Self-Organized Chemical Nanoscale Microreactors

M. Hildebrand,[1] M. Kuperman,[2] H. Wio,[2] A. S. Mikhailov,[1] and G. Ertl[1]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin*
[2]*Centro Atomico Bariloche and Instituto Balseiro, Consejo Nacional de Investigaciones Cientificas y Technicas,*
8400 Bariloche, Rio Negro, Argentina
(Received 6 January 1999)

Nonequilibrium localized structures of submicrometer and nanometer sizes, carrying the reaction, can spontaneously develop under reaction conditions on a catalytic surface. These self-organized microreactors emerge because of the coupling between the reaction and a structural phase transition in the substrate. The corresponding localized solutions are constructed using the singular perturbation approximation and reproduced in numerical simulations.

PACS numbers: 82.20.Wt, 05.65.+b, 47.54.+r, 82.65.Jv

The competition between short-range activation and long-range inhibition in reaction-diffusion systems may lead to the formation of nonequilibrium stationary localized structures (spots) [1]. Various instabilities of such spots, leading to breathing, static deformations, replication, and translational motion, were investigated [2,3]. The minimum spatial size of a spot in a reaction-diffusion system is limited by the diffusion length of the activator species. In surface chemical reactions this characteristic length typically exceeds a micrometer. Nanoscale nonequilibrium structures in chemical systems can however be formed if attractive interactions between reacting particles are included (see, e.g., [4]). Nonequilibrium pattern formation in reaction-diffusion systems with attractive interactions has been intensively investigated in the last years. It was found that a nonequilibrium chemical reaction can, for instance, terminate the growth of spatial domains in phase-separating polymer blends and give rise to extended stationary microstructures [5] and that similar stationary microstructures are possible in reactive adsorbates [6]. Furthermore, traveling nanoscale structures were shown to exist in reactive two-component adsorbates with attractive lateral interactions [7]. Experiments with fast scanning tunneling microscopy and field ion emission microscopy gave evidence of a rich variety of spatiotemporal nanoscale pattern formation in adsorbed monolayers [8]. Traveling atomic strings on solid surfaces in the presence of a phase transition were recently observed using atomic force microscopy [9]. Moreover, chemical catalysis on microstructured surfaces has been studied [10]. The surface microstructures employed in the latter experiments were fabricated by microlithography methods and their minimum spatial sizes were in the range of tens of micrometers.

The aim of this Letter is to show that microreactors with submicrometer and nanometer sizes may *spontaneously* develop in surface chemical reactions by a nonequilibrium self-organization process. The self-organized microreactors are found for a *single* reactive species *without* attractive interactions between adsorbed particles. They represent localized structures (spots) resulting from the interplay between the reaction, diffusion, and an adsorbate-induced structural transformation of the surface. The examples of adsorbate-induced structural transitions include a transition from a 1 × 2 reconstructed structure of the clean surface to the 1 × 1 bulklike structure of the CO-covered surface in the oxidation of CO on Pt(110) [11]. A similar phenomenon is observed in the NO + CO reaction on Pt(100), where sufficiently high coverages of NO and CO lift the quasihexagonal reconstruction ("hex") of the top layer of the substrate in favor of the 1 × 1 phase [12]. The growth kinetics of adsorbate islands in the absence of reactions was thoroughly investigated [13]. The existence of nonstationary nanoscale or submicrometer NO/CO-covered 1 × 1 reactive islands on a hex background was invoked to explain complex kinetic oscillations in the respective reactions [14].

