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Diffusion of Particles Adsorbed on a Reconstructive Surface

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Abstract. The influence of surface reconstruction on diffusion of particles, adsorbed on the surface, is investigated in the framework of symmetrical four-position model. The analytical expressions for the free energy and chemical and jump diffusion coefficients are obtained assuming the lateral interaction between the particles is negligibly small. The coverage dependencies of the tracer, jump and chemical diffusion coefficients are calculated using the expressions and MC simulations. The results demonstrate clearly a drastic change of the behavior of all diffusion coefficients on the reconstructed surface.

Keywords: lattice gas, surface reconstruction, surface diffusion, phase transitions

1. Introduction

Phase transitions in two-dimensional systems have not only a fundamental but also a practical, technological interest. One of the most prominent examples of such phenomena is the adsorption-induced surface reconstruction. Surface reconstruction can be a spontaneous or adsorbate-induced phenomenon. The effect of chemisorption is the restructuring of the substrate surface resulting in a completely new surface structure. One of the best studied systems which regard to the adsorbate-induced surface reconstruction is the hydrogen adsorbed on the face (001) of tungsten, $H/W(001)$. Since its discovery in 1971 (Yonehara and Schmidt, 1971) the system has been a subject of numerous investigations. The surface layer W atoms displace along the surface diagonals by ∼0.2 Å, forming zigzag chains parallel to the [110] direction and resulting reconstructed phase has a $C(2 \times 2)$ order. The theoretical description of various surface phenomena in such systems presents a considerable challenge. It is not surprising that a great deal of efforts is devoted to develop simple models, which have the advantage of the exact treatment, despite their oversimplification of the real situation. The lattice gas models of this phenomenon possessing all symmetry elements were developed by Roelofs and Wendelken in 1986 (see also Tarasenko and Chumak, 1993, 1995; Tarasenko et al., 1999). In these models, each surface atom can be located in four equilibrium positions, placed symmetrically around the square lattice vortices. Neglecting the adsorbate-adsorbate interactions, an analytical treatment is performed which gives well-known analytical expression for the free energy of the system. In the framework of this model we study the influence of the adsorption-induced surface reconstruction on the surface diffusion of the adsorbed particles. The jump and chemical diffusion coefficients are evaluated by using the analytical expressions obtained in the local equilibrium approximation. We use the Monte Carlo simulations to obtain the tracer diffusion coefficient and to check the theoretical dependencies of the jump and chemical diffusion coefficients.

2. Model and Hamiltonian

In the following we will consider an ideal solid surface with square symmetry. According to the model of reconstruction every surface atom can occupy any of the four minima of the potential relief placed symmetrically around sites of square lattice as shown in Fig. 1. Guest particles are adsorbed in the positions on

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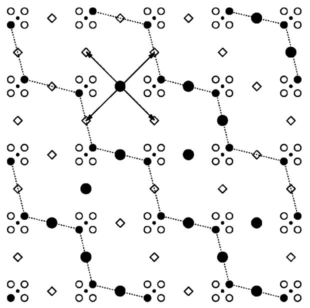

Figure 1. Schematic view of the reconstructive lattice. Empty and filled small circles denote the potential minima and surface atoms, correspondingly. Diamonds and big filled circles denote adsorption sites and adsorbed particles. Arrows denote four possible jumps of a particle to its *nn* empty adsorption sites. Thin lines show zigzag chains of the surface atoms in the ordered reconstructed phase.

the middle of any bond of the host lattice. The surface atom position in the ith lattice site is determined by a vector $\vec{s}_i = (s_i^x, s_i^y)$. We define two normalized components of its displacement as $s_i^{x,y} = \pm 1$ along the OX and OY directions, respectively. The signs of the components s_i^x (s_i^y) depend on whether the surface atom is located in the right/left (up/down) minima, as follows

$$s_i^x = \begin{cases} +1, & \text{a right minimum is occupied,} \\ -1, & \text{a left minimum is occupied,} \end{cases}$$
$$s_i^y = \begin{cases} +1, & \text{an up minimum is occupied,} \\ -1, & \text{a down minimum is occupied.} \end{cases} \quad (1)$$

