PHYSICAL REVIEW E, VOLUME 65, 033102

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

V. N. Kuzovkov[1,*] and G. Zvejnieks[1,2]
[1]*Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV–1063 Riga, Latvia*
[2]*FB Physik, Universitat Osnabruck, Barbarastrasse 7, D-49069, Osnabruck, Germany*

(Received 4 September 2001; published 15 February 2002)

We reply to the Comment by Zhdanov [preceding paper, Phys. Rev. E **65**, 033101 (2002)] on our recent paper [G. Zvejnieks and V. N. Kuzovkov, Phys. Rev. E **63**, 051104 (2001)]. We demonstrate that our quite different viewpoints result, in fact, entirely from nonunique definitions of the master equation, which has nothing to do with neglecting important physical principles, as Zhdanov claims.

DOI: 10.1103/PhysRevE.65.033102 PACS number(s): 82.20.Wt, 05.50.+q, 82.65.+r

As is well known, a wide class of physical problems, including the kinetics of heterogeneous catalytic reactions, is traditionally described in terms of the master equations (ME). The definition of ME allows us not only to perform Monte Carlo (MC) simulations, but also to develop at the same time appropriate analytical methods [mean field (MF), cluster approximations, etc.] [1]. ME is formally defined when all possible states of a system and the transition rates between these states are specified. This is enough to define only the transition rates $K(i\rightarrow j)$ for such *elementary processes* as particle adsorption, desorption, diffusion, reaction, etc., from the initial state *i* to the final state *j*. ME is a purely axiomatic theory, e.g., the actual form of the transition rates $K(i\rightarrow j)$ is completely arbitrary. When neglecting adsorbate-adsorbate lateral interaction (AALI), various MC methods have to give (and indeed they give) essentially the same reaction kinetics (if we neglect unavoidable fluctuation effects). For illustration, the MC methods used in Refs. [2,3] differ from one another as considerably as standard random walks differ from continuous-time random walks [4]. However, both methods give the equivalent kinetics [5] when applied to the same Kuzovkov-Kortlüke-von Niessen (KKN) model [6–10]; the only difference is in the speed of the particular computer codes.

However, the situation qualitatively changes when AALI is taken into account. The AALI is introduced into the ME formalism through Gibbs statistics, which is imposed as a kind of ME boundary condition. It is assumed that for reversible processes the ME gives the equilibrium distribution at an asymptotically large time. This boundary condition still weakly restricts the possible form of the transition rates through the detailed balance principle (DBP). In fact, the DBP determines exclusively the ratio of the transition rates, and only for *reversible processes*,

$$\frac{K(i\rightarrow j)}{K(j\rightarrow i)}=\frac{W^{eq}(j)}{W^{eq}(i)}. \tag{1}$$

Here $W^{eq}(i)$ and $W^{eq}(j), W^{eq}(i)+W^{eq}(j)=1$, are the probabilities to find the system in the states *i* and *j* for a local equilibrium, which are dependent on the AALI. In the case of irreversible processes DBP does not hold.

Therefore, the DBP is unable to introduce AALI uniquely into the ME formalism. Any transition rate definitions, which satisfy Eq. (1), drive the reversible processes to the equilibrium state. This nonuniqueness had no effect in the MC simulations of the thermodynamical equilibrium, but it becomes indeed actual, when *the kinetics of the processes* is involved. The mentioned nonuniqueness indicates that any theory based on DBP is logically incomplete. This is why the kinetic models including AALI have to be completed by means of additional definitions, in order to define uniquely the transition rate dependence on the AALI. Similar logical incompleteness is a problem of many physical theories, which, however, are widely used in natural sciences.

The additional definitions in axiomatic theories are impossible to achieve entirely using physical arguments. For example, a similar situation occurs in the theory of the stochastic differential Ito-Stratonovich equation [11], where the same equations are interpreted (i.e., defined) following either Ito or Stratonovich. The choice of additional definitions, that is, the use of different axiomatic, leads to a simultaneous coexistence of all dynamics mentioned by Zhdanov: Metropolis (MP), Glauber (GL), and initial-state (IS) dynamics. In our opinion, the variety of dynamics and their simultaneous use indicates weakness of a general theory. The actual formalism chosen depending on the proclivity of the investigator and each approach has its proponents. However, it is not acceptable for a many scientists that some physical problems cannot be solved entirely by physical arguments.

Let us formulate the basic requirements of an axiomatic approach. Additional definitions have not only to define uniquely the transition rates for the reversible elementary processes, but also to determine the transition rate dependence on AALI for the irreversible processes. These definitions have to be universal, i.e., they have to be independent on the particular nature of the states *i* and *j*. Moreover, taking into account that the definition of the initial and final states *i* and *j* is relative, the additional definitions have to be symmetrical with respect to the exchange of *i* and *j*.

