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Coupling of orthogonal diffusion modes in two-dimensional nonhomogeneous systems

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Collective diffusion coefficient in a two-dimensional lattice gas on a nonhomogeneous substrate is investigated using variational approach. In our model particles reside and jump randomly between adsorption sites modeled as potential wells with different depths. Site blocking is the only allowed particle-particle interaction mechanism. It is shown that the value of the diffusion coefficient in one lattice direction depends nontrivially on the rate and the character of the particle jumps in other directions. The collective diffusion coefficient increases, eventually approaching values predicted within the mean-field approximation when the jump rate increases in the direction perpendicular to that in which the diffusion coefficient is measured. Analytical predictions of our model are supported by the Monte Carlo simulation performed for selected systems.

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I. INTRODUCTION

Particle diffusion processes on a lattice play a decisive role in various physical phenomena of both fundamental and technological interests. Thermally activated particle jumps between adsorption sites are the fundamental microscopic processes resulting in diffusion. Geometry of the adsorption sites lattice and a topology of the potential-energy surface, as seen by the jumping particle, depend on a type of the substrate lattice, direction in which the crystal is cut, chemical properties of adsorbed particles and those of the substrate, and interactions among all of them. A topology of the potential-energy surface and its role in particle diffusion for substrates of various geometries have been the subject of intensive studies.[1]

Measurements show that diffusion over surfaces which are anisotropic, such as fcc (110), fcc (311), fcc (331), bcc (211), or bcc (321) is also anisotropic.[1] The above surfaces have a striped structure. For such surfaces when particle jumps across rows are blocked the diffusion has a one-dimensional (1D) character. For some systems, however, rates of jumps across rows may be higher than those along rows. Therefore for surfaces of the same geometric type, depending on the chemical properties of the substrate and the adsorbate, i.e., depending on the ratio of jump rates along mutually perpendicular directions, we may observe anything from truly (1D) diffusion to "mean-field" diffusion in which jumps in one of two perpendicular directions dominate. In the intermediate regime diffusion is genuinely two-dimensional (2D).

As long as we can treat particles as independent, such as in diluted systems, a collective diffusion behavior can be described in terms of a single-particle diffusion, i.e., diffusion of a collection of independent particles. When, however, particle-particle interactions come into play, collective diffusion in a many-particle system may drastically depart from this behavior.[2–7] The most striking example is that in which the system undergoes an ordering transition due to the interactions within the adsorbate,[8–13] but even when the interactions are limited to merely preventing double occupations of adsorption sites the dynamical behavior within the many-particle system has interesting properties which cannot be understood in terms of jumps of independent particles. It is well known[14] that as long as the underlying substrate lattice is homogeneous the site blocking alone does not affect collective diffusion and the diffusion coefficient remains independent of an adsorbate density. When, however, adsorption sites are not equivalent, collective diffusion does depend strongly on the adsorbate density even in the absence of interactions other than the site blocking.[15–22]

Adsorption sites may be nonequivalent due to interactions with the substrate[23,24] or because the surface is stepped.[25,26] In this work we discuss the collective diffusion in 2D systems in which interactions are limited to the site blocking only, but the local site potential-energy landscape changes from site to site, i.e., when the underlying substrate is not homogeneous. The inhomogeneity is modeled here in terms of Schwoebel barriers.[25,26] Mean-field treatment of the collective diffusion in a Schwoebel barrier system were proposed by Merikoski and Ying.[15,16] Series of Monte Carlo simulation results were reported by Masin *et al.*,[17] and theoretical mean-field analysis of these results, based on an approach balancing nonequilibrium particle fluxes in opposite directions, are due to Chvoj *et al.*[20]

We have shown recently that a developed variational approach to collective diffusion in Refs. 13, 22, and 27–31 provides a very efficient and systematic method of describing collective diffusion in inhomogeneous 1D systems. In this paper we extend the analysis from Ref. 22 to a class of two-dimensional systems. We demonstrate that the diffusion is not a simple superposition of one-dimensional collective diffusions in two main directions of the lattice. Whereas the diffusion coefficient of a single particle/single hole over such a lattice (a limit approached at low/high densities, respectively) always factorizes so the diffusion coefficients in both directions can be calculated independently, this is no longer the case in a many-particle system in which the site blocking alone induces dynamical correlations between jumps in different directions. Properly selected variational parameters lead to expressions for the collective diffusion coefficient which nontrivially depend on all present in the model jump rates in all directions. When for different systems considered the rate of jumps in one direction varies from zero to infinity, the resulting diffusion coefficients in perpendicular direction evolve from effectively 1D of Ref. 22 to the 2D mean-field theory result of Refs. 15 and 16. In fact, only in these two extreme cases the diffusion coefficient depends only on the jump rates in the diffusion direction.

We compare here the diffusion coefficients for an adsorbate on a surface with striped structure with that on a checkered anisotropic one. For both these structures we have the same 1D and the mean-field limits for the adsorbate density dependence of the diffusion coefficient. They differ, however, for all finite values of the jump rate in the direction perpendicular to the one in which the diffusion coefficient is measured. In case of the striped structure the diffusion proceeds on a surface with rows, such as fcc (110), which due to the interactions with the substrate have several nonequivalent adsorption sites. For the checkered structures, such as NaCl(100) surface, every second site in both principal directions is different. For either system the particle migration processes in two mutually perpendicular directions are coupled to each other due to stochastic site blocking even if, at a microscopic level, the particle jumps in each direction are independent of each other. Applying the variational approach[22] to properly tailored model, we obtain simple analytical expressions for the adsorbate density-dependent collective diffusion coefficients. Our approach allows one not only to interpret correctly the role played by kinematic coupling of particle jumps in different directions but also offer the possibility to compare analytic results with those of the Monte Carlo simulations performed for the same model systems.

The model and the variational approach to collective diffusion are summarized in Sec. II. It is applied to the striped and checkered substrate lattices in Secs. III and IV, respectively. Comparison with the results of the Monte Carlo simulations for selected systems is presented in Sec. V, followed by brief conclusions in Sec. VI.

