of possible events instead of the real space as the ordinary kMC algorithm does. There are no rejected attempts which results in a high efficiency of the BKL algorithm. It has been described in detail elsewhere [16].

We used the kMC simulations for calculations of the tracer and jump diffusion coefficients, adsorption isotherms, and isothermal susceptibility. The chemical diffusion coefficient has been determined via the Kubo–Green relation, here written as:

$$D_c = \theta D_j \frac{N_p(N - N_p)}{N\langle(\delta n)^2\rangle}, \qquad (20)$$

where N_p is the number of sites inside the probe area, and $\langle(\delta n)^2\rangle$ is the mean square fluctuation of the particle number in this area [17]. The shape of the probe area may be arbitrary.

The dependencies $\mu(\theta)$ have been calculated using the method of local states [18]. The idea of the method is rather simple. The energy of any particle can take the $2(z + 1)$ values: $E_i = -\varepsilon_{d,s} + n\varphi$, $n = 0, 1, 2, \ldots, z$, depending on the number of NNs. The energies define the local states of the particles. The set of conjugate states is determined for holes (empty sites). All conjugate states have the same zero energy. The frequencies of occurrence (ensemble average populations) of the ith local state and its conjugation are denoted as σ_i and σ_i'. They are related by the condition of the detailed balance as follows

$$\mu = \ln(\sigma_i/\sigma_i') + E_i, \quad i = 1, \ldots, 2(z + 1). \qquad (21)$$

To smooth out the fluctuations it is advisable to average μ over the most probable local states and exclude rare configurations.

We have averaged over 40 000–160 000 initial configurations, depending upon the lateral interaction strength φ. The accuracy has been judged by monitoring the change of computed quantities as a function of the number of initial configurations.
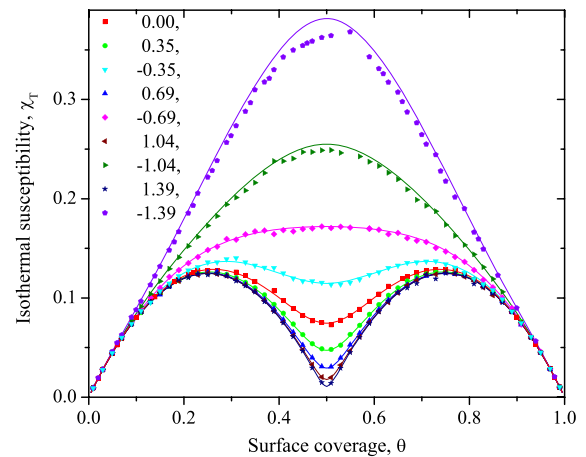
5. Results and discussion

Using the RSRG and MC methods we have calculated the adsorption isotherms, pair correlation function, isothermal susceptibility, tracer, jump, and chemical diffusion coefficients for attractive and repulsive lateral interaction between the particles adsorbed on an inhomogeneous honeycomb lattice. The inhomogeneity parameter is the same for all dependencies: $\varepsilon_d - \varepsilon_s = 7 \ln 2$.

To illustrate the accuracy of the RSRG method used for the calculations of the thermodynamic quantities we plot the coverage dependencies of the chemical potential μ (adsorption isotherms), correlation function P_{00} and isothermal susceptibility χ_T in figures 1, 2, and 3, respectively, for some representative values of the lateral interaction parameter φ. These quantities are necessary for calculations of the jump and chemical diffusion coefficients. For adsorption isotherms and correlation functions, the agreement between the RSRG results and the kMC data is excellent over the entire temperature and coverage range for attractive and repulsive interactions. These quantities are expressed via the first derivatives of the free energy over its arguments. The isothermal susceptibility, being the second derivative of the free energy over the chemical
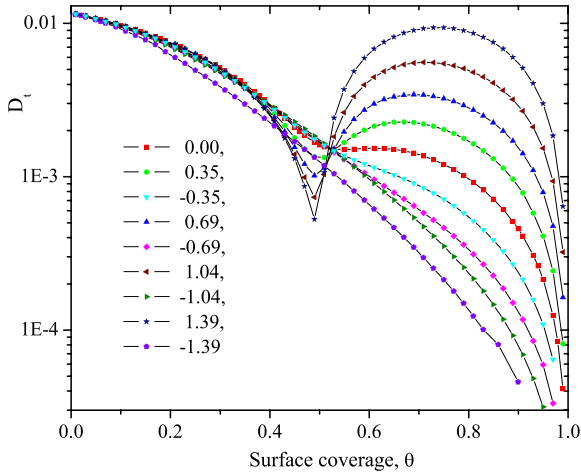
Figure 4. The tracer diffusion coefficient D_t versus θ. The kMC data only. Symbols are connected by lines to guide the eyes.
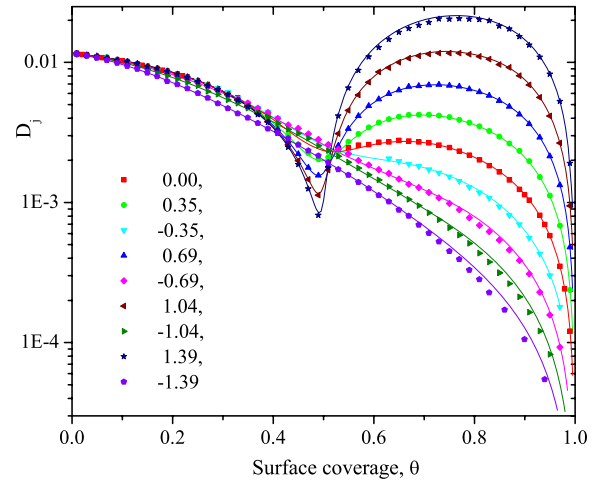

