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Surface Science 532–535 (2003) 588–593

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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 adsorbed particles is investigated in the framework of simple two-position symmetrical model. Exact expressions for the free energy and diffusion coefficient are obtained neglecting the lateral interaction between the adsorbed particles. The critical behavior of the system is described by an anisotropic Ising spin model. The coverage dependencies of the chemical diffusion coefficient are calculated for different temperatures and interaction parameters. The dependencies show clearly the strong influence of the phase transitions, occurring in the system, on the particle migration. The chemical diffusion coefficient turns to zero at the critical points of the system.

Keywords: Models of surface kinetics; Non-equilibrium thermodynamics and statistical mechanics; Surface diffusion

The reconstruction on solid surfaces have strong impact on the properties of materials. Particles adsorbed on a surface can change the lateral interaction between surface atoms, thus inducing or inhibiting surface reconstruction. Adsorbate-induced reconstruction has been observed in different adsorption systems (see, for example, Refs. [1,2]). The reconstruction in the $H/W(001)$ adsorption system may be is the most popular and studied example of this phenomenon [3–5].

The statistical study of systems of strongly interacting particles is rather difficult. 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 phenomena. Some simple models of surface reconstruction have been proposed to investigate the influence of a surface reconstruction on kinetics of elementary rate processes and diffusion of particles [6–10].

We have investigated the diffusion of adsorbed particles over the reconstructive surface, using the model of reconstruction, considered in Ref. [9]. In this model every atom from the surface layer can occupy any of the two minima of the potential relief placed symmetrically around the sites of square lattice (see Fig. 1). The distance between the minima is small as compared with the lattice constant a. Particles can be adsorbed in the so-called “bridge” positions on the middle of any bond of the lattice. We assume that any surface atom interacts with its four nearest neighbor (nn) surface atoms and with the particles, adsorbed on the bonds connecting the surface atom with its nns. The state of a surface atom in the ith site is determined by the sign of its displacement, which is equivalent to the Ising spin $s_i = 1$, if the atom

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doi:10.1016/S0039-6028(03)00413-8

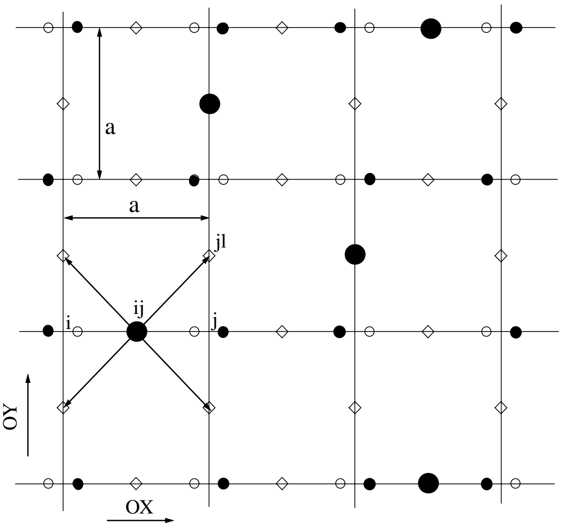

Fig. 1. Schematic view of the reconstructive lattice. Open circles denote the stable positions for the surface atoms, shown as the filled circles. Empty diamonds at the middles of the square lattice bonds denote adsorption sites. Adsorbed particles are denoted by the big filled circles. Arrows show four possible jumps of the adsorbed particle.

occupies the right minimum and $s_i = -1$, when it is in the left minimum. According to the definition, the top layer of surface atoms is equivalent to a square Ising spin model. The state of the adsorbed particle subsystem is described completely by the set of occupation numbers of the adsorption sites $\{n_{ij}\}$. Index ij labels bond connecting the ith and the jth sites and

$$n_{ij} = \begin{cases} 1 \text{ if the } ij\text{th bond is occupied,} \\ 0 \text{ if the } ij\text{th bond is empty.} \end{cases} \tag{1}$$

