Self-organized nanostructures in surface chemical reactions: Mechanisms and mesoscopic modeling

M. Hildebrand
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany
(Received 30 August 2001; accepted 17 December 2001; published 21 February 2002)

Nanoscale patterns can form in reactive adsorbates on catalytic surfaces as a result of attractive lateral interactions. These structures can be described within a mesoscopic theory that is derived by coarse graining the microscopic master equation thus providing a link between microscopic lattice models and reaction–diffusion equations. Such mesoscopic models allow to systematically investigate mechanisms responsible for the formation of nanoscale nonequilibrium patterns in reactive condensed matter. We have found that stationary and traveling nanostructures may result from the interplay of the attractive lateral interactions and nonequilibrium reactions. Besides reviewing these results, a detailed investigation of a single reactive adsorbate in the presence of attractive lateral interactions and global coupling through the gas phase is presented. Finally, it is outlined how a mesoscopic theory should be constructed for a particular scanning tunneling microscopy experiment [the oxidation of hydrogen on a Pt(111) surface] in order to overcome the failure of a corresponding reaction–diffusion model to quantitatively reproduce the experiments. © 2002 American Institute of Physics. [DOI: 10.1063/1.1448807]

The interplay of chemical reactions and cohesion in condensed matter may lead to the development of nonequilibrium nanostructures. Because the characteristic length scale of these structures is small, fluctuations may be important. A mesoscopic theory is formulated for such systems in terms of continuous concentrations including noises that reflect the discreteness of the microscopic dynamics. It is used to systematically explore mechanisms for the formation of nanoscale patterns in simple models for reactive surface adsorbates with attractive lateral interactions. These mechanisms are general and may play a role in other condensed reactive systems such as reactive polymer blends or biological membranes.

I. INTRODUCTION

In heterogeneous catalysis surface chemical reactions typically take place in open flow reactors. Hence, such systems are far from thermal equilibrium and the formation of dissipative structures is possible. The discovery of temporal oscillations of the reaction rate in the oxidation of carbon monoxide on a platinum wire in the early 1970s1,2 triggered a series of investigations of nonlinear aspects in this model reaction (see, e.g., Refs. 3 and 4). A systematic exploration of mechanisms responsible for oscillations and other self-organized phenomena was facilitated by the use of single crystal surfaces under ultra high vacuum (UHV) conditions.5,6 In this case, the catalytic reactions can be regarded as strictly isothermal and the possible interplay of the surface structure with the adsorbate is well defined. A breakthrough was achieved in the late 1980s when the development of photoelectron emission microscopy (PEEM) allowed to monitor nonequilibrium patterns in surface chemical reactions such as standing or traveling waves or rotating spirals, with characteristic length scales ranging from a few micrometers to several hundreds of micrometers in real time.7–9 These patterns could be relatively well described by classical reaction–diffusion (RD) models that neglect fluctuations and lateral interactions in the adsorbate.10

The development of novel experimental techniques such as field ion microscopy11,12 and fast scanning tunneling microscopy (STM)13 has opened the possibility to monitor some surface chemical reactions with an atomic resolution in real time. These experiments have clearly shown that the fast kinetic processes are typically accompanied by the appearance of nanoscale structures.14–16 The small characteristic length scales of the observed nanostructures can be attributed to the presence of lateral interactions between adsorbed molecules.17 The interactions can be either of a direct (van der Waals, electrostatic, bond formation) or an indirect, substrate-mediated nature.18 The latter type of interactions can be attractive, repulsive, or alternating. It can result from local changes of the surface electronic wave functions which are induced by adsorbed molecules and usually extend over several lattice lengths.11,19,20 On the other hand, the presence of an adsorbate can also modify the local crystallographic structure of the substrate’s surface layer and thus produce deformations and stresses in the crystal. This effect leads to long-range indirect elastic interactions between adsorbed molecules and their clusters.21–24

Because of significant interactions between adsorbed molecules and the presence of catalytic surface reactions, the adsorbates can be viewed as reactive condensed matter.25,26 In typical situations, such as the CO-oxidation on platinum single crystal surfaces, the diffusion length of mobile adsorbed reactants lies in the micrometer range. Because it represents the minimal characteristic length scale in corresponding RD models, they fail to describe the formation of nanoscale structures. The RD approach treats an adsorbate...
like a two-dimensional reactive ideal gas. Therefore, interactions can only be phenomenologically taken into account by assuming a coverage dependence of diffusion coefficients or desorption rates.

On the other hand, microscopic lattice models take explicitly into account the random motion of individual molecules and probabilistic reactions between them. Based on some rather general assumptions (see, e.g., Ref. 27) and the underlying physics, a master equation can be constructed that completely describes the microscopic dynamics of the system. Numerical realizations of the master equation are obtained in kinetic Monte Carlo (MC) simulations. Local and nonlocal lateral interactions between adsorbed molecules have been taken into account in such simulations. On the one hand, however, computational limitations have to be faced when intending to quantitatively describe long-range interactions or the interplay of short-range lateral interactions with the fast reaction–diffusion kinetics in the adsorbates. Such large differences between the microscopic length scales and the diffusion length may be overcome by the use of hybrid models combining local MC simulations with large scale mean field models, the numerical solution of coarse grained master equations, or the use of finite elements with locally coarse grained dynamics. The hybrid treatment is particularly useful for the description of reactions between a highly mobile noninteracting species and an immobile species with interactions. On the other hand, MC simulations are essentially numerical experiments and, as such, they do not constitute an analytic theory. They do not allow to make predictions concerning the properties and the evolution of structures.

To bridge the gap between the “macroscopic” RD approach, which neglects fluctuations and interactions, and the microscopic lattice theory that primarily addresses statistical properties of the fluctuating system a mesoscopic theory is desirable. In previous publications we have constructed such models by coarse graining the microscopic master equation. Similar to RD models, they are formulated in terms of continuous concentrations (coverages) of adsorbed particles. The mesoscopic evolution equation is however stochastic including internal noises that reflect the discreteness of the microscopic dynamics. The deterministic limit of this equation allows the systematic investigation of pattern forming mechanisms with standard techniques from bifurcation theory and nonlinear dynamics. The effect of strong internal interactions between the particles, the coarse graining is performed by introducing a system of boxes, each containing a large number of lattice sites but still smaller than the radius of lateral interactions between the particles. The fluctuating local concentrations (coverages) are then defined as the fraction of lattice sites inside a box occupied by the considered kind of particles. Using the Kramers–Moyal expansion, the master equation is approximately transformed into a functional Fokker–Planck equation which, in turn, corresponds to a stochastic partial differential equation for the fluctuating local coverage.