Therefore, the state of the surface is determined by two sets of the Ising spins $\{s_i^x\}$, $\{s_i^y\}$, where index i labels the sites. The state of the adsorbed particles is described, as usual, by a set of occupation numbers of the adsorption sites, $\{n_{(ij)}\}$, where $n_{(ij)}$ is equal to 1(0) if the (ij)th bond is occupied (empty). One can obtain the Hamiltonian of the model quite easily, expanding the energy of lateral interaction between the particles into a series about small displacements of surface atoms

$$H = \sum_{hb} \left\{\varphi_{\parallel} s_i^x s_j^x + \varphi_{\perp} s_i^y s_j^y + \lambda\left(s_i^x - s_j^x\right) n_{(ij)}\right\} + \sum_{vb} \left\{\varphi_{\parallel} s_i^y s_j^y + \varphi_{\perp} s_i^x s_j^x + \lambda\left(s_i^y - s_j^y\right) n_{(ij)}\right\} - \varepsilon_a N_a. \quad (2)$$

Here ε_a is the depth of the adsorption minima; $\varphi_{\parallel,\perp}$ are the pair interaction energies of the *nn* spins s_i^x in the OX and OY directions, respectively; λ is the interaction energy between the adsorbed particle and its *nn* spins; symbols *hb* and *vb* denote summation over the horizontal and vertical bonds, respectively.

The grand partition function, Q, and the number of particles, N_a, have the following forms

$$Q = \sum_{\{\vec{s}_i, n_{(ij)}\}} \exp(\mu N_a - H), \quad N_a = \sum_{hb,vb} n_{(ij)} \quad (3)$$

where μ is the chemical potential (henceforth we use the system of units with $k_{\mathrm{B}}T = 1$).

Equation (3) can be reduced to the analytic form after summation over all dummy variables $n_{(ij)}$

$$Q = \exp 2N(\alpha + F_I) \quad \text{where}$$
$$F_I = \frac{1}{2\pi} \int_0^{\pi} \ln \times [2(\cosh 2I_1 \cosh 2I_2 + k^{-1}\sqrt{1 + k^2 - 2k\cos 2\theta})] d\theta. \quad (4)$$

Here F_I is the free energy of an anisotropic Ising model (Baxter, 1982) and other quantities are defined as follows

$$\begin{aligned} I_1 &= |\varphi_{\parallel} + \phi|, \quad I_2 = |\varphi_{\perp}|, \\ k &= (\sinh 2I_1 \sinh 2I_2)^{-1}, \\ \phi &= \alpha - \ln(1 + \exp\mu), \\ \alpha &= \ln\{[1 + \exp(\mu + 2\lambda)]\,[1 + \exp(\mu - 2\lambda)] \\ &\quad \times (1 + \exp\mu)^2\}/4, \end{aligned} \quad (5)$$

where the depth of the potential relief, ε_a, is absorbed into the chemical potential, μ.

To investigate the kinetic properties of the system, one must know the detailed mechanisms of the particle transitions between the potential minima. We suppose that the adsorbed particles can jump to their *nn* empty minima only. The surface atoms can jump along the sides of an elementary square only: $s_i^x \to -s_i^x$ or $s_i^y \to -s_i^y$. The diagonal jumps $\vec{s}_i \to -\vec{s}_i$ are forbidden.

