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Surface diffusion of particles adsorbed on a lattice with two non-equivalent sites

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Abstract

We investigate the surface diffusion in a system of particles adsorbed on a lattice with two non-equivalent sites, whose number in the unit cell and adsorption energy are different. When the adsorption energies are comparable, the adparticle diffusion proceeds by uncorrelated adparticle jumps. In the opposite case, the adparticle migration proceeds by pairs of consecutive jumps. The contributions to the surface diffusion of these jump sequences depend considerably on the adparticle surface coverage and the relation between the adsorption energies. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

We have recently considered thermodynamic properties of a lattice gas adsorbed on a surface with fourfold hollow and twofold bridge adsorption sites using the real-space renormalization group (RSRG) and Monte Carlo methods [1,2]. In this paper we consider the collective diffusion on such lattice.

In the previous papers the transport properties of adparticles in this lattice gas model had been investigated in the framework of the quasi-chemical approximation [3]. The adparticle dynamics in systems with strong interactions have been intensively investigated by almost all methods of the non-equilibrium statistical mechanics. The Monte Carlo simulations, being the most reliable and simple approach, are used in the widest scale [4–7].

We have solved the balance equation for slowly varying small disturbances of the adparticle surface coverage and obtained explicit expressions for the chemical diffusion coefficient. Then we have calculated all necessary quantities using the RSRG method.

The outline of this paper is as follows: the system Hamiltonian and expressions for the chemical diffusion coefficient are described in Section 2. The coverage dependencies of the diffusion coefficient are discussed in Section 3, and the summary of results is presented in Section 4.

2. The system Hamiltonian and model of migration

We consider an ideal solid surface with the symmetry of the fcc(1 0 0) crystal face. The adsorbed particles occupy the minima of the potential

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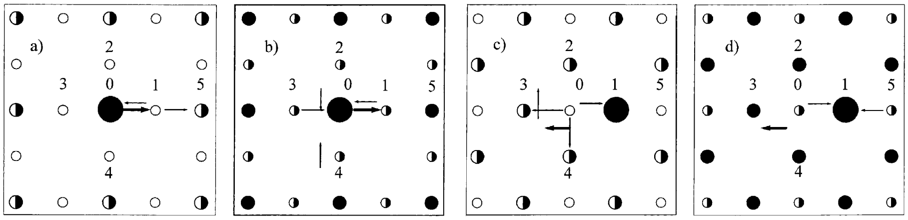

Fig. 1. Four types of the pair successions of the adparticle jumps. The open, half filled and filled circles denote empty, partially and completely occupied sublattices, respectively. The thick and thin arrows denote the first, the second jumps of the jump succession. (a) $\varepsilon_c - \varepsilon_b \gg 1$, $\theta < 1/3$; (b) $\varepsilon_c - \varepsilon_b \gg 1$, $\theta > 1/3$; (c) $\varepsilon_b - \varepsilon_c \gg 1$, $\theta < 2/3$; (d) $\varepsilon_b - \varepsilon_c \gg 1$, $\theta > 2/3$.

relief, which forms a two-dimensional lattice shown in Fig. 1. The thermodynamical state of the adparticle system is completely described by a set of the site occupation numbers $\{n_i\}$ with

$$n_i = \begin{cases} 1, & \text{if site } i \text{ is occupied,} \\ 0, & \text{if site } i \text{ is empty,} \end{cases} \tag{1}$$

where index i labels the N sites of the lattice.

These sites have different symmetry, i.e., fourfold c-sites in the vertices of the square lattice and twofold b-sites in the middle of the square lattice bonds. In principle, the depths of the b-sites, ε_b, and c-sites, ε_c, can be also different. We consider the lateral interaction φ between the nearest neighbor (nn) pairs of adparticles only. Then, the adparticles number N_a and Hamiltonian H_a can be written as follows

$$N_a = \sum_i n_i,$$
$$H_a = -\varepsilon_c \sum_c n_i - \varepsilon_b \sum_b n_i + \varphi \sum_{nn} n_i n_j. \tag{2}$$

