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# Manifestation of Onsager's off-diagonal fluxes in diffusion of coadsorbed particles

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## ABSTRACT

According to Onsager's phenomenological theory, the diffusion fluxes of coadsorbed particles are expressed via the gradients of their chemical potentials and can contain the off-diagonal terms. In the conventional two-dimensional lattice-gas models with jumps of monomers to nearest-neighbour vacant sites, such terms are absent at the mean-field (MF) level or in the framework including the statistical correlations related to lateral interaction between particles but neglecting the dynamical correlations. The role of the off-diagonal terms in these models with dynamical correlations and in other unconventional models is still not clear. Herein, the situation in this area is clarified from two perspectives by using Monte Carlo simulations and analytically, respectively. First, the scale of the related effects is shown for conventional diffusion with emphasis on the concentration profiles under steady-state conditions and diffusion-limited associative desorption under transient conditions. In these cases, the role of the off-diagonal terms is well manifested at the level above the MF approximation provided the coverages are appreciable and the difference between the jump rates of different particles is appreciable as well. Second, the off-diagonal terms are demonstrated to be available and important already at the MF level in unconventional diffusion occurring via concerted exchange and pair jumps.

## 1. Introduction

Diffusion of particles (atoms and molecules) adsorbed on a solid surface is of considerable intrinsic interest and also important in the context of various applications. For these reasons, this rate process has attracted attention of experimenters and theoreticians already many decades, and its various aspects have been comprehensively studied (reviewed by Gomer [1], Barth [2], Ala-Nissila et al. [3], Villarreal et al. [4], and Zhdanov [5]). In surface science, the focus was/is primarily on diffusion of adsorbates of one type. Diffusion of coadsorbed particles of two or more types has attracted much less attention although the latter is also physically interesting and practically relevant first of all in the context of heterogeneous catalysis where it occurs in systems with very different chemical compositions and catalyst structures including polycrystalline materials and single crystals [6,7], composites [8,9], and supported nanoparticles [10,11]. One of the reasons of reduced attention was/is that experiments with coadsorbed species are complex due to the need to measure accurately and simultaneously the spatio-temporal distribution of at least two species. In fact, accurate measurements of the rate of diffusion of coadsorbed particles are now lacking. In the context of theoretical applications to the kinetics of catalytic reactions, on the other hand, the adsorbate diffusion was/is

often considered to be important but not central. In particular, this process was long recognized to be usually fast compared to the rate-limiting reaction steps, and accordingly can often (especially under steady-state conditions) be excluded from the analysis by assuming the adsorbed reactants to be located at random (as in the classical Langmuir-Hinshelwood model) or according to the grand canonical distribution if the lateral adsorbate-adsorbate interactions are appreciable [5]. The kinetic models of this category are very widely and successfully used already many decades both in academic and applied studies. In the case of bistable and oscillatory spatio-temporal kinetics in rapid reactions such, e.g., as CO oxidation on the (100) and (110) faces of Pt [12,13], diffusion of coadsorbed species can play a more explicit and important role. In these classical and other examples of complex behaviour of heterogeneous catalytic reactions, the underlying mechanisms include usually the steps (e.g., surface restructuring or oxide formation) which can hardly be accurately described by the conventional mass-action law. With these steps, the employed kinetic models were/are inevitably coarse-grained. Under such circumstances, it is often makes no sense to pay much attention to the details of diffusion, and accordingly this process was/is usually described at the simplest possible level by using the textbook Fick law or slightly more complex equations [as Eq. (3) presented below]. In the absence of surface

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restructuring or oxide formation in CO oxidation, the reaction conditions are defined much better, and the role of diffusion of coadsorbed CO and O was theoretically studied in detail [7,14,15]. Deeper understanding of the mechanistic aspects of diffusion of coadsorbed particles is, however, still desirable because it can extend the basis for scrutiny both in experiments and theory. Among other areas where diffusion of coadsorbed particles may be important, I can mention, e.g., protein adsorption at solid supports in general (reviewed by Rabe et al. [16] and Adamczyk [17]) and surface of nanoparticles in particular (reviewed by Ke et al. [18] and Zhdanov [19]). Biological or biology-related media contain usually various proteins, and their coadsorption may result in the formation of complex structures (such, e.g., as a protein corona around nanoparticles [18,19]). The corresponding mechanistic details can depend on protein diffusion along the solution-solid interface although its role appears to be not so important as that of attachment and detachment.

In reality, diffusion of adsorbed particles is usually complicated by lateral interactions, and this effect can often be described in the framework of the two dimensional (2D) lattice-gas model by scrutinizing the balance of jumps of particles to nearest-neighbour (nn) vacant sites. The corresponding jump rate constants or probabilities should satisfy the detailed balance principle. Axiomatically, this prescription can be realized in different ways [20]. One of the physically reasonable approaches is to employ the transition state theory and introduce the lateral interactions of a particle in the ground and activated states,  $\epsilon_i$  and  $\epsilon_i^*$  (the index  $i$  characterizes the arrangement of particles adjacent to a pair of nn sites where a diffusion jump takes place), so that the change of the activation energy for a jump is  $\epsilon_i^* - \epsilon_i$  [5]. For diffusion of particles coadsorbed competitively and cooperatively on a uniform surface with one or two types of sites, it was done, respectively, in Refs. [21] and [22] (see also [5]). The diffusion fluxes of particles were expressed via their chemical potentials,  $\mu_A$  and  $\mu_B$ . It can be done in terms of the gradients of adsorbate coverages (or concentrations),  $\nabla\theta_A$  and  $\nabla\theta_B$ , or potentials,  $\nabla\mu_A$  and  $\nabla\mu_B$ . For conventional competitive coadsorption of A and B particles on the same sites (each site can be vacant or occupied by A or B), for example, the total diffusion flux of A particles (the sum of Eqs. (1) and (4) in [21]) can be represented as