Figure 5. The jump diffusion coefficient D_j versus θ.

Figure 6. The chemical diffusion coefficient D_c versus θ.

potential, is more sensitive to the accuracy of the calculations. There are visible discrepancies between the data obtained by the different methods for strong attraction ($\varphi = -2\ln 2$) at the half monolayer coverage.

The calculations of the diffusion coefficients require knowledge of the correlation functions, equation (11), which cannot be obtained by the RSRG method. For the Langmuir lattice gas the functions are simply powers of the corresponding vacancy densities:

$$P_3 = (1-\theta_d)(1-\theta_s)\left[(1-\theta_d)(2+\theta_d) + \theta_s(3-\theta_s)\right], \quad (22)$$

where θ_d and θ_s are the average occupancy of the d and s sublattices, respectively. Such an approximation is fairly good for $\theta < \frac{1}{2}$, where the particles can be considered as noninteractive. But for higher densities it gives noticeable discrepancies. In this case we expressed all necessary functions via the simplest two-site correlator we have at hand, P_{00}, as follows

$$
\begin{aligned}
\langle h_0 h_1 \ldots h_k\rangle &\approx P_{00}^k (1-\theta_d)^{1-k}, & 0 \in d, \\
\langle h_0 h_1 \ldots h_k\rangle &\approx P_{00}^k (1-\theta_s)^{1-k}, & 0 \in s.
\end{aligned}
\quad (23)
$$

This approximation works well at both ends of the coverage interval and gives small deviations at half-monolayer coverage, $\theta = \frac{1}{2}$.

For the homogeneous systems and $\varphi = 0$, the tracer diffusion coefficient is a monotone decreasing convex function of the surface coverage θ. The jump diffusion coefficient is a linear function of the surface coverage $D_j(\theta) \propto 1-\theta$, and the chemical diffusion coefficient does not depend on the surface coverage at all.

The tracer, jump, and chemical diffusion coefficients are equal in the limit of zero surface coverage, $D_t(0) = D_j(0) = D_c(0) \approx 2D_d$. In a completely occupied lattice (diffusion of a single vacancy) tracer and jump diffusion coefficients are also equal, $D_j(1) = D_t(1) = 0$, but their ratio $D_t(1)/D_j(1) \neq 1$. It depends on the dimensionality and symmetry of the lattice. The physical reason for the different behavior of the tracer
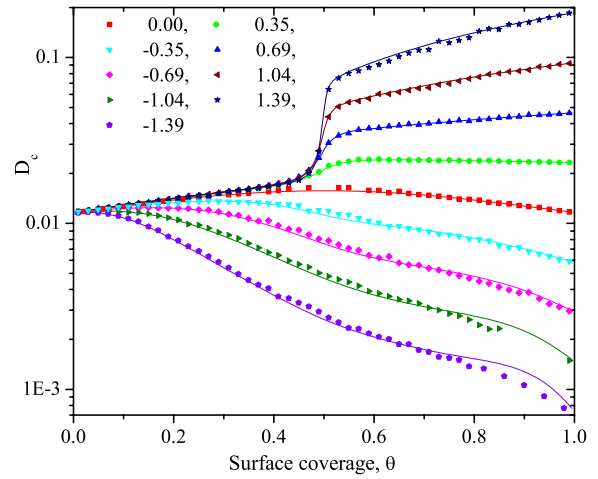
diffusion coefficient is the following: any particle left an empty site behind itself after every jump. If the other NN sites are empty there is no effect, but if some of them are occupied, the probability for the backward jump is greater than for the forward or sideward jumps. The backward correlation is taken into account by a correlation factor, $f(\theta)$, as follows:

$$D_t(\theta) = f(\theta)D_j(\theta). \quad (24)$$

The coverage dependencies of the tracer, jump, and chemical diffusion coefficients are plotted in figures 4–6, respectively. The dependencies for D_t were obtained by the kMC simulations only. We have no analytical expression for the tracer diffusion coefficient.