Here symbols i, c, b and nn denote summation over all sites, c-sites, b-sites and the nn pairs, respectively. For the investigations of the adparticle migration one must define the model of the adparticles jumps. Any adparticle can jump to one of its nn sites, if the destination is empty. The adparticle must surmount the potential barrier E_{if} between the initial site i and the final site f. The jump frequency, ν_{if}, exponentially depends on the activation energy E_{if}, (we use the system of units with $k_B T = 1$)

$$\nu_{\text{if}} = \nu_0 \exp(-E_{\text{if}}). \tag{3}$$

The activation energy of jumps is affected by the presence of adjacent adparticles. We assume that the lateral interactions influence the minima of the periodic potential only. Then, for example, if adparticle jumps from the 0th site to the 1st site (see Fig. 1), the activation energy, E_{01}, depends on the occupation numbers as follows

$$E_{01} = \varepsilon_c - \varphi(n_2 + n_3 + n_4). \tag{4}$$

The reverse jumps from the 1st site to the 0th site are influenced by an adparticle occupying the 5th site only:

$$E_{10} = \varepsilon_b - \varphi n_5. \tag{5}$$

The jump frequency, ν_{if}, satisfies the principle of the microscopic reversibility

$$\langle \nu_{\text{if}} n_{\text{i}}(1 - n_{\text{f}}) \rangle = \langle \nu_{\text{fi}} n_{\text{f}}(1 - n_{\text{i}}) \rangle. \tag{6}$$

In order to obtain the chemical diffusion coefficient we start from the balance equation for the adparticle occupation numbers, which describes the evolution of the occupation numbers due to the separate uncorrelated jumps of adparticles [8]

$$[n_i(t + \Delta t) - n_i(t)]/\Delta t = \sum_j (\nu_{ji} n_j h_i - \nu_{ij} n_i h_j) + J_i^{\text{L}}. \tag{7}$$

Here summation is carried out over all nns of the ith site; $h_i \equiv 1 - n_i$; J_i^{L} is the Langevin source of the occupation number fluctuations. Using the local-equilibrium approximation, the balance equation Eq. (7) is reduced to the ordinary diffusion equation with the chemical diffusion coefficient, D_c, determined by the following expression:

$$D_c = \nu_0 a^2 \exp(\mu) P_{00} / 6\chi_T. \tag{8}$$

Here μ is the chemical potential of the adparticles; $P_{00} \equiv \langle h_i h_f \rangle$ and χ_T is the isothermal susceptibility. The expression for the chemical diffusion coefficient Eq. (8) works rather well on the lattices with one kind of the lattice sites: honeycomb [9], square [10,11] and triangular symmetries [12].

It should be noted, that the successive jumps of adparticles became correlated in some sense when the adsorption energies ε_b and ε_c differ substantially $|\varepsilon_c - \varepsilon_b| \gg 1$. In this case one sublattice becomes deep and the other sublattice is shallow. The jump frequency from the deep sites is considerably lower than the jump frequency from the shallow sites. Then the adparticle migration is controlled by the slow jumps from the deep sites only. The elementary act of migration consists of a pair of consecutive jumps: any slow jump of an adparticle from a deep site to a shallow site is followed by a fast jump of an adparticle from a shallow site to a deep site. There are some types of such pairs of slow + fast pairs of jumps. Their contributions to the migration depend on the relation between ε_b and ε_c and on the surface coverage of adparticles θ. We investigate these types separately and derive corresponding expressions for the chemical diffusion coefficient.

Let us consider the case $\varepsilon_c - \varepsilon_b \gg 1$ at first. The c-sublattice is deep and b-sublattice is shallow. There is a characteristic coverage $\theta = 1/3$, which separates two distinctly different regions, where the adparticle migration is controlled by different pairs of jumps. If $\theta < 1/3$, the shallow sublattice is almost empty and deep sublattice is partially occupied as shown in Fig. 1a. The most probable are the pairs of jumps performed by the same adparticle. At first, adparticle jumps from the initial 0th deep site to the 1st site. If the next deep 5th site is occupied, the adparticle immediately returns back to the initial site. If $n_5 = 0$, the adparticle has two options with equal probability: proceed further or return back. Other possible pairs of jumps give exponentially small contributions to the chemical diffusion coefficient and can be neglected. The expression for the chemical diffusion coefficient has the following form:

$$D_1 = v_0 a^2 \exp(\mu) P_{cbc}/6\chi_{\mathrm{T}}, \tag{9}$$

where $P_{cbc} \equiv \langle h_0 h_1 h_5 \rangle$ is the probability to find three nn empty sites.