$$J_A = -S \exp(\mu_A/T) D_A^\circ T^{-1} \nabla\mu_A, \quad (1)$$

with  $S = \sum_i \mathcal{P}_{00,i} \exp(-\epsilon_i^*/T)$ , where  $D_A^\circ$  is the diffusion coefficient at low coverages,  $\mu_A$  is the chemical potential defined so that  $\mu_A = T \ln(\theta_A)$  at low coverages, and  $\mathcal{P}_{00,i}$  is the probability that a pair of empty nn sites has the environment being marked by index  $i$  (the Boltzmann constant is omitted in order to keep the equations compact). For Langmuir particles (without lateral interactions), we have

$$S = (1 - \theta_A - \theta_B)^2 \quad \text{and} \quad \exp\left(\frac{\mu_A}{T}\right) = \frac{\theta_A}{1 - \theta_A - \theta_B},$$

and accordingly Eq. (1) yields

$$J_A = -\theta_A (1 - \theta_A - \theta_B) D_A^\circ T^{-1} \nabla\mu_A, \quad \text{or} \quad (2)$$

$$J_A = -(1 - \theta_B) D_A^\circ \nabla\theta_A - \theta_A D_A^\circ \nabla\theta_B. \quad (3)$$

For B particles, the equations are similar. (Eq. (3) for Langmuir particles of two types or similar simple equations for arbitrary number of particle types were independently obtained and used e.g. in Refs. [21,23,24]; for recent application of such equations, see e.g. Ref. [25].)

The derivation of Eq. (1) implies local equilibrium and is based on the use of the grand canonical distribution. Thus, Eq. (1) takes accurately the statistical correlations into account. On the other hand, Eq. (1) and its simple versions (2) and (3) for Langmuir particles do not fully describe dynamical correlations. The latter is clear from its derivation and structure. The illustration of the effect of such correlations on the diffusion coefficient corresponding to the diagonal fluxes with respect to coverage was given by Evans et al. (Fig. 8 in Ref. [14] and Fig. 10 in Ref. [15]).

In the context of applications, the advantage of Eq. (1) is that the diffusion flux is expressed via  $\nabla\mu_A$  and does not contain the off-diagonal term proportional to  $\nabla\mu_B$ . This feature is, however, also a shortcoming of Eq. (1) [or (2) and (3)], because in the case of coadsorption such terms are expected on the basis of Onsager's phenomenological theory [26] (reviewed in Section 3.5 in [7]; see also a recent comment [27]). Although Onsager did not analyze diffusion of coadsorbed particles in the framework of the 2D lattice-gas model, using his theory one can represent the diffusion fluxes as

$$J_A = -\Lambda_{AA} \nabla\mu_A - \Lambda_{AB} \nabla\mu_B \quad \text{and} \quad J_B = -\Lambda_{BA} \nabla\mu_A - \Lambda_{BB} \nabla\mu_B$$

with  $\Lambda_{AB} = \Lambda_{BA}$ , but cannot obtain explicit expressions for the corresponding coefficients ( $\Lambda_{AA}$ ,  $\Lambda_{AB}$ ,  $\Lambda_{BA}$ , and  $\Lambda_{BB}$ ). For Langmuir particles, this aspect was scrutinized by Quastel [28] (reviewed by Liu et al. [7]), and the outcome of his heuristic analysis is that the off-diagonal terms are related to the specifics of the self-diffusion coefficients,  $D_A^*$  and  $D_B^*$ . In particular, using his equations, one can verify that in the case of A and B coadsorption the off-diagonal terms are negligible provided these coefficients are represented in the MF form,  $D_A^* = (1 - \theta_A - \theta_B) D_A^\circ$  and  $D_B^* = (1 - \theta_A - \theta_B) D_B^\circ$ . This means that the corrections are related to the deviation of  $D_A^*$  and  $D_B^*$  from these expressions. His analysis alone does not, however, allow one to obtain explicit expressions for the corresponding corrections either.

The off-diagonal diffusion coefficients introduced in terms of the gradients of concentrations of species were discussed and described in various approximations in many other areas of natural sciences as reviewed by Vanag and Epstein [31]. Onsager's results are often mentioned in the corresponding articles and are mentioned in their review as well. The results reported there are, however, not directly applicable to diffusion of coadsorbed particles.

The introduction above shows that diffusion of adsorbed particles merits additional attention from various perspectives. Herein, I focus on the theoretical aspects of diffusion of particles of two types, A and B, coadsorbed competitively at a uniform surface with the sites of one type or, more specifically, on the features related to Onsager's off-diagonal terms. Neglecting lateral interactions, I show by using Monte Carlo (MC) simulations how the deviations from the MF approximation [Eq. (3)] for conventional diffusion can be manifested in the coverage profiles and diffusion fluxes under steady-state conditions (Section 2) and transient kinetics of associative desorption (Section 3). In addition, I show analytically that Onsager's off-diagonal terms are not necessarily related to the dynamic factors which are beyond the MF approximation or, in other words, that these terms can be obtained in this approximation, but this is possible for various unconventional mechanisms of diffusion (Section 4).