II. MODEL

A system of N particles forming an adsorbate is distributed over a two-dimensional nonhomogeneous substrate. We treat diffusion within the adsorbate using a kinetic lattice-gas model. Basic assumptions are standard: kinetics of the microstates of the lattice gas is due to the stochastic hopping of particles to neighboring sites, only one particle in the gas hops at any given instant, an average residence time of particles at the adsorption sites is much longer than the transit time between the sites, and the transition rates of these hops depend on the potential-energy landscape experienced by the hopping particle. Thus, particles jump between neighboring sites provided the target site is unoccupied with the hopping rates that depend on the type of the site which the particle jumps from. The time evolution of this system is governed by the set of Markovian master rate equations for the probabilities $P(\{c\},t)$ that a microscopic *microstate* $\{c\}$ of a lattice gas occurs at time t,

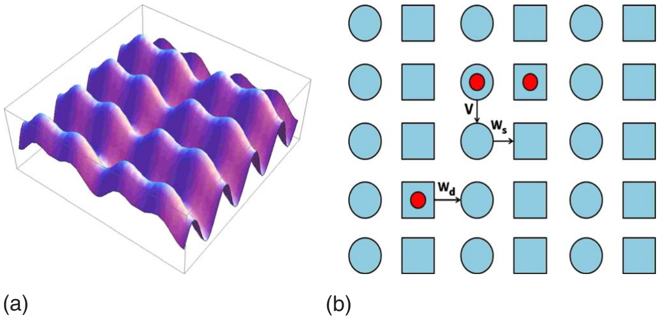

FIG. 1. (Color online) Potential geometry and jump schema in the system with striped substrate lattice.

$$\frac{d}{dt}P(\{c\},t) = \sum_{\{c'\}} [W(\{c\},\{c'\})P(\{c'\},t) - W(\{c'\},\{c\})P(\{c\},t)]. \tag{1}$$

$\{c\}$ is understood as a set of variables specifying which particular sites in the lattice are occupied and which are not. $W(\{c\},\{c'\})$ is a transition probability per unit time (transition rate) that the microstate $\{c'\}$ changes into $\{c\}$ due to a jump of a particle from an occupied site to an unoccupied neighboring site. The rates W satisfy the detailed balance conditions;

$$W(\{c\},\{c'\})P^{\mathrm{eq}}(\{c'\}) = W(\{c'\},\{c\})P^{\mathrm{eq}}(\{c\}). \tag{2}$$

Here, $P^{\mathrm{eq}}(\{c\})$ is the equilibrium probability of a configuration $\{c\}$. In the absence of interparticle interactions the rate depends only on the local potential-energy landscape experienced by the hopping particle. For thermally activated jumps it depends on the difference between the potential energy of the particle at the top of the potential-energy barrier between the sites involved and that at the initial site.

In order to investigate how the collective diffusion coefficient in a given direction is controlled by the particle jumps and the geometry of the lattice in the direction perpendicular to it, we analyze diffusion over two types of two-dimensional lattices, as shown in Figs. 1 and 2. They consist of periodically repeated patterns of site potentials and intersite barriers. Elementary cell of the striped lattice (Fig. 1) is 2×1: there are two nonequivalent sites along x axis, and all sites are identical along y axis. The checkered lattice has a $(\sqrt{2}\times\sqrt{2})45°$ elementary cell with two nonequivalent adsorption

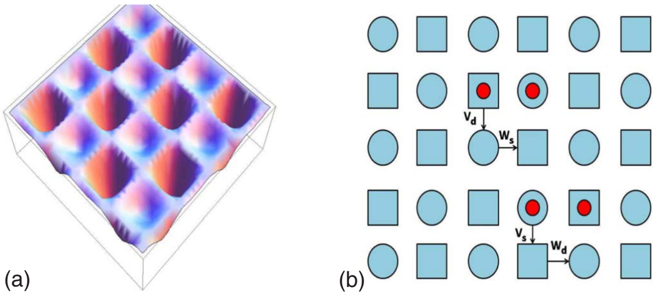

FIG. 2. (Color online) Potential geometry and jump schema in the system with checkered substrate lattice.

sites but is more convenient to consider a larger 2×2 "periodic" cell with two pairs of such sites in it. In general, for either structure, we have $n_x \times n_y$ periodic cells repeating L_x and L_y times in the x and y directions, respectively, i.e., the directions along which the elementary jumps between the nearest sites are only possible. The potential energy at the top of all barriers between the sites is assumed to be the same. Therefore, the system under study is a 2D box of $L_x \times L_y$ unit cells containing $L_x n_x \times L_y n_y$ sites. Periodic boundary conditions are assumed, and eventually, thermodynamic limit $L_x, L_y \to \infty$, with the adsorbate density kept constant, is taken.

We employ the variational approach to extract the diffusion coefficient from Eq. (1).[22,27–30] To this end, microscopic states of the systems need to be properly parametrized. Following Ref. 27 we identify a microstate $\{c\}$ by selecting one particle as a *reference particle* and specify positions of all remaining $N-1$ particles with respect to it. Position $\vec{X}+a\vec{l}_0$ of the reference particle in systems with nonequivalent sites is specified using two variables:[22] (i) position $\vec{X}$ of the periodic cell in which it resides and (ii) position $a\vec{l}_0$ within the cell. For two-dimensional systems $\vec{X}$ and $\vec{l}_0$ are vectors with two components and a is a distance between the adsorption sites referred to as a fractional lattice constant in what follows. Then a microstate $\{c\}$ may be identified by the following set of $2(N+1)$ numbers:

$$\{c\} = [\vec{X}; \vec{\ell}_0 : \vec{m}_1, \vec{m}_2, \ldots, \vec{m}_{N-1}] \equiv [\vec{X}; \{\vec{m}\}], \tag{3}$$

where $\vec{m}_j = (m_x, m_y)_j$ is a pair of integers indicating how far, in units of the fractional lattice constant a, the jth particle $(j=1,2,\ldots,N-1)$ is away from the reference particle. The set of $2N$ integers, $\{\vec{m}\} = [\vec{\ell}_0 : \vec{m}_1, \vec{m}_2, \ldots, \vec{m}_{N-1}]$, is referred to as a *configuration*, which accounts for the relative arrangement of particles in a given microstate $\{c\}$. The transition rate between two microstates depends on their configurations only, i.e., $W(\{c\},\{c'\}) \equiv W_{\{\vec{m}\},\{\vec{m}'\}}$. This allows us to take an advantage of the lattice periodicity by taking a lattice Fourier transform,

$$P_{\{\vec{m}\}}(\vec{k},t) = \sum_{\vec{X}} e^{i\vec{k}\vec{X}} P_{\{\vec{m}\}}(\vec{X},t), \tag{4}$$