The so-called standard model (or the standard dynamics) that was proposed earlier by us [1,12] and only very briefly described in Ref. [2], results from the consequent application of the philosophical principle by Ockam: "Essences should

---

[*] Electronic address: kuzovkov@latnet.lv

not be multiplied without necessity.'' For *all* the elementary processes, the only additional definition introduced is

$$K(i \rightarrow j) = QW^{eq}(j), \quad K(j \rightarrow i) = QW^{eq}(i), \tag{2}$$

where Q is a cofactor energetically independent on the states i and j. It was shown in a number of papers [1,2,12] that the use of this definition, Eq. (2), leads to a unique definition of the ME, independently of the inclusion or neglect of the AALI. Since Eq. (2) satisfies Eq. (1), the standard model for the equilibrium system automatically gives the Gibbs distribution, as expected.

Let us compare now some consequences of our standard model and analogous consequences arising from definitions introduced by Zhdanov. It was shown in [1,2,12] that according to the definition, Eq. (2), the transition rates for irreversible processes, are AALI-independent. The paper [13] however contains the strange statement: ''The effect of lateral interactions on the A-decomposition rate is for simplicity neglected (if necessary it can be taken into account . . .).'' This means that Zhdanov (i) can make the arbitrary transition rate to be AALI dependent in a given way, (ii) he knows how to specify this AALI dependence for the irreversible process. This is quite a fundamental point about the Zhdanov approach: his axiomatic is obviously incomplete since the transition rates for irreversible processes remain undefined. The point is that the dynamics described above are borrowed exclusively from the simulations of reversible processes. As far as models describing the kinetics of heterogeneous catalytic reactions always have irreversible processes, the methods have to be completed with the help of additional definitions. Strictly speaking, only our standard model has a unique definition of the transition rates for all processes. Alternative methods, like MP, GL, or IS, in practice, are also completed by their users but in an irregular way.

The standard model is not equivalent to the GL dynamics, as stated by Zhdanov, despite reproducing the dynamics for the Ising model. We want to stress that the dynamics in the standard model is defined for all processes in the same way. In contrast, in the papers by Zhdanov, as he writes himself, ''For NO adsorption and desorption, I used the IS dynamics. . . . I employed the MP dynamics'' for diffusion. The simultaneous application of the two different dynamics in a single model is quite characteristic of Zhdanov. The reader is, of course, welcome to choose alternative ways, e.g., to use the IS dynamics for diffusion and the MP dynamics for adsorption/desorption (the number of possible combinations becomes quite large). The preference for a particular dynamics with an argument that it gives ''agreement with available experimental data,'' i.e., using physical arguments, sounds strange, especially in light of this discussion. Superposition of several dynamics is a consequence of the fact that a single additional definition in our standard model, Eq. (2), is substituted by a number of particular definitions for each elementary process (or for groups of elementary processes). However, we insist on our point of view that the universal definitions and their symmetry is a key point in the development of axiomatic principles of any theory. The kinetics of heterogeneous catalytic reactions is not an exception. All particular additional definitions have an obvious disadvantage–they introduce a subjective factor, e.g., a number of possible asymmetric combinations of various dynamics mentioned above.

The use of the transition state theory in the comment by Zhdanov is another attempt to find independent additional arguments. The author forgets, however, that this theory in fact stems from DBP, i.e., from Eq. (1). As a consequence, this theory is logically incomplete, in analogy to the formalism of ME with AALI incorporation. The transition state theory introduces a purely intuitive assumption of so-called activated states (not used in the original definition of considered models) characterized by an undefined parameter $\omega \in [0,1]$ (known as the Brønsted-Polanyi coefficient [14]). This uncertainty is a direct consequence of the logically incomplete theory. Its additional definition is substituted by the choice of a particular parameter ω. In this way one can develop the alternative dynamics that differ by the value of ω. In a practice, mainly the three limiting cases are considered; $\omega = 0, \omega = 1$, and $\omega = 0.5$. A characteristic disadvantage of this method is that a particular choice of this parameter varies for different authors. For example, one can define a model where only adsorption is governed by AALI, but not a desorption. However, an opposite point of view (desorption depend on AALI, but not an adsorption) could be assumed equally well. The choice of a particular ω value in the papers that use the transition state theory often is based on the speculative assumptions about the properties of activated states. Exactly in this case practical application of the philosophical principle by Ockam is not only advisable but necessary.

Point (2) of the Zhdanov Comment is a typical illustration of application of a particular choice of ω. Instead of saying that he defines the dynamics with a particular ω value, the author gives an illustration (Fig. 1) and discusses which states (initial or final) is closer to the activated state. Obviously, for a particular choice of a parameter ω, e.g., $\omega = 0$, the alternative dynamics with $\omega = 1$ looks absurd, which is well demonstrated by Zhdanov.

The arguments that some dynamics was introduced as the first or is actively used somewhere else are not important. Physics, as a science, is developing and its definitions constantly become more and more elaborate. Thus, the MP dynamics historically was just a simple algorithm for searching for the equilibrium state in the lattice models using the MC method when the transition to the equilibrium state (kinetics) was unimportant. The dimensionless transition probabilities in the MP method are bounded from above by the nonanalytical conditions that contain energies of the initial and final states. In historically later developed dynamics, like GL and the standard model, all transition probabilities are not only bounded from above, but the corresponding conditions are analytical and have a high symmetry with respect of the exchange of forward and backward processes. This gives us additional possibilities to use analytical methods. One has to remember that the MC simulations are only a part of the ME ideology. A choice of a particular dynamics determines both, the corresponding MC procedure and a form of the kinetic equations [1], used e.g., in the mean-field approximation. For example, the GL dynamics was first proposed to describe the kinetics analytically.

Let us summarize now. The main problem is not which of possible dynamics fits better a given process, but that the very procedure of the ME development with AALI is not unique. Taking into account the growing interest of scientific community in the heterogeneous catalytic reactions, and the role of AALI in particular, a number of researchers facing the described problem and giving each time their subjective solution to the problem continuously increases. As a result, even now a comparison of the results obtained by different groups is almost impossible. We do believe that the real solution is a transition to a universal scheme and our standard model is one of the possibilities: it is very comprehensive and has the highest symmetry. We would like to stress that the theory was developed to describe a wide class of problems, which contain both reversible and irreversible processes.

Point 4 lies beyond the scope of the article being criticized [2], and continues the discussion started in papers [15,16] with new arguments suggested by Zhdanov. He ignores the fact that AALI is not used in the papers with KKN [6–10,15] but is suspicious of the fact that we use AALI, but in a hidden form. In his papers (see [13], and references therein) Zhdanov assumes that the surface reconstruction phenomena can be interpreted exclusively from the point of view of AALI. Any alternative approach is assumed by him to be wrong by default.

We agree with Zhdanov that the adsorbate induced surface reconstruction is a phase transition. But Zhdanov ignores that there exist kinetic phase transitions and recognizes only *statistical* phase transitions based on *energetic* interactions. Our model is a purely *kinetic* that needs no energetic parameters. The absence of ALLI in the definition of the model makes the DBP unnecessary. No doubt, there exist energetic interactions on the atomic length scale, but these remain unknown. A kinetic model therefore should be preferred in order to avoid manipulation with numerous unknown energetic parameters. Even more important is the fact that the adsorbate induced surface reconstruction shows almost no temperature dependence [17].

Our papers [10,15] once more support Ockams principle in practice. They give a purely kinetic interpretation of the phenomena, i.e., the peculiarities of the surface reconstruction of the Pt(100) surface (and other surfaces as well) is connected with the asymmetric diffusion of the adsorbants from one phase to another (the membrane effect). The extreme simplicity of the suggested mechanism is supported by both the MC method [10] and analytical estimates [15]. The KKN theory has a minimum number of parameters: both critical adsorbate concentrations (NO and CO) depend on a single parameter characterizing the diffusion asymmetry across a phase boundary. In the interpretation by Zhdanov, each critical concentration has a different origin and a total number of unknown energetic parameters that are necessary for the kinetics is four.

We would like to stress that the statement of Zhdanov [16] that the DBP is violated in the papers by KKN, and then repeated in the Comment, could be true when (i) the model of KKN is taking into account AALI, and (ii) the choice of transition rates contradicts Eq. (1). However, as was mentioned earlier, the KKN model ignores the AALI. Instead, the common principles of diffusion of noninteracting particles in spatially inhomogeneous media are only used [18]. The jump rate of the particle to the nearest neighboring site depends not on the initial or final surrounding of the particle (AALI neglected), but entirely by the fact whether both sites belong to the same phase or lie on the phase boundary. In the latter case the backward and forward jump rates over a phase boundary could be different.

In Point 5 Zhdanov returns to our paper [2], but focusing now on the Lotka model used there. The general nature of the Lotka model was stressed by us in Ref. [2], as well as in earlier paper [19], where the importance of the model was compared with the Ising model in the theory of phase transitions. Similarly to the fact that the Ising model is not a model of a real ferromagnet, the Lotka model is not an accurate model of any real catalytic process. However, nobody criticizes, e.g., the theory of phase transition for using simplified models. Theoretical models are images of real systems aimed to reproduce the most important aspects of the system and neglects less important details. The Lotka model [19] is the simplest (single parameter) model that allows us to investigate the fundamental properties of synchronization of oscillations and resonance properties as a response to an external modulation by the means of the MC simulations. We think that the synchronization of oscillations is ‘‘the basic properties of real catalytic systems.’’ However, the problem of synchronization has no direct connection with the reality of the used catalytic model, and thus it can be investigated with quite abstract models. So, the observed resonance properties of the Lotka-type model, which are similar to experimental result for CO oxidation on a Pt surface, were shown [19]. Nevertheless, the Lotka-type model has nothing in common with the traditional CO oxidation models, including the KKN model [6–9].

The reality of the models often is quite relative. As it is stressed [15], the complete kinetic scheme of the $NO+H_2$ reaction [13] contains ten microscopical elementary reaction processes in which eight adsorbate species occur. However, according to Zhdanov [13], ‘‘ . . . our reduced scheme of the $NO+H_2$ reaction on Pt(100) contains only two steps, namely reversible NO adsorption and decomposition. . . . Thus, we have only one adsorbed species, NO.’’ Comments here are unnecessary.

In conclusion, we are greatly indebted to V. P. Zhdanov for giving us the opportunity in this Reply to focus on the hidden ME problems that are not explained in the classical textbooks. We agree that this problem grows with time, with increasing interest to a role of AALI in heterogeneous catalysis. However, the solution of the problem suggested by us fundamentally differs from that by Zhdanov. We also totally disagree with him with respect to the level of abstraction necessary for modeling complex physico-chemical processes.

[1] E. A. Kotomin and V. N. Kuzovkov, *Modern Aspects of Diffusion-Controlled Reactions: Cooperative Phenomena in Bimolecular Processes*, Vol. 34 of Comprehensive Chemical Kinetics (Elsevier, Amsterdam, 1996).
[2] G. Zvejnieks and V.N. Kuzovkov, Phys. Rev. E **65**, 051104 (2001).
[3] R.J. Gelten, A.P.J. Jansen, R.A. van Santen, J.J. Lukkien, J.P.L. Segers, and P.A.J. Hilbers, J. Chem. Phys. **108**, 5921 (1998).
[4] E.W. Montroll and G.H. Weiss, J. Math. Phys. **6**, 167 (1965).
[5] J. Lukkien (private communication).
[6] V.N. Kuzovkov, O. Kortlüke, and W. von Niessen, J. Chem. Phys. **108**, 5571 (1998).
[7] O. Kortlüke, V.N. Kuzovkov, and W. von Niessen, J. Chem. Phys. **110**, 11523 (1999).
[8] O. Kortlüke, V.N. Kuzovkov, and W. von Niessen, Phys. Rev. Lett. **81**, 2164 (1998).
[9] O. Kortlüke, V.N. Kuzovkov, and W. von Niessen, Phys. Rev. Lett. **83**, 3089 (1999).
[10] V.N. Kuzovkov, O. Kortlüke, and W. von Niessen, Phys. Rev. Lett. **83**, 1636 (1999).
[11] C. W. Gardiner, *Handbook of Stochastic Methods for Physics*, Chemistry and the Natural Sciences (Springer, Berlin, 1983).
[12] J. Mai, V.N. Kuzovkov, and W. von Niessen, J. Phys. A **29**, 6205 (1996).
[13] V.P. Zhdanov, Phys. Rev. E **59**, 6292 (1999).
[14] *Handbook of Heterogeneous Catalysis*, edited by G. Ertl, H. Knözinger, and J. Weitkamp, (Wiley, Weinheim, 1997), Vol. 3.
[15] V.N. Kuzovkov, O. Kortlüke, and W. von Niessen, Phys. Rev. E **63**, 023101 (2001).
[16] V.P. Zhdanov, Phys. Rev. E **63**, 023102 (2001).
[17] A. Hopkinson, J. Bradley, X.-C. Guo, and D. King, Phys. Rev. Lett. **71**, 1597 (1993).
[18] *Diffusion in Condensed Matter*, edited by J. Kräger, P. Heitjans, and R. Haberlandt (Vieweg, Wiesbaden, 1998).
[19] G. Zvejnieks and V.N. Kuzovkov, Phys. Rev. E **61**, 4593 (2000).