## 2. Conventional diffusion under steady-state conditions

Let us consider diffusion of coadsorbed Langmuir A and B particles in the  $x$  direction on a square lattice at the strip with  $0 \leq x \leq L$  in the presence of gradients of their coverages,  $\theta_A$  and  $\theta_B$ , under steady-state conditions,

$$\frac{\partial J_A}{\partial x} = 0 \quad \text{and} \quad \frac{\partial J_B}{\partial x} = 0, \quad (4)$$

with fixed non-zero A and B coverages at  $x = 0$ , non-zero B coverage  $x = L$ , and  $\theta_A(L) = 0$ . This generic situation can be described in the MF approximation and also exactly by employing the MC technique. The difference in the corresponding results can be used as a measure of the role of Onsager's off-diagonal terms.

In the MF approximation, the diffusion flux of A particles is given by (3). Diffusion of B particles is described by analogy. With this specification, the solution of the diffusion equations for the A and B coverages yields

$$\theta_A(x) = \theta_A(0)(1 - x/L), \quad (5)$$

$$\theta_B(x) = \theta_B(0) + [\theta_B(L) - \theta_B(0)]x/L, \quad (6)$$

and the corresponding diffusion fluxes are represented as

$$J_A = D_A^\circ \theta_A(0)[1 - \theta_B(L)]/L, \quad (7)$$

$$J_B = D_B^\circ [\theta_B(0) - \theta_B(L) + \theta_A(0)\theta_B(L)]/L. \quad (8)$$

The corresponding kinetic MC simulations were performed on a  $L \times L$  square lattice with periodic boundary conditions along the  $y$  direction by using one of the conventional algorithms (see, e.g., Refs. [29,30]):

- (i) A site is chosen at random.
- (ii) If the site selected is vacant, a trial ends.
- (iii) If the site is occupied, an A or B particle located there tries to diffuse. In particular, a NN site is randomly selected, and if this site is vacant, the particle jumps to it with probability  $p_A$  or  $p_B$ , respectively. On the left- and right-hand side boundaries, the jumps are performed with the corresponding specifics.
- (iv) After each trial, the time is incremented by  $\Delta t = |\ln(\rho)|/L^2$ , where  $0 < \rho \leq 1$  is a random number.

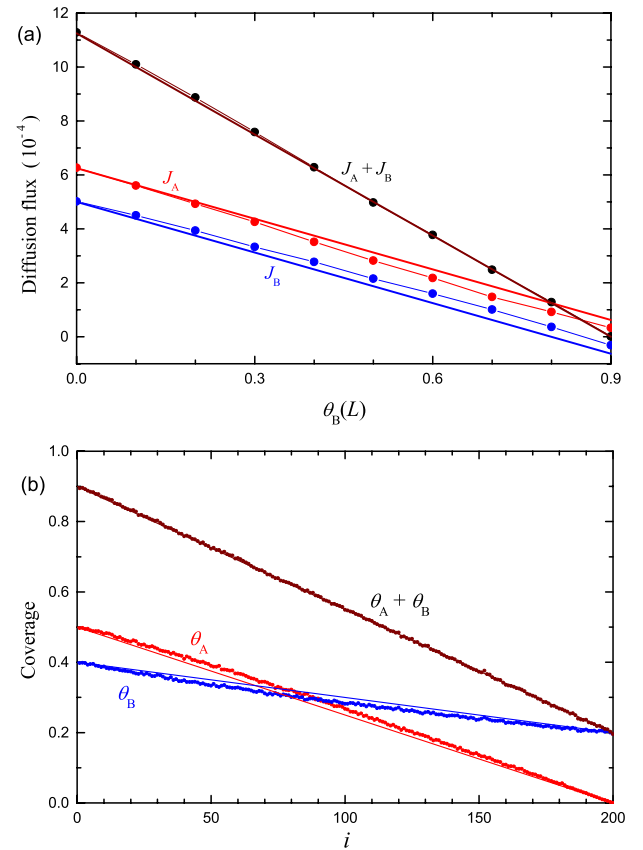
The time was measured in the so-called MC steps (MCS). One MCS was identified with  $\Delta t = 1$ . For the average value of  $\ln(\rho)$ , we have  $\langle |\ln(\rho)| \rangle = 1$ ; and accordingly 1 MCS defined in this way corresponds on average to  $L \times L$  trials of diffusion jumps. In this framework, the A and B diffusion at low coverages are given by  $D_A^\circ = p_A/4$  and  $D_B^\circ = p_B/4$ , provided the lattice spacing is used as the unity of length.

The initial A and B distribution was generated in agreement with the MF one [Eqs. (5) and (6)]. At the vertical border rows of sites with  $i = 1$  and  $i = 200$  ( $i$  enumerates the sites along the  $x$  direction), the occupation of sites was maintained according to the grand canonical distribution with prescribed average coverages. This procedure makes it possible to take fluctuations into account and simultaneously to keep the fixed average coverages at the boundary sites. The latter is by analogy with the boundary conditions introduced above for the phenomenological diffusion equations.

During each MC run, the first interval with the duration of  $2 \times 10^5$  MCS was used to reach the steady state. Then, the additional interval with the duration of  $2 \times 10^5$  MCS was employed to calculate the average diffusion fluxes,  $J_A$  and  $J_B$ , by accounting all the particles jumping between the nearest-neighbour vertical rows of sites located in the center (at  $i = L/2$  and  $i = L/2 + 1$ ) and dividing the net number of intersections of A or B particles (i.e., the difference of the numbers of jumps in the two directions) by  $L$  and the corresponding time ( $2 \times 10^5$ ).