We consider a simple model system where the state of the surface is characterized by a continuous order parameter. Without the adsorbate, the surface is found in one state, but its presence triggers a structural transformation into a different state. The driving force is the gain in adsorption energy and hence the surface region in the latter state is attractive for adsorbate molecules; therefore it represents a potential well for them. Molecules diffusing across the surface are trapped by such a region and a growing adsorbate island is formed. On the other hand, the reaction removes molecules from the island and slows down its growth. The competition between these two processes can lead to the formation of stationary reactive islands. Indeed, the total diffusion flux of adsorbed particles into an island is proportional to its perimeter. On the other hand, the total rate of removal of particles from the island due to the reaction is proportional to its area. For small islands the incoming diffusion flux should therefore dominate over the reaction and such islands must grow. If an island is large, the reaction is prevailing and its size decreases. The two processes exactly balance each other at a certain radius that gives the size of the stationary localized structure. To analytically investigate this phenomenon, an approximate kinetic description of the considered reactive system with a surface phase transition is needed. We assume that the free energy associated with the first-order surface phase transition is given by a Ginzburg-Landau functional (cf. [15])

$$F[\eta, c] = \int \left(\frac{1}{2}\,\kappa^2 (\nabla \eta)^2 + \varphi(\eta, c) + h(c) \right) d^2\mathbf{x}\,, \tag{1}$$

where $\varphi(\eta, c) = \chi[(\frac{4}{3}\eta^3 - 2\eta^2)c + \eta^4 - \frac{8}{3}\eta^3 + 2\eta^2]$ and $h(c) = k_B T n_0[(1 - c)\ln(1 - c) + c\ln(c)]$ is the contribution corresponding to a free lattice gas of adsorbed particles. Here the factor χ controls the magnitude of variations of the free energy density φ, κ specifies the strength of spatial energetic coupling between neighboring elements of the surface, and n_0 is the number of adsorption sites for the considered molecules per unit surface area. We assume that the order parameter η of this phase transition is not conserved and its relaxation kinetics is described by the equation [16] $\partial_t \eta = -\Gamma \delta F[\eta, c]/\delta \eta(\mathbf{x}, t)$, or, explicitly,

$$\tau \frac{\partial \eta}{\partial t} = \eta(1 - \eta)(\eta + c - 1) + l^2 \nabla^2 \eta\,, \tag{2}$$

where Γ is the relaxation rate constant for the order parameter η, $\tau = (4\chi\Gamma)^{-1}$, and $l = \kappa/\sqrt{4\chi}$. The system has always two stable uniform steady states $\eta = 0$ and $\eta = 1$ and an unstable uniform state $\eta = 1 - c$. When $c < 1/2$ the state with $\eta = 0$ has a lower free energy, whereas for $c > 1/2$ the state with $\eta = 1$ corresponds to the deepest minimum of this function. Thus, the system models an adsorbate-induced phase transition.

The molecules arrive at the surface from the gas phase, move diffusively across the surface, and desorb from it. The thermal desorption and the motion of the adsorbed molecules over the surface are influenced by the local chemical potential $\mu(\mathbf{x}) = n_0^{-1}\delta F/\delta c(\mathbf{x}) = U(\eta) + k_B T \ln[c/(1 - c)]$ with $U(\eta) = n_0^{-1}\partial_c \varphi(\eta, c) = -2n_0^{-1}\chi(\eta^2 - \frac{2}{3}\eta^3)$. The evolution of the adsorbate coverage is governed by the kinetic equation $\partial_t c = k_a p_0(1 - c)\{1 - \exp[(\mu(\mathbf{x}) - \mu_0)/k_B T]\} + \nabla[(D/k_B T)c(1 - c)\nabla\mu(\mathbf{x})] - k_r c$. Here, $\mu_0 = k_B T \ln(k_a p_0/k_{d,0})$, p_0 is the constant partial pressure of the molecules in the gas phase, k_a is their sticking coefficient, $k_{d,0}$ is the desorption rate constant for the phase $\eta = 0$, k_r is the rate constant of the considered nonequilibrium reaction, and D is the surface diffusion constant of the molecules at temperature T. The explicit form of this evolution equation is

$$\frac{\partial c}{\partial t} = k_a p_0(1 - c) - k_{d,0}\exp[U(\eta)/k_B T]c - k_r c + \frac{D}{k_B T}\nabla[(1 - c)c\nabla U] + D\nabla^2 c\,. \tag{3}$$

Note that this equation contains not only the diffusion term but also a term that describes a viscous surface flow of the adsorbate induced by the gradient of the potential U (cf. [17,18]).

