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Diffusion on anisotropic lattices of square and hexagonal symmetry

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ABSTRACT

We calculate diffusion coefficients of many particles jumping over a few types of crystal lattices of square and hexagonal symmetry. Lattices differ by particle jump rates modified by the surface reconstruction or presence of some defects. We use the variational approach invented for the analysis of the collective diffusion coefficients. When all adsorption sites have the same energy and only the site blocking interactions are present, the collective diffusion coefficient is expressed by the same formula as the one for the single particle diffusion. Our calculations show in several examples how the arrangement of different jump rates along the lattice affects direction and character of the particle diffusion.

1. Introduction

Diffusion plays an important role in various processes that occur on crystal surfaces, for example crystal growth or formation of nanostructures such as islands or chains. In each system particles are adsorbed at sites of surface lattice of given geometry. Particles jump from site to site with rates depending on the potential energy landscape, which in turn is related to the symmetry of concrete crystal surface. Regular lattices of adsorption sites of square or hexagonal symmetry quite often change due to reconstruction of the surface [1,2], impurities [3], defects [4], presence of adsorbed atoms [5,6] or the strain inside the crystal [7,8]. Deformation of the surfaces results in changes of the individual jump rates. It often leads to the anisotropic diffusion [9,10]. In this work we study diffusion of particles over some deformed lattices of square and hexagonal symmetry as the (1 1 1) face of fcc metals and the (0 0 0 1) face of hcp metals. The (1 1 0) face of bcc metals can be considered as a distorted hexagonal lattice [11]. Due to reconstruction it can also appear at the (1 0 0) face of Au or Pt [12,13]. Structures similar to those studied here can emerge also by reconstruction of Si (0 0 1) and Si (1 1 1) [14]. Transition rates of jumping particles at reconstructed surfaces can be modified due to the change of the energy of some sites [15], or by reduction or increase of the energy barrier between two sites of the same energy [9]. Below only the second case will be studied.

2. Variational approach

Lattice gas systems are quite effective in modelling systems of particles diffusing over lattices of different geometries. Diffusion of many particles treated as one assembly is called collective diffusion or chemical diffusion. It is studied in a system of a gas of particles which reside at adsorption sites in a lattice where double occupancy is forbidden. Time evolution of the whole system is defined by a set of master rate equations for the probabilities $P(\{c\}, t)$ that a microscopic *microstate* $\{c\}$ of a lattice gas occurs at time t.

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

$\{c\}$ 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.

We model dynamics over reconstructed surfaces by inhomogeneous lattice systems. In particular when all sites have the same equilibrium energy, all changes are set to the jump barriers between consecutive sites. As we will see below the collective diffusion problem in such a case is given by the same equations as these for the single-particle diffusion. First we will derive these equations in the same way as it was done in Ref. [16] for homogeneous systems and then the same property of particle diffusion will be seen in the variational approach we apply to the problem. If a particle jumps between sites of the same energy, transition rates in two opposite directions are equal, we have $W(\{c\}, \{c'\}) = W(\{c'\}, \{c\})$. Now, let us sum both sides of the Eq. (1) over all the microstates $\{c\}$ under condition that one chosen site i is occupied. In such a way

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we get equation for a local density of particles $\rho_i(t) = \sum_{\{c\}} n_i P(\{c\}, t)$ at site of position specified by vector $\mathbf{i}$, where $n_\mathbf{i} = 0, 1$ is the site occupation. Particles jump only between nearest neighboring sites, hence the only nonzero elements of the transition matrix are $W(\{c\}, \{c'\}) = W(\mathbf{i}, \mathbf{j})$ and describe rate of jump between site $\mathbf{i}$ and neighboring site $\mathbf{j}$. Now, the equation for time dependence of the mean density is

$$\frac{d}{dt}\rho_\mathbf{i}(t) = \sum_{<\mathbf{j}>} [W_{\mathbf{j},\mathbf{i}} P(n_\mathbf{j}, 1 - n_\mathbf{i}, t) - W_{\mathbf{i},\mathbf{j}} P(n_\mathbf{i}, 1 - n_\mathbf{j}, t)] \tag{2}$$

where $P(n_\mathbf{j}, 1 - n_\mathbf{i}, t)$ is the joint probability of finding a particle at the site $\mathbf{j}$ and not finding one at the site $\mathbf{i}$ at the time t and the sum is performed over all the neighboring sites of $\mathbf{i}$. Because finding a particle at a site and not finding one at the same site are mutually exclusive events, the following identities hold:

$$\begin{aligned} P(n_\mathbf{j}, 1 - n_\mathbf{i}, t) + P(n_\mathbf{j}, n_\mathbf{i}, t) &= \rho_\mathbf{j}(t) \\ P(n_\mathbf{i}, 1 - n_\mathbf{j}, t) + P(n_\mathbf{i}, n_\mathbf{j}, t) &= \rho_\mathbf{i}(t) \end{aligned} \tag{3}$$

Now, when we use the symmetry of transition rates $W_{\mathbf{i},\mathbf{j}} = W_{\mathbf{j},\mathbf{i}}$ and insert relations (3) into (2), the master equations (1) reduce to the form:

$$\frac{d}{dt}\rho_\mathbf{i}(t) = \sum_{<\mathrm{ij}>} W_{\mathbf{i},\mathbf{j}} [\rho_\mathbf{j}(t) - \rho_\mathbf{i}(t)] \tag{4}$$

This is the master equation for a local density of particles diffusing on the lattice with the jump rates $W_{\mathbf{i},\mathbf{j}}$. Variable $\rho_\mathbf{i}$ is calculated for many-particle system and means average occupation value at site $\mathbf{i}$, but for a single particle it can be replaced by a probability of finding a particle at a site $\mathbf{i}$. When we do such replacement, we have master equation for a single particle wandering over potential landscape described by values of transition rates $W_{\mathbf{i},\mathbf{j}}$. This identity proves that single particle diffusion and collective particle diffusion are given by the same equations as long as the equilibrium energy at each lattice site is the same, what gives $W_{\mathbf{i},\mathbf{j}} = W_{\mathbf{j},\mathbf{i}}$ symmetry. Below we show that the variational approach invented for the many-particle systems is a very effective method to describe this kind of diffusion over two-dimensional lattices.

The variational approach to collective diffusion was first proposed in [17] and then applied in [18–23] for various systems. It is based on the idea that the diffusion coefficients come from the lowest eigenvalue of the rate matrix $\hat{M}$ [24,25] which appears in the Fourier-transformed master equation (1):

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

Elements $P_{\{m\}}(\mathbf{k}, t)$ of the vector $\mathbf{P}(\mathbf{k}, t)$ are labelled by the configuration $\{m\}$ – the relative arrangement of the particles in the microstate $\{c\}$. They are the Fourier transforms of $P(\{c\}, t)$. Elements of the transformed rate matrix $\hat{M}$ depend on the jump rates of a particle and are also labelled by the configuration $\{m\}$. In order to approximate the lowest eigenvalue of the matrix we assume some trial eigenvector and calculate the expression:

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

$\phi(\vec{k})$ is a trial eigenvector in this variational approach. Rate matrix $\hat{M}$, eigenvalue λ and eigenvector ϕ operate in the Fourier space of $\vec{k}$ wavevectors. This approach is applied below to various systems with the same site energies, and different jump barriers from site to site. The diffusing particles interact with each other only through blocking interactions (multiple occupancy is forbidden). In such cases components $\phi_{\{m\}}$ of a trial eigenvector can be assumed in the following shape:

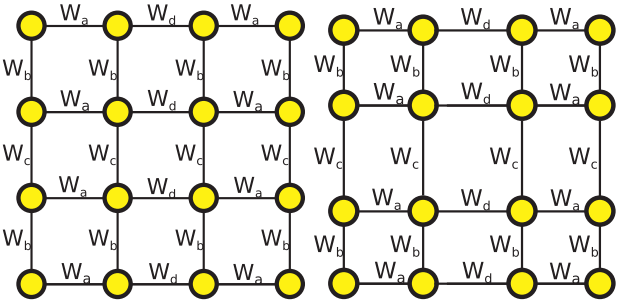

Fig. 1. Rates of jumps in the first lattice of square symmetry and lattice distorted for a concrete choice of jump rates.

$$\phi_{\{m\}}(\vec{k}) = e^{i(k_x\delta_0^x + k_y\delta_0^y)} + \sum_{j=1}^{N-1} e^{i(k_x x_j + k_y y_j + k_x\delta_j^x + k_y\delta_j^y)} \tag{7}$$

where position of the j-th particle in relation to the arbitrarily chosen reference particle is given by the (x_j, y_j) vector and N is the total number of the particles in the system. The values of the variational parameters δ_j^x and δ_j^y (δ_0^x and δ_0^y for the reference particle) should be chosen in such a way that λ_D^{var} has the smallest possible value. It is done by differentiating λ_D^{var} with respect to those parameters.

$\hat{D}_{var}$ can be also written as the ratio:

$$\vec{k}\hat{D}_{var}\vec{k} = \frac{\mathcal{M}(\vec{k})}{\mathcal{N}(\vec{k})} \tag{8}$$

where $\mathcal{M}(\vec{k})$ is the numerator of (6) and in our case

$$\mathcal{M}(\vec{k}) = \sum_{<j,k>}^{N} W_{j,k}[k_x(x_k - x_j) + k_y(y_k - y_j) + k_x(\delta_k^x - \delta_j^x) + k_y(\delta_k^y - \delta_j^y)]^2 \rho(1 - \rho) \tag{9}$$

$W_{j,k}$ is the probability of the particle jump from site j to k and ρ is the system density. Denominator $\mathcal{N}(\vec{k})$ now reduces to

$$\mathcal{N}(\vec{k}) = N\rho(1 - \rho) \tag{10}$$

and the diffusion coefficients will not depend on the system density in agreement with the previously derived Eq. (4).

3. Results

We study collective diffusion over a few lattices of square and hexagonal symmetry with jump rates ordered in various ways using the approach described above. Each choice of jump rate patterns corresponds to different lattice reconstruction if we assume that value of jump rate is inversely proportional to the length of links between sites. In general case both diffusion coefficients will depend on all the transition rates in the system due to the coupling of diffusion in the x and y directions. In addition to D_{xx} and D_{yy} coefficients in some models we'll get also D_{xy}, which is responsible for rotation of the main axes of diffusion. Let us first analyse a lattice where the rates of jumps both in the x-direction and the y-direction alternate along their own directions (Fig. 1). At the right side of Fig. 1 links between sites are moved according to the specific choice of jump rates, i.e. the smaller rate the longer the corresponding link is. The following diffusion coefficients:

$$D_{xx} = \frac{2W_aW_d}{W_a + W_d}, \quad D_{yy} = \frac{2W_bW_c}{W_b + W_c} \tag{11}$$