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Reply to ''Comment on 'Surface restructuring, kinetic oscillations, and chaos in heterogeneous catalytic reactions' ''

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In my numeration, the criticism of my simulations of kinetic oscillations in NO reduction by H_2 on Pt(100) [V. P. Zhdanov, Phys. Rev. E **59**, 6292 (1999)] by Kuzovkov, Kortlüke, and von Niessen [preceding paper, Phys. Rev. **63**, 023101 (2001)] contains 19 comments. I show that four comments are irrelevant. The other 15 comments are wrong, because they either contradict the basic principles of the theory of phase transitions, Monte Carlo simulations, and catalytic chemistry or ignore numerous experimental data on adsorbate-induced restructuring of the Pt(100) surface.

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I appreciate that Kuzovkov, Kortlüke, and von Niessen (KKN) start their Comment by referring to the general principle which I believe [1] should be used in simulations of oscillations, chaos, and pattern formation in heterogeneous catalytic reactions. Bearing in mind this principle, I have executed Monte Carlo (MC) simulations of oscillations in reactions accompanied by adsorbate-induced surface restructuring (AISR) [2,3(a,b)] and oxide formation [3(c)]. My analysis of oscillations related to AISR is based on the well-defined lattice-gas model [4] describing this phenomenon in terms of the statistical theory of first-order phase transitions (FOPT's). Specifically, I have treated NO reduction by H_2 [2] and CO [3(a)] and CO oxidation [3(b)] on Pt(100). Characterizing the earlier MC simulations of these reactions, I noted [2(a)]: ''In all the available MC models ..., the purely mathematical rules employed to realize the steps related to surface restructuring are far from those prescribed by statistical mechanics. For example, surface diffusion of CO (or NO) molecules is neglected or considered to be independent of the state of metal atoms. With such prescriptions, well-developed phases with atomically sharp phase boundaries, that are possible, are lacking, e.g., CO (or NO) molecules are not able to induce the formation of (1×1) islands at relatively low coverages, because there is no driving force for phase separation.'' Among the available MC models, I mentioned that proposed for CO oxidation by KKN [5(a)] (see also their more recent similar simulations [5(b)–(d)]). The Comment by KKN is aimed at my articles but actually they try to defend their results. Below, I show that my characterization of their works was right.

The KKN comments on my simulations [2(a)] of the $NO+H_2$ reaction are numerous. To keep the line, I reproduce their criticism in italic type together with my commentaries written in roman type.

(1) ... *the arguments given by Zhdanov are rather peculiar and the resulting model has nothing in common with a chemically reasonable model for the $NO+H_2$ reaction on Pt(100).*

Below, I show that the general conclusion above has no any grounds.

(2) *A consequence of this model ... is that all systems with a dissociative adsorption show the same nonlinear phenomena which is not true.*

In my paper, I note that the proposed reduced model of the $NO+H_2$ reaction is generic in the sense that it contains a minimal number of elementary steps. I, however, never claimed that the results predicted by this model are applicable to all systems with dissociative adsorption. Moreover, I have deliberately noted (p. 6296) that even in the case of the $NO+H_2$ reaction the applicability of the model is limited by special conditions.

(3) *The ... reaction steps are arbitrary ruled out because the reaction rates of these steps are either small or large, respectively.*

I rule out some of the slow steps on the basis of the available experimental data. Rapid steps were not ruled out (see item 5 below). Thus, the word ''arbitrary'' in the comment above makes no sense. The words ''ruled out'' used for rapid steps do not make sense either.

(4) *Jansen and Niemenen [7] showed that ...*

In NO reduction by H_2, we have several parallel channels of removing the reaction products from the surface. Some of these channels are slow and I neglect them. For example, the N_2O formation is often slow compared to N_2 desorption and accordingly was neglected. KKN try to criticize this standard (in catalytic chemistry) approach by referring to slow adsorption of a nonreaction species. The fact that such species can dramatically effect the reaction kinetics is well known (the example of kinetic oscillations based on this idea was proposed [6] long before the paper published by Jansen and Niemenen) but irrelevant because in our case we have no nonreacting species.