The main simulations were performed on a lattice with  $L = 200$ . The corresponding results are shown in Figs. 1–3 for  $\theta_A(0) = 0.5, \theta_B(0) = 0.4, \theta_A(L) = 0$ , and different values of  $\theta_B(L)$ . In particular, Fig. 1(a) exhibits the diffusion fluxes as a function of  $\theta_B(L)$  for maximal A and B jump-rate probabilities,  $p_A = p_B = 1$ . Typical coverage profiles [for  $\theta_B(L) = 0.2$ ] are shown in Fig. 1(b). Fig. 2 exhibits similar results for  $p_A = 0.1$  and  $p_B = 1$ , whereas Fig. 3 is for  $p_A = 1$  and  $p_B = 0.1$ . In all these cases, the MC coverage profiles are seen to be fairly close to the MF profiles [Figs. 1(b), 2(b), and 3(b)]. The MC diffusion fluxes are close to the MF ones provided the A and B jump probabilities are equal [Fig. 1(a)] and for the particles with the lower jump probability [Figs. 2(a) and 3(a)]. The MC diffusion fluxes for particles with higher jump probability are, however, appreciably smaller than the MF ones [Figs. 2(a) and 3(a)]. Physically, the latter is related to the presence of the regions where the coverage of the adsorbate with lower jump probability is high. Such regions are poorly conductive for the adsorbate with higher jump probability, and accordingly the diffusion flux of the latter adsorbate is controlled there by the diffusion jumps of the former adsorbate.

The MC results presented in Figs. 1–3 were obtained for the lattice with  $L = 200$ . This lattice size can be considered to be large, because in the problem under consideration there are no domain or island growth



**Fig. 1.** (a) Diffusion fluxes as a function of  $\theta_B(L)$  for  $p_A = p_B = 1$  and (b) typical coverage profiles under steady-state conditions according to the MC simulations (filled circles and thin lines used to guide eyes) and MF approximation (thick lines). The coverages are fixed at the boundaries as  $\theta_A(0) = 0.5, \theta_B(0) = 0.4$ , and  $\theta_A(L) = 0$ . The way of calculation of the MC diffusion fluxes is described in the text. The MC coverage profiles represent the average coverage at the vertical rows of sites in the end of the MC runs.

and no correlations on this length scale. For such large lattices, the coverages calculated under steady-state conditions and presented as a function of the normalized coordinate,  $x = i/L$ , are expected to be independent on  $L$ , whereas the diffusion fluxes are expected to scale as  $J \propto 1/L$ , i.e., the product of  $J$  and  $L$  should be independent of  $L$ . This was confirmed e.g. by comparing the results MC simulations performed for  $L = 200$  and  $100$  (not shown). As already noticed, each MC run described above included two intervals each of  $2 \times 10^5$  MCS. This duration is sufficiently long in order to reach steady state and get reliable statistics. This was confirmed by performing similar simulations on the  $200 \times 200$  lattice with longer intervals,  $4 \times 10^5$  MCS each. The difference of the results obtained with the intervals of  $2 \times 10^5$  and  $4 \times 10^5$  MCS was nearly not distinguishable to the eye (not shown).

Concerning the main subject of this study, I can notice that the results presented (Figs. 1–3) were obtained in the cases when the total adsorbate coverage is high at one side and spans the whole range of coverages at the other side. Such cases are instructive in the context of Onsager's off-diagonal terms because in the opposite limit (when the coverages are low everywhere) these terms are negligible. The general conclusion drawn from the simulations presented above is that the diffusion flux of the adsorbate with higher jump rate can be appreciably suppressed by the adsorbate with lower jump rate. It is of interest that the extent of suppression is much smaller than the difference in the jump rates. From this perspective, the suppression is not dramatic. Compared to the 2D case discussed here, this suppression is well known to be much stronger in the 1D “single-file” lattice models [32] and expected to be less pronounced in 3D diffusion, where there are more

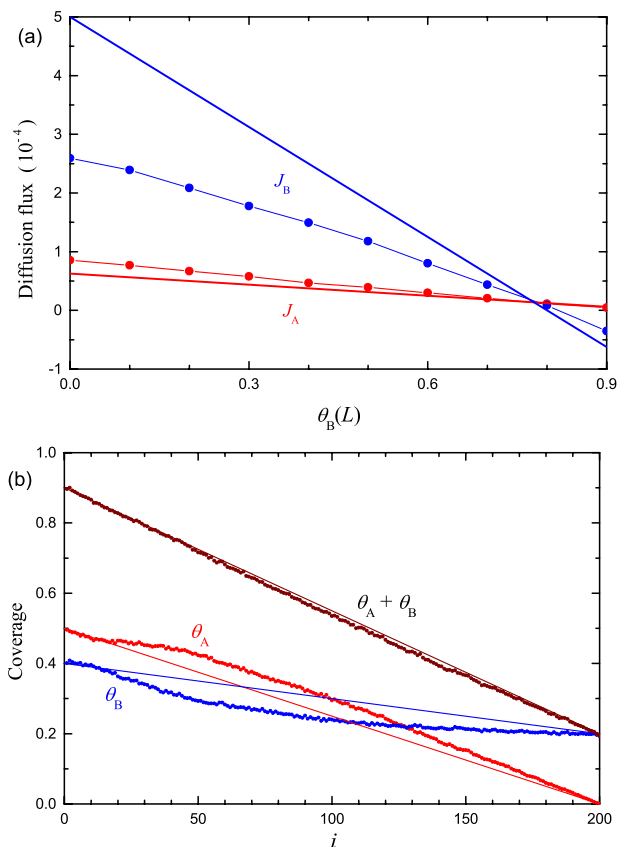


Fig. 2. As Fig. 1 for  $p_A = 0.1$  and  $p_B = 1$ .