If $\theta > 1/3$, the deep sublattice is completely occupied and shallow sublattice is partially occupied (see Fig. 1b). Again migration of adparticles proceeds by pairs of successive jumps. But in this case the most probable are pairs of jumps performed by different adparticles. At first, an adparticle jumps from the 0th site to the 1st site. The most probable next event will be the jump of another adparticle from the 2nd, 3rd or 4th site to the empty 0th site. The probability that the initial adparticle returns to the 0th site depends on the occupation numbers of the nn sites. If all nns are empty, the adparticle immediately returns back. If any one, two or three nns are occupied, any adparticle can fill the deep 0th site with the probability equal to 1/2, 1/3 and 1/4, respectively. The expression for D_{c} involves correlation functions of three, four and five nn sites

$$D_2 = v_0 a^2 \exp(2\mu + \varepsilon_b - \varphi) \times \langle h_0 h_1 (3h_2 + 3h_3 + 4h_2 h_3 + 2h_2 h_3 h_4) \rangle / 36\chi_{\mathrm{T}}. \tag{10}$$

In the case $\varepsilon_b - \varepsilon_c \gg 1$ the b-sublattice is deep and c-sublattice is shallow. The characteristic coverage is equal to 2/3. If $\theta < 2/3$, the shallow sublattice is almost empty and deep sublattice is partially occupied as shown in Fig. 1c. The main contribution to the chemical diffusion coefficient comes from the consecutive pairs of jumps performed by the same adparticle. An adparticle jump from the 1st site to the 0th site is followed by the fast jump of the adparticle to the next deep site (2nd, 3rd and 4th if some of these sites are empty). The possibility for the return jump depends on the occupation numbers of the 2nd, 3rd and 4th sites. If all these sites are occupied, the adparticle returns back. If any one, two or three nns are empty, the adparticle jumps to the empty sites (including the 1st site) with probability 1/2, 1/3 and 1/4, respectively. The expression for D_{c} involves correlations between three, four and five nns

$$D_3 = v_0 a^2 \exp(\mu) \times \langle h_0 h_1 (3h_2 + 3h_3 - 4h_2 h_3 + h_2 h_3 h_4) \rangle / 18\chi_{\mathrm{T}}. \tag{11}$$

If surface coverage exceeds 2/3, the deep sublattice is completely occupied and the shallow sublattice is partially occupied as shown in Fig. 1d.

An adparticle jump from the 1st site to the 0th site is followed by the jump of another adparticle from the 5th site (if it is occupied) to the 1st empty site. The probability of the return jump is equal to 1/2, if the 5th site is occupied, and 1, if the 5th site is empty. These pairs of jumps result in the following expression for D_c

$$D_4 = v_0 a^2 \exp(2\mu + \varepsilon_c - 3\varphi) P_{cbc}/6\chi_T. \tag{12}$$

Due to the strong inequality $|\varepsilon_c - \varepsilon_b| \gg 1$ the migration proceeds in the partially occupied sublattice. Only one definite type of the successive pairs of jumps plays dominant role, depending on the coverage. In the transition regions $|\theta - 1/3| \ll 1$ or $|\theta - 2/3| \ll 1$ the both types give comparable contributions to D_c, therefore, the total chemical diffusion coefficient is determined by sum $D_c = D_1 + D_2$ if $\varepsilon_c - \varepsilon_b \gg 1$ or $D_c = D_3 + D_4$, if $\varepsilon_b - \varepsilon_c \gg 1$.