(5) *Even more peculiar is the neglect of ... N_2 desorption because it is rather fast. ... This can be clearly seen in the ... model ... [8] or ... [9,10] where the microscopic reactions are infinitely fast ...*

I do not neglect N_2 desorption in the sense discussed in item (4). In contrast, I consider that this process is so fast compared to other steps that the N coverage is negligibly low. To justify this assumption, I refer (p. 6296) to the experimental data indicating that the N_2 desorption is really fast (the activation energy obtained for this process from thermal desorption measurements is about 20 kcal/mol). Under such conditions, there is no need to simulate N_2 desorption explicitly. One can simply remove N particles formed on the surface during NO decomposition just after decomposition. This reasonable and self-consistent approximation used in my work is not original. In catalytic chemistry, it has been successfully employed many decades [for a relevant example, see simulations [7] of oscillations in the NO-CO reaction on Pt(100)]. KKN try to criticize this point by referring to the simulations (Refs. [8–10] in the Comment) where the adsorbate coverages were appreciable or the macroscopic reaction rate was slow even if the microscopic reaction rate was infinitely fast. This trivial effect observed in the quoted simulations is directly connected with the fact that reactant diffusion was ignored or considered to be slow compared to reaction. In real systems, reactant diffusion (CO, NO, or N) is known to be relatively fast (this important point is ignored in the KKN simulations; e.g., they erroneously assume that the reaction between adsorbed O and CO is limited by CO diffusion). For this reason, the examples mentioned by KKN are irrelevant.

(6) *. . . the conclusion that ''the adsorbate-induced restructuring of the (100) face of Pt should be described in terms of the theory of first-order phase transitions'' is not correct.*

According to the theory of phase transitions, the free energies of different phases are different for FOPT and coincide for second-order phase transitions. In our case [for NO reduction or CO oxidation on Pt(100)], we have two phases: an almost clean ''hex'' phase and the (1×1) phase covered primarily by NO (or CO). The fact that the free energies of these phase are different is firmly established experimentally [8,9]. On the clean surface, for example, the energy of the (1×1) phase is higher by about 5 kcal/mol than that of the ''hex'' phase. After NO or CO adsorption, the energy of the (1×1) phase becomes lower than that of the ''hex'' phase. Thus, there is no doubt that this phase transition is of the first order. This finding forms a basis of the mean-field (MF) kinetic models [10,11] of CO oxidation on Pt(100) (these models are actually much more realistic than those proposed by KKN).

(7) *All models for surface reconstruction which are based on the theory of FOPT's have one decisive disadvantage: They predict a complete segregation of the phases, completely independent of their specific definition. . . .*

The theory of phase transitions predicts unlimited growth of islands or domains only in closed systems. In open chemically reactive systems, the island or domain growth can easily be terminated (this well established fact was first explicitly demonstrated in Ref. [12]). Thus, the comment above is wrong.

(8) *The . . . nonlinear island growth rate which has been observed by Hopkinson et al. [15,16] cannot be explained with a FOPT . . .*

Hopkinson *et al.* studied the dependence of the island growth rate on CO coverage in the case when the growth is accompanied by CO adsorption and desorption. The FOPT theory does not provide any strict prescriptions for this case. For this reason, the data obtained by Hopkinson *et al.* do not contradict the FOPT theory. Thus, the comment above is not correct.

(9) *Therefore . . . even the definition of the model by Zhdanov . . . contradicts experimental observations.*

From my commentaries in items 6–8, it is clear that this general conclusion is wrong.

(10) *Zhdanov draws the conclusion that the* (CO or NO) *desorption rate should be large on the* α (hex) *phase and very small on the* β *phase. But this conclusion cannot be drawn . . .*

This conclusion does not belong to me. The fact that this is the case was firmly established in the experiments (see, e.g., Refs. [9,11]). KKN ignore this finding in their simulations.

(11) *. . . the energetic interactions on the atomic length scale are almost unknown.*

At present, the scale of the interactions is known from the experiment (see, e.g., item 6), and my model takes into account the available information. In contrast, the KKN models ignore numerous experimental data.