The characteristic length l characterizes the width of an interface between two surface phases and can therefore be estimated as a few lattice lengths, i.e., it would be of the order of a nanometer [19]. On the other hand, the characteristic diffusion length of adsorbed molecules $L_{d,0} = \sqrt{D/k_{d,0}}$ is typically much larger (e.g., for CO molecules adsorbed on platinum at $T = 500$ K it is equal to a few micrometers). Hence, the ratio $\lambda = l/L_{d,0}$ of these two characteristic lengths is a small parameter. The dimensionless parameters $\epsilon = \chi n_0^{-1}/k_B T$, determining the relative strength of the adsorbate-substrate interactions, $\alpha = k_a p_0/k_{d,0}$ and $\nu = k_r/k_{d,0}$ can also be conveniently introduced.

Stationary localized solutions of Eqs. (2) and (3) represent spots. As an example, Fig. 1 shows a spot obtained by numerical integration of these equations in the one-dimensional case. We see that inside the spot the surface is in the state with $\eta = 1$. The coverage c is high in this region and slightly increases from the center towards its boundary. The shown spot has a radius close to the diffusion length. The width of the interface forming the spot's boundary is of order l. The spot is a reactive island that sucks adsorbate molecules from the surrounding surface. Therefore the coverage is decreased in the vicinity of this structure. To analytically construct the spot solutions and investigate their properties, a singular perturbation approximation using the small parameter λ has been developed. In this approximation a cross section through a spot can be divided into three zones: a sharp interface, where the order parameter η and the adsorbate coverage c rapidly change on a scale of order l, and outer and inner regions, where η is approximately constant and the adsorbate coverage c varies slowly on the characteristic diffusion length scale $L_{d,0}$.

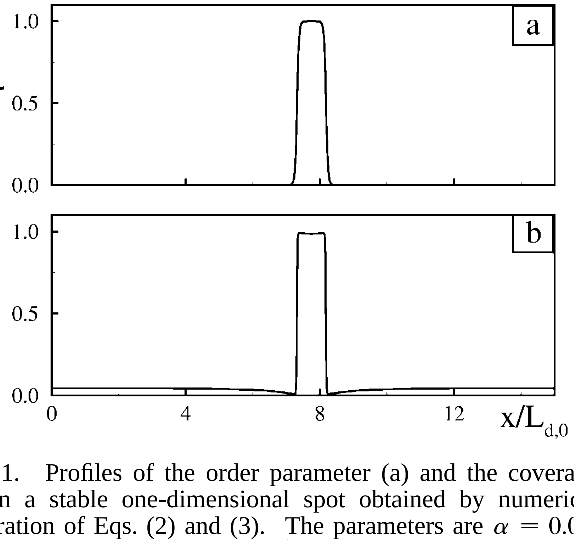

FIG. 1. Profiles of the order parameter (a) and the coverage (b) in a stable one-dimensional spot obtained by numerical integration of Eqs. (2) and (3). The parameters are $\alpha = 0.05$, $\nu = 0.1$, $\epsilon = 15$, $\tau = (15k_{d,0})^{-1}$, and $\lambda = 0.032$.