Though the derivation is technically complicated, the final result is simple. If there is only one kind of particles which can adsorb, desorb, diffuse, react, and attract each other, the stochastic evolution equation for the local coverage \( c(r,t) \) is (see Ref. 38)

\[
\frac{\partial c}{\partial t} = k_a p (1 - c) - k_d c - k_r c + \frac{1}{k_B T} \nabla \left[ D(r) \left( \nabla c + (1 - c) \nabla U \right) \right] + \xi(r,t).
\]

The first term on the right-hand side of this equation describes the adsorption of particles (\( p \) is the constant partial pressure in the gas phase above the crystal, \( k_a \) is the sticking coefficient), the second term corresponds to thermal desorption of particles, and the third term describes the reaction. The next term takes into account Fickian diffusion and the viscous flow of particles over the surface induced by the gradient of the local potential \( U(r) \) for adsorbed particles. This nonuniform potential is due to attractive lateral interactions between the particles,

\[
U(r) = \int u(r - r') c(r') \, dr',
\]
where \( u(\mathbf{r}) \) is the two-particle interaction potential and the integration extends over the whole surface. Except when noted explicitly, the following attractive Gaussian pair potential will be used below:

\[
u(r) = -\frac{u_0}{(2\pi r_0^2)^{d/2}} \exp \left( -\frac{r^2}{r_0^2} \right)
\]

with the parameter \( u_0 \) specifying the interaction intensity and \( r_0 \) determining the interaction radius; \( d \) is the spatial dimension of the system (typically \( d = 2 \)), \( T \) is the temperature, and \( k_B \) is the Boltzmann constant. The rate constant for the thermal desorption process depends on the potential as

\[ k_d = k_{d0} \exp\left( U(\mathbf{r})/k_BT \right). \]

In contrast, the rate constant for the reaction \( k_r \) does not depend on the surface potential \( U \), because it is assumed that the energy released in a reaction event is much larger than any local differences in the surface potential. The monomolecular reaction may correspond to photoinduced desorption or a bimolecular reaction with a second species which is present in abundance and its spatial distribution is uniform as a result of fast diffusion. Note that an evolution equation similar to Eq. (1) but without the reactive and the fluctuating terms has been independently constructed for binary alloys in the limit of long-range interactions.

The diffusion coefficient \( D(\mathbf{r}) \) in Eq. (1) depends on the microscopic model for the hopping process. Two limiting cases can be distinguished: If it is assumed that \( U(\mathbf{r}) \) varies linearly between two neighboring adsorption sites, the Metropolis algorithm should be chosen. In this case, the microscopic hopping rate depends on the energy difference \( \Delta U = U(\mathbf{r}_1) - U(\mathbf{r}_2) \) between the two adjacent sites at \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) and the diffusion coefficient is independent of \( \mathbf{r} \). i.e., \( D(\mathbf{r}) = D \) where \( D = k_{d0}/T \) is determined by the microscopic hopping frequency in the absence of interactions \( k_{d0} \) and the lattice length \( l_0 \). On the other hand, often it is more natural to regard the hopping between adjacent sites as an activated process (termed Arrhenius diffusion). In this case, it is assumed that before reaching a neighboring site a moving adsorbate particle assumes an intermediate “activated” state in which it does not feel the energetic influence of the attractive lateral interactions. Then, the diffusion coefficient is given by

\[
D(\mathbf{r}) = D \exp\left( U(\mathbf{r})/k_BT \right).
\]

The differential equation (1) includes the internal noise \( \xi(\mathbf{r},t) \). It takes into account fluctuations resulting from the stochastic nature of the system, approximately described by this evolution equation. Its intensity and functional form are determined by the master equation specifying the detailed stochastic evolution of the system. In the considered case we have

\[
\xi(\mathbf{r},t) = Z^{-1/2}[\sqrt{k_d p (1-c)}f_d(\mathbf{r},t) + \sqrt{k_c f_c(\mathbf{r},t)} + \sqrt{k_r f_r(\mathbf{r},t)} + \nabla(\sqrt{2D(\mathbf{r})c(1-c)}f(\mathbf{r},t))].
\]

Each process (i.e., adsorption, desorption, reaction, and diffusion) gives rise to its own independent internal noise. The internal noises are multiplicative and compatible with the fluctuation–dissipation principle. In Eq. (6) \( f_d(\mathbf{r},t) \), \( f_d(\mathbf{r},t) \), and \( f_r(\mathbf{r},t) \) of the vectorial white random force \( f(\mathbf{r},t) \) are white random noises of unit intensity.

The stochastic partial differential equation (1) should be interpreted in the Ito sense. The parameter \( Z \) is the number of lattice sites per unit surface area, it is related as \( Z = 1/l_0^d \) to the lattice length \( l_0 \). As we have already noted above, the stochastic evolution equation is obtained by applying coarse-graining over surface elements of a certain linear size \( l \), such that \( l_0 \gg l \gg l_0 \). Therefore, it correctly retains only fluctuations with the characteristic lengths exceeding \( l \) and the characteristic times exceeding the mixing time \( \tau = l^2/D \) within the surface element of length \( l \).

III. NANOSCALE PATTERN FORMATION IN ADSORBATES WITH STRONG ATTRACTION LATERAL INTERACTIONS

A. Mesoscopic modeling of phase transitions

In the absence of the nonequilibrium reaction \( (k_r = 0) \) Eq. (1) describes an equilibrium first-order phase transition in the two-dimensional nonideal gas of adsorbed particles if the attractive lateral interactions are strong enough \( (u_0 > 4k_BT) \). If in addition thermal desorption and adsorption of particles are absent \( (k_d = k_p = 0) \), the total number of adsorbed particles is conserved. It can be shown that in this case the nonlocal evolution equation (1) reduces to the local Cahn–Hilliard equation, used in the kinetic theory of first-order phase transitions, in the vicinity of the critical point, when fluctuations are neglected, and the formal limit \( r_0 \to 0 \) is taken. Our numerical simulations of the nonlocal evolution equation (1) for the case of a conserved mean coverage have shown that it is capable to describe stochastic nucleation, spinodal decomposition and Ostwald ripening even in parameter regions far away from the critical point. Examples of the spatiotemporal stochastic evolution of a two-dimensional system for two different average coverages \( \langle c \rangle \) are displayed in Fig. 1. When \( \langle c \rangle = 0.3 \) [Fig. 1(a)], stochastic nucleation of the dense phase on the background of the dilute phase takes place. Subsequently, competition between the growing supercritical nuclei sets in, so that the smaller nuclei disappear. When \( \langle c \rangle = 0.5 \) [Fig. 1(b)], the uniform phase is absolutely unstable and spinodal decomposition is observed.

If adsorption and thermal desorption processes are taken into account, the total number of particles on the surface is not conserved and hence the properties of the phase transition are modified. The kinetics of such a phase transition, combining the features typical for systems with conserved and nonconserved order parameters, has been considered by us in Ref. 38 using Eq. (1) with \( k_r = 0 \). Figure 2 shows the early stage of the stochastic nucleation process in the two-dimensional system. In the beginning, individual islands of the dense phase appear. As these islands grow and their number increases, they start to interact due to the depletion of the
adsorbate in the region surrounding a growing island. As a consequence, the islands grow much slower than in the initial stage after their nucleation, fluctuations in the regions between the islands are suppressed, and the formation of new nuclei in those regions is prevented. The interface velocity in the deterministic limit and the mean rate of spontaneous nucleation were determined numerically in one-dimensional simulations of the mesoscopic evolution equation in Ref. 38. In the following, an equation for the interface motion in the deterministic limit was derived through homogenization and asymptotics.\(^5\) Thus, macroscopic laws of interface velocity, surface tension, mobility, and critical nucleus size were obtained that show a direct dependence on the interaction potential.