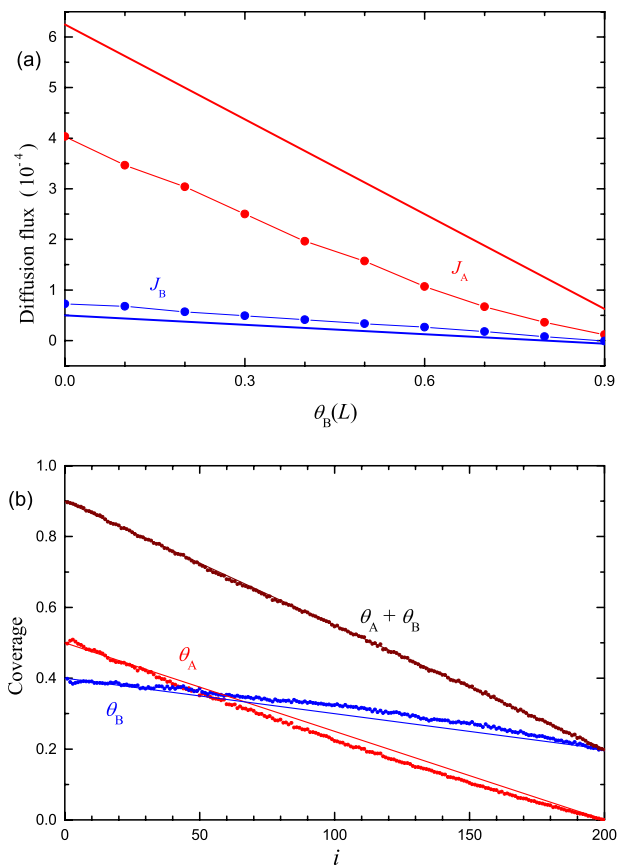


Fig. 3. As Fig. 1 for  $p_A = 1$  and  $p_B = 0.1$ .

possible routes to diffuse around the slow particles.

### 3. Associative desorption under transient conditions

In heterogeneous catalytic reactions, as noticed in the Introduction, the diffusion of coadsorbed particles or at least of some of them is usually fast compared to the rate-limiting reaction steps, and accordingly can often, especially under steady-state conditions, be excluded from the analysis. In other words, the diffusion plays perfectly its role so that an increase of its rate does not influence the kinetics. Of course, this is not always the case. In rapid reactions such e.g. CO oxidation on the Pt-group metals, CO diffusion is much faster than O diffusion, and, as already noticed in the Introduction, both these channels of diffusion can be manifested in the reaction kinetics especially under transient conditions [14,15] (reviewed in Liu et al. [7]). Another example is “reactive phase separation” at relatively low temperatures (reviewed in Section 7.3 in [7]). The full-scale classification of the transient regimes of the kinetics of catalytic reactions and the identification of the cases where Onsager’s off-diagonal corrections are important are still lacking. To clarify one of the related scenarios, I present MC simulations of diffusion-limited association of adsorbed A particles in the presence of B particles. In the MF approximation [Eq. (3)], the rate of A diffusion depends on the B coverage but does not depend on the rate of B diffusion, and one could accordingly expect that the kinetics of A association occurring at constant B coverage would be independent or at least weakly dependent on the rate of B diffusion. This is, however, not the case for the same reasons as for diffusion under steady-state conditions (Section 2; Refs. [7,14,15]). In fact, as demonstrated below, the scale of the effect of B diffusion on A association may be much more appreciable compared to what was shown in Section 2.

The corresponding kinetic MC simulations were performed on a square  $200 \times 200$  lattice with periodic boundary conditions by using the algorithm similar to that described in detail in Section 2. In particular, diffusion of A and B particles was realized via jumps to randomly chosen vacant nn sites with probabilities  $p_A$  and  $p_B$ , and the MC time was calculated as in Section 2. The diffusion-limited A association was mimicked by employing  $p_A = 1$  and removing an A particle from the lattice provided that after a jump it contacts one or more A particles in the nn sites. Among the latter particles, one was chosen at random and removed from the lattice as well. Initially, A and B particles were located at random. The initial A coverage was fixed to be 0.1 (the nn A-B pairs were excluded). The B coverage and jump probability,  $\theta_B$  and  $p_B$ , were used as governing parameters. For each  $\theta_B$  (0.2, 0.5, and 0.8), the simulations were done with  $p_B = 1, 10^{-1}, 10^{-2}$ , and  $10^{-3}$ .

The effect of the rate of B diffusion on the kinetics of A association is found to be nearly negligible provided  $\theta_B \leq 0.2$  [the results for  $\theta_B = 0.2$  are shown in Fig. 4(a)]. If  $\theta_B$  is appreciable, e.g., 0.5 [Fig. 4(b)], this effect is relatively weak during the first rapid phase of the kinetics (with  $\theta_A$  decreasing from 0.1 to 0.5) and strong later on. If  $\theta_B$  is high, e.g., 0.8 [Fig. 4(c)], the kinetics of A association is dramatically slowed down with decreasing the rate of B diffusion.