of both sides of the rate [Eq. (1)]. $P_{\{\vec{m}\}}(\vec{X},t)$ stands here for $P(\{c\}=[\vec{X};\{\vec{m}\}],t)$. It is convenient to treat $P_{\{\vec{m}\}}(\vec{k},t)$ as an $\{\vec{m}\}$th component of a one-column array $\mathbf{P}(\vec{k},t)$ with a macroscopic number of components—each component corresponds to an admissible microscopic configuration of the system. The Fourier-transformed rate equations can be written in a compact form,

$$\frac{d}{dt}\mathbf{P}(\vec{k},t) = \mathbb{M}(\vec{k}) \cdot \mathbf{P}(\vec{k},t), \tag{5}$$

where "·" denotes multiplication following usual "rows times columns" multiplication rules. The matrix elements of $\mathbb{M}(\vec{k})$ (referred to as the rate matrix from now on) are, in general, expressed in terms of the rates $W_{\{\vec{m}\},\{\vec{m}'\}}$, except for $\{m\}$ to $\{m'\}$ transitions involving a jump of the reference atom across a boundary between neighboring elementary cells. For such jumps elements of $\mathbb{M}$ are multiplied by an additional $\vec{k}$ dependent factor $\exp(\pm k_x n_x)$ or $\exp(\pm k_y n_y)$. For details of the matrix $\mathbb{M}$ properties and the derivation of all formulas see Refs. 22 and 27–30.

Eigenvalues of the rate matrix which are always negative account for the temporal decay of a $\vec{k}$th Fourier component of a density fluctuation from equilibrium. The eigenvalue vanishing such as $|\vec{k}|^2$ in the long-wavelength limit, $-\lambda_D(\vec{k})$, is referred to as a diffusive eigenvalue and yields the collective diffusion coefficient. The corresponding eigenvector of $\mathbb{M}(\vec{k})$ is referred to as the diffusive eigenvector. This eigenvalue is estimated calculated on using variational principle,[22]

$$\lambda_D^{\mathrm{var}}(\vec{k}) \equiv \frac{\tilde{\phi} \cdot [-\mathbb{M}(\vec{k})] \cdot \phi}{\tilde{\phi} \cdot \phi} \geq \lambda_D(\vec{k}) = -D|\vec{k}|^2, \tag{6}$$

where $\tilde{\phi}$ is a trial (variational) left eigenvector, possibly $\vec{k}$ dependent and containing appropriate variational parameters to be determined by minimizing λ_d and ϕ is the corresponding right eigenvector with components,

$$\phi_{\{\vec{m}\}} = P^{\mathrm{eq}}_{\{\vec{m}\}} \tilde{\phi}^*_{\{\vec{m}\}}. \tag{7}$$

Here, $P^{\mathrm{eq}}_{\{\vec{m}\}}$ is an equilibrium probability of a configuration $\{m\}$—it is a component of a right eigenvector of $\mathbb{M}(\vec{k}=0)$ corresponding to its zero eigenvalue.

For a nonhomogeneous substrate, we propose, following Ref. 22, that the trial left eigenvector has $\{\vec{m}\}$th component equal to a sum of phase factors associated with all *occupied sites* in the configuration $\{\vec{m}\}$;

$$\tilde{\phi}_{\{\vec{m}\}}(\vec{k}) = e^{i\vec{k}a(\vec{\delta}_{\vec{\ell}_0}+\vec{\Delta}_{\vec{\ell}_0})} + \sum_{j=1}^{N-1} e^{i\vec{k}a(\vec{m}_j+\vec{\delta}_{\vec{\ell}_j}+\vec{\Delta}_{\vec{\ell}_j})}. \tag{8}$$

The phase contributed by the jth particle is determined not only by its distance $a\vec{m}_j$ from the reference particle (it is a sole contribution to the phase for a homogeneous system). It receives two additional distinct contributions $\vec{\delta}_{\vec{\ell}_j} = (\delta_{x\vec{\ell}_j}, \delta_{y\vec{\ell}_j})$ and $\vec{\Delta}_{\vec{\ell}_j} = (\Delta_{x\vec{\ell}_j}, \Delta_{y\vec{\ell}_j})$ which play a role of the variational parameters allowing us to minimize $\lambda_D^{\mathrm{var}}(\vec{k})$. Both depend on the position $a\vec{\ell}_j$ within a periodic cell of the site at which the jth particle resides. The first one, $\delta_{\vec{\ell}_j}$, called the *geometrical phase*, accounts for an inhomogeneity at the substrate within a periodic cell and does not depend on the presence of other particles in the system. It is always possible to select one particular site (the same within each periodic cell) which, if occupied, contributes the geometrical phase $\delta_0=0$. The other phase, $\Delta_{\vec{\ell}_j}$, called the *correlational phase*, is introduced to account for correlations between the jth particle and all the remaining ones, and in principle, it depends on the state of occupation of all sites in the system. Following previous work[22] we assume that it is sensitive to the occupation of sites nearest to $\vec{\ell}_j$ only. Thus correlational phases $\Delta_{\vec{\ell}_j}$, associated with a pair of particles at $\ell_{xj}-1, \ell_{yj}$ and $\vec{\ell}_j = \ell_{xj}, \ell_{yj}$, will appear in all equations as a sum of contributions to the phase of the particle at the position $\vec{\ell}_j$ due to its left neighbor and of the phase of the particle at the position $\ell_{xj}-1, \ell_{yj}$ due to its right neighbor $\vec{\Delta}_{\vec{\ell}_{xj}}=\vec{\Delta}^R_{\ell_{xj}-1,\ell_{yj}}+\vec{\Delta}^L_{\ell_{xj}\ell_{yj}}$. Similarly the phase $\vec{\Delta}_{\vec{\ell}_{yj}}$ appears with neighbors along direction y. Different phases associated with particle pairs are additive. Summarizing: a phase related to each particle in the system depends on (i) the distance of the particles from the reference particle, (ii) an address within the periodic cell of the site which it occupies (geometrical phase), and (iii) the state of occupation of the sites adjacent to it (correlational phase).

Periodic boundary conditions in two dimensions imply in the wave-number ($\vec{k}$) domain that the conditions,

$$e^{ik_x a n_x L_x}=1, \quad e^{ik_y a n_y L_y}=1, \tag{9}$$

must be used in the calculations before the long-wavelength limit $|\vec{k}a|^2 \ll 1$ is applied (recall, L_x and n_x are the number of periodic cells and the number of sites within the cell, respectively, along x).