**B. Stationary nanostructures**

The kinetic behavior of an adsorbate undergoing a phase transition can be significantly affected by a nonequilibrium chemical reaction. If the nonequilibrium reaction is neither too strong nor too weak, the phase separation can be frozen leading to the formation of stationary nonequilibrium nanostructures.\(^4\) The development and the final form of such nanostructures are described by the mesoscopic evolution equation (1). Similar reaction-induced patterns have been theoretically predicted\(^5\) and experimentally observed\(^5\) in polymer blends undergoing phase separation.

Independent of the specific choice of the hopping rate and of the binary interaction potential, the uniform stationary states \(c_0\) of the deterministic limit of Eq. (1) are given by the

![Image](https://example.com/image1.png)

**FIG. 1. Two-dimensional phase separation in (1) in the absence of local kinetics \((k_r=k_p=k_d=0)\) for system size \(L=16, u_0=6\, k_B\, T, r_0=0.2, D =1, Z=4000,\) and \((\epsilon)=0.3\) in (a), and \((\epsilon)=0.5\) in (b). The time intervals between subsequent frames (shown from top left to bottom right) are \(\Delta t =2.5.\) The local surface coverage \(c\) is shown in gray scale, with darker areas corresponding to higher coverages.

![Image](https://example.com/image2.png)

**FIG. 2. Spontaneous nucleation in the stochastic two-dimensional system (1) for \(k_r=0\) (from top left to bottom right). The time interval between subsequent frames is \(\Delta t=5k_B\, T.\) Moreover, \(u_0=6\, k_B\, T, k_p=0.0753k_d, r_0=0.2(D/k_d)^{1/2},\) and \(Z=2\times10^3(k_d/D);\) the grid size is \(\Delta x =0.1(D/k_d)^{1/2}\) and the system size is \(L=16(D/k_d)^{1/2};\) gray-scale coding as in Fig. 1.

The kinetic behavior of an adsorbate undergoing a phase transition can be significantly affected by a nonequilibrium chemical reaction. If the nonequilibrium reaction is neither too strong nor too weak, the phase separation can be frozen leading to the formation of stationary nonequilibrium nanostructures.\(^4\) The development and the final form of such nanostructures are described by the mesoscopic evolution equation (1). Similar reaction-induced patterns have been theoretically predicted\(^5\) and experimentally observed\(^5\) in polymer blends undergoing phase separation.

Independent of the specific choice of the hopping rate and of the binary interaction potential, the uniform stationary states \(c_0\) of the deterministic limit of Eq. (1) are given by the

![Image](https://example.com/image3.png)

**FIG. 1. Two-dimensional phase separation in (1) in the absence of local kinetics \((k_r=k_p=k_d=0)\) for system size \(L=16, u_0=6\, k_B\, T, r_0=0.2, D =1, Z=4000,\) and \((\epsilon)=0.3\) in (a), and \((\epsilon)=0.5\) in (b). The time intervals between subsequent frames (shown from top left to bottom right) are \(\Delta t =2.5.\) The local surface coverage \(c\) is shown in gray scale, with darker areas corresponding to higher coverages.

![Image](https://example.com/image4.png)

**FIG. 2. Spontaneous nucleation in the stochastic two-dimensional system (1) for \(k_r=0\) (from top left to bottom right). The time interval between subsequent frames is \(\Delta t=5k_B\, T.\) Moreover, \(u_0=6\, k_B\, T, k_p=0.0753k_d, r_0=0.2(D/k_d)^{1/2},\) and \(Z=2\times10^3(k_d/D);\) the grid size is \(\Delta x =0.1(D/k_d)^{1/2}\) and the system size is \(L=16(D/k_d)^{1/2};\) gray-scale coding as in Fig. 1.

The kinetic behavior of an adsorbate undergoing a phase transition can be significantly affected by a nonequilibrium chemical reaction. If the nonequilibrium reaction is neither too strong nor too weak, the phase separation can be frozen leading to the formation of stationary nonequilibrium nanostructures.\(^4\) The development and the final form of such nanostructures are described by the mesoscopic evolution equation (1). Similar reaction-induced patterns have been theoretically predicted\(^5\) and experimentally observed\(^5\) in polymer blends undergoing phase separation.

Independent of the specific choice of the hopping rate and of the binary interaction potential, the uniform stationary states \(c_0\) of the deterministic limit of Eq. (1) are given by the

![Image](https://example.com/image5.png)

**FIG. 1. Two-dimensional phase separation in (1) in the absence of local kinetics \((k_r=k_p=k_d=0)\) for system size \(L=16, u_0=6\, k_B\, T, r_0=0.2, D =1, Z=4000,\) and \((\epsilon)=0.3\) in (a), and \((\epsilon)=0.5\) in (b). The time intervals between subsequent frames (shown from top left to bottom right) are \(\Delta t =2.5.\) The local surface coverage \(c\) is shown in gray scale, with darker areas corresponding to higher coverages.

![Image](https://example.com/image6.png)

**FIG. 2. Spontaneous nucleation in the stochastic two-dimensional system (1) for \(k_r=0\) (from top left to bottom right). The time interval between subsequent frames is \(\Delta t=5k_B\, T.\) Moreover, \(u_0=6\, k_B\, T, k_p=0.0753k_d, r_0=0.2(D/k_d)^{1/2},\) and \(Z=2\times10^3(k_d/D);\) the grid size is \(\Delta x =0.1(D/k_d)^{1/2}\) and the system size is \(L=16(D/k_d)^{1/2};\) gray-scale coding as in Fig. 1.

The parameter \(D_0\) in Eq. (8) is equal to the constant \(D\) for the case of the Metropolis algorithm, while it is given by \(D_0 = D\, \epsilon\) for activated surface diffusion. Assuming that the pair potential satisfies the scaling relation \(u(r) = f(r/r_0),\) the dispersion relations (8) are identical for both cases if the wavelength \(\lambda = 2\pi/k\) and the interaction radius \(r_0\) are rescaled to the characteristic length scale \(L_{\text{diff}} = (D_0/k_r)^{1/2}.\)
The case when the two-particle interaction potential is given by Eq. (3) and $D_0=D$ has been investigated in Ref. 41. It was shown that the self-organized stationary nanostructures can form as a result of a Turing-type bifurcation if the nonequilibrium reaction is neither too strong nor too weak. For sufficiently small interaction radii $r_0$ the wavelength of the first unstable mode can be estimated as

$$\lambda_0 \sim \sqrt{r_0 L_{\text{dir}}}.$$  \hspace{1cm} (10)

Equation (10) reflects the fact that the reaction-induced stationary nanostructures occupy an intermediate position between purely kinetic Turing structures and spatially modulated equilibrium phases of a purely energetic origin. We have performed a weakly nonlinear analysis \(^4^0\) for the one-dimensional system and the case when the pair potential is given by Eq. (3) showing that the Turing-instability is supercritical if the interaction radius is large enough and the thermal desorption is not too strong.