The behavior of the dependencies for the tracer and jump diffusion coefficients becomes non-monotonic due to the different character of the particle migration. The tracer and jump diffusion coefficients have pronounced minima at the half-monolayer coverage, but the minimum on the coverage dependencies $D_c(\theta)$ is absent as the isothermal susceptibility, χ_T, and the jump diffusion coefficient, D_j, have minima at the same coverage which compensate each other. The

nature of these minima can be explained as follows. At the stoichiometric coverage $\theta = \frac{1}{2}$ all d sites are occupied and all s sites are empty. The overwhelming majority of jumps will be unsuccessful. Any particle jumping from a d site to the NN s site cannot find another empty d site and returns back to the initial empty site. The total displacement will be close to zero. The isothermal susceptibility, tracer, and jump diffusion coefficients reach their minima at this coverage.

Any deviation from the stoichiometric value increases the particle diffusivity. For $\theta < \frac{1}{2}$ some d sites are empty, and there are vacancies in the d sublattice. So it is possible for activated particles to perform pair jumps to occupy other vacancies. For $\theta > \frac{1}{2}$ all d sites are occupied and some excess particles occupy the s sites. If a particle from a d site jumps to an empty NN s site, another excess particle from another NN s site can occupy the vacancy created by the previous particle.

The dependencies for the jump diffusion are very similar to those for the tracer diffusion coefficient. The RSRG and MC data coincide rather well.

The dependencies for the chemical diffusion coefficient D_c are shown in figure 6. There is a rather strong effect of the lateral interaction on the particle diffusion. The chemical diffusion coefficient grows from its initial value D_0 almost linearly for $\theta < \frac{1}{2}$ and then jumps at $\theta = \frac{1}{2}$. At this coverage the lateral interaction is switched on and particles begin to 'feel' each other. The chemical diffusion coefficient grows very fast if the coverage exceeds slightly the stoichiometric value.

In the limit $\theta \rightarrow 1$, a jumping particle has two NNs. Therefore, the limiting value of the chemical diffusion coefficient at the monolayer coverage is equal to

$$\lim_{\theta \rightarrow 1} D_c = D(0) \exp(2\varphi). \tag{25}$$

Attraction inhibits the particle migration. The relaxation of the coverage disturbances became slower and slower as the interaction parameter $|\varphi|$ increases.

The numerical data for the chemical diffusion coefficient are obtained using the Kubo–Green relation. The good coincidence between the data obtained by the analytical and numerical methods shows the applicability of the Kubo–Green relation for this model.

6. Summary

We have investigated the diffusion of particle on inhomogeneous lattices with two kinds of sites. Such systems display specific peculiarities which qualitatively affect the particle diffusion as compared to homogeneous lattices. Notably, the lattice inhomogeneity causes specific correlation between the particle jumps. This results in a qualitatively different non-monotonic behavior of the diffusion coefficients: the appearance of a minimum $D_t(\theta)$ and $D_j(\theta)$.

The numerical BKL technique as well as the analytical RSRG method have been used to compute the adsorption isotherms and the coverage dependencies of the pair correlation function, isothermal susceptibility, jump, tracer, and chemical diffusion coefficients at different values of

the lateral interaction between the adsorbed particles. The excellent agreement between the data indicates that the RSRG method can be applied successfully for investigations of the thermodynamic properties of the lattice gas systems with strong lateral interactions.

The standard model of single jumps works rather well in simple lattice gas systems provided the lattice inhomogeneity is not substantial. However, the model is doomed to failure even at a qualitative level of accuracy in the case of a strongly inhomogeneous potential surface. An extension to the model of jump pairs has been proposed which forms a sound basis for the quantitatively correct description of the particle diffusion in such cases. This approach is quite general. The analytical expressions for the chemical diffusion coefficient derived on the basis of this model extension are valid for inhomogeneous lattices of different symmetry and dimensionality. The proposed model of jump pairs gives a simple and natural explanation of the peculiar characteristics of surface diffusion on inhomogeneous lattices as mentioned above.

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