One can obtain the Hamiltonian of the whole system "spins + particles" quite easily, expanding the energy of pair interactions between the particles into a series about small displacements of surface atoms and keeping only the first non-vanishing terms in the series

$$H = \sum_{\text{hb}} \{\varphi_{\|} s_i s_j + [\lambda(s_i - s_j) - \varepsilon] n_{ij}\} + \sum_{\text{vb}} (\varphi_{\perp} s_i s_j - \varepsilon n_{ij}). \tag{2}$$

Here ε is the depth of the adsorption minima; $\varphi_{\|,\perp}$ are the nn pair interaction parameters of the surface atoms in the OX and OY directions, respectively, λ is the pair interaction energy between the nearest neighbor particle and surface atom; symbols hb and vb mean summation over horizontal and vertical lattice bonds, respectively. As the distance between any surface atom and its nn particles, adsorbed on the vertical bonds, does not change during atom transitions from the left minimum to the right and vice versa, the energy does not change also. Therefore, particles, adsorbed on the vertical bonds, do not influence the surface layer reconstruction.

All necessary thermodynamic quantities can be calculate via the grand partition function Q. As we neglect the particle lateral interaction, the grand partition function can be reduced to a partition function of the anisotropic Ising model after summation over all particle occupation numbers n_{ij}. The result of the summation can be written as follows:

$$Q = (1 + \exp\mu)^N \exp\{N[\varrho + F_I(I_1, I_2)]\}, \tag{3}$$

where, as usual, the depth of the potential minima ε is absorbed into the chemical potential μ; $F_I(I_1, I_2)$ is the free energy of an anisotropic Ising model

$$F_I(I_1, I_2) = \frac{1}{2\pi} \int_0^{\pi} \ln\{2[\cosh 2I_1 \cosh 2I_2 + \sqrt{1 + k^2 - 2k\cos 2\vartheta}]\} \, d\vartheta \tag{4}$$

and other quantities are defined as follows

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

At high temperatures, surface atoms are distributed randomly over the minima and the system is in a disordered state. As the temperature is lowered, the lateral interactions between surface atoms cause formation of an ordered phase, with a definite symmetry. The symmetry of the ordered phase is determined by the signs of the interaction parameters of the Hamiltonian of the system $\varphi_{\|,\perp}$.

There are four possible ordered phases of the clean reconstructed surface, corresponding to the four combinations of signs of the interaction parameters. The critical temperature of the surface reconstruction T_c is determined by the well-known equation: $\sinh 2I_1 \sinh 2I_2 = 1$. As adsorption of particles modifies the interaction parameter I_1, the critical temperature of reconstruction depends on the particle surface coverage θ.

One interesting property of the atom–particle interaction should be noted. As adsorbed particles try to orientate nn spins in the opposite directions (independently on the sign of the interaction parameter λ), they will inhibit reconstruction for $\varphi_\parallel < 0$ or increase the critical temperature in the case $\varphi_\parallel > 0$. Strong enough atom–particle interaction $|\lambda| > 2|\varphi_\parallel|$ would destroy the initially ordered phase and cause reconstruction into a phase with the symmetry, corresponding to the positive sign of interaction parameter $\varphi_\parallel$ [9].

To investigate the particle migration, one must know the microscopic mechanism of the particle transition from one adsorption site to another. We suppose that particles jump to their nn empty minima only, as shown in Fig. 1. Any particle can jump in the four possible directions. The jumping particle must surmount the potential barrier between the initial site and the final site. The height of the barrier is affected by the presence of adjacent surface atoms. Usually the interaction between an activated particle at the saddle point of the potential barrier ant its nns is neglected. Than, the jump frequency for a particle, jumping from the ijth to any empty nn adsorption site, for example, jlth, as shown in Fig. 1, has the following form: $v_{ij,jl} = v\exp[-\lambda(s_i - s_j)]$. We will consider the relaxation of the low-frequency, long-wavelength disturbances of the surface coverage in the so-called hydrodynamic limit. In this case the chemical diffusion coefficient, D_c, is expressed via the thermodynamic quantities [11].

$$D_c = D_0\theta_{vb}(1 - \theta_{hb})/\chi_T, \qquad (6)$$

where $D_0 = v\exp(-\varepsilon)a^2/2$ is the diffusion coefficient for non-interacting particles; $\theta_{vb,hb}$ are the mean values of the particle occupation numbers of the adsorption sites on the vertical and horizontal lattice bonds, respectively and χ_T denotes the isothermal susceptibility or the mean square surface coverage fluctuations: $\chi_T = \partial^2 F/\partial\mu^2$.