The general case can be qualitatively discussed by analyzing Eq. (8): The four first terms on the right-hand side of this equation are local contributions which dominate in the limit when the reaction radius is much smaller than the characteristic diffusion length. The last term corresponds to the nonlocal contributions. For purely attractive binary interactions $[u(r)<0 \text{ for all } r]$ it is always negative. For $\varepsilon>4$ however, the effective diffusion coefficient $D_{\text{eff}}(c) = D_0 [1-\varepsilon c (1-c)]$ can become negative enough to induce the formation of stationary nanostructures for small interaction radii. On the other hand, in the case of monotonously decaying purely repulsive interactions $[u(r)>0 \text{ and } u'(r)<0 \text{ for all } r]$ the nonlocal contribution to the dispersion is destabilizing. It can be shown however that always $\gamma_k < -k_d p -k_r -k_d \exp(-\varepsilon c_0)$, i.e., the nonlocal term never becomes large enough to destabilize the uniform stationary state. If the binary interaction potential is alternating, it follows from Eq. (8) that the instability can only take place if $u(r)$ is effectively attractive, i.e., if $\varepsilon>0$.

Numerical simulations have shown that the Turing-type instability leads to the formation of stationary nonequilibrium structures of different morphologies, such as spot arrays and complex labyrinthine phases. \(^4^1\) The characteristic length scale of these patterns is roughly determined by the wavelength (10) of the first unstable mode. Figure 3 shows an example of a stochastic simulation of a labyrinthine nanostructure in the presence of internal noises. Three snapshots of the two-dimensional system corresponding to subsequent time moments are displayed here. Measured in elementary lattice lengths $l_0$, the interaction radius is $r_0=6$ and the diffusion length is $L_{\text{dir}}=149$. The total linear size of the system is just $L=506$ elementary lattice lengths. We see that though the fluctuations are significant, they do not destroy the labyrinthine morphology of the nanostructure.

C. The influence of global coupling through the gas phase

Local variations of the catalytic activity on the surface lead to changes of the partial pressure in the gas phase. Typically, the local variations of the partial pressure equilibrate instantaneously on the characteristic time scale of the adsorbate kinetics. For example, in the CO-oxidation on platinum single crystal surfaces under UHV conditions the mean velocity of a gas particle is about $1000$ m/s and hence in a typical container, the effective equilibration of the local pressure variations takes place in less than $10^{-3}$ s. \(^3^4\) Therefore, in addition to being subject to nonlocal lateral interactions, in principle, adsorbed particles interact globally through the gas phase.

The influence of global coupling on reacting surface adsorbates has been the subject of various theoretical studies (see, e.g., Refs. 43 and 55). Kevrekidis et al. \(^5^5\) have investigated the influence of gas phase coupling on a single species that can adsorb, desorb, react, and is subject to strong attractive lateral interactions. Their analysis was however limited to uniform states. The model consisted of two coupled ordinary differential equations for the uniform coverage and the gas phase partial pressure of the considered species. Though they showed that the system could possess a limit cycle solution, they were not able to prove the stability of these homogeneous oscillations, because fluctuations and spatial couplings for inhomogeneous adsorbate distributions were not taken into account.

In order to address this open question we have generalized the evolution equation (1) to the case when the adsorbate particles are globally coupled through the gas phase. The partial pressure $p$ in Eq. (1) can be interpreted as a spatially uniform dynamical variable. Aside from the dependence of $p$ on the mean adsorption and desorption rates, the interaction of the reactor with the external environment must be taken into account. It is open in the sense that gas particles are continuously pumped into and out of it. For a constant inlet partial pressure $p_1$, the temporal evolution of the outlet partial pressure $p$ can be described as \(^4^0\)

$$\frac{\partial p}{\partial t} = \frac{p_1-p}{\tau_r} + p^* (k_d \exp(U(r)/k_B T) - k_d p (1-c)).$$ \hspace{1cm} (11)

The first term on the right-hand side of this equation corresponds to pressure variations resulting from flows into and out of the reactor, $\tau_r$ is the mean residence time of a gas particle in the reactor. The second term on the right-hand side of Eq. (11) describes the pressure variations in a closed reactor, which are proportional to the net amount of particles entering the gas phase from the surface. In this term, $\langle \cdots \rangle$ denotes spatial averaging and $p^*$ is the change of the partial
pressure which would be caused by the desorption of a monolayer. If the gas phase is sufficiently dilute, it is given by \( p^* = N_g k_B T_g V^{-1} \), where \( N_g \) is the number of particles corresponding to a monolayer, \( T_g \) is the temperature of the gas, and \( V \) is the reactor volume.

The dynamics of the partial pressure (11) is coupled to the stochastic evolution equation (1) for the adsorbate coverage. Now, it is implicitly assumed that in the monomolecular nonequilibrium reaction adsorbed particles are converted into gas particles of another species. The following linear stability analysis will be again limited to one-dimensional systems in the deterministic limit. The influence of surface defects and internal fluctuations on the dynamics, which was studied in numerical simulations, is presented at the end of this section.

The stationary uniform coverages \( c_0 \) of the system of Eqs. (1) and (11) are given by the roots of the equation

\[
k_a p_1 (1 - c_0) - k_d d c_0 \exp(-\varepsilon c_0) - k_r c_0 - k_r \tau_c k_a p^* c_0 (1 - c_0) = 0. \tag{12}
\]

The corresponding stationary partial pressure \( p_0 \) depends linearly on \( c_0 \)

\[
p_0 = p_1 - k_r \tau_c p^* c_0. \tag{13}
\]

Depending on the parameters, Eq. (12) has a single or three different solutions.

The stability of uniform stationary states is tested by adding small perturbations \( \delta c \exp(\gamma t + i k x) \) and \( \delta p \exp(\gamma t) \) to \( c_0 \) and \( p_0 \), respectively. Choosing the Gaussian pair potential given by Eq. (3), the following expression for the linear growth rate \( \gamma \) is obtained:

\[
\gamma = -k_a p_0 + k_d d c_0 \exp(-\varepsilon c_0) \left[ c_0 \exp(-r_0^2 k^2/4) - 1 \right] - k_r c_0 - k_r \tau_c k_a p^* c_0 \left[ 1 + \exp(-r_0^2 k^2/4) \right] \times \exp(-\varepsilon c_0) \left[ 1 - \exp(-r_0^2 k^2/4) \right] \times \left[ \gamma + \tau_c^{-1} + k_a p^* (1 - c_0) \right]^{-1} \delta k, 0.
\tag{14}
\]

For \( k \neq 0 \), this expression coincides with Eq. (8) which we have obtained above for the absence of gas phase coupling, and hence, the Turing-type bifurcation leading to the formation of stationary nanostructures can take place. At \( k = 0 \) the dispersion relation (14) is discontinuous due to the presence of global coupling. Moreover, \( \gamma_{k=0} \) can be complex. The real part of \( \gamma_{k=0} \) can change its sign, while the imaginary part remains finite, i.e., the system undergoes a Hopf bifurcation. In parameter space, this instability is determined by the condition

\[
-k_a p_0 - k_r c_0 \exp(-\varepsilon c_0) \left[ \gamma + \tau_c^{-1} + k_a p^* (1 - c_0) \right]^{-1} = 0,
\tag{15}
\]

together with the steady state conditions (12) and (13). Furthermore, the following inequality has to be satisfied:

\[
k_a p^* (1 - c_0) - (\tau_c k_r)^{-1} \left[ -k_a p_0 - k_r \right] + k_a d d c_0 - 1 \exp(-\varepsilon c_0) = 0.
\tag{16}
\]

In Fig. 4 the growth rate \( \gamma_k \) is displayed as a function of the dimensionless wave number \( k(D/k_d,d)^{1/2} \) for the case when the uniform stationary state undergoes a Hopf bifurcation (dispersion relation). The discontinuity at \( k = 0 \) is apparent.