An activated particle must surmount the potential barrier between the initial site and the final site. The activation barrier, E_a, is given by the difference between the saddle point energy E_s and the initial state energy E_i. The height of the barrier is affected by the presence of adjacent atoms due to the lateral interactions. The model of the jumps includes the lateral interactions at the saddle point as follows $E_s = \eta(E_i + E_f)$, where E_f is the particle energy in the final state. The expression for the saddle point energy, E_s depends on the parameter η, which characterizes the “freedom” of an activated particle in the saddle point. If $\eta = 0$, the particle in the saddle point does not interact with its surrounding. Using the local equilibrium approximation one can obtain easily the following expressions for the chemical diffusion coefficients (Chumak and Tarasenko, 1980, 1996)

$$\begin{aligned} D_c^{\text{para}} &= D_0 \exp(\mu - 2\alpha) \\ &\quad \times \left\{ \left[\mathcal{A} + \langle s_i^x s_{i+1}^x \rangle \mathcal{B} \right]^2 + \langle s_i^x \rangle^2 \mathcal{C}^2 \right\} \chi_T^{-1}, \\ D_c^{\text{perp}} &= D_0 \exp(\mu - 2\alpha) \\ &\quad \times \left\{ \left[\mathcal{A} + \langle s_i^x s_{i+1}^x \rangle \mathcal{B} \right]^2 - \langle s_i^x \rangle^2 \mathcal{C}^2 \right\} \chi_T^{-1}. \qquad (6) \end{aligned}$$

Here D_c^{para} and D_c^{perp} are the chemical diffusion coefficients along and across the surface atoms chains, correspondingly; the angle brackets $\langle \cdots \rangle$ mean the ensemble averaging; $\theta = N_a/2N$ is the surface coverage of the adsorbed atoms; $D_0 = D_c(\lambda = 0)$ and other quantities have the following forms:

$$\begin{aligned} \chi_T &= \partial^2\alpha/\partial\mu^2 + \left(\partial^2 F_I/\partial I_1^2\right)(\partial\phi/\partial\mu) \\ &\quad - \langle s_i^x s_{i+1}^x \rangle \partial^2\phi/\partial\mu^2, \qquad \langle s_i^x \rangle = (1 - k^2)^{1/8}, \\ \theta &= \partial\alpha/\partial\mu - \langle s_i^x s_j^x \rangle \partial\phi/\partial\mu, \\ \langle s_i^x s_j^x \rangle &= -(\partial F_I/\partial I_1)\, \text{sign}(\varphi_\parallel + \phi), \\ \beta &= \ln[1 + \exp(\mu + 2\lambda)][1 + \exp(\mu - 2\lambda)]^{-1}/4, \\ \mathcal{A} &= \cosh^2(\beta - \eta\lambda)\cosh\phi \\ &\quad - \sinh^2(\beta - \eta\lambda)\sinh\phi, \\ \mathcal{B} &= \cosh^2(\beta - \eta\lambda)\sinh\phi \\ &\quad - \sinh^2(\beta - \eta\lambda)\cosh\phi, \\ \mathcal{C} &= 2\cosh(\beta - \eta\lambda)\sinh(\beta - \eta\lambda)\exp(-\phi). \qquad (7) \end{aligned}$$

3. Results and Discussion

There are four possible ordered phases of the clean reconstructed surface, corresponding to the four combinations of signs of the interaction parameters I_1 and I_2. We consider here the case when the both interaction parameters are positive and equal ($\varphi_\parallel = \varphi_\perp = 100$ K). For this set of parameters the temperature of the reconstruction for clean surface, T_c is about 227 K. The adsorption of the half monolayer increases T_c to 238 K ($\lambda = 100$ K).

We have calculated the coverage dependencies of the mean square surface coverage fluctuations, χ_T, and the tracer, D_t, jump, $D_j = D_c\chi_T/\theta$, and chemical, D_c, diffusion coefficients for $\eta = 0$. To show clearly the influence of the surface reconstruction on the particle diffusion the temperature is chosen well below critical ($T = 120$ K). The reconstructed $C(2 \times 2)$ phase has a twofold symmetry and diffusion of particles on it is anisotropic. The coverage dependencies of the diffusion coefficients along and across the surface atoms chains are essentially different.