The second derivative of the free energy F over the chemical potential μ, is proportional to the second derivative of the free energy over the interaction parameter I_1, which has the well-known logarithmic divergence at the critical points of the system. Therefore, the chemical diffusion coefficient, D_c has the universal critical slowdown behavior $D_c \propto |\ln|T - T_c||^{-1}$.

We have calculated the coverage dependencies of the chemical diffusion coefficient for some values of the interaction parameters. As the particle adsorption influences only the atom–atom interaction along OX direction, there are two principally different cases only, that should be considered separately.

At first we consider the case of repulsive interaction between the atoms, $\varphi_\parallel > 0$. The coverage dependencies of the chemical diffusion coefficient are plotted in Fig. 2. At high temperatures the coverage dependence of the diffusion coefficient is rather weak (see curve 5 in Fig. 2). There is a smooth curve with a wide small maximum at $\theta \approx 0.75$. The dependency is qualitatively similar to those obtained for the diffusion of repulsive

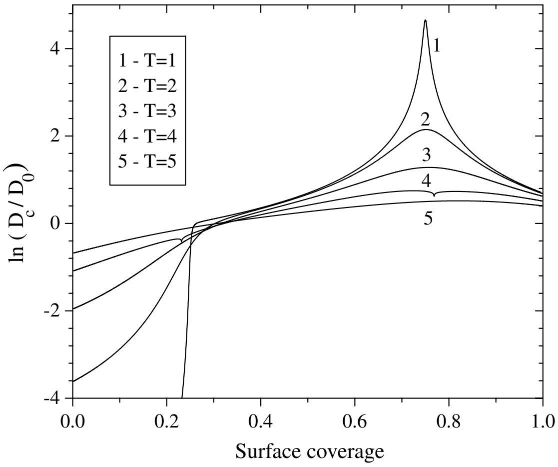

Fig. 2. The coverage dependencies of the chemical diffusion coefficient, $\ln D_c/D_0$ vs. θ. The values of the interaction parameters are the following: $\varphi_\parallel = 2\varphi_\perp > 0$, $\lambda = 5\varphi_\perp$. The temperature, T, is measured in the dimensionless units $k_B T/\varphi_\perp$.

particles on the honeycomb and square lattices [12,13]. As it was mentioned above, any particle tends to set nn spins in the opposite directions, thus creating unfavorable conditions for adsorption of other particles in its close vicinity. It is equivalent to an effective repulsive interaction between the adsorbed particles.

For small coverage the diffusion coefficient grows exponentially with the coverage as the average number of nns increases which causes the increase of the indirect repulsion energy between the particles. This effect is more pronounced at low temperatures, when the surface atom layer is ordered. In this case the nn spins are antiparallel. Therefore, the adsorption sites on the horizontal bonds have different depth in the alternating order. There are "deep" sites with depth equal to $\varepsilon + 2|\lambda|$ and "shallow" ones with the depth $\varepsilon - 2|\lambda|$.

At low coverage the diffusion of the particles proceeds mainly by jumps from the deep sites as particles are adsorbed in these sites. The diffusion coefficient $D_c(\theta = 0)$ is less than the diffusion coefficient of non-interacting particles D_0. It should be noted that the relaxation of the coverage disturbances proceeds by the particle jumps from sites with different depth. In this case the most slow process governs the total migration of the particles.

For high coverage ($\theta \to 1$) diffusion of particles is effectively described by the the jumps of "holes"—empty adsorption sites. It is easy to show that the lateral interaction between the holes is the same as between the particles. All holes are located in the "shallow" sites. Then, $D_c(\theta = 1) > D_0$ and the diffusion coefficient grows exponentially with the increasing of the hole coverage.