Figure 5 shows the bifurcations for uniform stationary states \((c_0, p_0)\) in the parameter plane \((k_a p_1/k_d,d, e)\). Inside the cusp region multiple uniform stationary states coexist. In the presence of the gas phase coupling, the node which is born at the saddle node bifurcations (solid lines) can be unstable while it is always stable in its absence. The Hopf bifurcations (dashed–dotted lines) are typically subcritical inside the cusp region, while outside they are supercritical. As can be seen from Fig. 5(a), the oscillatory region lies within the region, where stationary nanostructures exist (dashed lines). In the infinite system this is always the case because the limit \( \gamma_{k=0} = -k_a p_0 - k_r c_0 \left[ \gamma + \tau_c^{-1} - k_a p^* (1 - c_0) \right]^{-1} \exp(-\varepsilon c_0) \) is always positive if Eq. (15) is satisfied.

In a finite system of length \( L \) however uniform oscillations do not have to coexist with spatially periodic nanostructures because only a discrete set of modes with wave numbers \( k_n = 2 \pi n/L \) \((n = 0,1,2,...)\) can be excited. If the system is sufficiently small, all possible inhomogeneous modes will be damped despite a positive growth rate of the homogeneous mode. Increasing the system size beyond a critical

![FIG. 4](image_url)

**FIG. 4.** Dispersion relation \(\text{Re}(\gamma_k) \) vs \( k(D/k_d,d)^{1/2} \) for \( r_0 = (D/k_d,d)^{1/2} \), \( e = 5.1 \), \( k_a p_1 = 0.146 k_d,d \), \( p^* = 0.225 p_1 \), \( \tau_c = 30.1 (k_d,d)^{-1} \), and \( k_r = 0.033 k_d,d \). The black dot corresponds to \(\text{Re}(\gamma_{k=0}) \) while the white dot marks the limit \(\text{Re}(\gamma_{k=0})\).

![FIG. 5](image_url)

**FIG. 5.** (a) Bifurcation diagram for uniform stationary states as obtained by linear stability analysis. The solid lines are saddle-node bifurcations of uniform stationary states, the dashed–dotted curves correspond to Hopf bifurcations, and the dashed curves mark the Turing-type instability; in (b) a close-up of the cusp region in (a) is displayed; parameters are \( e = 14 \), \( p^* = 0.4 p_1 \), \( \tau_c = 30.1 (k_d,d)^{-1} \), and \( k_r = 0.033 k_d,d \).
value $L_c$, the growth rate $\gamma_k$ becomes positive for the first spatial mode with wave number $k_1 = 2\pi/L$ and then successively for the modes with higher wave numbers. Regarding $L$ as an additional bifurcation parameter, the transition at $L_c$ together with a Hopf bifurcation with respect to uniform perturbations corresponds to a codimension two point for the uniform stationary solution $(c_0,p_0)$, which is mathematically similar to the Turing–Hopf bifurcation previously investigated in reaction–diffusion systems.\(^{36}\) From these studies, two basic scenarios for the dynamics in the vicinity of the codimension two point are known. In the first one, stable mixed-mode oscillations can be found for $L$ close to $L_c$, where the system oscillates between homogeneous states and spatially periodic states (with wave number $k_1$). In the second scenario, the mixed-mode oscillations are unstable and the homogeneous oscillations and the stationary microstructured state coexist for values of $L$ close to $L_c$. Investigating the size-dependent bifurcation scenario in the parameter plane $(kdp_1/k_{d,0},\varepsilon)$, we have indeed observed both cases in deterministic one- and two-dimensional simulations of Eqs. (1) and (11). At the boundaries of the region enclosed by the Hopf bifurcations we have predominantly found the scenario where stable mixed modes are formed, while in the interior of this region the bistable scenario with unstable mixed modes is observed. In the latter case, the uniform oscillations coexist with stationary nanostructures for $L > L_c$. In deterministic simulations of the one-dimensional system with size $L > L_c$, and homogeneous initial conditions close to the unstable stationary state we observe the nanostructures at the boundaries of the oscillatory region in the parameter plane $(kdp_1/k_{d,0},\varepsilon)$, while in its interior the system relaxes to homogeneous oscillations. The latter region shrinks upon increasing the size of the system, reflecting that the basin of attraction for the homogeneous oscillations becomes smaller upon increasing $L$.

Figure 6(a) shows a typical stable mixed-mode oscillation, where the system oscillates between a homogeneous state and a state which is spatially modulated by the first mode, for a numerical simulation of the one-dimensional system (1), (11) in the absence of fluctuations. Similar to the case of uniform oscillations, for mixed modes, the mean coverage exhibits harmonic oscillations with small amplitude or relaxation oscillations with large amplitude, depending on the ratio of the characteristic time scales of $c$ and $p$. For some parameter values we find mixed-mode oscillations, where the system undergoes various homogeneous oscillation cycles between two successive inhomogeneous states [see Fig. 6(b)]. Moreover, for relatively small values of $\varepsilon$ and system sizes slightly below $L_c$ we have found a period doubling scenario for the mixed modes; Fig. 6(c) shows a mixed-mode oscillation of period two. We have also performed deterministic simulations of the two-dimensional system, which qualitatively confirm the results presented above for the one-dimensional system. For periodic boundary conditions the observed mixed modes correspond to an oscillation between a uniform state and a square-shaped pattern.\(^{49}\)

In experiments crystals of several mm\(^2\) size are typically used. On the other hand, the largest length scale relevant for the formation of patterns is the diffusion length which is typically of the order of several micrometers for fast adsorbates. Hence, the size of the surface will be much larger than the critical system size $L_c$, which is proportional to $\sqrt{r_0}$ as follows from Eq. (10), and the mixed-mode oscillations will not be observed in a typical experiment. Still, one might set up an experiment with a surface of size close to $L_c$. Then however, the reactor must be of similar size because otherwise the parameter $p^*$ in Eq. (11) and thus the oscillatory region in parameter space would become too small to observe the desired mixed-mode oscillations. On the other hand, homogeneous oscillations may coexist with the stationary nanostructures for large systems, i.e., when $L \gg L_c$. The question remains, whether these oscillations may be observed if internal fluctuations in the adsorbate coverage and surface heterogeneities are present.

Despite very diligent preparation procedures, typical catalytic surfaces are characterized by the presence of surface defects or steps between neighboring terraces where the average sticking coefficient is increased or decreased in comparison to the rest of the surface. We have qualitatively taken into account the presence of such surface defects by a space-dependent ansatz for the sticking coefficient $k_d(\mathbf{r}) = [1 + \alpha_d(\mathbf{r})] \langle k_d \rangle$ in the model (1), (11), where $\alpha_d(\mathbf{r})$ represents the defect profile with $\langle \alpha_d \rangle = 0$.\(^{49}\) Numerical simulations for different defect profiles show that systems of size $L > L_c$ react very sensitively to the presence of surface defects: The uniform oscillations are destroyed, even if the sticking coefficient is only infinitesimally modulated in space (in the sense of the available computational accuracy). Thus it can be expected, that in a realistic experiment no oscillations can be observed as a result of gas phase coupling due to the natural roughness of the catalytic surface. The formation of stationary nanostructures is to be expected instead.
A similar dynamic response of the system is found if the sticking coefficient is kept constant, but the internal fluctuations in Eq. (1) are taken into account. For \(L > L_c\), again the homogeneous oscillation are destroyed by the formation of stationary nanostructures. For \(L < L_c\) however, oscillations that become irregular as a result of the fluctuations or surface defects can still be observed in numerical simulations. Figure 7 shows the space-time evolution of noisy mixed-mode oscillations for systems with rather weak (a) and rather strong (b) internal fluctuations for the case when stable mixed mode oscillations are found in the deterministic limit.