We first consider the one-dimensional problem. Introducing the fast coordinate $\xi = x/l$, we find from Eq. (3) that to the order $O(\lambda^2)$ the coverage distribution inside the interface region satisfies the equation $\partial_\xi[\partial_\xi c + c(1 - c)\partial_\xi U(\eta)/k_B T] = 0$. Taking into account that the order parameter approaches the constant values $\eta = 1$ and $\eta = 0$ on the left and right boundaries of the interface, this equation can be integrated twice. Thus we obtain in the zeroth order of the small parameter λ a relationship connecting the order parameter η and the adsorbate coverage $c = c^{(0)}(\eta)$ inside the interface: $c^{(0)}(\eta) = \{1 + (1 - c_-)c_-^{-1}\exp[U(\eta)/k_B T]\}^{-1}$. Here c_- represents the asymptotic value of the coverage at the right boundary of the interface. Substituting this into (2) and using the boundary conditions for the order parameter η, we find the adsorbate coverages c_+ and c_- on both sides of the interface. To the zeroth order in λ they are $c_\pm = [1 + \exp(\mp\epsilon/3)]^{-1}$. Outside the interface the order parameter is constant and Eq. (3) is linear. In the one-dimensional case, its solutions are then given by combinations of exponentials with characteristic scales given by the respective diffusion lengths $L_{\mathrm{in}} = L_{d,0}[\alpha + \nu + \exp(-2\epsilon/3)]^{-1/2}$ and $L_{\mathrm{out}} = L_{d,0}[\alpha + \nu + 1]^{-1/2}$ inside, respectively, outside the island. The spot radius R_0 is determined by an additional matching condition. It corresponds to the equality of the diffusion fluxes of molecules coming into the interface from the outer region and entering the inner region from the interface, i.e., the equation $D\partial_x c_{\mathrm{in}}(R_0) = D\partial_x c_{\mathrm{out}}(R_0)$ should hold. We have checked that for $\lambda = 0.032$ the numerically obtained equilibrium radius agrees with the singular perturbation results within a few percent.

In the two-dimensional geometry, the line tension—an analog of the surface tension in three dimensions—plays a significant role and must be taken into account. If the interface width l is small as compared with the spot size, the free energy term associated with the interface can be written as $\Delta F = \frac{1}{2}\kappa^2 \int d^2\mathbf{x}\,(\nabla\eta)^2 \approx \sigma L$, where L is the length of the spot boundary ($L = 2\pi R_0$ for a circular spot). The line tension coefficient σ is then given as $\sigma = \gamma(\epsilon) n_0 l k_B T$, where $\gamma(\epsilon) = 2\epsilon\int_{-\infty}^{\infty}(\partial_\xi\eta)^2 d\xi = \epsilon\int_0^1\{\frac{2}{3} - \frac{8}{3}\eta^3 + 2\eta^4 + \frac{2}{\epsilon}\ln[c_+^{-1}c^{(0)}(\eta)]\}^{1/2}\,d\eta$ depends in the zeroth order of λ only on the dimensionless parameter ϵ and is numerically calculated [see Fig. 2(a)].

In the two-dimensional case, the coverage distributions in the inner and the outer regions are given by modified Bessel functions. In the region inside the spot one obtains in the singular perturbation limit $c_{\mathrm{in}}(r) = c_1 + (\tilde{c}_+ - c_1)I_0(r/L_{\mathrm{in}})I_0^{-1}(R_0/L_{\mathrm{in}})$ with $c_1 = [1 + \nu/\alpha + \alpha^{-1}\exp(-2\epsilon/3)]^{-1}$. In the outer region we have $c_{\mathrm{out}}(r) = c_0 + (\tilde{c}_- - c_0)K_0(r/L_{\mathrm{out}})K_0^{-1}(R_0/L_{\mathrm{out}})$, where $c_0 = [1 + \nu/\alpha + \alpha^{-1}]^{-1}$. The line tension for curved interfaces provides additional cohesion, such that the coverages $\tilde{c}_\pm$ at the interface edges of a circular spot are increased by an amount $\delta c = \gamma(\epsilon)\mathrm{cosech}(\epsilon/3)l/R_0$ as compared to the values $c_\pm$ for planar interfaces. The radius R_0 of the stationary spot is then given as a solution of the equation