We see from Eq. (6) that the diffusion coefficient D_{var} is a ratio,

$$D_{\text{var}}=-\frac{\lambda_D^{\text{var}}}{|\vec{k}|^2}=\frac{\mathcal{M}(\vec{k})}{\mathcal{N}(\vec{k})|\vec{k}|^2}, \tag{10}$$

of the "expectation value" numerator,

$$\mathcal{M}(\vec{k})=\sum_{\{m\},\{m'\}}^{\text{no rep}} P^{\text{eq}}_{\{m'\}} W_{\{m\},\{m'\}} |\tilde{\Phi}^*_{\{m'\}}(\vec{k})-\tilde{\Phi}^*_{\{m\}}(\vec{k})|^2, \tag{11}$$

to the "normalization" denominator,

$$\mathcal{N}(k)=\sum_{\{\vec{m}\}} P^{\text{eq}}_{\{\vec{m}\}} |\tilde{\Phi}_{\{\vec{m}\}}(\vec{k})|^2. \tag{12}$$

Equations (7) and (8) have been used to get the final expression for the numerator in Eq. (11). Due to the detailed balance condition (2) each term in Eq. (7) corresponds to a pair of configurations ($\{\vec{m}\},\{\vec{m}'\}$) for transitions from $\{\vec{m}'\}$ to $\{\vec{m}\}$ and back. Each such pair should then appear in the sum only once [as indicated by the comment "no rep" above the sum in Eq. (11)] in order to avoid double counting. In fact, it was shown in Ref. 22 that the dependence of the diffusion denominator $\mathcal{N}(k)$ on variational parameters, $\vec{\delta}_{\ell_j}$ and $\vec{\Delta}_{\ell_j}$, can be ignored in the long-wavelength limit and that

$$\lim_{k\to 0}\mathcal{N}(k)=\left[N\left(\frac{\partial(\beta\mu)}{\partial \ln \theta}\right)_T\right]^{-1} \equiv \langle N^2\rangle-\langle N\rangle^2. \tag{13}$$

Here μ is the chemical potential and $\beta=(k_B T)^{-1}$ is usual thermodynamic parameter for a system of temperature T. The diffusion denominator reduces to the square of the particle number fluctuation in the system, whereas the numerator $\mathcal{M}(k)$ depends on the details of particle dynamics and on all variational parameters of the model.

III. STRIPED LATTICE

Let us consider first the striped lattice shown in Fig. 1. It consists of rows of sites, with alternating deep and shallow potential-energy minima. Transition rates of jumps along x are $W_d=\nu\exp(-\beta E_d)$ for a jump from a deep well and $W_s=\nu\exp(-\beta E_s)$ for a jump from a shallow well. Energies E_d and E_s are activation energies for a jump out of deep and shallow potential minima, respectively, and ν measures an attempt frequency of these jumps. All jumps along y axis have the same rate $V=\nu\exp(-\beta E_v)$, depending on the activation energy E_v. A ratio $r=W_d/W_s=\exp[-\beta(E_d-E_s)]$ between both rates along x axis depends on the difference of the site energies. It is the only parameter which determines the equilibrium properties of the system at a given density of particles. With the site blocking interactions, preventing double site occupation, the mean equilibrium densities are

$$\theta_s=\frac{r\exp(\beta\mu)}{1+r\exp(\beta\mu)} \tag{14}$$

for the shallow and

$$\theta_d=\frac{\exp(\beta\mu)}{1+\exp(\beta\mu)} \tag{15}$$

for the deep sites. The chemical potential μ determines the total particle density $\theta=(\theta_s+\theta_d)/2$, understood as a fraction of adsorption sites that are occupied, and θ_s and θ_d are, respectively, the mean occupation numbers for the shallow and the deep well sites. The denominator $\mathcal{N}(0)$ given by Eq. (12) in the limit $(|\vec{k}|a)^2\to 0$ depends only on the equilibrium properties of the system. With no interactions other than the site blocking we have

$$\mathcal{N}(0)=\theta_s(1-\theta_s)+\theta_d(1-\theta_d). \tag{16}$$

In order to derive the numerator $\mathcal{M}(\vec{k})$, given in Eq. (11), we use variational vector $\tilde{\Phi}_{\{m\}}(\vec{k})$ [Eq. (8)]. There are four types of different jumps for particles in the striped lattice: from deep to shallow site and from shallow to deep site along the x axis and between two deep sites or between two shallow sites along the y axis. The sum in Eq. (11) contains a macroscopic number of terms. Grouping the terms with the same jump rate is done by surrounding two sites between which the hopping occurs by "correlated" sites whose occupation state affects both the hopping rate and, more importantly, values of geometrical and correlational phases to be used. Such a cluster of sites, termed as an active cell, contains in our case eight sites, out of which six may be in any occupation state. This results in 2^6 phase terms in the sum which are multiplied by the same jump rate. Adding these phase terms is a relatively straightforward matter, particularly in the long-wavelength limit, because of the symmetrical arrangement of sites within the active cell. The number of different variational parameters to be determined is significantly reduced due to symmetry. Thus, selecting a deep well site as a reference for geometrical phases we can set the geometrical phase due to a particle residing at a deep well site to be zero, $\delta^S_d=0$. This leaves only one geometrical phase, δ^S_s, due to a particle in a shallow well site which, however, also vanishes for the substrate with potential energies of all barriers being the same. Due to the same reason, all correlational phases are either Δ^S_x or $-\Delta^S_x$ for a particle in a shallow potential well with the neighboring deep well site to its right/left occupied. For the particle residing in the deep site well the corresponding correlational phases are $-\Delta^S_x$ and

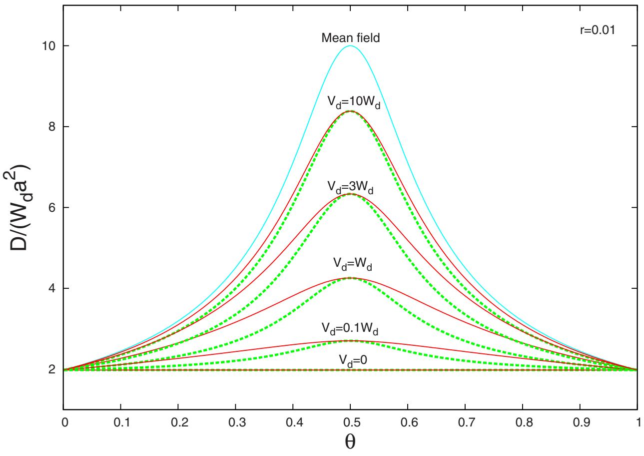

FIG. 3. (Color online) Adsorbate density dependence of the collective diffusion coefficient $D_x(\theta)$ on a striped (dashes) and a checkered (solid lines) substrate lattices. Jump rates along y direction on striped lattices are related to the jump rates on checkered lattices for the corresponding diffusion curves like $V=\sqrt{V_dV_s}=V_s\sqrt{r}$. The lowest line corresponds to 1D case, $V=V_s=V_d=0$. The topmost line for $V=V_s=V_d\to\infty$ reproduces the mean-field result from Refs. 15 and 16.