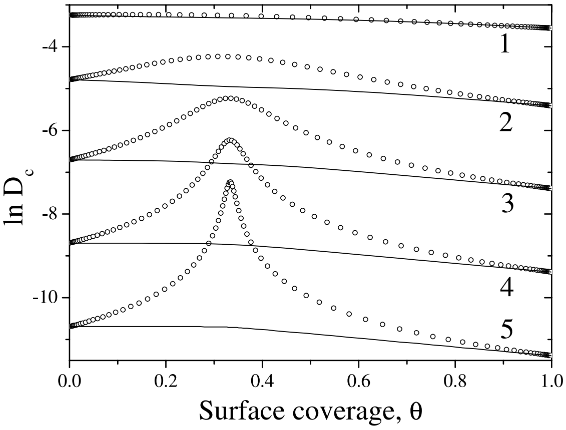

Fig. 2. $\ln D_c$ vs. θ for $\varphi = 0$. The lines and symbols represent $D_c = D_1 + D_2$ and Eq. (8), respectively. The values of the parameters are the following: $\varepsilon_b = 1$, $\varepsilon_c = 2n$, where n is the number of the curve.

3. Results

We have calculated the coverage dependencies of the chemical diffusion coefficient by the RSRG method. The rather exact RSRG transformation with cluster of 34 lattice sites used for these calculations is described in the previous papers [10,11].

We begin with the Langmuir lattice gas ($\varphi = 0$). We have calculated the coverage dependencies for the chemical diffusion coefficients determined by the separate adparticle jumps, Eq. (8) and by the pairs of the successive jumps, $D_1 + D_2$. The dependencies are plotted in Fig. 2.

It should be noted that the discrepancies are very small, if the adsorption energies are comparable $|\varepsilon_c - \varepsilon_b| \leqslant 1$ (see curve 1 in Fig. 2, plotted for $\varepsilon_c - \varepsilon_b = 1$). In this region ordinary expression for the diffusion coefficient Eq. (8) works well. Also the chemical diffusion coefficient, based on the successive jumps pairs, fits close the ordinary diffusion coefficient. But the discrepancies increase considerably, when the difference of the site depths grows. The coverage dependencies become qualitatively different. The uncorrelated jumps give sharp maximum at the characteristic coverage $\theta = 1/3$, but the pair sequences give monotone decreasing dependencies without any peculiarities. The maximal disagreement between the curves is reached at the characteristic coverage. It clearly shows the decisive contribution of the return jumps. At the characteristic coverage, the system of adparticles is well ordered even without interaction. Deep sublattice is completely occupied and shallow sublattice is completely empty. Therefore many jump sequences are unsuccessful. There is the same qualitatively behavior for the case $\varepsilon_b > \varepsilon_c$. The ordinary diffusion coefficient coverage dependencies have sharp maxima at $\theta = 2/3$ and the pair sequences give monotone growth of the chemical diffusion coefficient.

We use simple approximations for the three, four and five particle correlation functions in order to obtain a qualitative behavior of the chemical diffusion coefficient coverage dependencies for the case $\varphi \neq 0$. The normalized dependencies are plotted in Figs. 3 and 4 for $\varepsilon_c > \varepsilon_b$ and $\varepsilon_b > \varepsilon_c$, respectively ($D_0 = D_c(\theta = 0)$).

It should be noted the rather weak dependence on the interaction for $\theta < 1/3$ ($\varepsilon_c > \varepsilon_b$) and $\theta < 2/3$ ($\varepsilon_b > \varepsilon_c$). Such behavior is quite obvious. The jump frequency depends on the interaction due to the presence of nns. If the coverage is less than its characteristic value, almost all adparticles occupy deep sites and the number of nns is very small.