Another interesting peculiarity of the $C(2 \times 2)$ structure is the discrepancy between the theoretical results and MC data in the direction perpendicular to the surface atoms chains. The theoretical expressions for $D_{j,c}^{\text{para}}$ coincide very well with the corresponding MC data. The same expressions for $D_{j,c}^{\text{perp}}$ give quantitatively and even qualitatively different coverage dependencies as compared with the MC simulations (see corresponding curves in Fig. 3). To understand why the analytical expressions give perfect description in one direction and almost completely fail in other direction, we consider the migration of the particles in detail. The reconstruction results in the rows of the deep and shallow adsorption sites. There are two types of the particle jumps, which may be called as slow (from the deep sites) and fast (from the shallow sites). The main contribution to the particle migration along the chains give jumps of the same type: slow ($\theta < \frac{1}{2}$ML) or fast ($\theta < \frac{1}{2}$ML). It is possible to say that in this direction particles jump over a homogeneous lattice. The approximations used for the derivation of the analytical expressions Eq. 6 work very well on the homogeneous lattices (Tarasenko et al., 1999) The coverage dependency of the chemical diffusion coefficient, D_c^{para}, have a step-like form and coincide rather well with the numerical data.

When migrating across the chains, particles perform slow and fast jumps in an alternative order. Such alternating jump successions are typical for inhomogeneous square lattices (Tarasenko and Jastrabik, 2002; Tarasenko et al., 2004). The coverage dependencies of the diffusion coefficients are rather similar in the both cases also. It was shown in the above mentioned references that the correct description of the particle diffusion on the heterogeneous lattices should account for the correlation between the successive jumps of a particle from a deep site to its *nn* shallow site and the backward jump to the initial site. The exact calculation of the correlation is impossible. We can only to make estimations of the chemical and jump diffusion coefficients in the limit of low temperatures $\exp 4|\lambda| \gg 1$.

The coverage dependencies of the tracer diffusion coefficient are plotted in Fig. 2. It should be noted that

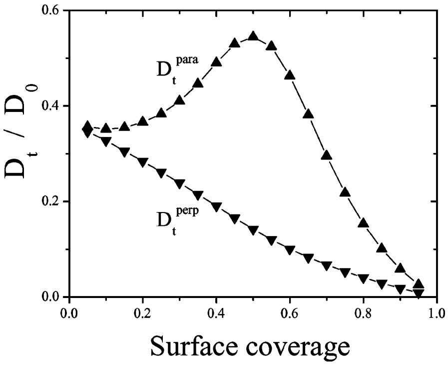

Figure 2. The tracer diffusion coefficients D_t^{perp} and D_t^{para} vs. coverage θ. The MC data only.

the dependencies $D_t^{\text{perp}}(\theta)$ and $D_t^{\text{para}}(\theta)$ are very similar to the corresponding dependencies for the jump diffusion coefficient $D_j^{\text{perp}}(\theta)$ and $D_j^{\text{para}}(\theta)$ despite the strong interaction with the surface atoms.

In Fig. 3 we present coverage dependencies of the jump and chemical diffusion coefficients across and along the chains. The both components, $D_{j,c}^{\text{para}}$ and $D_{j,c}^{\text{perp}}$, behave very different. The tiny minimum in D_c^{perp} at the half monolayer arises due to the singular behavior of the correlation factor and has a non-physical origin. Nevertheless, the MC data are better fitted by the dependencies calculated with the account for the correlations between the successive jumps (solid lines). The correlation decreases the particle diffusion across the chains, especially at the half monolayer coverage $\theta = \frac{1}{2}$ML.