The chemical diffusion coefficient has a strong narrow maximum at $\theta = 3/4$-ML at low temperatures (see curve 1 in Fig. 2). At this coverage all deep sites are occupied (and all sites on the vertical lattice bonds are occupied also). This ordered phase is rather stable and the surface coverage fluctuations are strongly suppressed. The isothermal susceptibility has deep and narrow minimum at this coverage. Therefore, the diffusion coefficient has maximum.

At some temperatures the variation of the surface coverage, θ, causes the second order phase transitions of the atom surface layer from a disordered state to an ordered phase (surface reconstruction) and vice versa. The effective interaction energy between the surface atoms $I_1 = |\varphi_\parallel + \phi|$ depends on the coverage. The dependence is rather specific. The adsorbed particles do not influence the interaction at $\theta = 0$, ($\mu = -\infty$), which is quite obvious, and $\theta = 1$, ($\mu = \infty$), which is less obvious. The maximal influence takes place at the half monolayer coverage, $\mu = 0$ (see Eq. (5)). The critical line or dependence of the temperature of the surface layer reconstruction on the surface coverage, $T_c(\theta)$, is a convex function of the coverage, symmetrical about $\theta = 1/2$-ML. Fixing the temperature in the region $T_c(0) < T < T_c(0.5)$ and changing the surface coverage from zero to the monolayer, one crosses the critical line two times. In these critical points the chemical diffusion coefficient drops to zero (see curve 2 in Fig. 2). The critical slowdown of the diffusion coefficient, D_c, is determined by the logarithmic divergence of the isothermal susceptibility, χ_T.

More distinctly all critical peculiarities of the chemical diffusion coefficient are manifested for the case of attractive interaction between the atoms, $\varphi_\parallel < 0$ (the corresponding coverage dependencies of the chemical diffusion coefficient are

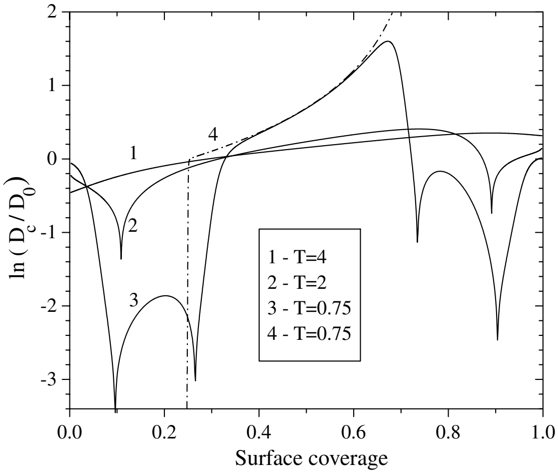

Fig. 3. The coverage dependencies of the chemical diffusion coefficient, $\ln D_c/D_0$ vs. θ. The values of the interaction parameters are the following: $\varphi_\parallel = -2\varphi_\perp < 0$, $\lambda = 5\varphi_\perp$ ($\varphi_\parallel = 2\varphi_\perp > 0$ for curve 4).

plotted in Fig. 3). It should be noted that the adsorbed particles produce the effective interaction, ϕ, with the sign opposite to the sign of the original lateral interaction $\varphi_{\|}$.

At high temperatures there is a weak coverage dependence of the chemical diffusion coefficient on the surface coverage. The surface layer is disordered and the influence of the atom–particle interaction on the migration is almost negligible. If the temperature decreases and falls into the region $T_c(0) > T > T_c(0.5)$, the surface layer is ordered at low and high coverages and disordered in the intermediate region as in this case the critical temperature is a concave function of the coverage, symmetrical around $\theta = 1/2$-ML. There is a critical slowdown of the chemical diffusion coefficient in the two critical points (curve 2 in Fig. 3).