Δ_x^S. The correlational phases corresponding to the direction along y are zero because the substrate is homogeneous along this direction. With all that, components of a trial eigenvector are

$$\tilde{\phi}_{\{m_j\}}(\vec{k})=\sum_{j=1}^{N-1}e^{ik_xa(m_{xj}+\Delta_{xj}^S)+ik_yam_{yj}},\tag{17}$$

with $\Delta_y^S=0$, $\delta_s^S=\delta_d^S=0$ and Δ_{xj}^S equal to either $\pm\Delta_x^S$ or zero depending on the occupancy of neighboring sites. After solving the variational equation minimizing $\mathcal{M}(\vec{k})$ we get

$$\Delta_x^S=\frac{W_s-W_d}{W_s+W_d+V},\tag{18}$$

resulting in the expression for the diffusion coefficient along the x direction,

$$D_x^S=a^2\frac{2W_s}{W_s+W_d+4V}\left[W_d+\frac{4V\theta_s(1-\theta_d)}{\theta_s(1-\theta_s)+\theta_d(1-\theta_d)}\right]\tag{19}$$

while for the y direction we get

$$D_y^S=a^2V.\tag{20}$$

The adsorbate density dependence of the diffusion coefficient $D_x^S(\theta)$ for a striped substrate lattice is plotted in Fig. 3 (dashed lines).

Setting $V=0$ in Eq. (19) we get

$$D_x^{1\mathrm{D}}=a^2\frac{2W_sW_d}{W_s+W_d},\tag{21}$$

which is the result for the diffusion coefficient in 1D system with alternating shallow and deep potential well sites, obtained in Ref. 22. In this limit diffusion does not depend on the adsorbate density, as illustrated by the lowest line in Fig. 3. For all nonzero values of V, however, the diffusion coefficient along x axis depends on the adsorbate density θ. This dependence changes as the jump rate along y direction, V, varies. While the diffusion coefficient due to a migration of an isolated particle ($\theta\to 0$) or hole ($\theta\to 1$) remains the same no matter what the jump rate along the y direction is, the diffusion coefficient values for intermediate densities increase with increasing V. In the limit $V\to\infty$, on the other hand, we get

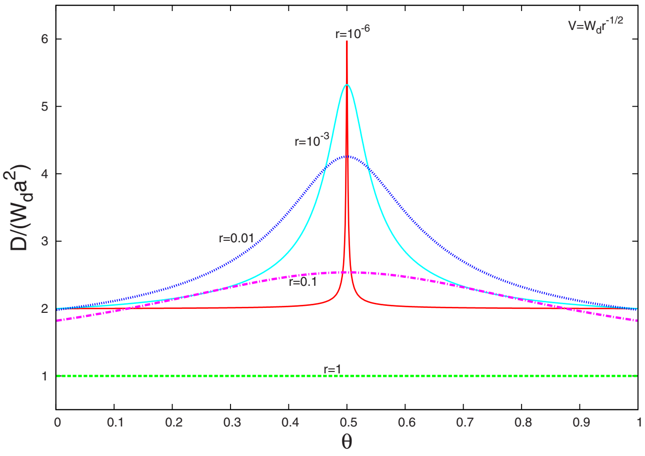

FIG. 4. (Color online) Adsorbate density dependence of the collective diffusion coefficient $D_x(\theta)$ on a striped substrate lattice for different values of r [defined above Eq. (14)]. The jump rate along y direction is equal to the geometrical mean value of rates in x direction $V=W_d/\sqrt{r}$.

$$D_x^{\mathrm{inf}}=a^2\frac{2W_s\theta_s(1-\theta_d)}{\theta_s(1-\theta_s)+\theta_d(1-\theta_d)},\tag{22}$$

which reproduces exactly the result for the collective diffusion coefficient obtained in the mean-field approximation in Refs. 15 and 16.

We can see that V the rate of the jumps along y axis controls the character of the density dependence of the diffusion coefficient. With increasing V we observe a smooth transition from a purely one-dimensional to the mean-field behavior. While the former limit is obvious, the latter one can be understood in such a way that a particle, capable of a fast travel along y axis, detects mean-field occupation of the neighboring site and instantaneously adjusts to it.

The character of the density dependence of the diffusion coefficient depends strongly on the ratio r of rates from the deep and shallow sites along the direction under study. In Fig. 4 we show how the diffusion changes with r. The jump rates along y axis increase with decreasing r such as $V=W_d/\sqrt{r}$, slower than the quicker of two rates along x, $W_s=W_d/r$. We see in Fig. 4 that with such a choice of parameters, the curves become higher and steeper as r decreases, approaching to the limiting behavior in which diffusion coefficient has value $D=2W_d$ for all densities except at a one discrete point of $\theta=0.5$ for which $D=6W_d$.

To illustrate the consequences of the transition from 1D to 2D character of dynamics for a striped substrate lattice, we

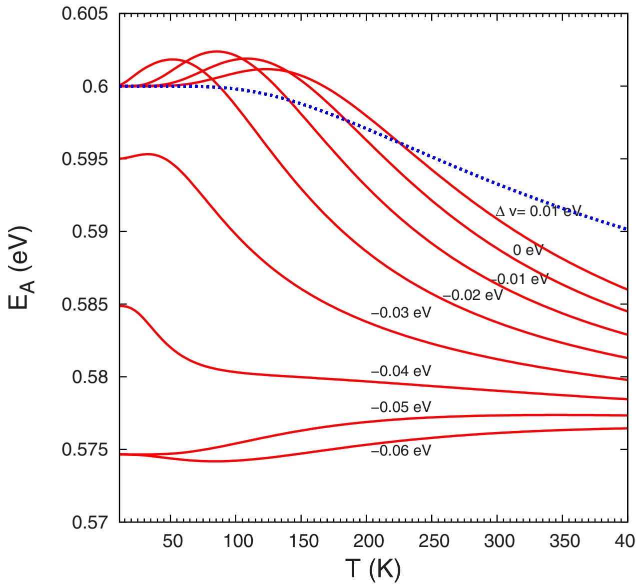

FIG. 5. (Color online) Temperature dependence of the activation energy $E_A(T,\theta{=}0.5)$ for a striped substrate lattice for $E_s-E_d=0.05$ eV and varying $\Delta v=E_v-E_d$. E_A for 1D diffusion, when $\Delta v\to\infty$, is plotted by a dotted line.

have calculated the effective activation energy $E_A(T,\theta)$ defined as follows:

$$D = \nu e^{-\beta E_A}. \tag{23}$$

An expression for E_A may be obtained by differentiating a logarithm of D [Eq. (19)] with respect to β. For an arbitrary θ it results in a rather complicated expression, but it simplifies for $\theta{=}0.5$ considerably,

$$E_A(T,\theta=0.5) = E_d + (2E_v - E_s - E_d)\frac{Vr^{1/2}}{W_d + 2Vr^{1/2}} + [(E_d - E_s)W_d + 4(E_v - E_s)V]\frac{r}{W_d(1+r) + 4Vr}, \tag{24}$$

in which T enters through V and W_d. In Fig. 5 we see the dependence of E_A on the temperature T for several values of $\Delta v=E_v-E_d$, the difference between actual activation energies for jumps along and across rows and a typically reported[1,3,19,23] activation energy difference $E_d-E_s=0.05$ eV for jumps from the deep and shallow well along x direction. The parameter Δv is positive when jumps are slower across than they are along the rows and negative when jumps across the rows are quicker. The dotted line shows the temperature dependence of activation energy for an independent particles diffusion $(\theta{=}0)$ at the same surface. Diffusion coefficient along the x direction for the independent particles does not depend on the rate V and is equal to the collective diffusion coefficient in a 1D case. In Fig. 6 we show $E_A(T{=}100\ \text{K},\theta)$ as a function of the surface coverage at $T{=}100$ K. In general, the observed activation energy depends on both the temperature and the coverage.

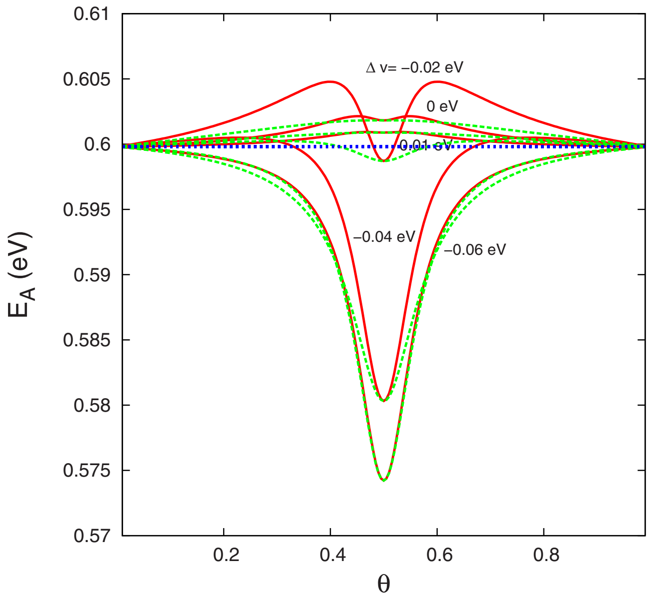

FIG. 6. (Color online) Adsorbate density dependence of the activation energy $E_A(T{=}100\ \text{K},\theta)$ for $E_s-E_d{=}0.05$ eV at $T=100$ K and varying Δv for a striped (solid lines) and checkered (dashed lines) substrate lattices. E_A for 1D diffusion, when $\Delta v\to\infty$, is plotted by a dotted line.

IV. CHECKERED LATTICE

Let us now consider a checkered substrate lattice which has the same structure in both x and y directions. We assume that the potential energy at every second adsorption site in either direction is the same, i.e., the shallow and the deep adsorption sites alternate along both directions (see Fig. 2). Jumps rates out of the shallow sites in x direction are given by $W_s=\nu\exp(-\beta E_s)$ and those in y directions are given by $V_s=\nu\exp(-\beta E_s^V)$, with the jump rates out of the deep sites are $W_d=\nu\exp(-\beta E_d)$ and $V_d=\nu\exp(-\beta E_d^V)$, respectively. All rates are proportional to the same attempt frequency ν and are determined by the appropriate activation energies. The condition,

$$\frac{W_d}{W_s} = \frac{V_d}{V_s} = r, \tag{25}$$

has to be fulfilled. The equilibrium occupancies are again given by Eq. (14) for the shallow site and by Eq. (15) for the deep site. Consequently, the diffusion denominator is again given by Eq. (16). As before, all geometrical phases δ are equal to zero due to equal height of all potential-energy barriers. There are now two nonzero correlational phases. Minimizing the diffusive eigenvalue [or $\mathcal{M}(\vec{k})$] yields the correlational phase associated with a pair of particles oriented along x direction;

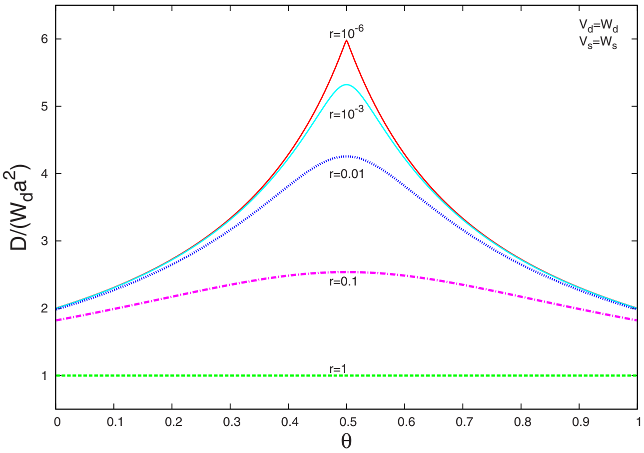

FIG. 7. (Color online) Adsorbate density dependence of the collective diffusion coefficient D_x for a checkered substrate lattice for several values of r. Rates of jumps out of a given adsorption site in the x and y directions are equal to each other.

$$\Delta_x^C = \frac{(W_s - W_d)\theta_s(1-\theta_d)}{(W_s + W_d)\theta_s(1-\theta_d) + 2V_d[\theta_d(1-\theta_d) + \theta_s(1-\theta_s)]}, \tag{26}$$

and another one associated with similar pair along oriented along y direction,

$$\Delta_y^C = \frac{(V_s - V_d)\theta_s(1-\theta_d)}{(V_s + V_d)\theta_s(1-\theta_d) + 2W_d[\theta_d(1-\theta_d) + \theta_s(1-\theta_s)]}. \tag{27}$$

The resulting diffusion coefficient along x direction is (the superscript C refers to "checkered")

$$D_x^C = a^2 \frac{2W_s\theta_s(1-\theta_d)(W_d + 2V_d)}{(W_d + W_s)\theta_s(1-\theta_d) + 2V_d[\theta_d(1-\theta_d) + \theta_s(1-\theta_s)]}, \tag{28}$$

and for diffusion along y we must replace in the above expression all V and W rates with W and V, respectively, with the same subscript s or d.

D_x^C as a function of θ for several values of rates V_s and V_d is plotted in Fig. 3 (solid lines). Maxima of the diffusion coefficient at $\theta=0.5$ for the striped and checkered substrate lattices are equal to each other if we relate the rates of jumps along y direction in both model systems as follows: $V=\sqrt{V_s V_d}=V_s\sqrt{r}$. They all merge at the dilute system limits, $\theta=0$ and 1. For all other densities the diffusion coefficient for the checkered substrate lattice is somewhat larger than the one for the striped substrate lattice. The 1D and the mean-field limits, $V\rightarrow 0$ and $V\rightarrow\infty$, respectively, are the same for both types of substrate.

In Fig. 7 we follow the changes in the shape of the density dependence of the diffusion coefficient with changes in r [see Eq. (25)] for the checkered substrate lattice. We keep here $V_s=W_s$ and $V_d=W_d$.

For $E_s-E_d=0.05$ eV and choosing $E_d^V=\Delta v+0.025$ eV to assure that $V=\sqrt{V_s V_d}$, all the activation energy curves $E_A(T,\theta=0.5)$ plotted in Fig. 5 for the striped substrate lattice are indistinguishable from the similar ones for the checkered system. This is obvious because the condition $V=\sqrt{V_s V_d}$ was designed specifically to match the diffusion coefficient between the two model systems at $\theta=0.5$. For other densities the effective activation energies differ as seen in Fig. 6. These differences are consistent with those observed in Fig. 3.

V. MONTE CARLO SIMULATIONS

In order to verify the accuracy of the variational approach to diffusion in a lattice gas on an inhomogeneous substrate and that of the resulting analytical expressions for the adsorbate density dependence of the collective diffusion coefficient, we have simulated such systems for selected set of system parameters using Monte Carlo dynamical approach. We have used the Boltzmann-Matano analysis of the shape of a steplike density profile after letting it decay via diffusion process.[32,33] Results of this analysis are shown in Fig. 8 for a striped (left panel) and a checkered substrate lattices with $r=0.01$ and three different jump rates along the y direction. In particular, the lowest lines represent results for $V=V_d=0$ which do not depend on the coverage in agreement with the results for a 1D system. For the two other sets of parameters (lines in the middle) for which the diffusion has genuinely 2D character, the maxima of the diffusion coefficient differ by a factor of 2 between them, as seen also in the Monte Carlo results despite considerable noise present. Unfortunately due to a considerable noise the differences between the two types of analyzed substrate lattices, seen in Fig. 3 for analytic results, are too small to be clearly visible in the simulation data. It is evident, however, that the evolution of the adsorbate density dependence of the diffusion coefficient with varying jump rates along the y axis (V and V_d) for both substrate lattice types, observed in Fig. 3, is confirmed by simulations.

VI. CONCLUSIONS

We have shown that the recently formulated variational approach to the collective diffusion, originally designed for 1D systems, is an effective and a promising method of dealing also with diffusion in 2D systems. We have applied this method here to describe collective diffusion in a system of particles adsorbed on nonhomogeneous substrates with two types of the potential-energy landscape experienced by the adsorbed particles. The resulting density dependence of the collective diffusion coefficients depending on all jump rates present in either system are given by simple analytic expressions. The predicted density dependence agrees with the Monte Carlo simulation results for such system parameters for which running the simulations was feasible. An example of such a comparison have been shown here.

We show that the kinetics diffusion in two-dimensional system is interesting and far from trivial even if the site blocking is the only interaction that particles experience. In contrast to a single-particle (dilute) systems, collective diffusion along each of the two directions in which particles can jump depend nontrivially on microscopic jump rates in both

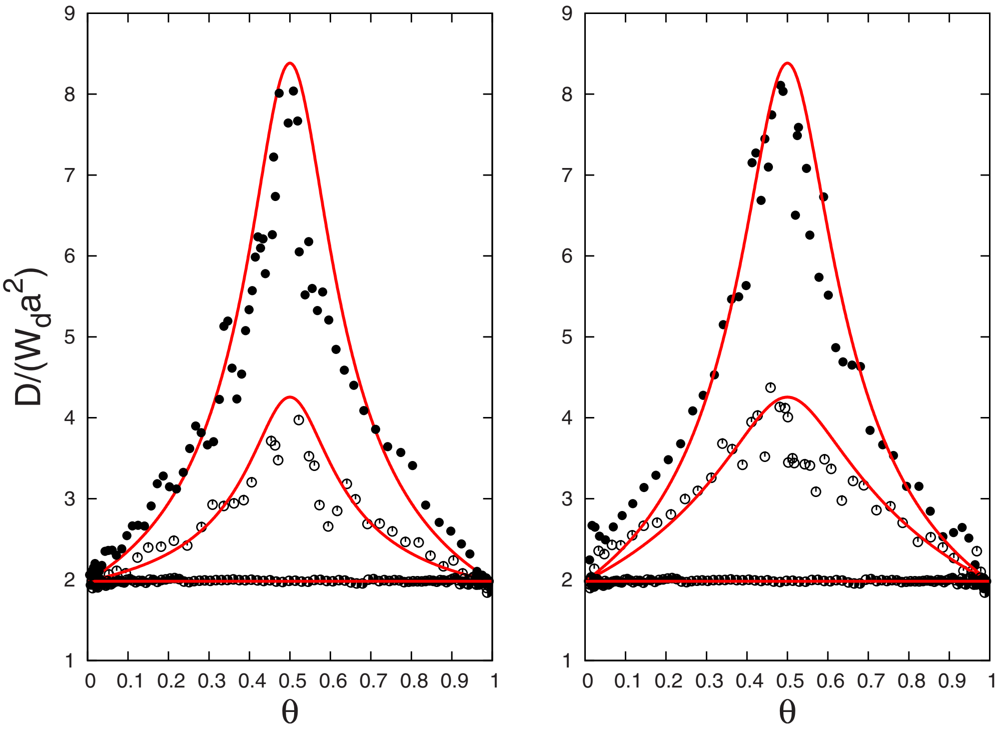

FIG. 8. (Color online) Comparison of Monte Carlo (open and full circles) with analytical results (solid lines) for the diffusion coefficient D_x dependence on the adsorbate density (coverage) θ for $r=0.01$ for striped (left panel) with and for checkered (right panel) with substrate lattice. Full circles: $V=100W_d$ (left panel; striped system) and $V_d=\sqrt{r}V=10W_d$ (right panel; checkered system). Open circles: $V=10W_d$ (left panel; striped system) and $V_d=\sqrt{r}V=W_d$ (right panel; checkered system). The lowest data sets in both panels are for $V=V_d=0$.

directions, e.g., collective diffusion along x, say, depends on jump rates in x and y directions. This effect is due to the site blocking and nonhomogeneity of the substrate lattice. It is not present in a system of many independently moving particles without the site blocking interactions, and it is not present in a homogeneous system with the site blocking.

We have demonstrated that the character of diffusion changes continuously from a one-dimensional one to the mean-field-like when the rates of jumps in direction perpendicular to the one along which diffusion is observed are varied from very slow to the very fast ones. We can understand this as a result of an activation of alternative diffusion pathways when the direct pathway is blocked. Transition from the 1D to the 2D behavior is highly nontrivial even if particles do not interact with each other except for hard-core interactions preventing multiple occupancy of the adsorption sites.

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[1] G. Antczak and G. Ehrlich, Surf. Sci. Rep. **62**, 39 (2007).
[2] D. A. Reed and G. Ehrlich, Surf. Sci. **102**, 588 (1981).
[3] R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).
[4] A. Danani, R. Ferrando, E. Scalas, and M. Torri, Int. J. Mod. Phys. B **11**, 2217 (1997).
[5] T. Ala-Nissila, R. Ferrando, and S. C. Ying, Adv. Phys. **51**, 949 (2002).
[6] J. W. Haus and K. Kehr, Phys. Rep. **150**, 263 (1987).
[7] A. R. Allnatt and A. B. Lidiard, Rep. Prog. Phys. **50**, 373 (1987).
[8] W. Zwerger, Z. Phys. B: Condens. Matter **42**, 333 (1981).
[9] H. J. Kreuzer and J. Zhang, Appl. Phys. A **51**, 183 (1990).
[10] H. J. Kreuzer, J. Chem. Soc., Faraday Trans. **86**, 1299 (1990).
[11] S. H. Payne and H. J. Kreuzer, Phys. Rev. B **75**, 115403 (2007).
[12] J.-S. McEwen, S. H. Payne, H. J. Kreuzer, and C. Bracher, Int. J. Quantum Chem. **106**, 2889 (2006).
[13] M. A. Załuska-Kotur and Z. W. Gortel, Phys. Rev. B **72**, 235425 (2005).
[14] R. Kutner, Phys. Lett. **81**, 239 (1981).
[15] J. Merikoski and S. C. Ying, Surf. Sci. **381**, L623 (1997).
[16] J. Merikoski and S. C. Ying, Phys. Rev. B **56**, 2166 (1997); **58**, 15912 (1998).
[17] M. Mašín, I. Vattulainen, T. Ala-Nissila, and Z. Chvoj, J. Chem. Phys. **122**, 214728 (2005).
[18] M. Mašín, I. Vattulainen, T. Ala-Nissila, and Z. Chvoj, J. Chem.

Phys. **126**, 114705 (2007).

[19] Z. Chvoj, H. Conrad, V. Chab, M. Ondrejeck, and A. M. Bradshaw, Surf. Sci. **329**, 121 (1995).

[20] Z. Chvoj, M. Mašín, and T. Ala-Nissila, J. Stat. Mech.: Theory Exp. (2006) P10003.

[21] A. A. Tarasenko, Z. Chvoj, L. Jastrabik, F. Nieto, and C. Uebing, Phys. Rev. B **63**, 165423 (2001).

[22] M. A. Załuska-Kotur and Z. W. Gortel, Phys. Rev. B **76**, 245401 (2007).

[23] M. Ceriotti and M. Bernasconi, Phys. Rev. B **76**, 245309 (2007).

[24] J. K. Garleff, M. Wenderoth, R. G. Ulbrich, C. Surgers, H. v. Lohneysen, and M. Rohlfing, Phys. Rev. B **76**, 125322 (2007).

[25] R. L. Schwoebel and E. J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).

[26] R. L. Schwoebel, J. Appl. Phys. **40**, 614 (1969).

[27] Z. W. Gortel and M. A. Załuska-Kotur, Phys. Rev. B **70**, 125431 (2004).

[28] Ł. Badowski, M. A. Załuska-Kotur, and Z. W. Gortel, Phys. Rev. B **72**, 245413 (2005).

[29] M. A. Załuska-Kotur, Ł. Badowski, and Z. W. Gortel, Physica A **357**, 305 (2005).

[30] M. A. Załuska-Kotur and Z. W. Gortel, Phys. Rev. B **74**, 045405 (2006).

[31] M. Yakes, M. Hupalo, M. A. Załuska-Kotur, Z. W. Gortel, and M. C. Tringides, Phys. Rev. Lett. **98**, 135504 (2007).

[32] M. A. Załuska-Kotur, S. Krukowski, and Ł. A. Turski, Surf. Sci. **441**, 320 (1999).

[33] M. A. Załuska-Kotur, S. Krukowski, Z. Romanowski, and Ł. A. Turski, Surf. Sci. **457**, 357 (2000).