(12) *The processes (2.1) and (2.2)* (NO or CO desorption and diffusion) *are . . . combined in the author's model . . . But there is no reason for this forced combination of both processes. . . .*

CO (or NO) adsorption is reversible. CO (or NO) diffusion jumps are reversible as well. For this reason, the rates of these processes should be calculated in accordance with the detailed balance principle. This was done in my MC simulations and also in the earlier MF simulations by Gruyters *et al.* [11] (in particular, they take into account that due to the adsorbate-substrate interaction, the difference of the activation energies for CO desorption from different phases is the same as that for the CO exchange between the phases). In the KKN simulations, all these effects crucial for a physically reasonable description of AISR are ignored.

(13) *Consider an almost homogeneous surface . . . with large terraces and only a few . . . steps. The . . . terraces can be regarded as different ''phases.'' The desorption is then completely independent of the phase, . . . but in the diffusion from one phase one phase to the other there exist an asymmetry . . .*

In this example, the individual terraces cannot be regarded as different ''phases'' because the adsorption energies on the terraces are equal. To describe this system properly, one needs [19] to introduce adsorption on step sites and define the jump rate from these sites to the terraces and back in agreement with the detailed balance principle. Then, one can easily show that despite the asymmetry of the diffusion jumps from the terraces to the step sites the average coverages of different terraces will be equal at equilibrium (even if there are no adsorption and desorption processes). The latter result cannot be obtained if one excludes step sites and introduce an asymmetry for jumps between the terraces as proposed by KKN. Thus, the KKN example is wrong because they violate the detailed balance principle.

(14) *In the model introduced by Zhdanov . . . the difference of the Boltzmann factors for the nucleation and for phase border propagation (island growth) is small . . .* $\sim$0.1. *This is a clear contradiction to the experiment where it has been shown that the nucleation is a very rare process . . . [17].*

The kinetic parameters used in my simulations have been chosen to describe the reaction kinetics at $T\simeq500$ K. Even at these relatively high temperatures, the model predicts that in the case discussed by KKN the nucleation rate is appreciably lower than the phase propagation rate. In the experiments of Ritter *et al.* (Ref. [17] in the Comment), the growth of the (1×1) phase at submonolayer NO coverage was studied by scanning tunneling microscopy (STM) at 295 K. They conclude that the removal of the ''hex'' phase occurs via a ''nucleation and growth'' mechanism but do not present any quantitative estimates of the relative rates of these processes. From their data (Fig. 5), it is clear that the growth is faster than nucleation. One can however hardly estimate the ratio of the rates, because it is not quite clear whether the patterns on the left bottom side of the panels should be attributed to the growth of new or already existing islands. For these reasons, these data do not contradict my model. In addition, it is appropriate to note that in my model the nucleation rates of the phase transitions are strongly dependent on the arrangement of adjacent adsorbed particles. In contrast, KKN ignore this important effect in their simulations.

(15) *A further point is that the rates of adsorption and nucleation in Ref. [3] are of the same order of magnitude and are coupled because of the definition of the model. This is a further contradiction to experiment . . . [18].*

Here I may recall once more that I simulated the reaction kinetics on the Pt(100) surface at relatively high temperatures, $T \simeq 500$ K. Even at these temperatures, the nucleation rate in my simulations is appreciably lower than the adsorption rate. Gritsch *et al.* (Ref. [18] in the Comment) studied by using STM a very initial stage of the CO-induced (1×2)→(1×1) phase transition on the Pt(110) surface at submonolayer coverages. In their work, the time scale of adsorption was much shorter than that of nucleation, because the experiments were executed at 300 K. Thus, these experimental data do not contradict my simulations. In addition, I may note that the quoted data are irrelevant for our discussion, because the CO-induced (1×2)→(1×1) phase transition on Pt(110) is different (much softer) compared to the CO- or NO-induced ''hex''→(1×1) phase transition on Pt(100). My simulations [2,3] are focused on the latter system. AISR of Pt(110) was treated earlier [13] by using the model which has a little in common with that employed in my recent works. In contrast, KKN use their model for both systems. This means that their model does not take into account the specifics of AISR of the Pt (100) and (110) surfaces.

(16) *The simulation procedure performed by Zhdanov is as follows. . . . The processes are divided into groups on account of their relative weights. In each group there exist additional division with additional weights. . . . At the end of this chain the process which occurs is chosen . . . according to the Metropolis* (MP) *rule.*

The last sentence in this comment is not quite right. I use the MP dynamics only for NO diffusion and surface restructuring. The other processes (NO adsorption, desorption and decomposition) are simulated by employing the other types of dynamics.

