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Comment on "Monte Carlo simulations for a Lotka-type model with reactant diffusion and interactions"

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Discussing the effect of adsorbate-adsorbate lateral interactions on the kinetics of heterogeneous catalytic reactions, Zvejnieks and Kuzovkov [Phys. Rev. E **63**, 051104 (2001)] conclude that in the case of adsorbed particles the Metropolis Monte Carlo dynamics is meaningless and propose to use their own dynamics, which is equivalent to the Glauber dynamics. In this Comment, I show that these and other conclusions and prescriptions by Zvejnieks and Kuzovkov are not in line with the general principles of simulations of rate processes in adsorbed overlayers.

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The kinetics of chemical reactions in gas and liquid phases are usually described by employing the conventional mass-action law equations. The laws governing the kinetics of heterogeneous catalytic reactions are as a rule much more complex due to adsorbate-adsorbate lateral interaction (AALI), surface heterogeneity, spontaneous and adsorbate-induced changes in a surface, and/or limited mobility of some of the reactants [1]. The most straightforward way of simulations of the reaction kinetics complicated by these factors is based on the use of the Monte Carlo (MC) technique. To employ this technique, one needs to understand the relation between the conventional Metropolis (MP), Glauber (GL), or Kawazaki MC dynamics; dynamics inherent to adsorbed overlayers, and the general principles of the theory of rate processes on solid surfaces. These aspects of MC simulations have recently been discussed by Zvejnieks and Kuzovkov (ZK) in the paper [2] aimed at illustrating the effect of AALI on the kinetics of a model heterogeneous reaction occurring via the Lotka mechanism. In the Introduction, referring to my MC simulations [3] of oscillatory kinetics of NO reduction by H_2 on Pt(100), they write that the MP dynamics should not be used in studies of the kinetics of catalytic reactions in general and surface diffusion in particular, because "*this method is defined only for equilibrium systems, where the kinetic aspects of the model are neglected*." Then, ZK propose to employ their own "*standard*" dynamics, which is essentially equivalent to the GL dynamics. From our point of view, the ZK criticism of the MP dynamics, their prescriptions to use the GL dynamics, and some other their statements are misleading for the following reasons:

(1) According to the MP rule, the normalized dimensionless transition probability is defined by

$$P_{\mathrm{MP}}=\begin{cases}1 & \text{for } \epsilon_f \leqslant \epsilon_i\,,\\ \exp[-(\epsilon_f-\epsilon_i)/k_{\mathrm{B}}T] & \text{for } \epsilon_f > \epsilon_i\,,\end{cases} \tag{1}$$

where ϵ_i and ϵ_f are AALI in the initial and final states. For the GL dynamics, we have

$$P_{\mathrm{GL}}=1/(1+\exp[(\epsilon_f-\epsilon_i)/k_{\mathrm{B}}T]). \tag{2}$$

To relate these dynamics to more specific dynamics corresponding to adsorbed particles, it is instructive to focus on surface diffusion and to recall the general principles of describing this process [1,4] in the simplest case when it occurs via jumps of adparticles to nearest-neighbor (NN) vacant sites. Under thermal conditions, the rate constants of such jumps can be calculated by employing the transition state theory. According to this theory, the jump rate of a given particle at a given arrangement of adjacent particles depends on the energy difference between the activated and initial (ground) states, and accordingly can be represented as

$$k_i=k_o\exp[-(\epsilon_i^*-\epsilon_i)/k_{\mathrm{B}}T], \tag{3}$$

where k_o is the jump rate at low coverages and ϵ_i^* is the lateral interaction between the activated complex and adjacent particles. Comparing Eqs. (1)–(3) shows that the relevance of the MP and GL dynamics for surface processes depends not on whether the system is close to equilibrium, as claimed by ZK, but rather on the type of AALI in the activated state.

(2) To illustrate the point noted in item (1) more explicitly, let us consider diffusion of particles with attractive NN AALI ($\epsilon_i \leqslant 0$) on a square lattice (Fig. 1). In this case, the distance between the activated complex and adjacent (nonactivated) adparticles is larger than that between NN adparticles. Taking into account that AALI rapidly decreases with increasing distance, one can conclude that AALI in the activated state is often weak compared AALI in the initial state.

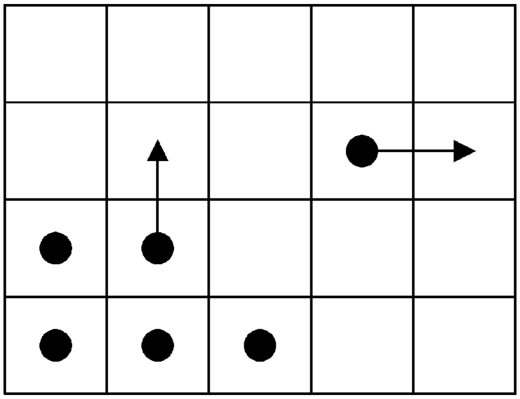

FIG. 1. Jumps of a single particle and a particle located on the island boundary. In the latter case, the particle has two neighbors, and accordingly, its energy is $\epsilon_i=2\epsilon_1$.