It should be mentioned that the surface diffusion of adsorbed hydrogen on reconstructive surface W(001) was investigated experimentally by the field emission fluctuation method (Daniels and Gomer, 1995) and by the linear optical diffraction technique (Lei Cai et al., 2002). The results of the investigations are rather controversial. In the former investigation three diffusion regimes have been found: temperature independent (tunneling) for $T < 140$ K, followed by a slightly activated diffusion between 140 and 220 K and strongly activated for $T > 220$ K. There is some diffusion anisotropy have been detected for tunneling and weakly activated regimes. The temperature dependencies for slightly activated and strongly activated regimes have Arrhenius form without any peculiarities. In the latter investigation the anomalous, non-Arrhenius behavior of the chemical diffusion coefficient have been observed. The temperature

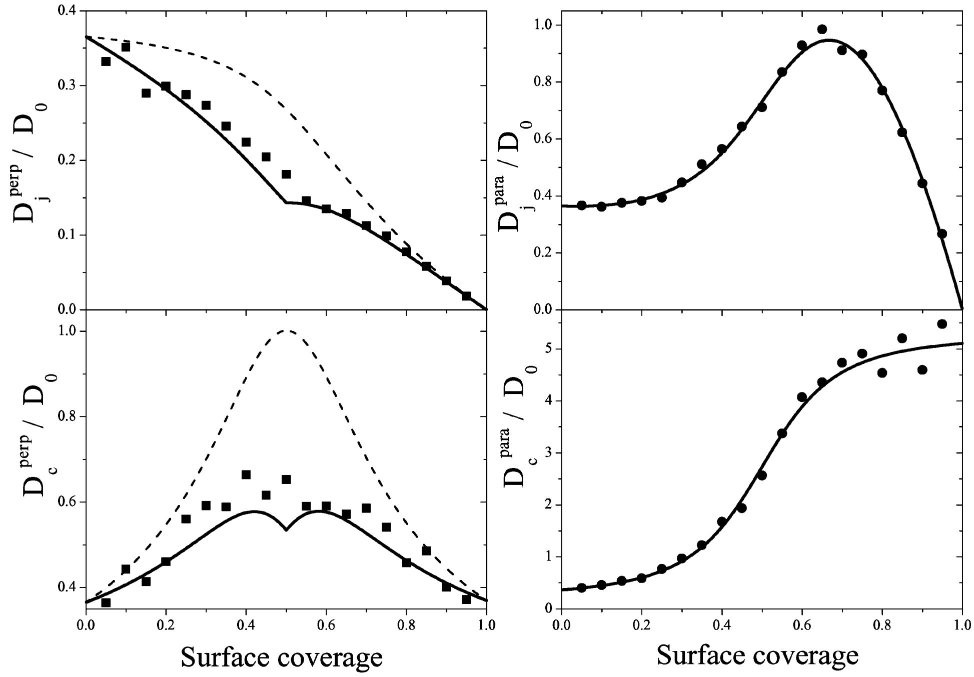

Figure 3. The coverage dependencies of the jump and chemical diffusion coefficients, $D_{j,c}^{\text{perp}}$, $D_{j,c}^{\text{para}}$. The solid and dash lines denote $D_{j,c}^{\text{perp}}$ calculated with and without account of the correlations between the successive jumps, correspondingly. Symbols denote MC data.

dependence has strong dip at the transition temperature. The dip had been predicted theoretically in the framework of the continuous displacive model of the surface reconstruction (Ala-Nissila et al., 1992). Authors did not find any noticeable anisotropy of the diffusion coefficient. The absence of the anisotropy may be explained by the averaging of the experimental data over two orthogonal degenerate domains of the reconstructed phase. The critical slowdown of the diffusion coefficient demonstrates clearly the strong influence of the surface reconstruction on the particle migration.

Summing up the results one should conclude that the theoretical description of the diffusion of particles adsorbed on the reconstructive surface is rather nontrivial. The surface reconstruction causes anisotropy of the particles migration. The coverage dependencies of the tracer, jump and chemical diffusion coefficients along and across the chains are qualitatively different. The analytical expressions for the jump and chemical diffusion coefficients give very good description of the surface diffusion in the direction parallel to the rows of the surface atoms only, when the particle migration proceeds over one type of sites (deep or shallow). In the perpendicular direction particles jump over deep and shallow sites in alternating order. For this direction the correlation between the successive jumps plays significant role and should be accounted for the correct description of the surface diffusion.

Acknowledgments

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