Concerning the lattice size,  $L = 200$ , used in the simulations under consideration, the situation is here similar to that in Section 2, i.e., the size can be considered to be large and does not influence the kinetics. This was confirmed by comparing the results obtained for  $L = 200$  and 100 (not shown).

### 4. Diffusion including exchange and pair jumps

As already noticed, diffusion of chemically adsorbed particles is usually considered to occur via individual jumps to nn vacant sites as in the conventional lattice-gas model. Other mechanisms of diffusion are also possible. For example, the activation barrier for diffusion can be comparable with the lateral interaction, and adsorbed particles can form incommensurate structures so that the lattice-gas approximation is not applicable, and the diffusion occurs via collective rearrangement of

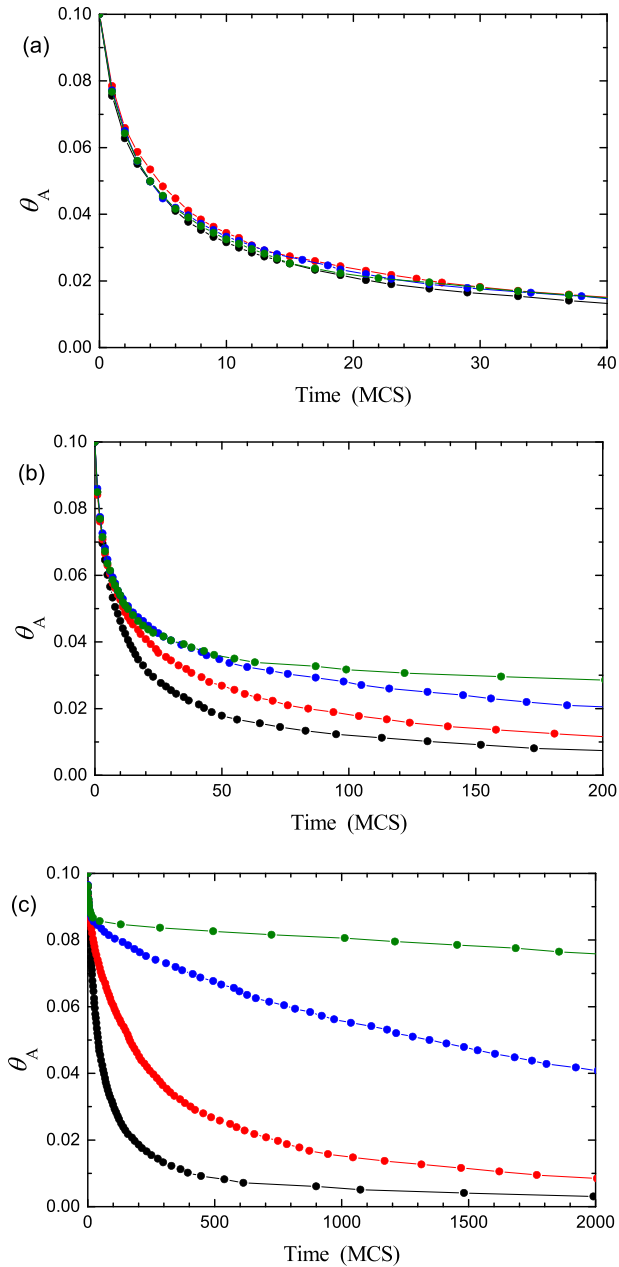


Fig. 4. MC kinetics of diffusion-limited association of A particles with  $\theta_A(0) = 0.1$  in the presence of B particles with  $\theta_B = 0.2$  (a),  $0.5$  (b), and  $0.8$  (c). In each case, the results are shown for  $p_B = 1, 10^{-1}, 10^{-2}$ , and  $10^{-3}$ . With decreasing  $p_B$ , the kinetics become slower.

a few or many particles (for related models, see, e.g., [33]). In the framework of the lattice-gas approximation, collective rearrangements can be introduced as well. In principle, for example, jumps of single particles to nn vacant sites may occur in parallel with concerted exchange of particles located in nn sites or by concerted jumps of pairs of particles located in nn sites to nn pairs of vacant sites. Such mechanisms of diffusion have not attracted attention in the areas of surface science and heterogeneous catalysis. The exchange mechanism of diffusion has, however, been scrutinized in the context of 1D “single-file” diffusive transport through finite-length nanopores (see [32] and references therein). Under certain conditions, this mechanism of diffusion is expected to be operative also in the case of adsorption of proteins at a solid surface. The specifics of proteins is that they are flexible and prone to reconfiguration. Acts of adsorption of proteins are usually considered to occur at vacant areas and include reconfiguration after adsorption

(reviewed in Rabe et al. [16]). At high coverage, the experiments can, however, sometimes be interpreted assuming the exchange mechanism where attachment of one protein occurs via concerted replacement of another already adsorbed protein with simultaneous reconfiguration of both proteins [34] (see also Section 5.1 in the review by Rabe et al. [16]). By analogy, diffusion of adsorbed proteins via concerted exchange or pair jumps is expected to be also possible under suitable conditions. From the tutorial point of view, these mechanisms of diffusion are instructive in the context of the Onsager theory. From this perspective, it makes sense to simplify the model up to the level allowing one to easily obtain exact results illustrating the key message. This strategy is used below. To be specific, the diffusion is discussed in terms corresponding to protein adsorption.

