



## Coarse-graining the computations of surface reactions: Nonlinear dynamics from atomistic simulators

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### ABSTRACT

We review and discuss the use of equation-free computation in extracting coarse-grained, nonlinear dynamics information from atomistic (lattice-gas) models of surface reactions. The approach is based on circumventing the explicit derivation of macroscopic equations for the system statistics (e.g., average coverage). Short bursts of appropriately initialized computational experimentation with the lattice-gas simulator are designed “on demand” and processed in the spirit of the coarse timestepper introduced in Theodoropoulos et al. (2000) (K. Theodoropoulos, Y.-H. Qian, I.G. Kevrekidis, Proc. Natl. Acad. Sci. USA 97 (2000) 9840). The information derived from these computational experiments, processed through traditional, continuum numerical methods is used to solve the macroscopic equations without ever deriving them in closed form. The approach is illustrated through two computational examples: the CO oxidation reaction, and the NO + CO/Pt(100) reaction.

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### 1. Introduction

Complex systems are typically characterized by the emergence of macroscopic, coherent behavior from the interactions of microscopic degrees of freedom – molecules, individuals in a population – among themselves and with their environment. In modeling such systems we often start with a description at a fine scale, microscopic/atomistic level, and attempt to derive – through appropriate assumptions and closures – macroscopic, coarse-grained descriptions (e.g., obtain the Navier-Stokes equations starting from kinetic theory, Chapman and Cowling [1]). Deriving *accurate* such macroscopic equations in closed form is a formidable task that often cannot be successfully carried through; detailed simulations with the atomistic/microscopic models appears then to be the only way of extracting information about the system’s behavior, its dependence on parameters etc. This approach suffers from the tremendous space and time scale gap between the level at which a good physical model is available (e.g., molecular dynamics) and the level at which information is required (e.g., design of a chemical reactor). Multiscale computational methods (ranging from Car-Parinello molecular dynamics [2] to the quasi-continuum method of Ortiz and Phillips [3]) attempt to bridge this gap. In this paper the complex, multiscale problems of interest are heterogeneous catalytic reactions on metal single crystal lattices, and the fine scale, microscopic models are of the lattice-gas type. The purpose

of the paper is to briefly review the application of the so-called Equation-Free approach to modeling complex/multiscale systems [4–6] to the systems level analysis of the nonlinear dynamics of such reactions/models. In particular, we will explore coarse-graining the dynamics of reactions that involve lateral adsorbate interactions.

Lateral interactions between adsorbed species on catalyst surfaces have been studied for many years in an effort to understand their effects on chemical reaction dynamics. It is well known that, due to lateral interactions, strong spatial correlations and ordered adsorbed layers (microstructures) arise on the catalyst surface. Microstructures of adsorbed and coadsorbed particles have been found and analyzed with a variety of methods, including low-energy electron diffraction [7] and scanning tunneling microscopy (STM) [8].

In order to mathematically describe the influence of lateral interactions on the reaction kinetics, equations of a mean-field (MF) type are widely used. However, these equations ignore spatial correlations in the adsorbed layer; the absence of correlations in the occupation of sites is inconsistent with the presence of lateral interactions. As a result, the rates of chemical reactions predicted by MF models can be quite inaccurate, and the comparison between theory and experiment becomes inconclusive. In order to take the lateral interactions into account, more sophisticated approximations can be constructed (e.g., quasi-chemical approximation); yet it is difficult to control the accuracy of these approximations, especially for reactions involving several interacting adsorbates and different adsorption sites. Theoretically, the

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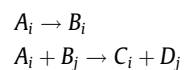
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non-ideal lattice-gas problem can be solved “exactly” using kinetic Monte Carlo (KMC) simulations. At present, this technique is widely used in modeling heterogeneous catalytic reaction kinetics (e.g., [9–13]). With current computing capabilities, KMC simulations in combination with transition state theory and density functional theory (DFT) may yield unprecedentedly deep insights in surface science problems [14–18].

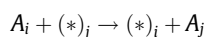
Our paper uses two illustrative examples, the CO + O<sub>2</sub> and NO + CO/Pt(100) catalytic reactions, to demonstrate the use of equation-free computation. We review, discuss and slightly extend results from previous publications on the subject [19–21]. The paper is organized as follows: In Section 2 we set the stage by describing both the direct (KMC) lattice-gas simulations and the equation-free computation of coarse-grained bifurcation diagrams (coarse-KMC). Sections 3 and 4 review the computational exploration of the nonlinear dynamic behavior of our two model systems. Coarse turning points as well as coarse Hopf bifurcations are detected. We conclude with a brief discussion and some thoughts about the scope and future applications of the approach.

## 2. KMC simulations and coarse-KMC bifurcation analysis for a lattice-gas model

We consider a set of elementary reactions, such as adsorption, desorption, migration, bimolecular reaction etc. A catalyst surface is represented by a perfect lattice with  $N = N_1 \times N_2$  adsorption sites and periodic boundary conditions. Elementary reactions may involve one or two adsorption sites:



Here,  $i$  and  $j$  are nearest-neighbor (NN) lattice sites. Each lattice site can be occupied by an adsorbed particle (say, of type A) or it can be empty [ $A = (*)$ ]. The list of possible microscopic events includes the elementary events of migration:



which describe the individual jumps of adsorbed particles to their NN vacant sites. The set of all possible elementary reactions constitutes the reaction mechanism.

We take into account lateral interactions only between the NN adsorbed species, and also interactions of the activated complexes with neighboring adparticles. Second-, third- etc., NN interactions can be included in the model in a straightforward manner. In addition, it is quite easy to extend the model by taking into account the different adsorption sites (on-top, bridge, fourfold etc.). We assume that the lateral interactions are pairwise additive; three- and more-particle interactions are neglected. Due to lateral interactions, the activation energies of elementary reactions may depend on the local environment, and because of these interactions an ordered adsorbed layer forms on the lattice.

The time evolution of the probability distribution for the adparticles populations can be described by the chemical master equation:

$$\frac{dP_x(t)}{dt} = \sum_{x'} \{W_{x' \rightarrow x} P_{x'}(t) - W_{x \rightarrow x'} P_x(t)\},$$

where  $P_x(t)$  [ $P_{x'}(t)$ ] denotes the probability of finding the system in configuration  $x$  [ $x'$ ] at time  $t$ , and the  $W_{x \rightarrow x'}$  are used to denote transition probabilities per unit time which specify the rate of the adsorbed layer changes due to various elementary reactions. The transition probabilities can be interpreted as microscopic rate constants that are described by the Arrhenius equation using activation energies and pre-exponential factors. Unfortunately, even for very

small lattice sizes, the chemical master equation consists of an enormous number of ordinary differential equations (ODEs), and it is practically impossible to integrate it directly. Therefore, one has to either use some uncontrolled approximations in order to derive macroscopic evolution equations, or to implement detailed KMC simulations which are able to simulate the “exact” dynamical evolution of the reacting system.

The basic steps of the KMC algorithm we have implemented are as follows [22,23]:

1. Prescribe a lattice configuration at  $t = 0$ .
2. Calculate transition probabilities per unit time (rates),  $W_\alpha(i, j)$ , for all elementary reactions  $\alpha$  at all lattice sites  $i$ .
3. Calculate the total transition probability  $W = \sum_\alpha \sum_{i,j} W_\alpha(i, j)$  in order to find the expected time  $\Delta t$  that the system spends in the current configuration:  $\Delta t = -\ln(\xi)/W$ , where  $\xi$  is a random number taken from a uniform distribution on  $(0, 1)$ . Update the current time by an increment  $\Delta t$ .
4. Using a random number uniformly distributed on the unit interval, select one reaction from the set of all possible microscopic events, with a probability proportional to its rate.
5. Perform the selected kinetic event, and update the appropriate  $W_\alpha(i, j)$  values in order to take the local compositional changes on the lattice into account.
6. Repeat the previous three steps while  $t < \tau$ .

This KMC algorithm constructs one realization of the master equation solution by generating the sequence of configurations and the times when these configurations change from one to the other. This algorithm can be viewed as a stochastic time-stepper which solves an initial value problem. It uses the species distribution on a lattice at  $t = 0$  and generates a final distribution at  $t \geq \tau$ .

Realistic description of surface diffusion is one of the main implementation problems for KMC simulations of catalytic reactions under typical experimental conditions. In most practical cases, especially under UHV conditions, adspecies hop rates are many orders of magnitude greater than all other rates. For example, DFT calculations give a rule-of-thumb estimate for the diffusion barrier at about only 12% of the binding energy of the adsorbed state [24].

On the other hand, due to fast diffusion of adsorbates, at each time instant the adsorbed layer can be thought of as being in an equilibrium state for the current adsorbate coverages and temperature. This feature turns disadvantage into advantage: it can be shown that, in the limit of infinite diffusion and lattice sizes, the macroscopic system behavior can be described in terms of ordinary differential equations for coverages [25]. In this work, we assume “infinitely” fast diffusion of adsorbed species. This assumption, in particular, allows us to suggest that the long-term, macroscopic system behavior can be described in terms of average coverages only: higher order correlation functions are quickly slaved to (become functionals of) the coverages. This is analogous to a quasi-steady state approximation: the higher order moments evolve first quickly to a *slow manifold*, and then evolve slowly on this manifold parameterized by the coverages [4–6]. One can observe the evolution of trajectories on this manifold through the coverages of the corresponding distributions.

We assume that the evolution of the adspecies coverages in the lattice-gas model can indeed be described by a system of “coarse” ODEs:

$$\frac{d\Theta}{dt} = F(\Theta; p) \quad (1)$$

Here,  $\Theta \in \mathbb{R}^m$  is a vector containing the system state,  $m$  is the number of different adsorbed species,  $F: \mathbb{R}^{m+1} \rightarrow \mathbb{R}^m$ , and  $p$  is a real scalar denoting the dependence of the kinetics on a parameter,

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