The most interesting critical behavior of the chemical diffusion coefficient proceeds at the low temperatures in the case of strong atom–particle interaction, $|\lambda| > 2|\varphi_{\|}|$. There is a sequence of the order-disorder phase transitions and the diffusion coefficient is a rather complex, non-monotone function of the surface coverage (see curve 3 in Fig. 3). At low and high coverages, $\theta < 0.1$ and $\theta > 0.9$, the influence of the adsorption is weak and the surface layer of atoms is ordered. In the central region, $0.27 < \theta < 0.73$ the influence of the adsorption is maximal. The lateral effective atom–atom interaction changes its sign. It becomes repulsive despite the original attractive interaction, $\varphi_{\|} < 0$. The indirect atom–atom interaction via the adsorbed particles, ϕ, is strong enough to cause the reconstruction of the atom surface layer into the ordered phase with the symmetry corresponding to the repulsive atom–atom interaction, $\varphi_{\|} > 0$. These ordered phases are separated by the regions of the surface coverage where the atom surface layer is completely disordered even at $T = 0$. It means that the effective lateral atom–atom interaction parameter I_1 is equal to zero. Therefore, changing the surface coverage from zero to the monolayer, one crosses the critical lines four times. In the critical points the chemical diffusion coefficient turns to zero (see curve 3 in Fig. 3).

It is interesting to note the influence of ordering on the diffusion of particles. The chemical diffusion coefficient has the same values for the opposite values of the interaction parameter $\varphi_{\|}$ in the region where surface layer of atom has the same ordering. Curve 4 in Fig. 3 is plotted for the strong repulsive interaction, $\varphi_{\|} > 0$ (other interaction parameters are the same). The dependencies of the chemical diffusion coefficient coincides rather well if the surface coverage is not too close to the critical points. It is possible to say that the type of the ordering of the atom surface layer plays the decisive role in the adsorbed particles migration on this reconstructive surface.

It should be pointed out that the relation between the interaction parameters, we choose for the dependencies plotted in Figs. 2 and 3, is not such unrealistic as it may be thought at the first glance ($|\lambda| = 2.5|\varphi_{\|}|$). The interaction parameters are not the real interaction energies, but only the changes of the interaction energies, which are proportional to the first derivatives of the corresponding energies over the distance between the particles. Therefore, the atom–particle interaction energy can be markedly less that the atom–atom interaction energy but for the first derivatives the inequality can be reversed due to the fact that the distance between an atom and its nn adparticles is two times smaller as compared with the distance between the nn surface atoms.

Summing up all results one can conclude that surface diffusion can be significantly dependent on the surface reconstruction. For the model of reconstruction considered here the chemical diffusion coefficient has universal slowdown behavior $D_c \propto |\ln|t - T_c||^{-1}$ in the close vicinity of the critical points.

Acknowledgement

This work has been supported by the grant LN00A015 of the MSMT of Czech Republic.

References

[1] T.E. Felter, R.A. Barker, P.J. Estrup, Phys. Rev. Lett. 38 (1977) 1138.
[2] M.K. Debe, D.A. King, J. Phys. C 10 (1977) L303.

[3] L.D. Roelofs, J.F. Wendelken, Phys. Rev. B 34 (1986) 3319.

[4] W.K. Han, S.C. Ying, Phys. Rev. B 46 (1992) 1849.

[5] L.D. Roelofs, T. Ramseyer, L.N. Taylor, D. Singh, H. Krakauer, Phys. Rev. B 40 (1989) 9147.

[6] V.P. Zhdanov, Surf. Sci. Rep. 12 (1991) 183.

[7] A.A. Tarasenko, A.A. Chumak, Ukr. Phys. J. 40 (1995) 995;
A.A. Tarasenko, A.A. Chumak, Ukr. Phys. J. 40 (1995) 1074.

[8] A.A. Chumak, A.A. Tarasenko, Surf. Sci. 364 (1996) 424.

[9] A.A. Tarasenko, F. Nieto, V. Pereyra, C. Uebing, Surf. Sci. 441 (1999) 329.

[10] F. Nieto, A.A. Tarasenko, C. Uebing, V. Pereyra, Surf. Rev. Lett. 6 (1999) 323.

[11] A.A. Chumak, A.A. Tarasenko, Surf. Sci. 91 (1980) 694.

[12] A.A. Tarasenko, L. Jastrabik, C. Uebing, Phys. Rev. B 57 (1998) 10166.

[13] A.A. Tarasenko, L. Jastrabik, F. Nieto, C. Uebing, Phys. Rev. B 59 (1999) 8552.