#### 4.1. Diffusion including exchange of particles

Let us consider diffusion of A and B proteins adsorbed on an anisotropic support which is fabricated so that it can be viewed as a square lattice with the lattice size comparable with the protein size so that the protein adsorption can be described in terms of the simplest lattice-gas model (no lateral interactions). The diffusion is assumed to be possible in both directions. It may include jumps of monomers to nn vacant sites,  $A0 \rightleftharpoons 0A$  and  $B0 \rightleftharpoons 0B$ , and concerted exchange jumps,  $AB \rightleftharpoons BA$ . The gradients of the coverages along the y direction are considered to be negligible, and the focus is on the diffusion along the x direction. The anisotropy of the lattice is introduced at the level of the rate of diffusion jumps. In particular, the jumps along the y direction are assumed to be much faster than along the x direction so that the proteins are located in the rows of sites along the former direction at random and the correlations in the arrangement of proteins in the pairs of nn sites are negligible.

In the framework of the model described above, the correlations are negligible, and accordingly the MF approximation yields exact results. In particular, the channel including jumps of monomers to nn vacant sites is described by Eq. (3), and the corresponding diffusion fluxes expressed via the gradients of the chemical potential do not contain the off-diagonal terms. In the context of our present discussion, additional analysis of this channel is not needed. The diffusion fluxes related to the exchange channel can be described by scrutinizing the balance of jumps directly in terms of coverages,  $\theta_A$  and  $\theta_B$ , or in terms of chemical potentials,  $\mu_A$  and  $\mu_B$ , by using the grand canonical distribution. The former approach is more conventional, while the latter one is more straightforward. Below, both these approaches are used in order to explain better the latter approach and then to use it in the case of pair jumps (Section 4.2).

In the absence of correlations, the diffusion flux of e.g. A particles along the x direction can be expressed as the difference of the forward and backward fluxes between rows  $i$  and  $i + 1$  oriented along the y direction,

$$J_A = k[\theta_A(i)\theta_B(i+1) - \theta_A(i+1)\theta_B(i)], \quad (9)$$

where  $k$  is the coverage-independent exchange rate constant. The introduction of the diffusion fluxes and the use of the diffusion equations imply that the concentration gradients take place on the length scale much larger than the lattice spacing (this spacing is here used as the unit length), and accordingly we have

$$\theta_A(i+1) = \theta_A(i) + \frac{\partial \theta_A}{\partial x} \quad \text{and} \quad \theta_B(i+1) = \theta_B(i) + \frac{\partial \theta_B}{\partial x}. \quad (10)$$

Substituting these expressions into (9) yields

$$J_A = -k\theta_B \frac{\partial \theta_A}{\partial x} + k\theta_A \frac{\partial \theta_B}{\partial x}. \quad (11)$$

The chemical potentials of particles are given by (with  $T = 1$ )

$$\exp(\mu_A) = \frac{\theta_A}{1 - \theta_A - \theta_B} \quad \text{and} \quad \exp(\mu_B) = \frac{\theta_B}{1 - \theta_A - \theta_B}, \quad (12)$$

and we have

$$\frac{\partial \mu_A}{\partial x} = \frac{1 - \theta_B}{\theta_A(1 - \theta_A - \theta_B)} \frac{\partial \theta_A}{\partial x} + \frac{1}{1 - \theta_A - \theta_B} \frac{\partial \theta_B}{\partial x}, \quad (13)$$

$$\frac{\partial \mu_B}{\partial x} = \frac{1 - \theta_A}{\theta_B(1 - \theta_A - \theta_B)} \frac{\partial \theta_B}{\partial x} + \frac{1}{1 - \theta_A - \theta_B} \frac{\partial \theta_A}{\partial x}. \quad (14)$$

With these relations, the derivatives of coverages can easily be expressed via the derivatives of chemical potential and then these expressions can be used in (11) or in a similar expression for  $J_B$ . This yields

$$J_A = -k\theta_A\theta_B \frac{\partial \mu_A}{\partial x} + k\theta_A\theta_B \frac{\partial \mu_B}{\partial x}, \quad (15)$$

$$J_B = k\theta_A\theta_B \frac{\partial \mu_A}{\partial x} - k\theta_A\theta_B \frac{\partial \mu_B}{\partial x}. \quad (16)$$

To employ the chemical potentials more explicitly, Eq. (9) can be rewritten as

$$J_A = k[\mathcal{P}_{AB}(i, i+1) - \mathcal{P}_{BA}(i, i+1)], \quad (17)$$

where  $\mathcal{P}_{AB}(i, i+1)$  is the probability that a pair of nn sites in rows  $i$  and  $i+1$  is occupied by A and B [ $\mathcal{P}_{BA}(i, i+1)$  is defined by analogy]. According to the grand canonical distribution, we have

$$\mathcal{P}_{AB}(i, i+1) = \mathcal{P}_{00}(i, i+1)\exp[\mu_A(i) + \mu_B(i+1)], \quad (18)$$

$$\mathcal{P}_{BA}(i, i+1) = \mathcal{P}_{00}(i, i+1)\exp[\mu_B(i) + \mu_A(i+1)]. \quad (19)$$

where  $\mathcal{P}_{00}(i, i+1)$  is the probability that a pair of nn sites in rows  $i$  and  $i+1$  is vacant, and  $\mu_A(i)$ ,  $\mu_B(i+1)$ ,  $\mu_B(i)$  and  $\mu_A(i+1)$  are the corresponding chemical potentials. The probability  $\mathcal{P}_{00}(i, i+1)$  in (18) and (19) is the same, and the corrections related to accounting the gradients of A and B concentrations during its calculation can be neglected, i.e., it can be represented as

$$\mathcal{P}_{00}(i, i+1) = (1 - \theta_A - \theta_B)^2. \quad (20)$$

In contrast, the chemical potentials in rows  $i+1$  and  $i$  are slightly different and can be related by analogy with (10). Using these relations first in (18) and (19) and then in (17) and taking into account that the derivative  $\partial \mu_A / \partial x$  and  $\partial \mu_B / \partial x$  are small (because the length scale characterizing the gradients of concentrations is usually much larger than the lattice spacing) and the exponential functions containing these derivative can be expanded, one can obtain expression (15) for the diffusion flux of A particles. Expression (16) for B particles can be obtained by analogy.

Expressions (15) and (16) contain the off-diagonal terms with respect to the gradients of the chemical potentials in agreement with Onsager's theory.

#### 4.2. Diffusion including pair jumps

Now, let us consider diffusion of A and B proteins occurring along the  $x$  direction at the anisotropic support (as in Section 4.1) via A and B jumps to nn vacant sites,  $A0 \rightleftharpoons 0A$  and  $B0 \rightleftharpoons 0B$ , and concerted jumps,  $AB,00 \rightleftharpoons 00,AB$ , of nn AB pairs located in one row of sites to nn pairs of vacant sites located in an adjacent row of sites. The diffusion along the  $y$  direction is assumed to be rapid and may include exchange events so that the gradients of the coverages along the  $y$  direction are negligible and the correlations in the arrangement of particles are negligible as well (as in Section 4.1). In this model, the A diffusion flux related to pair jumps is represented as

$$J_A = k[\mathcal{P}_{AB,00}(i, i+1) - \mathcal{P}_{00,AB}(i, i+1)], \quad (21)$$

where  $k$  is the coverage-independent rate constant, and  $\mathcal{P}_{AB,00}(i, i+1)$  is the probability that a pair of nn sites in row  $i$  is occupied by A and B and

the nn pair of sites in row  $i+1$  is vacant [ $\mathcal{P}_{00,AB}(i, i+1)$  is defined by analogy]. The grand canonical distribution yields

$$\mathcal{P}_{AB,00}(i, i+1) = \mathcal{P}_{00,00}(i, i+1)\exp[\mu_A(i) + \mu_B(i)], \quad (22)$$

$$\mathcal{P}_{00,AB}(i, i+1) = \mathcal{P}_{00,00}(i, i+1)\exp[\mu_B(i+1) + \mu_A(i+1)]. \quad (23)$$

where  $\mathcal{P}_{00,00}(i, i+1)$  is the probability that two adjacent pairs of nn sites located in rows  $i$  and  $i+1$  are vacant, and  $\mu_A(i)$ ,  $\mu_B(i+1)$ ,  $\mu_B(i)$  and  $\mu_A(i+1)$  are the corresponding chemical potentials. Then, the diffusion flux defined by Eqs. (21)–(23) can be calculated by using the procedure similar to that employed in Section 4.1. In particular, taking into account that

$$\mathcal{P}_{00,00}(i, i+1) = (1 - \theta_A - \theta_B)^4, \quad (24)$$

and using expressions (12) for the chemical potentials, we obtain

$$J_A = J_B = -k\theta_A\theta_B(1 - \theta_A - \theta_B)^2 \left( \frac{\partial \mu_A}{\partial x} + \frac{\partial \mu_B}{\partial x} \right). \quad (25)$$

As in (15) and (16), the A and B diffusion fluxes are seen to contain the off-diagonal terms with respect to the gradients of the chemical potential in agreement with Onsager's theory.

## 5. Conclusion

The results presented in this study clarify the role of Onsager's off-diagonal terms in diffusion of coadsorbed particles from two perspectives.

First, the scale of the related effects is shown for conventional diffusion via jumps of monomers to nn vacant with emphasis on the concentration profiles and diffusion fluxes under steady-state conditions and diffusion-limited associative desorption under transient conditions. In these cases, the role of Onsager's corrections is manifested at the level above the MF approximation provided the coverages are appreciable and the difference between the jump rates of particles is appreciable as well.

Second, the diffusion occurring via unconventional mechanisms including concerted exchange and pair jumps has been scrutinized. In these cases, the role of Onsager's corrections can be well manifested at the MF level. On the basis of the analysis performed, this conclusion is expected to be applicable to more complex unconventional schemes of diffusion including concerted jumps. Concerning the simplest exchange and pair jumps, I can add that the corresponding equations [(15), (16), and (25)] can be straightforwardly generalized by analogy with the derivation of Eq. (1) in order to take lateral interactions into account.

Although, as many other theoretical studies of diffusion of adsorbed particles, this work is not focused on specific systems, the results obtained are potentially of interest in the context of applications. In particular, the conclusions drawn in Section 2 can be instructive in the case of processes occurring on nanocomposite surfaces. The results presented in Section 3 may be useful e.g. for the interpretation of associative desorption of hydrogen occurring from a metal surface in the presence of strongly bound coadsorbed species (such systems are numerous). The conclusions drawn in Section 4 are instructive e.g. in the context of the late stage of the formation of a protein corona around nanoparticles. At this stage, the protein coverage is appreciable and the protein attachment to, detachment from, and diffusion along the surface of nanoparticles may occur via the exchange mechanism.

## Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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