We have also performed simulations for a system consisting of two microsurfaces of size \(L < L_c\) which are coupled through a common gas phase, in order to get an idea whether oscillatory phenomena could be expected for artificially microstructured arrays similar to the ones investigated in Ref. 57 or as result of natural microstructuring of crystal surfaces into single-crystal terraces. We find, that for this configuration synchronized oscillations are also destroyed through the presence of internal fluctuations.

Thus it can be concluded that uniform oscillations induced by the presence of global coupling through the gas phase in the reactive one-variable model are very unlikely to be observed in realistic experiments. Instead, the formation of stationary nanostructures should be expected as in the absence of global coupling.

**D. Nanoscale traveling wave fragments**

There are only few examples for traveling nonequilibrium structures in condensed reactive systems. Such wave patterns have been experimentally observed in an illuminated Langmuir–Blodgett film, though a satisfactory theory of this effect is not yet available. In this case, the characteristic wavelength of a pattern was still relatively large, lying in the range of tens of micrometres. Propagating “atomic strings” with sizes of less than a micrometer have however recently been observed using atomic force microscopy on crystal surfaces under reaction conditions. In Refs. 39 and 42 we have presented a possible mechanism for the formation of such structures. It was shown that the competition of attractive lateral interactions and a nonequilibrium reaction between two different adspecies can lead to the formation of traveling nanoscale patterns.

As an example, we have considered a surface chemical reaction with the reacting species \(U\) and \(V\). Both species arrive through adsorption from the gas phase. The particles \(V\) are so strongly chemisorbed that they do not desorb thermally and cannot laterally move across the surface. On the other hand, the particles \(U\) are only weakly bound to the substrate; they are highly mobile and can desorb. When they meet adsorbed molecules \(V\), both molecules react and give rise to a product that immediately leaves the surface \((U + V \rightarrow 0)\). We assume that attractive lateral interactions between molecules \(U\) and between molecules \(U\) and \(V\) are present. The mesoscopic kinetic equations for the fluctuating local coverages \(u\) and \(v\) of both species are derived from the master equation for the full probability distribution of such a reactive lattice gas (see Ref. 39). They have the form

\[
\frac{\partial u}{\partial t} = k_{a,a} p_a (1-u) - k_{d,a} u - k_{a,v} u v + \nabla \left( \frac{D}{k_BT} u (1-u) \nabla W \right) + \nabla (D \nabla u) + \xi_a(r,t),
\]

\[
\frac{\partial v}{\partial t} = k_{a,a} p_a (1-v) - k_{d,v} u v + \xi_v(r,t).
\]

The local surface potential \(W(r)\) is determined by attractive interactions between particles

\[
W(r) = \int w_{a,a}(r-r') u(r') dr' + \int w_{a,v}(r-r') v(r') dr'.
\]

For simplicity, we assume that both attractive pair potentials \(w_{a,a}(r)\) and \(w_{a,v}(r)\) have the form of a Gaussian as in Eq. (5) with the same interaction radius \(r_0\) and different intensities \(w_{a,a}^{0}\) and \(w_{a,v}^{0}\). The desorption rate \(k_{d,\alpha}\) of molecules \(\alpha\) depends on the local potential as \(k_{d,\alpha} \approx k_{d,0} \exp[-W(r)/k_BT]\); the immobile molecules \(V\) do not desorb. The reaction rate \(k_r\) does not depend on the local potential since, as we assume, the chemical energy released in an individual reaction event is sufficiently high to overcome any local differences in the adsorption potential. The internal noises in these two equations are

\[
\xi_a(r,t) = Z^{-1/2} \left\{ \sqrt{k_{d,a} p_a (1-u)} f_{a,a}(r,t) + \sqrt{k_d u f_d(r,t)} + \sqrt{k_{a,v} u f_v(r,t)} + \nabla (\sqrt{2 D u (1-u)} f(r,t)) \right\},
\]

\[
\xi_v(r,t) = Z^{-1/2} \left\{ \sqrt{k_{d,a} p_a (1-v)} f_{a,a}(r,t) + \sqrt{k_d v f_d(r,t)} \right\},
\]

where \(f_{a,a}, f_{d,d}, f_{f,d}, f_{a,a}, \ldots\), and \(f\) are independent white random forces of unit intensity. Note that the reaction noise in both equations is exactly the same because each reaction event involves molecules \(U\) and \(V\).

A linear stability analysis has revealed that in this case the uniform stationary state can undergo a Hopf bifurcation with finite wave number (also called a “wave bifurcation”) (see Ref. 60), if the characteristic intensity of the cross-species interaction \(e^r = w_{a,v}^0/k_BT\) is strong enough. Again,
the wavelength of the first unstable mode scales as in Eq. (10) and numerical simulations confirm the formation of nonstationary nanoscale patterns. As $\epsilon'$ is lowered a special codimension-two situation is found, where the wave bifurcation and a Turing-type bifurcation take place simultaneously.\textsuperscript{39} Sufficiently below this point only stationary nanostructures can be observed.

The selection and stability of patterns in the vicinity of the wave bifurcation can be determined by calculating the coefficients of universal coupled dynamical equations for the amplitudes of unstable modes representing left- and right-propagating waves, which are nonlocal if the group velocity is finite.\textsuperscript{51} Such a weakly nonlinear analysis has been performed for the one-dimensional system in the absence of thermal desorption of the species $U$.\textsuperscript{40} We find that for very small interaction radii the wave bifurcation is always supercritical, while for larger values of $r_0$ it is supercritical. In the latter case traveling wave trains are selected which are stable with respect to spatial modulations of their amplitudes. The respective weakly nonlinear analysis for the Turing-type bifurcation in the considered system has not yet been performed.

In the macroscopic limit either traveling wave trains or standing waves can form as a result of the wave bifurcation. As an example, Fig. 8 displays a two-dimensional deterministic simulation, starting with small random perturbations added to the unstable uniform phase. The three snapshots (a)–(c) show the coverage distributions of the species $U$ at subsequent time moments. To characterize the dynamics of the pattern, Fig. 8(d) presents its temporal evolution along the central cross section shown by the dashed lines in the three snapshots. It can be seen that, in the early stage of the evolution, irregular patterns of distorted standing waves are formed. Later, however, the standing waves evolve into planar wave trains traveling at a constant velocity. These waves tend to form a periodic pattern containing pointlike defects. For other values of the parameters stable standing waves consisting of oscillations between orthogonal stripe patterns are observed in the deterministic simulations as displayed in Figs. 9(a)–9(d). The nodes of this standing wave become clearly visible in the one-dimensional cross section in Fig. 9(e).