(17) *A MC simulation which contains kinetic parameters is always connected with the corresponding master equations via the . . . rates for the elementary . . . processes. These transition rates give an unequivocal definition of the time scale and the probabilities for the MC simulation procedure [19–21]. This is missing in the author's model.*

This comment contains two mistakes. (i) The MC algorithm used in my simulations is not original. I employ one of the standard algorithms described in the classical review by Binder [14]. Reading that review (or other textbooks), one can find that the definition of MC probabilities, their relation with real rate constants, and also the relation of the MC and real time are not unique. All these details of MC simulations are different for different MC algorithms. With a correct choice of these details, different MC algorithms are known to give identical results. Thus, the KKN statement that the ''transition rates give an unequivocal definition of the time scale and the probabilities for the MC simulation procedure [19–21]'' is erroneous. (ii) In my simulations, I first define (p. 6299) the dimensionless parameters characterizing the relative rates of different processes and then describe (p. 6301) the relationship between these parameters and the rate constants of different processes and also the relation between the MC and real time. Thus, the KNN criticism (the last sentence in the comment) makes no sense.

(18) *Even worse is the use of the Metropolis rule . . .*

The MP dynamics is well known to be the simplest dynamics compatible with the detailed balance principle. In the situations when the details of real dynamics are not well established, the application of the MP dynamics is reasonable. For example, this dynamics is widely used to simulate various kinetic processes, e.g., phase transitions [15] or protein folding [16]. I employ the MP rule for NO diffusion and surface restructuring. At present, the understanding of the details of these processes is limited and accordingly the application of the MP dynamics is a reasonable first step. If necessary, one can use other dynamics for these processes as described in Ref. [17]. All these points have been explicitly noted in my papers, and accordingly the grounds for the KKN comment are in fact absent.

(19) *V. ALTERNATIVE MODEL . . .*

The main goal of my simulations was to show spatiotemporal patterns which are possible in oscillatory catalytic reactions accompanied by AISR. In Sec. V, using the same ideas and in their earlier MC simulations, KKN propose the MF equations describing AISR. These equations are very poor because they do not contain such key parameters as an average size of islands, etc. Accordingly, the results presented in Sec. V are irrelevant. Nevertheless, I may give a few comments on these equations in order to emphasize once more the type of shortcomings available in the KKN papers. (i) In the beginning, ignoring the experimental data, KKN assume that the rate constants of desorption from two phases are equal. The rate constants of jumps between the phase are, however, considered to be different. The description of these two steps contradicts the detailed balance principle. (ii) The KKN statement that ''the membrane effect in the diffusion at the phase border is the only driving force for phase separation'' is erroneous because the phase separation can be realized both via the adsorption-desorption steps and via surface diffusion. For this reason, all these steps should be described self-consistently. In the KKN simulations, this is not the case. (iii) Using then κ as a fitting parameter, KKN try to obtain the experimentally measured critical coverages for the coexistence of the (1×1) and ''hex'' phases. In reality, these coverages are however crucially dependent on lateral adsorbate-adsorbate and adsorbate-substrate interactions. For example, the upper critical coverage ($\simeq 0.5$) is determined by the nearest-neighbor repulsive interaction between CO molecules. This interaction, ignored by KKN, results in the local $c(2\times2)$ CO ordering on the (1×1) patches so that the formation of this phase becomes possible on the whole surface at $\theta_{\mathrm{CO}}\simeq 0.5$ (see experiment [8,18] and simulations [4]). Thus, the KKN model does not contain the key factors determining the values of the critical coverages. For this reason, their attempts to fit the experiment are physically senseless.

In summary, I conclude that four KKN comments [items (4), (5), (18), and (19)] are irrelevant. The other 15 comments are wrong, because they either contradict the basic principles of the theory of phase transitions, Monte Carlo simulations, and catalytic chemistry or ignore numerous experimental data on IASR of Pt(100). Despite this outcome, I believe that our discussion merits publication because it will help to understand and use the right level of description of oscillations and pattern formation in heterogeneous catalytic reactions. In particular, our discussion shows that the abstract models [5] proposed by KKN are far below that level.

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