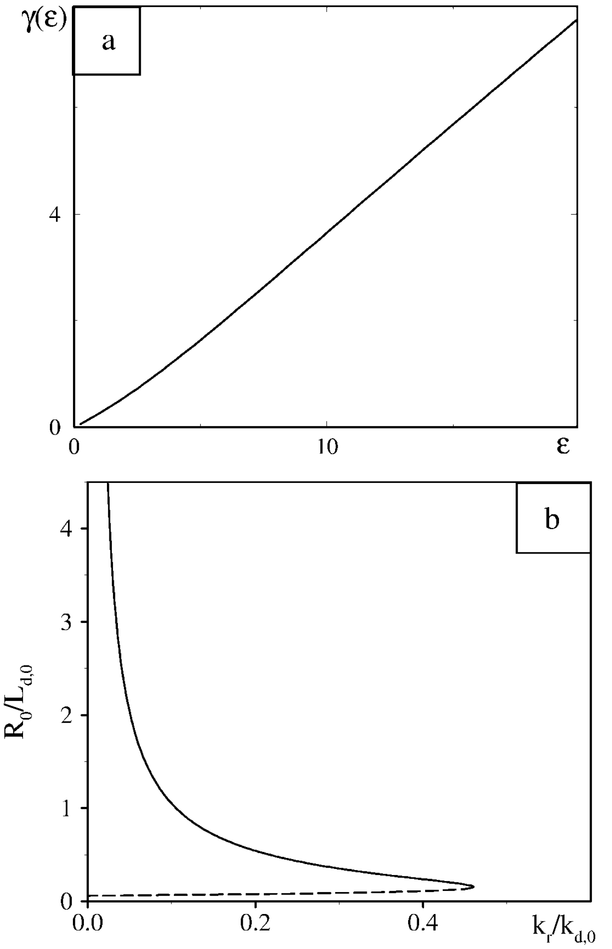

FIG. 2. (a) Dimensionless line tension coefficient γ as a function of ϵ. (b) Dependence of the spot radius R_0 on the reaction rate constant k_r; the same parameters as in Fig. 1.

$$\frac{1}{L_{\mathrm{out}}}\left(c_0 - c_- - \frac{\lambda\gamma(\epsilon)L_{d,o}}{R_0\sinh(\epsilon/3)}\right)K_1\left(\frac{R_0}{L_{\mathrm{out}}}\right)K_0^{-1}\left(\frac{R_0}{L_{\mathrm{out}}}\right)$$
$$= \frac{1}{L_{\mathrm{in}}}\left(c_+ - c_1 + \frac{\lambda\gamma(\epsilon)L_{d,o}}{R_0\sinh(\epsilon/3)}\right)I_1\left(\frac{R_0}{L_{\mathrm{in}}}\right)I_0^{-1}\left(\frac{R_0}{L_{\mathrm{in}}}\right). \tag{4}$$

Examining Eq. (4), we find that it has *two* roots [Fig. 2(b)]. The two solution branches meet and disappear at a certain critical reaction rate constant. The lower branch, shown by the dashed line in Fig. 2(b), is unstable and corresponds to the critical nucleus of the considered surface phase transition. The stability of the spots of the upper solution branch has to be tested in numerical simulations. For relatively high reaction rates their radius may be much shorter than the characteristic diffusion length $L_{d,0} = \sqrt{D/k_{d,0}}$; it diverges however upon reaching a certain minimal value of k_r.