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Neglecting ϵ_i^* and normalizing k_i to k_o, one then obtains the jump probability for the so-called initial-state (IS) dynamics,

$$P_{\mathrm{IS}} = \exp(\epsilon_i / k_{\mathrm{B}}T). \tag{4}$$

According to this dynamics proposed in the first simulations of surface diffusion [5,6] and now very widely used in surface science [1,4], the ratio of the jump rates of a particle located on the island boundary and a single particle is $\exp(n\epsilon_1/k_{\mathrm{B}}T)$, where ϵ_1 is AALI between two NN particles, and n is the number of NN particles (Fig. 1). The MP dynamics yields the same result. In contrast, the GL dynamics predicts that this ratio is equal to $2/[1+\exp(-n\epsilon_1)/k_{\mathrm{B}}T)]$. Thus, contrary to the ZK statements, the MP dynamics is more relevant in the case under consideration compared to the GL dynamics. This, of course, does not mean that the MP dynamics is universally applicable [one can construct practically important examples where both (MP and GL) dynamics fail], but that we can conclude from this example is that the MP dynamics is at least not worse than the GL one.

(3) In my simulations [3], the oscillations in the kinetics of the NO-H_2 reaction on Pt(100) are connected with NO-induced surface restructuring. To describe this process, I took into account attractive NO-Pt lateral interactions. For NO adsorption and desorption, I used the IS dynamics, which was validated by experiment. The details of the effect of surface restructuring on NO diffusion are not well known. For this reason, I employed the MP dynamics for this process, because in agreement with available experimental data [7] it predicts rather rapid diffusion on hex and (1×1) patches; rapid jumps at the phase boundaries from the hex to (1×1) phase, but slow jumps in the opposite direction. Taking into account the experimental data and also the points formulated in items 1 and 2 above, I conclude that the ZK attempt to criticize my simulations on the basis that the MP dynamics is irrelevant and their prescription to use the GL dynamics instead make no sense.

(4) Concerning NO or CO diffusion on Pt(100), it is instructive to discuss briefly how Kuzovkov *et al.* [8] treat the effect of surface restructuring on this process. (i) In their study, the adsorption sites are allowed to be in the states α and β (Fig. 2), corresponding in reality to the hex and (1×1) phases, respectively. (ii) The CO jumps from a site in the state α (β) to an NN site in the state β (α) are considered to be faster (slower) than those between the sites in the same state. (iii) The propagation of phase boundaries is simulated by analyzing the state of pairs of NN sites. If one of the sites is in the state β, another one is in the state α, and in addition the pair is occupied at least by one CO molecule, the latter site transits to the state β. If the pair does not contain CO molecules, the former site transits to the state α. The rates of these transitions are assumed to be equal. Here it is appropriate to note that assumptions (ii) and (iii) violate the detailed balance principle, which plays the key role in simulations of rate processes. To demonstrate this fact, let us scrutinize the jump rates of CO molecules shown in Fig. 2. According to Kuzovkov's rules, a CO molecule located in site 3 facilitates the $\alpha \rightarrow \beta$ transition in site 4. This means that Kuzovkov *et al.* implicitly take into account the lateral interaction between this particle and site 4. According to the detailed balance principle, this interaction should modify the rates of other processes as well. But, according to Kuzovkov's rules, this is not the case. For example, Kuzovkov *et al.* consider that the rate of the CO jump from site 3 to site 2 is the same as from site 6 to site 5.

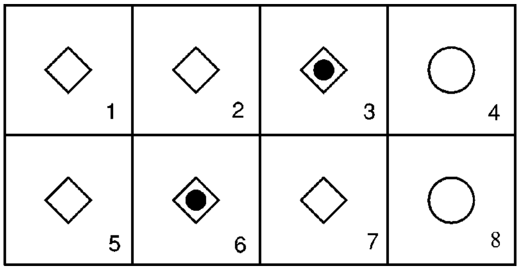

FIG. 2. Model of CO-induced restructuring of the Pt(100) surface proposed by Kouzovkov *et al.* [8]. The large open circles and diamonds show adsorption sites in the states α and β, corresponding in reality to the "hex" and (1×1) phases, respectively. The small filled circles indicate CO molecules.

(5) Introducing their version of the Lotka model, ZK write that it can be used "*to study the very basic properties of catalytic systems*." There are a few controversial points, which are as follows. (i) Here I may recall that Lotka proposed his oscillatory model in the beginning of the previous century [9]. Oscillations in heterogeneous catalytic reactions have actively been studied already three decades (see the first report [10] about observation of this phenomenon and reviews [7,11,12]). During this period, a multitude of models have been proposed to simulate such oscillations [11], but none of them includes the autocatalytic steps, $A_{\mathrm{ads}}+B_{\mathrm{ads}} \rightarrow 2B_{\mathrm{ads}}$ ("ads" means "adsorbed"), inherent for the Lotka model, because such steps do not occur in reality. (ii) In addition, in real catalytic reactions, surface diffusion of at least one of the reactants is usually so rapid that the bimolecular steps, $A_{\mathrm{ads}}+B_{\mathrm{ads}} \rightarrow \mathrm{Product}$, are not limited by diffusion as assumed by ZK (for the discussion of this aspect of simulations of the kinetics of heterogeneous reactions, see, e.g., the reviews [12,13]). Taking into account points (i) and (ii), one can hardly agree with the ZK statement quoted in the beginning of this paragraph, because the abstract model they use has a little in common with basic properties of real catalytic systems.

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