The stochastic simulation of Eqs. (17) including the internal noises (19) which is displayed in Fig. 10 leads to the conclusion that in this case the internal fluctuations have a stronger qualitative effect on the pattern evolution than in the case of the stationary nanostructures: The planar periodic wave train observed in a corresponding deterministic simulation is broken into many short fragments that form irregular spatial patterns seen in the snapshots (a)–(c). Nonetheless, examining the time evolution in the central cross section Fig. 10(d), we recognize that these fragments do not just fluctuate. They travel across the surface while undergo-

FIG. 8. Formation of coherent traveling wave patterns in a two-dimensional simulation of Eqs. (17) in the absence of internal fluctuations for $w_{\text{in}} = 5k_B T$, $w_{\text{des}} = 3k_B T$, $k_{\text{ads}} p_a = k_a = 0.5k_{\text{desb}}$, $k_{\text{ads}} p_e = k_e = 1.5k_{\text{desb}}$, and $r_0 = 0.07 L_{\text{des}}$. The snapshots (a)–(c) correspond to time moments $t = 18k_{\text{desb}}$ (a), $t = 45k_{\text{desb}}$ (b), and $t = 72k_{\text{desb}}$ (c). The temporal evolution is displayed in (d) during the interval $18k_{\text{desb}} < t < 85k_{\text{desb}}$ in the one-dimensional cross section indicated by the vertical dashed lines in the snapshots. The total size of the system is $L = 4.2L_{\text{des}}$. The local surface coverage of the species $U$ is shown in gray scale, with darker areas corresponding to higher coverages.

FIG. 9. Standing wave patterns in a two-dimensional simulation of Eqs. (17) in the absence of internal fluctuations for system size $L = 4.24L_{\text{des}}$, $k_{\text{ads}} p_e = 0$, and all other parameters and gray-scale coding as in Fig. 8. The time interval between subsequent snapshots of the coverage $u(x, y, t)$ in (a)–(d) is $\Delta t = 0.16k_{\text{desb}}^{-1}$. The temporal evolution is displayed in (e) during the interval $T = 8.8k_{\text{desb}}^{-1}$ in the one-dimensional cross section indicated by the dashed line in (a).

FIG. 10. Fluctuating traveling wave fragments as obtained by numerical integration of Eqs. (17) with internal fluctuations given by Eqs. (19); $Z = 1.07 \times 10^3 L_{\text{des}}^{-2}$, $k_{\text{ads}} p_a = 0.08k_{\text{desb}}$, $L = 1.7L_{\text{des}}$, $r_0 = 0.028L_{\text{des}}$; the other parameters and the gray-scale coding are the same as in Fig. 8. The two-dimensional snapshots (a)–(c) are separated by equal intervals $\Delta t = 0.89k_{\text{desb}}^{-1}$. The temporal evolution in the one-dimensional cross section (d) is shown during time $T = 44.6k_{\text{desb}}^{-1}$.

FIG. 11. Formation of nanoscale patterns as obtained by numerical solution of Eqs. (17) with internal fluctuations given by Eqs. (19); $Z = 1.07 \times 10^3 L_{\text{des}}^{-2}$, $k_{\text{ads}} p_a = 0.08k_{\text{desb}}$, $L = 1.7L_{\text{des}}$, $r_0 = 0.028L_{\text{des}}$; the other parameters and the gray-scale coding are the same as in Fig. 8. The two-dimensional snapshots (a)–(c) are separated by equal intervals $\Delta t = 0.89k_{\text{desb}}^{-1}$. The temporal evolution in the one-dimensional cross section (d) is shown during time $T = 44.6k_{\text{desb}}^{-1}$.
In a first attempt, modeling was performed within the framework of RD equations based on steps (II) and (III). For the small temperatures chosen in the experiments step (I) is neglected since it is slow, and O and OH are practically immobile due to strong bonding to the surface and strong mutual attractive interactions, respectively. Hence, water is the only mobile oxygen containing adspecies. Adsorbed H atoms are so mobile that the hydrogen distribution can be regarded as spatially uniform. Since in the experiments hydrogen is continuously supplied by adsorption from the gas phase, the H concentration can be safely set to 1. The following RD system was proposed:

\[
\begin{align*}
\frac{\partial u}{\partial t} &= -2k_3uv + k_2w + D\Delta u, \\
\frac{\partial v}{\partial t} &= -k_3uv, \\
\frac{\partial w}{\partial t} &= 3k_3uv - k_2w.
\end{align*}
\]

where \(u, v,\) and \(w\) correspond to the local surface coverages of adsorbed \(\text{H}_2\text{O},\) O, and OH, respectively. The system of Eqs. (20) was solved by two-dimensional numerical integration.

For a quantitative comparison with the STM results the kinetic parameters entering the set of RD equations (20) were determined in a set of independent experiments. Since the diffusion of water on the O-covered surface limits the overall mobility of \(\text{H}_2\text{O},\) the average diffusion coefficient for this process was used in the numerical simulations of Eqs. (20).

Quantitative model predictions about the dependence of the front velocity and width on temperature could thus be compared with the experimental data. As discussed in detail in Ref. 64, the temperature dependence of the front velocity was qualitatively reproduced with the RD system, but the absolute numbers were about one order of magnitude smaller. This is not considered to be a serious problem in view of the uncertainties associated with the kinetic parameters that were used in the simulations. The disagreement between experiment and theory was more pronounced for the temperature dependence of the front width: Whereas the experimental data show an increase with temperature, the simulations predict a slight decrease, and the absolute values from the simulations are up to three orders of magnitude higher.
These discrepancies express the limitations of the simple RD description that completely neglects the experimentally observed presence of strong attractive lateral interactions caused by the formation of hydrogen bonds between adsorbed particles. The macroscopic kinetic constants are therefore expected to depend on microscopic interaction parameters. In particular, the diffusion of adsorbed H$_2$O will be affected by strong attractive lateral interactions with adjacent water or OH particles, leading to clustering. Moreover, their motion will be influenced by the local oxygen coverage because of the hydrogen bonding between water molecules and the underlying atoms of the O(2×2) layer. Another aspect that has not been taken into account in the simple RD model (20) is related to the migration of adsorbed water molecules across the OH-covered zone: While the diffusion of H$_2$O adparticles is blocked by adsorbed OH, this process is presumably connected with hydrogen transfer from a water molecule to an adjacent OH particle, a fast process. It can be expressed by the reaction scheme

$$\text{H}_2\text{O}(r) + \text{OH}(r') \rightarrow \text{OH}(r) + \text{H}_2\text{O}(r'),$$  \hspace{1cm} (21)

where $r$ and $r'$ denote adjacent sites of the adsorption lattice which is assumed to be identical for adsorbed H$_2$O and OH molecules.

We have constructed a suitable mesoscopic model that takes these effects into account by coarse graining a corresponding microscopic master equation.\textsuperscript{67} It provides a mechanism for sharper interfaces, explaining the above mentioned discrepancies between the RD predictions and the experimental data. Moreover, the formation of water clusters behind the propagating front can be investigated.\textsuperscript{67}

V. SUMMARY AND PERSPECTIVES

In this article we have reviewed the construction and application of mesoscopic models for the description of nanoscale pattern formation in surface chemical reactions. It was shown that this theory can be very useful in bridging the gap between microscopic and macroscopic theories. In particular, it is capable of capturing the interplay of attractive lateral interactions acting on the microscale and macroscopic reaction--diffusion kinetics. Recently, fast numerical algorithms based on spectral methods\textsuperscript{68} and adaptive grids with variable time stepping\textsuperscript{69,70} have been developed which allow to efficiently solve deterministic or stochastic mesoscopic models used to investigate new mechanisms for the formation of nanoscale patterns or to model specific experiments in detail.