Our two-dimensional numerical simulations show that relatively small circular spots are stable. For example, we found stable spots of radius $R_0 = 0.387 L_{d,0}$ in a simulation with $\alpha = 1.5$, $\nu = 1.66$, $\epsilon = 3$, $\tau = (15\, k_{d,0})^{-1}$, and $\lambda = 0.0161$ in a system of size $L = 4.13 L_{d,0}$. Large spots are, however, unstable with respect to deformations of their shape. Figure 3 shows an example of a growing snowflake structure that develops for a spot with a stationary radius $R_0 = 2.045 L_{d,0}$ as a result of such an instability. Its origin is apparently related to the fact that the adsorbate coverage is depleted by diffusion in lagunas formed by the concave parts of the boundary. This behavior resembles crystal growth instabilities and static deformations of stationary spots in reaction-diffusion systems [2]. The bridges in the snowflake pattern are so thin that they would probably break when fluctuations are taken into account, leading to a spreading pattern of self-replicating domains. Detailed investigations of the spot instabilities will be performed in a separate publication.

Our theoretical study, based on a simple model, shows that stable circular spots with sizes smaller than the characteristic diffusion length and thus lying in the submicrometer and nanometer range are possible in surface chemical reactions. Though the reaction takes place everywhere on the surface, it would predominantly proceed inside the spots where almost all adsorbed molecules are concentrated. Hence, the spots can be viewed as microreactors. In contrast to prefabricated microreactors, such self-organized structures exist only so far as a nonequilibrium reaction is present and its rate exceeds a certain threshold. Their sizes may be controlled by changing the adsorption and reaction rates. These microreactors are dynamic objects and modifications of the considered simple model might also yield localized nanoscale structures that would breath or travel across the surface.

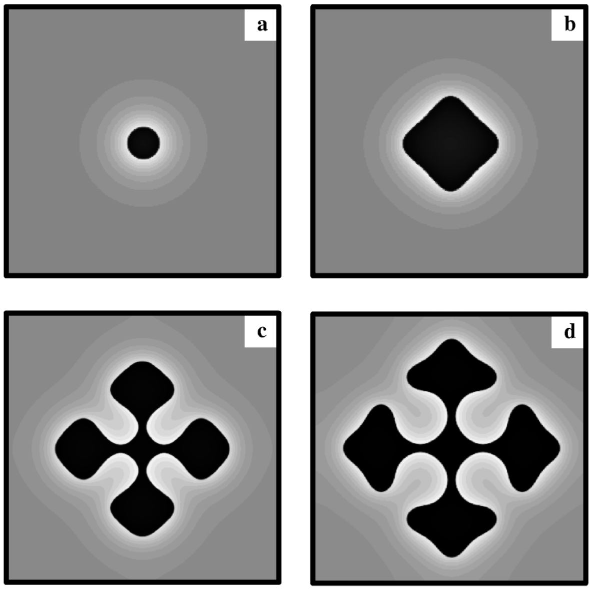

FIG. 3. Instability of a circular spot. Frames (a)–(d) correspond to the moments $t = 0, 65/k_{d,0}, 237/k_{d,0}$, and $363/k_{d,0}$, respectively; $\nu = 0.05$ and the other parameters as in Fig. 1. The local coverage c is shown in grey scale, increasing from white to black.

The authors thank R. Imbihl for stimulating discussions. The financial support of Fundación Antorchas (Argentina) is acknowledged.

[1] B. S. Kerner and V. V. Osipov, Sov. Phys. JETP **47**, 874 (1978); **52**, 1122 (1980); S. Koga and Y. Kuramoto, Prog. Theor. Phys. **63**, 106 (1980); B. S. Kerner and V. V. Osipov, Sov. Phys. Usp. **32**, 101 (1989); A. S. Mikhailov, *Foundations of Synergetics I. Distributed Active Systems* (Springer-Verlag, Berlin, 1990).

[2] T. Ohta, M. Mimura, and R. Kobayashi, Physica (Amsterdam) **34D**, 115 (1989).

[3] J. E. Pearson, Science **261**, 189 (1993); K. Krischer and A. S. Mikhailov, Phys. Rev. Lett. **73**, 3165 (1994); C. B. Muratov and V. V. Osipov, Phys. Rev. E **53**, 3101 (1996); M. