Collective diffusion of dense adsorbate at surfaces of arbitrary geometry

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Abstract. A convenient variational formula for collective diffusion of many particles adsorbed at lattices of arbitrary geometry is formulated. The approach allows us to find the expressions for the diffusion coefficient for any value of the system’s coverage. It is assumed that particles interact via on-site repulsion excluding double site occupancy. It is shown that the method can be applied to various systems of different geometry. Examples of real systems such as GaAs with specific energetic landscapes are also presented. Diffusion of Ga adatoms on GaAs(001) surface reconstructed in two different symmetries is studied. It is shown how increasing Ga coverage changes the character of diffusion from isotropic 2D into highly anisotropic, almost 1D. It is shown how important the role of the inter-particle correlations is, which influences the value of the collective diffusion coefficient at higher coverages.

Keywords: diffusion, stochastic particle dynamics, surface diffusion
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1. Introduction

Collective diffusion is a complex many-body process that plays an important role in many physical applications. During epitaxial crystal growth interplay between adsorption, desorption and surface diffusion is responsible for the character and the quality of the grown layers. Understanding diffusive processes is therefore important to gain a precise control over the crystal growth. Currently of particular interest is synthesis of atom-thick layers such as graphene [1, 2], semiconductors like MoS2 [3] or hexagonal-BN [4], or topological insulators such as Bi2Se3 [5, 6] or Bi2Te3 [6].

The value of the diffusion coefficient (or, in general, the diffusion tensor), which can be either measured in experiments or calculated using theoretical methods, strongly depends on the system’s energy landscape, which describes the depth of all the adsorption sites and the jump rates between them. Specifically, both the rate of diffusion and its anisotropy depend on the details of the energetic landscape. Those parameters play an important role during growth of both bulk crystals and various nanostructures at their surfaces.
Even though crystals usually crystallize in highly symmetric structures, the symmetry of their surfaces is often different from that of the bulk. One of the reasons for it is surface reconstruction, which can lead to a change of the height of the energy barriers \cite{7} and the geometry of the surface \cite{8, 9}. Other reasons can be presence of steps at the surface \cite{10, 11} or defects \cite{12}.

Theoretical calculations of diffusion coefficients require the knowledge of the system’s energetic landscape, which is usually determined from \textit{ab initio} methods or from experiments. Among common simulation approaches to diffusion problems are Monte Carlo and molecular dynamics, while analytical methods are based for example on Fokker–Planck, Kramers or master equation \cite{13–34}. Many studies have been devoted to the problems of diffusion over concrete crystal surfaces of complex energetic landscape \cite{24–28}. In such case description of single-particle diffusion already is a difficult task and the presence of many particles increases only the degree of complexity.

Our approach to calculating diffusion coefficients is a variational one and is based on analysis of master equation. It was first proposed in \cite{29} and has been subsequently developed to deal with various cases of surface diffusion \cite{26–34}. It has been shown that the approach is effective in analyzing diffusion in real systems, such as Ga adatom at GaAs(001) surface \cite{26} or Cu monomer and dimer on Cu(111) and Ag(111) surfaces \cite{27}. Recently using the variational approach we have derived a general formula for the collective diffusion coefficient for interacting particles in an arbitrary 1D potential \cite{28}.

For a small concentration of particles in the system their diffusive paths can be treated as independent and the collective diffusion coefficient can be considered as being equivalent to that of single-particle diffusion. In \cite{24} and \cite{25} analytical formulas for single-particle diffusion coefficients for various lattices of square, rectangular and hexagonal symmetry have been derived. It is known that collective diffusion in an energetic landscape consisting of adsorption sites of equal depth does not depend on the coverage if only site blocking interactions are considered \cite{35}. Therefore, in such cases collective diffusion is equivalent to that of a single particle in the same potential. In \cite{33} we presented diffusion coefficients for a few lattices of square and hexagonal symmetry with identical adsorption energies calculated using variational method. However, in the case of energetic landscapes with adsorption sites of different depths the collective diffusion coefficient may significantly depend on the system’s coverage even if no other interactions than site blocking are present. The degree to which the diffusion is influenced by the inter-particle correlations depends on the difference between the energies of the adsorption sites, the heights of the diffusive barriers and the number of the nearest neighbors, that is the geometry of the system.

In this article we show how to apply a variational approach to calculation of the diffusion coefficient of 2D many-particle systems. We calculate the collective diffusion coefficients for several systems. The method is variational and the proper choice of parametrization decides about the quality of the obtained results. Moreover, the calculations of the collective diffusion coefficient concern only small deviations from the equilibrium state \cite{13}, so for states that are far from the equilibrium the analysis is approximate. However, for dynamics close to the equilibrium the approach is general and can be applied in any case, regardless of the symmetry of the lattice.

Among various examples we study lattices considered in \cite{24} and \cite{25}, for which single-particle diffusion coefficients were calculated. We show density dependence of
the diffusion coefficient for all systems analyzed in [24, 25] by taking into account the role of the inter-particle correlations. In the low density limit our results reproduce the formulas obtained for single-particle diffusion. Next we use the presented method to calculate the density dependence of the diffusion on GaAs surface, studied earlier in [26]. We show that the diffusion anisotropy at this surface can be induced by the presence of other particles. Density-dependent particle diffusion on lattices with two different symmetries resulting from different surface reconstructions is compared.

2. Theory

2.1. Variational approach

We consider a gas of particles adsorbed at a lattice of arbitrary geometry. The lattice is periodic and consists of elementary cells, each of which contains several adsorption sites. In the system we assume periodic boundary conditions. From the physical point of view adsorption sites are energetic minima of the potential landscape that comes from the underlying surface. We assume that at any time a given adsorption site can be either free or occupied by exactly one particle, that is multiple occupancy is forbidden. Each microstate \( \{c\} \) of the system has a fixed number \( N \) of particles distributed over lattice sites and can be described as a vector

\[
\{c\} = [\vec{X}; \vec{l}_0; \vec{m}_1, \vec{m}_2, \ldots, \vec{m}_{N-1}] = [\vec{X}; \{\vec{m}\}],
\]

which specifies which of the adsorption sites at the lattice are occupied. It distinguishes one of the particles as the reference particle at the position \( \vec{X} + \vec{l}_0 \), where \( \vec{X} \) is the position of the origin of its elementary cell and \( \vec{l}_0 \) is its position within that cell. The set of the remaining vectors \( \{\vec{m}_1, \vec{m}_2, \ldots, \vec{m}_{N-1}\} \) gives the positions of all the other particles with respect to the reference particle. Since the system has translational symmetry we can define a configuration as

\[
\{\vec{m}\} = [\vec{l}_0; \vec{m}_1, \vec{m}_2, \ldots, \vec{m}_{N-1}],
\]

which specifies only the position of the reference particle with respect to the origin of any elementary cell and the positions of the remaining particles with respect to the reference particle. All the microstates in which the positions of the particles differ only by a linear combination of the lattice vectors (that is by \( \vec{X} \)) correspond to the same configuration.

Most of the time the adsorbed particles reside at their sites but from time to time they perform thermally activated jumps to neighboring sites. The jumps occur over the energetic barriers, which are the saddle points of the potential landscape between the two involved adsorption sites. The jump rate of a particle from the site \( A \) to the site \( B \) that changes the configuration \( \{c\} \) to the configuration \( \{c'\} \) is

\[
W(\{c\}, \{c'\}) = \nu \exp(-\beta(E(\{c\}, \{c'\}) - E(\{c\})))
\]

where \( E(\{c\}) \) is the energy of the system when the particle occupies the site \( A \) and \( E(\{c, c'\}) \) is the energy of the system when the particle is at the saddle point between
the sites $A$ and $B$. The prefactor $\nu$ is the attempt frequency, which is the measure of how many attempts per unit time the adsorbed particle performs to jump out of its site. Its value is determined by the vibrations of the atom lattice, that is phonons. Usually we will assume that it is equal to the typical phonon frequency in condensed matter, which is $\nu = 10^{13}$ s$^{-1}$. At thermal equilibrium detailed balance condition is fulfilled, which means that the probability of every microscopic process is equal to the probability of the reverse process

$$W(\{c\}, \{c'\})P_{\text{eq}}(\{c\}) = W(\{c'\}, \{c\})P_{\text{eq}}(\{c'\}),$$

(4)

where $P_{\text{eq}}(\{c\})$ is the equilibrium probability of the occupations in the state $\{c\}$.

In order to calculate collective diffusion coefficients understood as it is defined i.e. in [13] for the lattices considered in the next chapter we use the variational approach that was first proposed in [29]. For 1D collective diffusion it was possible to derive by means of that approach a general formula for the diffusion coefficient expressed in terms of jump rates, interaction constants, temperature and chemical potential [28]. Diffusion in one dimension can be considered as an extreme case of anisotropic surface diffusion. There is always only one channel of diffusion in one dimension since a diffusing particle must overcome all barriers ordered one after another to move to the next elementary cell. However, due to inter-particle correlations the dependence of the diffusion coefficient on the barriers is still not trivial and we showed that its behavior can depend not only on the height of those barriers but also on their order in an elementary cell.

Diffusion in two dimensions is a much more complicated process since there are a lot of different paths along which a particle can move. Because of that the diffusion depends not only on the values of the jump rates but also on the geometry of the lattice. We shall derive a variational formula for a non-interacting case, which depends on a set of variational parameters and can be explicitly written out for a system of arbitrary geometry. Then it can be used for finding the values of the variational parameters and therefore determining the diffusion coefficient.

The starting point in our variational approach is the master equation written for the lattice gas system

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

(5)

which describes the evolution of the probability $P(\{c\}, t)$ of finding the system in the microstate $\{c\}$ (1). We can use the definition of configuration to replace $W(\{c\}, \{c'\})$ in equation (5) by $W_{\{\vec{m}\},\{\vec{m}'\}}$. At given time we allow only for one jump of a particle between neighboring sites. For pairs of $\{\vec{m}\}$ and $\{\vec{m}'\}$ which fulfill that condition $W_{\{\vec{m}\},\{\vec{m}'\}}$ are equal to corresponding jump rates (3) and in the equilibrium $P(\{c\}, t) = P_{\text{eq}}(\{\vec{m}\})(\vec{X}, t)$ become $P_{\text{eq}}(\{\vec{m}\})$. For other pairs of configurations $W_{\{\vec{m}\},\{\vec{m}'\}}$ are equal to zero.

The periodicity of the system allows us to take a Fourier transform of the master equation (5) to get

$$\frac{d}{dt} \vec{P}(\vec{k}, t) = \hat{M}(\vec{k}) \cdot \vec{P}(\vec{k}, t),$$

(6)

which is a matrix equation where the position vector $\vec{X}$ has been replaced by the wave vector $\vec{k}$. The components of the vector $\vec{P}(\vec{k}, t)$ correspond to the configurations $\{\vec{m}\}$.
and \( M(\vec{k}) \) is the rate matrix, whose properties have been described in detail in [29–31], with elements

\[
M_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k}) = W_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k}) - \delta_{\{\vec{m}\},\{\vec{m}'\}} \sum_{\{\vec{m}''\}} W_{\{\vec{m}''\},\{\vec{m}\}},
\]

where \( W_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k}) = F_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k})W_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k}) \) with \( F_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k}) \) equal to 1 except when the reference particle crosses the boundary between elementary cells. In the latter case \( F_{\{\vec{m}\},\{\vec{m}'\}}(\vec{k}) = \exp(\pm i\vec{k}A) \), where \( A \) is the lattice vector between those cells and the sign depends on the direction of the jump.

When the system is brought out of the equilibrium state, it will start returning to that state with the rate described by the rate matrix’s eigenvalues, which are always real and negative and correspond to the decay of the \( k \)th eigenvalues, which are always that state with the rate described by the rate matrix depends on the direction of the jump.

Close to the equilibrium the eigenvalue \( \lambda_D(\vec{k}) \) with the lowest absolute value is proportional to \( k^2 = |\vec{k}|^2 \) and gives the diffusion tensor

\[
[k_x \ k_y] \begin{bmatrix} D_{xx} & D_{xy} \\ D_{xy} & D_{yy} \end{bmatrix} [k_x \ k_y] = -\lambda_D(\vec{k}).
\]

In order to find that eigenvalue we use a variational approach. We denote a trial eigenvector by \( \phi \) and we obtain its trial eigenvalue \( \lambda^D_{\text{var}}(\vec{k}) \) from

\[
-\lambda^D_{\text{var}}(\vec{k}) = -\lim_{k \to 0} \left( \frac{\phi \cdot \hat{M}(\vec{k}) \cdot \phi}{\dot{\phi} \cdot \phi} \right) = \lim_{k \to 0} \left( \frac{M(\vec{k})}{N(\vec{k})} \right),
\]

which is the variational formula used by us to solve various diffusional problems [26–34]. \( M(\vec{k}) \) and \( N(\vec{k}) \) have been referred to as the expectation value numerator and the normalization denominator, respectively. The most important step in the variational method is choosing the proper eigenvector. Following our earlier works we assume the form

\[
\hat{\phi}^{\ast}_{\{\vec{m}\}} = \sum_{i=0}^{N-1} \exp[i\vec{k}(\vec{m}_i + \tilde{\delta}_{\vec{m}_i} + \tilde{\Delta}_{\vec{m}_i})],
\]

where \( \vec{m}_i \) is the position of the \( i \)th particle in the \( \{\vec{m}\} \) configuration, while \( \tilde{\delta}_{\vec{m}_i} \) and \( \tilde{\Delta}_{\vec{m}_i} \) are the variational parameters, called geometrical and correlational phase, respectively, assigned to that particle in that configuration. We insert that trial eigenvector into the variational formula (10), which we then differentiate with respect to the variational parameters in order to find its minimal value.

The geometrical phase \( \tilde{\delta}_{\vec{m}_i} \) depends on the symmetry of the potential with respect to the site \( \vec{m}_i \). By that we understand not only the nearest neighbors of that site but also the global structure of the potential. On the other hand, the correlational phase \( \tilde{\Delta}_{\vec{m}_i} \) is in general non-zero when two neighboring sites with different adsorption energies.
are both occupied. For a given particle the value of $\delta m_i$ depends only on the position of that particle, while the value of $\Delta m_i$ depends also on the occupancy of neighboring sites. Both for the geometrical and the correlational phases one can use symmetry arguments in order to deduce some properties of the values they can assume. For lattices exhibiting some kind of symmetry one can prove that some of the phases are equal to zero, or one can relate the value of one phase to that of another one.

Since $N(k)$ for our choice of the trial vector does not depend on the variational parameters, we shall consider the factors $M(k)$ and $N(k)$ separately.

2.2. Equilibrium state

Collective diffusion coefficient is calculated for the system that approaches the thermal equilibrium state. Thus all probabilities that are used in the variational formula are calculated in this state. When diffusive processes take place in the closed system with conserved number of particles, the equilibrium probability is given by the canonical statistical distribution. However, it is well known that the value of the calculated thermodynamic variable does not depend on the choice of the statistical distribution. To derive the equilibrium values of the occupation and the correlation functions we can choose a distribution that is easiest to apply. That is why we use the grand canonical distribution in the calculation of the equilibrium probabilities of the system. All quantities depend on the chemical potential $\mu$, which in turn is given by the value of the mean particle density.

In the systems that are analyzed below there are no interactions between particles except double occupancy exclusion rule. The equilibrium probability that the site with the adsorption energy $E_A$ is occupied is

$$\theta_A = \frac{ze^{-\beta E_A}}{1 + ze^{-\beta E_A}}$$

where $z = e^{\beta \mu}$, $\mu$ is the chemical potential and $\beta = 1/k_B T$ is the Boltzmann factor. The mean coverage of the system is defined as

$$\theta = \frac{\sum_{i=1}^n \theta_i}{n},$$

where the sum is performed over all the adsorption sites in an elementary cell and $n$ is the number of those sites. The two equations above define occupation of each site for a given number of particles in the system. Note that due to equation (13) all probabilities are interrelated by one, density dependent chemical potential value. The chemical potential uniquely identifies value of mean density $\theta$ and equilibrium densities at all sites individually $\theta_A$ by (12) and (13). These relations will be used to determine the dependence of the diffusion coefficient on the density. The other quantities used in equations below are correlation functions of simultaneous occupation of two or more sites. Due to the lack of long-range interaction, these functions, controlled by the chemical potential in the formulation of the grand canonical distribution, can be written as a product of the probability of site occupation and such representation will be used in further calculations.
2.3. Denominator

For the trial vector (11) the denominator of equation (10) can be written as

\[ N(\vec{k}) = \sum_{\{\vec{m}\}} P^{eq}_{\{\vec{m}\}} \mid \tilde{\phi}_{\{\vec{m}\}}(\vec{k}) \mid^2, \tag{14} \]

which in the limit \( k \to 0 \) for particles with exclusion interactions only and when all correlation functions are expressed in the grand canonical approach has a very simple form

\[ N(0) = \sum_{i=1}^{n} \theta_i (1 - \theta_i). \tag{15} \]

2.4. Numerator

In order to minimize the trial eigenvalue given by the formula (10) it is enough to minimize its numerator \( M(\vec{k}) \). Following our earlier works we write

\[ M(\vec{k}) = \sum_{\{\vec{m}\}, \{\vec{m}'\}}^{\text{no rep}} P^{eq}_{\{\vec{m}\}, \{\vec{m}'\}} \mid \tilde{\phi}_{\{\vec{m}\}}(\vec{k}) - \tilde{\phi}_{\{\vec{m}'\}}(\vec{k}) \mid^2. \tag{16} \]

Then we insert the trial vector (11) into the above expression to find the values of the variational parameters for which the expression has the smallest possible value. In the limit \( k \to 0 \) and assuming that the configurations \( \{\vec{m}\} \) and \( \{\vec{m}'\} \) differ only by the position of one particle we can rewrite the numerator as

\[ M(\vec{k}) = \sum_{A,B}^{\text{no rep}} W_{AB} \theta_A (1 - \theta_B) \sum_{\{n_A^A\}\cup\{n_B^B\}} P^{eq}(\{n_A^A\}\cup\{n_B^B\}) \]

\[ \times [\vec{k} \cdot (\vec{a}_{AB} + \vec{\delta}_B - \vec{\delta}_A + \Delta_B(\{n_B^B\}) - \Delta_A(\{n_A^A\}))]^2, \tag{17} \]

where the first summation is done over all the possible jumps in the system, that is all pairs of nearest neighbors with \( A \) denoted as the site from which the jump starts and \( B \) as the site to which the particle jumps. The second summation is performed over all possible occupational states of the neighbors of sites \( A \) and \( B \). Because of the detailed balance condition (4) it is enough to consider each jump only in one direction, as indicated by the ‘no rep’ comment over the sum symbol. \( \{n_i^{A(B)}\} \) are sets of the occupation numbers of the neighbors of the \( A(B) \) site excluding the \( B(A) \) site. Sites \( A \) and \( B \) can in general have mutual neighbors, that is why in general \( P^{eq}(\{n_A^A\} \cup \{n_B^B\}) \neq P^{eq}(\{n_A^A\})P^{eq}(\{n_B^B\}) \). As mentioned before, the values of the correlational phases depend on the occupancy of the neighboring sites. \( \vec{a}_{AB} \) is the vector connecting the sites \( A \) and \( B \). Once we have the factors (16) and (14) expressed in terms of jump rates and equilibrium occupancies, the diffusion coefficient is the ratio of those factors.

Calculating the numerator directly from the equation (17) for a specific system is rather tedious as for each jump one has to consider all relevant configurations in
the system, that is in general all occupational states of the neighborhood of the sites involved in the jump. However, we shall show now that we can perform the second sum in equation (17) in a general case and obtain a formula which can be easily used for calculations. First of all, we assume that the total correlational phase of a particle is the sum of correlational phases related to all of its neighbors

$$\vec{\Delta}_A\{n_i^A\} = \sum_i n_i \vec{\Delta}_{Ai}. \quad (18)$$

Then let us rewrite the second sum in equation (17) as

$$M_{AB} = \sum_{\{n_i^A\} \cup \{n_i^B\}} P^{eq}(\{n_i^A\} \cup \{n_i^B\})[\vec{k} \cdot \vec{\Delta}_B - \vec{\Delta}_A]$$

$$+ \Delta_B(\{n_i^B\}) - \Delta_A(\{n_i^A\}))^2 = [\vec{k} \cdot (\vec{\alpha}_{AB} + \vec{\delta}_B - \vec{\delta}_A)]^2$$

$$+ \sum_{\{n_i^A\} \cup \{n_i^B\}} P^{eq}(\{n_i^A\}) \sum_{\{n_i^B\}} [\vec{k} \cdot (\Delta_B - \Delta_A)]^2$$

$$+ 2[\vec{k} \cdot (\vec{\alpha}_{AB} + \vec{\delta}_B - \vec{\delta}_A)] \sum_{\{n_i^A\} \cup \{n_i^B\}} P^{eq}(\{n_i^A\})$$

$$\times [\vec{k} \cdot (\Delta_B - \Delta_A)], \quad (19)$$

where we used the fact that the geometrical phases do not depend on the occupancy of the neighboring sites so we could pull them out before the sum, which is equal to 1 if there are no correlational phases under it. In the above expression we have two sums. The one in the mixed term can be rewritten as

$$\sum_{\{n_i^A\} \cup \{n_i^B\}} P^{eq}(\{n_i^A\} \cup \{n_i^B\})[\vec{k} \cdot (\Delta_B - \Delta_A)]$$

$$= \sum_{\{B\}} \theta_i \vec{k} \cdot \vec{\Delta}_B - \sum_{\{A\}} \theta_i \vec{k} \cdot \vec{\Delta}_A, \quad (20)$$

where \{A(B)\} denote the set of all neighbors of the site A(B) excluding the site B(A).

On the other hand, the sum with the squared term is

$$\sum_{\{n_i^A\} \cup \{n_i^B\}} P^{eq}(\{n_i^A\} \cup \{n_i^B\})[\vec{k} \cdot (\Delta_B - \Delta_A)]^2$$

$$= \sum_{\{n_i^B\}} P^{eq}(\{n_i^A\})[\vec{k} \cdot \Delta_A]^2 + \sum_{\{n_i^B\}} P^{eq}(\{n_i^B\})[\vec{k} \cdot \Delta_B]^2$$

$$- 2 \sum_{\{n_i^A\} \cup \{n_i^B\}} P^{eq}(\{n_i^A\} \cup \{n_i^B\})[\vec{k} \cdot \Delta_A][\vec{k} \cdot \Delta_B], \quad (21)$$

where the first sum on the right-hand side can be written as

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\[
\sum_{\{n_i^A\}} P^\text{eq}(\{n_i^A\}) [\vec{k} \cdot \vec{\Delta}_A]^2 = \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_A]^2
\]

\[
+ \sum_{i \neq j} \theta_i \theta_j [\vec{k} \cdot \vec{\Delta}_A] [\vec{k} \cdot \vec{\Delta}_A] = \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_A]^2
\]

\[
+ \left\{ \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_A] \right\}^2 - \sum_i \theta_i^2 [\vec{k} \cdot \vec{\Delta}_A]^2
\]

\[
= \left\{ \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_A] \right\}^2 + \sum_i \theta_i (1 - \theta_i) [\vec{k} \cdot \vec{\Delta}_A]
\]

(22)

and of course we can get an analogous expression for the second sum in (21). Similarly one can show that the last sum there is

\[
\sum_{\{n_i^A\}\cup\{n_i^B\}} P^\text{eq}(\{n_i^A\} \cup \{n_i^B\}) [\vec{k} \cdot \vec{\Delta}_A] [\vec{k} \cdot \vec{\Delta}_B]
\]

\[
= \sum_{i \neq j} \theta_i \theta_j [\vec{k} \cdot \vec{\Delta}_A] [\vec{k} \cdot \vec{\Delta}_B] + \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_A] [\vec{k} \cdot \vec{\Delta}_B]
\]

\[
= \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_A] \sum_i \theta_i [\vec{k} \cdot \vec{\Delta}_B] + \sum_i \theta_i (1 - \theta_i) [\vec{k} \cdot \vec{\Delta}_A] [\vec{k} \cdot \vec{\Delta}_B].
\]

(23)

Now after using the results above and collecting all terms in the expression (19) we can show that the final formula for the numerator in non-interacting case is

\[
M = \sum_{A,B} W_{AB} \theta_A (1 - \theta_B) \left\{ \left[ \vec{k} \cdot (\vec{\alpha}_{AB} + \vec{\delta}_B - \vec{\delta}_A) \right]
\]

\[
+ \sum_i \theta_i \vec{k} \cdot \vec{\Delta}_{Bi} - \sum_i \theta_i \vec{k} \cdot \vec{\Delta}_A \right\}^2
\]

\[
+ \sum_i \theta_i (1 - \theta_i) [\vec{k} \cdot (\vec{\Delta}_{Bi} - \vec{\Delta}_A)]^2 \right\}.
\]

(24)

After we assign variational parameters to the sites and to the pairs of neighbors in the system this formula is simple to use. In the next chapter we shall show a few examples illustrating how to use that formula to calculate the collective diffusion coefficient.
3. Results

We illustrate this method on several examples. Below we show coverage dependence of collective diffusion coefficients for lattices of complex energy landscapes calculated using variational approach. The formula (24), which is the starting point of our calculations, depends on a few variational parameters, called geometrical and correlational phases, with respect to which it must be minimized. In general, one assigns one geometrical phase to each adsorption site and one correlational phase to each pair of nearest neighbors, however, usually it is possible to reduce the number of independent variational parameters using symmetry arguments.

In order to minimize the variational formula, one has to solve a set of linear equations obtained from differentiating it with respect to the assumed parameters. Such set of equations is always soluble, for example by means of Cramer’s rule. Finally, the obtained values of the parameters are inserted into the formula (whose squared terms can be eliminated in the minimum, which simplifies the expression further) to get the diffusion coefficients as functions of jump rates, temperature and the system’s coverage.

The above procedure is always the same and does not depend on the lattice symmetry. However, depending on the complexity of the investigated system calculations can be shorter or longer. We start with three examples of square lattices, and then two different hexagonal lattices are analyzed. Finally we show results for lattices that model experimental system of Ga diffusing on GaAs(001) surface. Diffusion coefficients for two different reconstructions of this surface are compared.

3.1. Square lattice systems

3.1.1. Two equivalent sublattices. The first system we analyze is shown in figure 1. It is a lattice of square symmetry, similar to the checkered lattice considered in [32], however, in addition to jumps between different sites there are also jumps between identical sites. One elementary cell contains one $A$ and one $B$ site. All jumps are symmetric and there are 8 possible jumps per elementary cell: 2 between $A$ sites, 2 between $B$ sites and 4 between $A$ and $B$ sites.

Because of the central inversion of the lattice in every adsorption site, all the geometrical phases are equal to zero. The only non-zero variational phases will be correlational ones related to the $AB$ bonds. There will be 4 such phases in total, however, due to the lattice symmetry with respect to the rotation by 90 degrees, they will differ only by the direction. Therefore, they can be expressed by one variational parameter, $\Delta_{AB}^{\pm\pm} = \Delta_{AB}(\pm 1; \pm 1)$, where the index $\pm\pm$ refers to the orientation of the $AB$ bond at the lattice. The numerator of the variational formula is then

$$M = \{W_{AA}\theta_A(1 - \theta_A) [a^2 + 16\theta_B(1 - \theta_B)\Delta_{AB}^2]$$
$$+ W_{BB}\theta_B(1 - \theta_B) [a^2 + 16\theta_A(1 - \theta_A)\Delta_{AB}^2]$$
$$+ 4W_{AB}\theta_A(1 - \theta_B) \left[\frac{a}{2} + \Delta_{AB}(\theta_B - \theta_A)\right]^2$$
$$+ 3\Delta_{AB}^2 [\theta_A(1 - \theta_A) + \theta_B(1 - \theta_B)]\} (k_x^2 + k_y^2).$$  
(25)

https://doi.org/10.1088/1742-5468/aac142
After differentiating that formula with respect to $\Delta_{AB}$ and setting the derivative to zero we get

$$\Delta_{AB} = W_{AB}(\theta_A - \theta_B)a/\left\{2[4\theta_B(1 - \theta_A)(W_{AA} + W_{BB}) + W_{AB}(\theta_B - \theta_A)^2 + 3W_{AB}[\theta_A(1 - \theta_A) + \theta_B(1 - \theta_B)]]\right\}. \quad (26)$$

Using the condition for the derivative $\partial M/\partial \Delta_{AB} = 0$ we can eliminate the square terms in the expression (25) and

$$M = a^2\{a[W_{AA}\theta_A(1 - \theta_A) + W_{BB}\theta_B(1 - \theta_B) + W_{AB}\theta_A(1 - \theta_B)]$$

$$+ 2W_{AB}\theta_A(1 - \theta_B)\Delta_{AB}(\theta_B - \theta_A)\}(k_x^2 + k_y^2). \quad (27)$$

When phase (26) is inserted into equation (27) we obtain the final expression for the numerator

$$M = a^2\left\{W_{AA}\theta_A(1 - \theta_A) + W_{BB}\theta_B(1 - \theta_B)$$

$$+ W_{AB}\theta_A(1 - \theta_B) - W_{AB}^2\theta_A(1 - \theta_B)(\theta_B - \theta_A)^2$$

$$/\left\{4\theta_B(1 - \theta_A)(W_{AA} + W_{BB}) + W_{AB}(\theta_B - \theta_A)^2 + 3W_{AB}[\theta_A(1 - \theta_A) + \theta_B(1 - \theta_B)]\right\}\}(k_x^2 + k_y^2). \quad (28)$$
Since there is only one adsorption site of each type in an elementary cell, the denominator is

\[ N = \theta_A(1 - \theta_A) + \theta_B(1 - \theta_B). \]  

(29)

The diffusion is isotropic and \( D_x = D_y = M/(N(k_x^2 + k_y^2)) \).

The first three terms in equation (28), each of which contains one jump constant multiplied by adequate occupation probabilities, can be easily interpreted as contributions to the diffusion from respective paths without considering correlational effects. The term with \( W_{AA} \) corresponds to diffusion through \( A \) sites, the one with \( W_{BB} \) describes the diffusive path through \( B \) sites and the last one with \( W_{AB} \) accounts for the diagonal path that goes alternately through \( A \) and \( B \) sites.

On the other hand, the last term in equation (28) can be attributed to the inter-particle correlations in the system. It comes from the correlational phase that was initially assumed in the variational formula. That term is negative, which reflects the fact that the variational approach helps to estimate the upper value of the diffusion coefficient. Both in the limit \( \theta \to 0 \) (single particle) and \( \theta \to 1 \) (single hole) the correlation term vanishes. For a single particle the other terms together with the denominator (29) yield the diffusion coefficient

\[ D_p = a^2 \frac{W_{AA}W_{BA} + W_{BB}W_{AB} + W_{AB}W_{BA}}{W_{AB} + W_{BA}}, \]  

(30)

which is identical to the expression derived in [24] for the same lattice. We used the detailed balance conditions for \( A \) and \( B \) sites \( W_{AB}\theta_A(1 - \theta_B) = W_{BA}\theta_B(1 - \theta_A) \) while taking the single-particle limit. For a single hole the diffusion coefficient is

\[ D_h = a^2 \frac{W_{AA}W_{AB} + W_{BB}W_{BA} + W_{AB}W_{BA}}{W_{AB} + W_{BA}}. \]  

(31)

For \( W_{AA} = W_{BB} = 0 \) the diffusion at this lattice is the same as at the checkered lattice from [32], \( D_p = D_h \) and the maximum of the diffusion coefficient is for \( \theta = 0.5 \). However, when we add jumps between sites of the same type, represented by \( W_{AA} \) and \( W_{BB} \), then the dependence of the diffusion coefficient on the coverage will change significantly. In figure 2 we show the dependence of the collective diffusion coefficient on the mean coverage of the system for three different cases. In all of them the depths of the adsorption sites are assumed \( E_A = 0 \text{eV} \) and \( E_B = 0.05 \text{eV} \) and the barrier between them is \( E_{AB} = 0.07 \text{eV} \). The barriers for \( W_{AA} \) and \( W_{BB} \) jumps differ between the curves. The bottom curve represents the diffusion where those barriers are infinite, that is the corresponding jumps are blocked. That case is equivalent to diffusion at the checkered lattice [32]. The middle curve is for \( E_{AA} = 0.1 \text{eV} \) and jumps between \( B \) sites are blocked. We can see that activating a channel between \( A \) sites speeds up the diffusion. Because \( A \) sites are deeper than \( B \) sites, the change in the diffusion coefficient is bigger for lower values of the concentration. Finally, the upper curve shows the diffusion for \( E_{AA} = 0.1 \text{eV} \) and \( E_{BB} = 0.12 \text{eV} \). This time, as expected, the diffusion is more strongly accelerated for high values of \( \theta \). Even though \( E_{BB} > E_{AA} \), the effect is stronger than for the channel between \( A \) sites. That is because the value that decides about the jump rates is the difference between the barrier and the depth of the adsorption sites that are involved in the jump. In our case \( E_{BB} - E_B < E_{AA} - E_A \).
Collective diffusion of dense adsorbate at surfaces of arbitrary geometry

3.1.2. Lattice of square symmetry—inequivalent sublattices. Now let us consider a lattice shown in figure 3. It possesses square symmetry but differs significantly from the square lattice in figure 1. In the geometric sense the adsorption sites $A$ and $B$ are not equivalent. Each $A$ site connects to 4 other $A$ sites and to 4 sites $B$, while each $B$ site connects to 6 sites $B$ and to 2 sites $A$. Each elementary cell contains one $A$ site and, contrary to the previous examples, two $B$ sites. Those two $B$ sites differ by the angular orientation of the surrounding sites. They have the same adsorption energy but one of them is placed between the two $A$ sites in the horizontal direction and the other in the vertical one. Therefore, the total number of sites per elementary cell is 3. One should also note that there are two types of jumps between the $B$ sites. One of them is a short jump in the diagonal direction and the other one is a long jump in the horizontal or vertical direction. We will denote the corresponding jump rates by $W_{BB}^s$ and $W_{BB}^l$, respectively.

Again, there will be one correlation phase, which will possess four versions with respect to the angular orientation. As in the previous case they can all be expressed by one variational parameter $\Delta_{AB}$. The numerator is

$$M = \left\{ 2W_{AA}\theta_A(1 - \theta_B) \left\{ \left[ \frac{a}{2} + (\theta_B - \theta_A)\Delta_{AB} \right]^2 + \Delta_{AB}^2 \left[ \theta_A(1 - \theta_A) + 3\theta_B(1 - \theta_B) \right] \right\} + 2W_{AA}\theta_A(1 - \theta_A) \left[ a^2 + 4\theta_B(1 - \theta_B)\Delta_{AB}^2 \right] + 4W_{BB}^l\theta_B(1 - \theta_B) \left[ \left( \frac{a}{2} \right)^2 + 2\theta_A(1 - \theta_A)\Delta_{AB}^2 \right] + W_{BB}^l\theta_B(1 - \theta_B) \left[ a^2 + 4\theta_A(1 - \theta_A)\Delta_{AB}^2 \right] \right\} (k_x^2 + k_y^2).$$

(32)

Figure 2. Dependence of the collective diffusion coefficient on the mean coverage of the system for the lattice shown in figure 1. For all curves $E_A = 0$ eV, $E_B = 0.05$ eV and $E_{AB} = 0.07$ eV. For the bottom curve $E_{AA} = E_{BB} = \infty$, for the middle one $E_{AA} = 0.1$ eV and $E_{BB} = \infty$, and for the upper curve $E_{AA} = 0.1$ eV and $E_{BB} = 0.12$ eV. Temperature $T = 300$ K and attempt frequency $\nu = 10^{13}$ s$^{-1}$. 

$5 \times 10^{11}$

$6 \times 10^{11}$

$7 \times 10^{11}$

$8 \times 10^{11}$

$9 \times 10^{11}$

$1 \times 10^{12}$

$1.1 \times 10^{12}$

$1.2 \times 10^{12}$

$1.3 \times 10^{12}$

$0$

$0.2$

$0.4$

$0.6$

$0.8$

$1$

$D[a^2/s]$
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From there we obtain

$$\Delta_{AB} = W_{AB}(\theta_A - \theta_B)a/\left\{2\left\{W_{AB} \left[ (\theta_B - \theta_A)^2 + \theta_A(1 - \theta_A) 
+ 3\theta_B(1 - \theta_B)\right] + 2(1 - \theta_A)\theta_B \left[2(W_{AA} + W^s_{BB})
+ W^l_{BB}\right]\right\}\right\}$$

(33)

and

$$M = a^2\left\{2W_{AA}\theta_A(1 - \theta_A) + (W^s_{BB} + W^l_{BB})\theta_B(1 - \theta_B)
+ \frac{1}{2}W_{AB}\theta_A(1 - \theta_B) - W^2_{AB}\theta_A(1 - \theta_B)(\theta_B - \theta_A)^2
\right\} \left\{2\left\{W_{AB} \left[ (\theta_B - \theta_A)^2 + \theta_A(1 - \theta_A) + 3\theta_B(1 - \theta_B)\right]
+ 2(1 - \theta_A)\theta_B \left[2(W_{AA} + W^s_{BB}) + W^l_{BB}\right]\right\}\right\}\right\} (k_x^2 + k_y^2).$$

(34)

The denominator in this case is

$$N = \theta_A(1 - \theta_A) + 2\theta_B(1 - \theta_B).$$

(35)

The diffusion coefficient is calculated again by $D_x = D_y = M/(N(k_x^2 + k_y^2))$ and its dependence on the mean coverage for three sets of the jump rates is shown in figure 4. As can be expected when we decrease energy barrier for long distance-jumps between $B$ and $B$ sites $E^l_{BB}$, diffusion coefficients increase for all surface coverages. However, interestingly the increase of high-coverage diffusion coefficient is much faster. As a result for higher barrier low-coverage diffusion coefficient is higher than high-coverage diffusion coefficient, while for lower barrier high-coverage diffusion becomes higher by three orders of magnitude than the low-coverage one.
3.1.3. Square lattice with three different adsorption sites. We analyze diffusion at the lattice shown in figure 5. The lattice is of square symmetry with three different adsorption sites. In general they all differ by the adsorption energy. Sites A and B are geometrically equivalent to each other in the sense that they both have four C neighbors, one at each of the four main directions. Sites C, on the other hand, have two A neighbors placed either horizontally or vertically and two B neighbors placed in the perpendicular direction. Each elementary cell has one A site, one B site and two C sites. The two C sites differ by the angular orientation of their neighbors.

There are two types of jumps between adsorption sites: \(W_{AC}\) and \(W_{BC}\). Per elementary cell there are four \(W_{AC}\) jumps and four \(W_{BC}\) jumps. Again, because of the symmetry of the adsorption sites there are no geometrical phases. There are two correlational phases, \(\Delta_{AC}\) and \(\Delta_{BC}\), related to the respective pairs of neighbours. The numerator is

\[
M = \left\{ 2W_{AC}\theta_A(1 - \theta_C) \left\{ \frac{a}{2} + \Delta_{AC}(\theta_C - \theta_A) \right\}^2 + \Delta_{AC}^2 \left\{ \theta_A(1 - \theta_A) + 3\theta_C(1 - \theta_C) \right\} + 2\Delta_{AC}^2 \theta_B(1 - \theta_B) \right\} \\
+ \frac{a}{2} + \Delta_{BC}(\theta_C - \theta_B) \right\}^2 + \Delta_{BC}^2 \left\{ \theta_B(1 - \theta_B) + 3\theta_C(1 - \theta_C) \right\} + 2\Delta_{BC}^2 \theta_A(1 - \theta_A) \right\} \right\} \\
\times (k_x^2 + k_y^2). \tag{36}
\]

As before, in order to find the variational parameters we have to differentiate the above expression with respect to them and set the derivatives to zero. That will give us a set of two equations. In the case considered here each equation will contain only one phase so one can easily calculate their values

\[
\Delta_{AC} = aW_{AC}(\theta_A - \theta_C) \left\{ 2\left\{ W_{AC}\left( (\theta_C - \theta_A)^2 + \theta_A(1 - \theta_A) + 3\theta_C(1 - \theta_C) \right) + 2W_{BC}\theta_B(1 - \theta_A) \right\} \right\},
\]

\[
\Delta_{BC} = aW_{BC}(\theta_B - \theta_C) \left\{ 2\left\{ W_{BC}\left( (\theta_C - \theta_B)^2 + \theta_B(1 - \theta_B) + 3\theta_C(1 - \theta_C) \right) + 2W_{AC}\theta_A(1 - \theta_B) \right\} \right\}. \tag{37}
\]

Finally we get the numerator

\[
M = \frac{a^2}{2} \left\{ W_{AC}\theta_A(1 - \theta_C) + W_{BC}\theta_B(1 - \theta_C) - W_{AC}^2\theta_A(1 - \theta_C)(\theta_C - \theta_A)^2 \left\{ W_{AC}\left( (\theta_C - \theta_A)^2 + \theta_A(1 - \theta_A) + 3\theta_C(1 - \theta_C) + 2W_{BC}\theta_B(1 - \theta_A) \right\} \right\} \\
- W_{BC}^2\theta_B(1 - \theta_C)(\theta_C - \theta_B)^2 \left\{ W_{BC}\left( (\theta_C - \theta_B)^2 + \theta_B(1 - \theta_B) + 3\theta_C(1 - \theta_C) + 2W_{AC}\theta_A(1 - \theta_B) \right\} \right\} \right\} \\
\times (k_x^2 + k_y^2). \tag{39}
\]
The denominator is \( N = \theta_A(1 - \theta_A) + \theta_B(1 - \theta_B) + 2\theta_C(1 - \theta_C) \).

From the above expressions one can simply calculate the diffusion coefficient as the ratio \( D = M/(N(k_x^2 + k_y^2)) \). From equation (38) it is seen that there are two main
diffusive paths: one through $W_{AC}$ jumps and the other through $W_{BC}$ jumps. Again, the negative terms are due to the inter-particle correlations.

3.2. Hexagonal lattice systems

3.2.1. System of two hexagonal sublattices. Next we analyze a lattice of hexagonal symmetry shown in figure 6. Here each site contains 6 connections to sites of the same type and 3 connections to sites of the other type. Similarly to the previous cases, using symmetry arguments one can reduce the number of independent variational phases to one correlation phase between $A$ and $B$ sites.

The numerator of the diffusion coefficient is

$$M = \frac{3}{2} W_{AA} \theta_A (1 - \theta_A) \left[ a^2 + 6 \theta_B (1 - \theta_B) \Delta_{AB}^2 \right]$$

$$+ \frac{3}{2} W_{BB} \theta_B (1 - \theta_B) \left[ a^2 + 6 \theta_A (1 - \theta_A) \Delta_{AB}^2 \right]$$

$$+ \frac{3}{2} W_{AB} \theta_A (1 - \theta_B) \left[ \left( \frac{\sqrt{3}}{2} a + \Delta_{AB} (\theta_B - \theta_A) \right)^2 \right]$$

$$+ 2 \Delta_{AB}^2 \left[ \theta_A (1 - \theta_A) + \theta_B (1 - \theta_B) \right] \right\} (k_x^2 + k_y^2).$$

From there one can find the correlational phase

$$\Delta_{AB} = \sqrt{3} W_{AB} (\theta_A - \theta_B) \alpha \left\{ \frac{3}{2} [6 \theta_B (1 - \theta_A) (W_{AA} + W_{BB}) + W_{AB} (\theta_B - \theta_A)^2 + 2 W_{AB} \theta_A (1 - \theta_A) + \theta_B (1 - \theta_B)] \right\},$$

which gives the final value of the numerator

$$M = \frac{\alpha^2}{2} \left\{ 3 W_{AA} \theta_A (1 - \theta_A) + 3 W_{BB} \theta_B (1 - \theta_B) + W_{AB} \theta_A (1 - \theta_B) - W_{AB}^2 \theta_A (1 - \theta_B) (\theta_B - \theta_A)^2 \right\}$$

$$\div \left\{ 6 \theta_B (1 - \theta_A) (W_{AA} + W_{BB}) + W_{AB} (\theta_B - \theta_A)^2 + 2 W_{AB} \theta_A (1 - \theta_A) + \theta_B (1 - \theta_B) \right\} \left\} \right\} (k_x^2 + k_y^2).$$

The denominator is the same as for the case of two square sublattices, that is $N = \theta_A (1 - \theta_A) + \theta_B (1 - \theta_B)$ and again $D_x = D_y = M/(N(k_x^2 + k_y^2))$.

Expression (42) has in fact the same structure as the numerator (28) for the square lattice. The only difference is in the coefficients that stand by various terms. That is not surprising since both lattices contain two different adsorption sites per elementary cell and they are connected with each other similarly at both lattices. They differ by the number and the geometry of those connections but at both lattices the three main diffusive paths are along the $W_{AA}$, $W_{BB}$ and $W_{AB}$ jumps.
We show the collective diffusion coefficient for the hexagonal lattice in figure 7 for the same set of parameters as for the square lattice from figures 1 and 2. The behavior of the diffusion is qualitatively the same in both cases but we can see that here the diffusion is generally lower and the curves are flatter than in figure 2, especially the one for $E_{AA} = E_{BB} = \infty$. 

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Figure 6. Lattice of hexagonal symmetry containing two different adsorption sites. Dashed line shows an elementary cell.

Figure 7. Dependence of the collective diffusion coefficient on the mean coverage of the system for the lattice shown in figure 6. For all curves $E_A = 0$ eV, $E_B = 0.05$ eV and $E_{AB} = 0.07$ eV. For the bottom curve $E_{AA} = E_{BB} = \infty$, for the middle one $E_{AA} = 0.1$ eV and $E_{BB} = \infty$, and for the upper curve $E_{AA} = 0.1$ eV and $E_{BB} = 0.12$ eV. Temperature $T = 300$ K and attempt frequency $\nu = 10^{13}$ s$^{-1}$. 

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3.2.2. Lattice of hexagonal symmetry—three sublattices. In figure 8 we show another lattice with three different adsorption sites. All of them have the same geometry, each site of a given type has six connections to sites of two other types in that way that A site connects to 3 B and 3 C sites and so on.

There are three possible types of jumps in the system: \( W_{AB} \), \( W_{BC} \) and \( W_{CA} \) and per elementary cell each of those jumps exists in three angular versions. Contrary to the previous examples, in this case there are three independent correlational phases: \( \Delta_{AB} \), \( \Delta_{BC} \) and \( \Delta_{CA} \). The numerator is

\[
M = \left\{ 3W_{AB}\theta_A(1 - \theta_B) \left[ \frac{1}{2} \left[ \frac{\sqrt{3}}{3} a + \Delta_{AB}(\theta_B - \theta_A) \right] \right]^2 + [\theta_A(1 - \theta_A) + \theta_B(1 - \theta_B)]\Delta_{AB}^2 + \theta_C(1 - \theta_C) \left[ \frac{3}{2} (\Delta_{BC}^2 + \Delta_{CA}^2) + \Delta_{BC}\Delta_{CA} \right] \right. \\
+ 3W_{BC}\theta_B(1 - \theta_C) \left[ \frac{1}{2} \left[ \frac{\sqrt{3}}{3} a + \Delta_{BC}(\theta_C - \theta_B) \right] \right]^2 + [\theta_B(1 - \theta_B) + \theta_C(1 - \theta_C)]\Delta_{BC}^2 + \theta_A(1 - \theta_A) \left[ \frac{3}{2} (\Delta_{CA}^2 + \Delta_{AB}^2) + \Delta_{CA}\Delta_{AB} \right] \\
\left. + 3W_{CA}\theta_C(1 - \theta_A) \left[ \frac{1}{2} \left[ \frac{\sqrt{3}}{3} a + \Delta_{CA}(\theta_A - \theta_C) \right] \right]^2 + [\theta_C(1 - \theta_C) + \theta_A(1 - \theta_A)]\Delta_{CA}^2 + \theta_B(1 - \theta_B) \left[ \frac{3}{2} (\Delta_{AB}^2 + \Delta_{BC}^2) + \Delta_{AB}\Delta_{BC} \right] \right\} \times (k_x^2 + k_y^2). \tag{43}
\]

Unlike previous examples, here mixed terms (for example \( \Delta_{AB}\Delta_{BC} \)) enter the expression for the numerator. That means that the derivatives will contain also other phases than that with respect to which the expression is differentiated. We shall write the set of linear equations for the correlational phases in the matrix form

\[
\begin{bmatrix}
X_{11} & X_{12} & X_{13} \\
X_{21} & X_{22} & X_{23} \\
X_{31} & X_{32} & X_{33}
\end{bmatrix} \begin{bmatrix}
\Delta_{AB} \\
\Delta_{BC} \\
\Delta_{CA}
\end{bmatrix} = \begin{bmatrix}
Y_1 \\
Y_2 \\
Y_3
\end{bmatrix} \tag{44}
\]

where
Collective diffusion of dense adsorbate at surfaces of arbitrary geometry

\[ X_{11} = W_{AB}\theta_A (1 - \theta_B) \left[ (\theta_B - \theta_A)^2 + 2[\theta_A(1 - \theta_A) + \theta_B(1 - \theta_B)] + 3\theta_B(1 - \theta_A)(W_{BC}\theta_A(1 - \theta_C) + W_{CA}\theta_B(1 - \theta_B)) \right] \]
\[ X_{22} = W_{BC}\theta_B (1 - \theta_C) \left[ (\theta_C - \theta_B)^2 + 2[\theta_B(1 - \theta_B) + \theta_C(1 - \theta_C)] + 3\theta_C(1 - \theta_B)(W_{CA}\theta_B(1 - \theta_A) + W_{AB}\theta_A(1 - \theta_C)) \right] \]
\[ X_{33} = W_{CA}\theta_C (1 - \theta_A) \left[ (\theta_A - \theta_C)^2 + 2[\theta_C(1 - \theta_C) + \theta_A(1 - \theta_A)] + 3\theta_A(1 - \theta_C)(W_{AB}\theta_C(1 - \theta_B) + W_{BC}\theta_B(1 - \theta_A)) \right] \]
\[ X_{12} = X_{21} = W_{CA}\theta_C (1 - \theta_A)\theta_B(1 - \theta_B) \]
\[ X_{13} = X_{31} = W_{BC}\theta_B (1 - \theta_C)\theta_A(1 - \theta_A) \]
\[ X_{23} = X_{32} = W_{AB}\theta_A(1 - \theta_B)\theta_C(1 - \theta_C) \]
\[ Y_1 = -W_{AB}\theta_A (1 - \theta_B)(\theta_B - \theta_A)\frac{\sqrt{3}}{3}a \]
\[ Y_2 = -W_{BC}\theta_B (1 - \theta_C)(\theta_C - \theta_B)\frac{\sqrt{3}}{3}a \]
\[ Y_3 = -W_{CA}\theta_C (1 - \theta_A)(\theta_A - \theta_C)\frac{\sqrt{3}}{3}a. \]

(45)

Figure 8. Lattice of hexagonal symmetry containing three different adsorption sites. Dashed line shows an elementary cell.
As we can see this case is more complex than the previous ones and also it is more difficult to obtain the solution. However, one can solve the set of equations using Cramer’s rule

\[
\Delta_{AB} = \frac{\begin{vmatrix} Y_1 & X_{12} & X_{13} \\ Y_2 & X_{22} & X_{23} \\ Y_3 & X_{32} & X_{33} \end{vmatrix}}{\begin{vmatrix} X_{11} & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{vmatrix}}
\]

\[
\Delta_{BC} = \frac{\begin{vmatrix} X_{11} & Y_1 & X_{13} \\ X_{21} & Y_2 & X_{23} \\ X_{31} & Y_3 & X_{33} \end{vmatrix}}{\begin{vmatrix} X_{11} & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{vmatrix}}
\]

\[
\Delta_{CA} = \frac{\begin{vmatrix} X_{11} & X_{12} & Y_1 \\ X_{21} & X_{22} & Y_2 \\ X_{31} & X_{32} & Y_3 \end{vmatrix}}{\begin{vmatrix} X_{11} & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{vmatrix}}.
\] (46)

Again, we can simplify the expression (43) by using the condition of vanishing derivatives to get

\[
M = \frac{a^2}{2} \left\{ W_{AB}\theta_A(1 - \theta_B) + W_{BC}\theta_B(1 - \theta_C) \\
+ W_{CA}\theta_C(1 - \theta_A) + \frac{\sqrt{3}}{2} a \left\{ W_{AB}\theta_A(1 - \theta_B)(\theta_B - \theta_A)\Delta_{AB} \\
+ W_{BC}\theta_B(1 - \theta_C)(\theta_C - \theta_B)\Delta_{BC} \\
+ W_{CA}\theta_C(1 - \theta_A)(\theta_A - \theta_C)\Delta_{CA} \right\} \right\}
\times (k_x^2 + k_y^2).
\] (47)

Then we put the phases (46) into the above expression and after dividing it by the denominator

\[
N = \theta_A(1 - \theta_A) + \theta_B(1 - \theta_B) + \theta_C(1 - \theta_C)
\] (48)

we get the collective diffusion coefficient \(D\).
3.3. Diffusion on GaAs(001) surface

The variational method is not limited to lattices whose adsorption sites possess symmetry. It can be just as well used to analyze diffusion in systems where there is an asymmetry of the jumps from a given site. In such cases one should assume a geometrical phase related to that site. In general, one should look not only at the symmetry of the jumps from that site but also at the symmetry of the entire system. Even when the jumps are symmetric, the geometrical phase can be non-zero when the whole potential is not symmetric with respect to the site considered. The whole procedure of finding the diffusion coefficients is the same as for symmetric landscapes. The variational formula is minimized with respect to the parameters by simple differentiation, which gives a set of linear equations.

In this section we shall consider two examples of lattices which contain at least one site with respect to which the energetic landscape is asymmetric and consequently its geometrical phase cannot be set to zero. These examples model Ga adatoms diffusion on GaAs(001) surfaces in two different reconstructions. We show how diffusion anisotropy changes with the system coverage in both cases.

3.3.1. Ga adatoms on GaAs(001)-c(4×4). In figure 9 a simplified lattice for Ga adatom at reconstructed GaAs(001)-c(4×4) surface is shown. The scheme of jumps is based on ab initio calculations for that system in [36]. Based on those data diffusion coefficients for a single Ga atom were calculated in [25]. A more detailed landscape was found in [37], which contained a few more adsorption sites and energetic barriers. Single-particle diffusion coefficients based on those new data were found in [26] by means of our variational approach.

Here we shall calculate collective diffusion coefficients for the lattice shown in figure 9. Unlike earlier approaches, the result will depend on the coverage of the system as our method takes into account inter-particle correlations.

As usual, we start by writing out the variational formula for the lattice studied. As shown in figure 9 one elementary cell contains 1 A site, 2 B sites and 2 C sites. There are two types of jumps: \( W_{AB} \) and \( W_{BC} \). Per elementary cell there are 2 \( W_{AB} \) jumps and 4 \( W_{BC} \) jumps. Because of that we will have two correlational phases, each assigned to one pair of neighboring sites: \( \vec{\Delta}_{AB} \) and \( \vec{\Delta}_{BC} \). Depending on the orientation of a given pair in the lattice they will assume the values \( \vec{\Delta}_{AB}^\pm = (\pm \Delta_{AB}^x, 0) \) and \( \vec{\Delta}_{BC}^{\pm x\pm y} = (\pm \Delta_{BC}^x, \pm \Delta_{BC}^y) \). Since sites A and C are inversion centers of the lattice, the geometrical phases at those sites are equal to zero. On the other hand, site B does not have such symmetry, however, it has symmetry with respect to the \( x \) axis and two inequivalent B sites in an elementary cell are related to each other by the symmetry with respect to the \( y \) axis. Because of that the \( y \) component or its geometrical phases
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will vanish, while the $x$ component will differ by the sign between the $B$ sites neighboring to the left and to the right of the $A$ site, that is $\delta^\pm_B = (\pm\delta_B, 0)$. Taking all those facts into account we can write the numerator as

$$M = 2W_{AB}\theta_A(1 - \theta_B)\left\{\left[(a + \delta_B + \theta_B\Delta_{AB} + 2\theta_C\Delta_{BC}^x)^2\right.ight.$$

$$+ \theta_B(1 - \theta_B)\Delta_{AB}^2 + 2\theta_C(1 - \theta_C)(\Delta_{BC}^x)^2\Big[\frac{k^2}{2}\right.$$

$$+ 2\theta_C(1 - \theta_C)(\Delta_{BC}^x)^2k^2\Big]\right\}_x$$

$$+ 4W_{BC}\theta_B(1 - \theta_C)\left\{\left[(\delta_B + \theta_A\Delta_{AB} + (\theta_B + \theta_C)\Delta_{BC}^x)^2\right.$$

$$+ \theta_A(1 - \theta_A)\Delta_{AB}^2 + (\theta_B(1 - \theta_B) + \theta_C(1 - \theta_C))(\Delta_{BC}^x)^2\Big[\frac{k^2}{2}\right.$$

$$+ \left[(a - \Delta_{BC}^x(\theta_B - \theta_C))^2 + 2(\theta_B(1 - \theta_B)$$

$$+ \theta_C(1 - \theta_C))(\Delta_{BC}^x)^2\Big[\frac{k^2}{2}\right]\right\}. \tag{49}$$

We can see that the diffusion is anisotropic here, however, its main directions are always along $x$ and $y$ axes. The $x$-component depends on three parameters: $\delta_B$, $\Delta_{AB}$ and $\Delta_{BC}^x$, while the $y$-component depends only on one parameter, $\Delta_{BC}^y$. One has to minimize both components with respect to those parameters.

For the $x$-direction we get a set of three equations, which can be again written in the matrix form similar to (44)

$$\begin{bmatrix} X_{11} & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{bmatrix} \begin{bmatrix} \delta_B \\ \Delta_{AB} \\ \Delta_{BC} \end{bmatrix} = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \end{bmatrix} \tag{50}$$

with

$$X_{11} = W_{AB}\theta_A(1 - \theta_B) + 2W_{BC}\theta_B(1 - \theta_C)$$

$$X_{22} = X_{12} = X_{21} = [W_{AB}(1 - \theta_B) + 2W_{BC}(1 - \theta_C)]\theta_A\theta_B$$

$$X_{33} = 2[W_{AB}\theta_A(1 - \theta_B)\theta_C(1 + \theta_C)$$

$$+ W_{BC}\theta_B(1 - \theta_C)(\theta_B + \theta_C + 2\theta_B\theta_C)]$$

$$X_{13} = X_{31} = 2[W_{AB}\theta_A(1 - \theta_B)\theta_C$$

$$+ W_{BC}\theta_B(1 - \theta_C)(\theta_B + \theta_C)]$$

$$X_{23} = X_{32} = 2[W_{AB}(1 - \theta_B)\theta_C$$

$$+ W_{BC}(1 - \theta_C)(\theta_B + \theta_C)]\theta_A\theta_B$$

$$Y_1 = -aW_{AB}\theta_A(1 - \theta_B)$$

$$Y_2 = -aW_{AB}\theta_A(1 - \theta_B)\theta_B$$

$$Y_3 = -2aW_{AB}\theta_A(1 - \theta_B)\theta_C \tag{51}$$

and again we can obtain the phases
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\[ \delta_B = \frac{\text{det} \begin{bmatrix} X_1 & X_{12} & X_{13} \\ Y_1 & X_{22} & X_{23} \\ Y_3 & X_{32} & X_{33} \end{bmatrix}}{\text{det} \begin{bmatrix} X_1 & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{bmatrix}}, \]

\[ \Delta_{AB} = \frac{\text{det} \begin{bmatrix} X_1 & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{bmatrix}}{\text{det} \begin{bmatrix} X_1 & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{bmatrix}}. \]

\[ \Delta_{BC} = \frac{\text{det} \begin{bmatrix} X_1 & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{bmatrix}}{\text{det} \begin{bmatrix} X_1 & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{bmatrix}}. \]

The simplified formula (49) for the x-direction is

\[ M_x = 2W_{AB}\theta_A(1 - \theta_B)(a + \delta_B + \theta_B\Delta_{AB} + 2\theta_C\Delta_{BC})a, \]

(53)
to which we insert the phases (52) and obtain the diffusion coefficient.
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\[ D_x = \frac{M_x}{N}, \]

where

\[ N = \theta_A(1 - \theta_A) + 2\theta_B(1 - \theta_B) + 2\theta_C(1 - \theta_C). \]

Calculating diffusion coefficient in the \( y \)-direction at this lattice is much easier as it requires to minimise the terms in the formula (49) which stand by \( k_y^2 \) with respect to only one variational parameter, namely \( \Delta_{BC}^y \). After differentiating we get

\[ \Delta_{BC}^y = aW_{BC}\theta_B(\theta_B - \theta_C)\left\{ W_{AB}\theta_A(1 - \theta_B)\theta_C + W_{BC}\theta_B[(\theta_B - \theta_C)^2 + 2[\theta_B(1 - \theta_B) + \theta_C(1 - \theta_C)]]\right\}, \]

which inserted into simplified formula (49) for the \( y \)-direction gives

\[ M_y = 4W_{BC}\theta_B(1 - \theta_C)\left\{ 1 - W_{BC}\theta_B(\theta_B - \theta_C)^2 \right\}
\]

\[ \left\{ W_{AB}\theta_A(1 - \theta_B)\theta_C + W_{BC}\theta_B[(\theta_B - \theta_C)^2 + 2[\theta_B(1 - \theta_B) + \theta_C(1 - \theta_C)]]\right\}a^2 \]

and

\[ D_y = \frac{M_y}{N}. \]

In figure 10 we show the collective diffusion coefficients at that lattice as functions of the mean coverage. We take the values of the adsorption energies and the energetic barriers from [36]. We see that both coefficients start at around \( 2 \cdot 10^{-8} \text{ cm}^2 \text{s}^{-1} \) for \( \theta = 0 \), which is the value of the same order of magnitude as obtained in the Monte Carlo simulations in [36]. For low coverages the diffusion is almost isotropic. However, starting from \( \theta = 0.2 \) it becomes faster in the \( y \)-direction, while in the \( x \)-direction it remains constant. At \( \theta = 0.6 \) \( D_y \) reaches its maximal value while \( D_x \) starts to decrease rapidly. Diffusion in the \( y \)-direction becomes two orders of magnitude faster than in the \( x \)-direction for the single hole limit (\( \theta = 1 \)). Such anisotropy should be easy to verify in STM measurements or other experimental techniques.

3.3.2. Ga adatoms on GaAs(0 0 1)-(2 \times 4) \( \beta 2 \). We consider a different reconstruction of the GaAs(001) lattice, namely (2 \times 4) \( \beta 2 \). We show the scheme of the lattice in figure 11, which was based on \textit{ab initio} calculations in [38].

The lattice has two types of adsorption sites, to which we assign geometrical phases \( \vec{\delta}_A = (0, \delta_A) \) and \( \vec{\delta}_B = (\pm \delta_B, \delta_B^y) \), where the sign \( \pm \) refers to the \( B \) site lying closer either to the left or to the right of the \( A \) site. Each cell has one \( A \) site and two \( B \) sites. There is also one correlational phase \( \vec{\Delta}_{AB} = (\pm \Delta_{AB}^x, \Delta_{AB}^y) \) assigned to the \( AB \) bond, where \( \pm \) again refers to the position of the \( B \) site to the left or to the right with respect to the \( A \) site. The jumps per elementary cell are: one \( W_{AA} \), two \( W_{AB} \), one \( W_{BB}^h \) (horizontal), two \( W_{BB}^v \) (vertical) and two \( W_{BB}^d \) (diagonal). We write the numerator as

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\[ M = W_{AA}\theta_A(1-\theta_A)\{4\theta_B(1-\theta_B)(\Delta^x_{AB})^2k_x^2 + [a^2 + 4\theta_B(1-\theta_B)(\Delta^y_{AB})^2k_y^2]\] 
\[ + 2W_{AB}\theta_A(1-\theta_B)\left\{ \left[ \frac{3}{4}a + \delta_B^x + \theta_B\Delta^x_{AB} \right]^2 + \theta_B(1-\theta_B)(\Delta^x_{AB})^2 \right\}k_x^2 + \left[ \left( \frac{1}{4}a + \delta_B^y - \delta_A - \theta_B\Delta^y_{AB} \right)^2 + \theta_B(1-\theta_B)(\Delta^y_{AB})^2 \right]\}k_y^2 \] 
\[ + (W_{BB}^h + 2W_{BB}^d)\theta_B(1-\theta_B)\left\{ \left[ \frac{1}{2}a - 2\delta_B^x - 2\theta_A\Delta^x_{AB} \right]^2 + 2\theta_A(1-\theta_A)(\Delta^x_{AB})^2k_x^2 \right\} 
\[ + 2(W_{BB}^d + W_{BB}^v)\theta_B(1-\theta_B)a^2k_y^2 + 4W_{BB}^d\theta_A(1-\theta_A)(1-\theta_B)\right\}((\Delta^x_{AB})^2k_x^2 + (\Delta^y_{AB})^2k_y^2]. \] 

Again one has to minimize the above expression separately for the \( x \)- and the \( y \)-direction. For the \( x \)-direction we have

\[ \delta^x_B = a\left\{ (W_{AA} + W_{BB}^v)(1-\theta_A)\left[ (W_{BB}^h + 2W_{BB}^d)\theta_B 
\[ - \frac{3}{2}W_{AB}\theta_A \right] + \frac{1}{2}[W_{AB} + W_{BB}^h + 2W_{BB}^d] 
\times \left[ (W_{BB}^h + 2W_{BB}^d)\theta_B(1-\theta_A) - \frac{3}{2}W_{AB}\theta_A(1-\theta_B) \right] 
\[ + \frac{3}{4}W_{AB}(W_{BB}^h + 2W_{BB}^d)\theta_A(\theta_B - \theta_A) \left\} \left/ \left\{ (W_{BB} + W_{BB}^d)(1-\theta_A) \right\} \right. \right. \] 
\[ + 2(W_{BB}^h + 2W_{BB}^d)\theta_B(1-\theta_B) 
\[ + W_{AB}(W_{BB}^h + 2W_{BB}^d)\theta_A(\theta_A - \theta_B) 
\[ + 2(W_{AA} + W_{BB}^v)(1-\theta_A)W_{AB}\theta_A 
\[ + 2(W_{BB}^h + 2W_{BB}^d)\theta_B) \right\} \right. \right. \] 
\[ - (W_{BB} + W_{BB}^d)(1-\theta_B)W_{AB}(W_{BB}^h + 2W_{BB}^d) \right. \right. \] 
\[ \left/ \left\{ (W_{BB} + W_{BB}^d)(1-\theta_B) \right\} \right. \right. \] 
\[ + 2(W_{BB}^h + 2W_{BB}^d)\theta_B(1-\theta_A) 
\[ + W_{AB}(W_{BB}^h + 2W_{BB}^d)\theta_A(\theta_A - \theta_B) 
\[ + 2(W_{AA} + W_{BB}^v)(1-\theta_A)W_{AB}\theta_A 
\[ + 2(W_{BB}^h + 2W_{BB}^d)\theta_B) \right] \right. \right. \] 
\[ \Delta^x_{AB} = 2a(\theta_A - \theta_B)W_{AB}(W_{BB}^h + 2W_{BB}^d) \right. \right. \] 
\[ \left/ \left\{ (W_{BB} + W_{BB}^d)(1-\theta_B) \right\} \right. \right. \] 
\[ + 2(W_{BB}^h + 2W_{BB}^d)\theta_B(1-\theta_A) 
\[ + W_{AB}(W_{BB}^h + 2W_{BB}^d)\theta_A(\theta_A - \theta_B) 
\[ + 2(W_{AA} + W_{BB}^v)(1-\theta_A)W_{AB}\theta_A 
\[ + 2(W_{BB}^h + 2W_{BB}^d)\theta_B) \right] \right. \right. \] 
\[ \right. \right. \] 

\[ \text{The corresponding diffusion coefficient is} \] 

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\[ D_x = a \left( \frac{3}{2} W_{AB} \theta_A (1 - \theta_B) \left( \frac{3}{4} a + \delta x_B + \theta_B \Delta x_{AB} \right) \ight. \]
\[ + \left. \frac{1}{2} \left( W_{BB}^h + 2W_{BB}^d \right) \theta_B (1 - \theta_B) \left( \frac{1}{2} a - 2 \delta x_B \right) \right) \left\{ \theta_A (1 - \theta_A) + 2 \theta_B (1 - \theta_B) \right\} \].

Figure 10. Dependence of the collective diffusion coefficient on the mean coverage of the system for the lattice shown in figure 9. \( a = 0.37 \) nm, \( E_A = 0 \) eV, \( E_B = 0.18 \) eV, \( E_C = 0.48 \) eV, \( E_{AB} = 0.33 \) eV and \( E_{BC} = 0.63 \) eV. The bottom curve is for the \( x \)-direction and the upper one for the \( y \)-direction. Temperature \( T = 473 \) K and attempt frequency \( \nu = 2 \cdot 10^{13} \) s\(^{-1}\).

Figure 11. Lattice for Ga adatom diffusing at GaAs(001)-(2 \times 4) \( \beta 2 \), based on [38]. Dashed line shows an elementary cell.

\[ \text{https://doi.org/10.1088/1742-5468/aac142} \]
In the above we used the denominator $N = \theta_A (1 - \theta_A) + 2 \theta_B (1 - \theta_B)$ and the variational parameters should be taken from equation (60). The obtained formula is valid for any value of the coverage $\theta$. For $\theta \to 0$ we have $\Delta_{AB}^x = 0$ but $\delta_B^x \neq 0$ and

$$D_x = \frac{4W_{AB}W_{BA}(W_{BB}^h + 2W_{BB}^d)}{(2W_{AB} + W_{BA})(W_{BA} + 2W_{BB}^h + 4W_{BB}^d)} a^2,$$

which is the same expression as the one obtained in [25].

Now let us consider diffusion in the $y$-direction. There are three variational phases related to that direction: $\delta_A, \delta_B^y$ and $\Delta_{AB}^y$. However, they enter the numerator (59) only as the difference $\delta_B^y - \delta_A$. Therefore, we can use that difference as a new parameter $\delta_{AB}^y$ reducing the number of independent variational phases to two. After differentiating we get

$$\delta_{AB}^y = -\frac{a}{4}$$

$$\Delta_{AB}^y = 0.$$

Even though we allowed for a non-zero value of $\Delta_{AB}^y$ it turned out to be zero. It reflects the fact that the two channels of diffusion in the $y$-direction, one through $A$ sites and the other through $B$ sites, are independent from each other. The final result for the diffusion coefficient is

$$D_y = a^2 \frac{W_{AA} \theta_A (1 - \theta_A) + 2 (W_{BB}^h + W_{BB}^d) \theta_B (1 - \theta_B)}{\theta_A (1 - \theta_A) + 2 \theta_B (1 - \theta_B)}.$$

Figure 12. Dependence of the collective diffusion coefficient on the mean coverage of the system for the lattice shown in figure 11. $a = 1.13$ nm, $E_A = 0$ eV, $E_B = 0.3$ eV, $E_{AB} = 0.8$ eV, $E_{BB}^h = 0.7$ eV and $E_{BB}^v = E_{BB}^d = 0.9$ eV. The bottom curve is for the $x$-direction and the upper one for the $y$-direction. Temperature $T = 473$ K and attempt frequency $\nu = 2 \cdot 10^{13}$ s$^{-1}$.
Since the contributions to the diffusion in the $y$-direction from the $W_{AB}$ jumps cancel out, the above expression does not depend on that jump rate. It is easy to see that in the $\theta \to 0$ limit one again gets the result obtained in [25].

Again we illustrate the results by plotting the dependence of the diffusion coefficients as functions of the coverage in figure 12 with the values of the barriers taken from [38]. We can see that there is a high anisotropy in the whole range of the coverage. The behaviors of diffusion in the two directions are completely distinct. Diffusion along $x$-direction is mostly through three adsorption sites: one deeper ($A$) and two shallow ones ($B$). Therefore, it is similar to the 1D case discussed in [28]. There is a characteristic peak at $\theta = 1/3$ related to ordering of the system at that coverage, in which sites $A$ are completely filled while sites $B$ are free. On the other hand, diffusion along $y$-direction exhibits a behavior of switching between the deep and the shallow diffusive channel. Such behavior was earlier observed in the model of hills and valleys [34], where the number of sites in the deep channel and the shallow one was equal and the transition between them occurred at $\theta = 1/2$ instead of $\theta = 1/3$.

4. Conclusions

We have formulated in a simple way a variational method of analyzing collective diffusion of particles adsorbed at lattices of arbitrary geometry, interacting by infinite on-site repulsion, excluding double site occupancy. We have derived a convenient variational formula which is expressed by all jump rates and equilibrium occupancies of the adsorption sites in a given system, that is its energetic landscape. Finding diffusion coefficients from that formula is a simple and straightforward procedure. It has been shown how the method can be applied to various systems, including real ones with specific values of the energetic barriers.

We showed explicit calculations of the diffusion coefficient based on our variational approach for a few lattices taken from [24] and [25]. In each case our results reproduce the expressions for the single-particle diffusion coefficient (taking the limit $\theta \to 0$) calculated in those publications. Our approach allows to find the expressions for the diffusion coefficient for any value of the system’s coverage $\theta$. For the values of $\theta$ between 0 and 1 the effects of inter-particle correlations become important and the collective diffusion coefficient is different from the one obtained without assuming correlations in the system. Only in the case with identical adsorption energies of all sites the diffusion coefficient does not depend on the coverage [33, 35]. However, in real systems that condition is rarely fulfilled.

The presented method was applied to two different reconstructions of GaAs(001) surface and we can study the coverage dependence of the diffusion coefficient. Increasing Ga coverage not only changes the value of the diffusion coefficient, but also dramatically influences the ratio of diffusion in two main directions. At the surface of $c(4 \times 4)$ reconstruction diffusion changes from isotropic for low Ga coverages into strongly 1D for high Ga coverages, for which diffusion coefficients in two directions differ by three orders of magnitude. At the surface of $(2 \times 4)$ $\beta 2$ reconstruction symmetry diffusion of
Ga adatoms is faster in one direction for all coverages, but ratio between $D_x$ and $D_y$ changes from three orders of magnitude, then decreases to one for coverage 0.35 and for higher coverages increases again. Diffusion is never isotropic for this reconstruction of GaAs(001) surface.

It is important to note that the approach presented in this article is not limited to the examples shown in the section with the results. The variational method is not dependent on the symmetry of the lattice, it is the variational parameters whose values adjust to the geometry of the energetic landscape and the correlations between the diffusing particles to give a proper expression for the diffusion coefficient. Our approach is also not limited to two dimensions, without any modifications in the formalism one can apply it also to analyze bulk diffusion.

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Appendix

Grand canonical description of the lattice gas of adsorbed, diffusing particles is a very convenient tool. It allows us to calculate easily all equilibrium quantities that are used in our analysis of the diffusion process. The derivation of grand canonical formulas can be found in textbooks [39, 40]. Below we will show how variables needed in our calculations, such as local (12) and global density (13), compressibility (15) and correlation functions used in (17) or (24) can be expressed as functions of the chemical activity $z$. Our model is a lattice gas of sites of different local energies $E_i$, each of which can be either empty or occupied by a single adparticle. Variable $n_i = 0,1$ describes temporary occupation of the site. Hamiltonian of the system can be written as

$$H = \sum_i^n E_i n_i$$

and grand canonical analysis of this system starts with derivation of the partition function $Z$ and global density $\theta$, that in the case of Hamiltonian (A.1) can be expressed as

$$Z = \prod_{i=1}^n \sum_{n_i=0}^1 z^{n_i} e^{-\beta E_{ni}}$$

$$\theta = \frac{1}{n} \frac{1}{z} \frac{\partial}{\partial z} \ln Z = \frac{1}{n} \sum_{i} \frac{z e^{-\beta E_i}}{1 + z e^{-\beta E_i}}.$$  \hspace{1cm} (A.2)

The two equations written above are parametric formulation of the statistical description of equilibrium properties of the lattice gas model. Chemical activation constant $z$ is the parameter that is reduced when we solve these equations. After this procedure all properties are expressed as functions of the global density $\theta$. The first of such values that is used further in the evaluation procedure is the local density $\theta_i = \theta_A$ at the site of a given energy $E_A$. For the local density $\theta_A$ the expression (12) is easy to find as one
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of the terms in the last sum of the formula (66). The reduction of \( z \) variable from equations (12) and (66) analytically is usually not possible. In such a case typical procedure is to plot interesting curves parametrically, which means that we set some value of \( z \) and calculate \( \theta_A \) and \( \theta \) for this \( z \), then \( z \) is changed and the next point is calculated in the same way. For all other expressions within the article the same procedure is used. Besides the local density we calculate also the denominator of the diffusion coefficient with the help of grand canonical approximation, which gives us equation (15). It is calculated from equation (13) as

\[
\mathcal{N}(0) = n \frac{\partial \theta}{\partial \ln(z)}.
\]

(A.3)

In the form (15) of the denominator and also in all correlation functions that are derived to use in the numerator (24) it is easy to see that the local densities separate. This is a typical property of non-interacting particles, directly resulting from the form of the partition function (66). Densities factorize, however they are not completely separated, because they are dependent on the same chemical activity \( z \). For a system without interactions the solution presented here is exact. However, if particles interact with each other, one needs to use some approximation such as random phase or mean field approximation in order to find the equilibrium state. On the other hand, the correlations in the kinetic part of the diffusion coefficient are described by variational parameters and they do not factorize.

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