The derivation of the mesoscopic models is based on a local mean-field approximation and discrete lattice effects are only indirectly taken into account (the density of lattice sites enters into the mesoscopic equation). Therefore, it is best suited for the description of processes whose characteristic length scales are larger than the lattice length but might be less than the diffusion length associated with the reaction kinetics.\textsuperscript{38} First qualitative comparisons of mesoscopic and Monte Carlo simulations indicate a good agreement even for relatively short-range potentials with interaction radii of a few lattice lengths.\textsuperscript{56,71} The deterministic limit of the mesoscopic evolution equation for a single species provides an exact description of the microscopic dynamics if the range of the interactions is infinite.\textsuperscript{70,57} Suitable asymptotics can be used to relate phenomenological theories based on the Cahn--Hilliard equations\textsuperscript{48,52} with mesoscopic models.\textsuperscript{30,41} The kinetics of first-order phase transitions can be described by mesoscopic models even in parameter regions very far from the critical point.\textsuperscript{26,38}

The mesoscopic approach also allows to systematically investigate mechanisms responsible for the formation of nanoscale nonequilibrium patterns in catalytic surface reactions. Several examples were given where such structures result from the competition of short-range attractive lateral interactions and long-range reaction--diffusion kinetics. For a single reactive species a spatial symmetry breaking instability which is mathematically equivalent to the Turing instability in RD systems leads to the appearance of stationary spatially periodic nanostructures with spatial periods in the nanometer range.\textsuperscript{41} Physically, these structures occupy an intermediate position between purely kinetic Turing structures and spatially modulated equilibrium structures of a purely energetic origin.

Here, we have also presented the results of a detailed investigation\textsuperscript{40,49} on the effect of an additional global coupling of adsorbed particles through the gas phase. It was shown that uniform or mixed mode oscillations induced by the global coupling will not be observable in typical experiments. Instead, the formation of stationary spatially periodic nanostructures should be expected. To observe the oscillations the surface would have to be smaller than one $\mu$m$^2$, and the reactor would have to be many orders of magnitude smaller than in typical experiments.

For two different reactive species a wave bifurcation may lead to the appearance of traveling or standing weaves in the deterministic limit if the attractive cross-species interaction is strong enough. In the simple model analyzed in Refs. 39 and 42, the effect of strong internal fluctuations is more significant than for the stationary nanostructures in the one-variable model: The lateral coherence of planar traveling or standing waves is broken and a complex dynamics of interacting wave fragments is observed.

Although stationary and traveling nanoscale structures were found by us only in particular models of surface chemical reactions, the mechanisms responsible for their formation are general and similar structures can therefore be expected in other nonequilibrium soft matter, such as reactive polymer blends or biological membranes. These extremely small structures would perfectly fit into the characteristic dimensions of a single biological cell. Simple mesoscopic models have been applied for example to describe the sintering of alloys\textsuperscript{72} and the diffusion through membranes.\textsuperscript{46}

It should also be mentioned that there is another principal mechanism, not reviewed here, which leads to the formation of nonequilibrium adsorbate structures on scales smaller than the characteristic diffusion length even when attractive lateral interactions between adsorbed molecules are absent: Adsorbates on single crystal surfaces can induce a structural phase transition in the surface of the substrate where the adsorption of particles triggers a rearrangement of the metal
atoms leading to a surface structure different from the one found for the bare surface.\textsuperscript{73} In Refs. 69, 70, and 74 we have investigated a simple mesoscopic model for a single reactive adsorbate coupled to such a structural phase transition which shows the formation of disk-shaped localized stationary structures. They correspond to self-organized microreactors or to unreactive depletion holes in a dense reactive adsorbate layer.\textsuperscript{69} The stationary localized structures are stable if they are significantly smaller than the characteristic diffusion length. As the reaction parameter is changed they become larger and undergo a static instability with respect to shape perturbations leading to the formation of delocalized stationary structures.\textsuperscript{70}

So far, we have only considered systems with very simple reaction kinetics. More complex features like a precursor kinetics for the adsorption process, the presence of promoters, associative desorption, or the simultaneous presence of a structural phase transition in the surface of the substrate and attractive lateral interactions may be incorporated into mesoscopic models. The effect of nonlocal coupling in systems with a more complex reaction kinetics (e.g., bistable, oscillatory, or excitable) has been investigated in electrochemical models\textsuperscript{75} and RD systems where the nonlocal coupling arises from the adiabatic elimination of an additional variable\textsuperscript{76} or from a feedback.\textsuperscript{77} Though the details of the nonlocal coupling are different in those systems, similar phenomena can be expected for reactive adsorbates with attractive lateral interactions.

The mesoscopic theory may be used to develop detailed models for specific experiments. As an example, we have discussed the propagation of reaction fronts in the oxidation of hydrogen on a Pt(111) single crystal surface as observed with scanning tunneling microscopy (STM). The limitations of a simple reaction–diffusion model were revealed in a quantitative comparison with experimental data. Microscopic effects like the formation of hydrogen bonds between oxygen containing species were pointed out that can be taken into account in a detailed mesoscopic model. Note, however, that despite such examples the applicability of the STM (or of field emission microscopy) for the \textit{in situ} observation of catalytic surface reactions is very limited due to a relatively low time resolution (scanning rate $<$ 20 Hz) and strong interactions between the tip and molecules participating in the reaction, e.g., via adsorption of particles from the gas phase on the tip or via the influence of the electric field of the tip on the adsorbate dynamics. These problems explain why the stationary and traveling nanostructures predicted by our simple models have not yet been observed. Hopefully, the current experimental limitations can be overcome by the development of novel techniques which are less invasive and allow a higher temporal resolution such as sophisticated devices involving synchrotron radiation of variable photon energy and an energy filter (see, e.g., Ref. 78).

\section*{Acknowledgments}

The results presented in Sec. II C were obtained in close collaboration with F. Ulmar. The author thanks J. Wintterlin for helpful comments during the preparation of Sec. IV. The author is grateful for the inspiring collaboration with A. S. Mikhailov and the continuous support from G. Ertl. Moreover, he acknowledges financial support from the Alexander von Humboldt-Stiftung in the year 2000.
The apparent contradiction contained in the statement that thermal equilibrium is reached in an open reactor can be resolved by showing that Eq. (1) also describes the adsorption–desorption kinetics of an adsorbate in a closed container containing a number \( N \) of particles that is much larger than the total number of adsorption sites on the surface \( N_s \). Taking into account global coupling of adsorbed particles through the gas phase for the case of the closed reactor, the temporal evolution of the partial pressure is described by Eq. (11) with the first term on the right-hand side of this equation being absent. Applying the ideal gas law for \( p^* \) in Eq. (11) we obtain \( p^* = p N_s / N \) implying that \( p^* \to 0 \) for \( N_s / N \to 0 \). Therefore the partial pressure in the closed container can be regarded as stationary in this limit and the evolution equation (1) applies for this case as well.

\[ p^* = \frac{p N_s}{N} \]

- D. G. Vlachos (private communication).