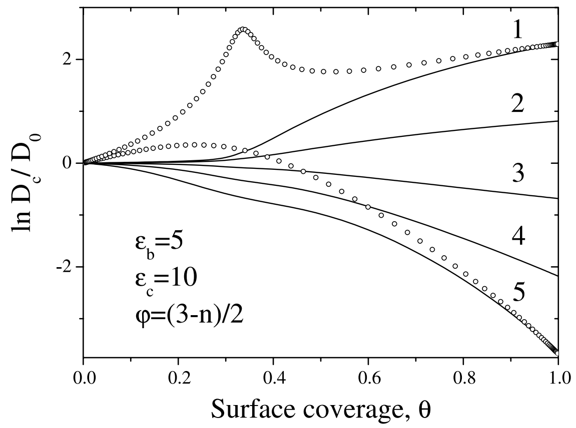

Fig. 3. $\ln D_c/D_0$ vs. θ. The lines and symbols represent the pair jump contributions $D_c = D_1 + D_2$ and ordinary diffusion coefficient Eq. (8), respectively.

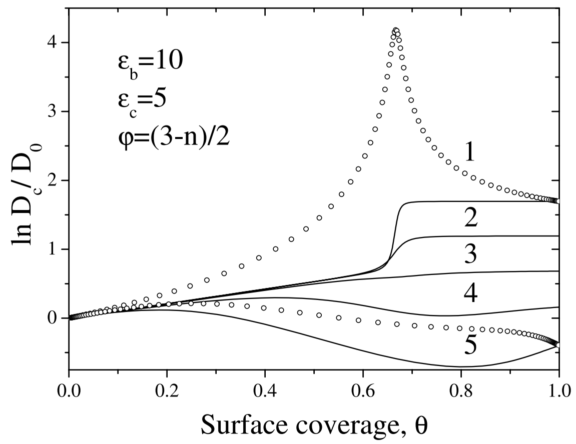

Fig. 4. $\ln D_c/D_0$ vs. θ. The lines and symbols represent the sum of the pair jumps contributions $D_3 + D_4$ and ordinary diffusion coefficient, respectively.

Therefore, the frequency of the slow jumps, which control the surface diffusion, remains almost unchanged. If the coverage exceeds its characteristic value, the slow jump frequency increases, if adparticles repel each other, and decreases if the interaction is attractive.

The comparison of the curves plotted for the same interaction in Figs. 3 and 4 shows clearly that the diffusion coefficient is markedly more sensitive to the interaction when $\varepsilon_c > \varepsilon_b$. It can be explained easily. At the monolayer coverage the frequencies of jumps from the *b*- and *c*-sites are equal to $\nu_0 \exp(-\varepsilon_b + \varphi)$ and $\nu_0 \exp(-\varepsilon_c + 3\varphi)$, respectively. For $\varepsilon_c > \varepsilon_b$ slow jumps proceed from the *c*-sites and the slow jump frequency is affected by the interaction in the greater extend as compared to the case $\varepsilon_b > \varepsilon_c$, when slow jumps proceed from the *b*-sites.

4. Summary

We investigated the surface diffusion in a lattice gas system with two different kinds of adsorption sites, the number of which in the unit cell and adsorption energies is different. The expressions for the chemical diffusion coefficient are obtained for the cases when the adsorption energies are close to each other and when the difference of these energies exceeds considerably the thermal energy k_BT. When adsorption energies are comparable, the surface migration proceeds by the uncorrelated jumps of adparticles. When adsorption energies are considerably different, the jumps of adparticles became correlated: any slow jump is followed by a fast jump. Therefore, the surface migration proceeds by the correlated pairs of jumps. There are four qualitatively different types of such correlated jump pairs. It is shown that depending on the surface coverage θ and relation between the adsorption energies ε_b and ε_c only one definite type of successive jumps plays the dominant role in the adparticle diffusion. Using the local equilibrium approximation we have obtained the explicit expressions for the chemical diffusion coefficient corresponding to the different types of jump pairs. We have calculated the coverage dependencies of D_c for some representative values of the adsorption energies difference $|\varepsilon_c - \varepsilon_b|$ and interaction parameter φ, using the RSRG approach. The dependencies are qualitatively different for the case of uncorrelated jumps and for the case of correlated jump pairs. We have also investigated the effect of the lateral interaction on the chemical diffusion coefficient. Attraction between adparticles inhibits and repulsion accelerates their migration over the surface as it should be. The effect is the most pronounced at the monolayer coverage.

Acknowledgements

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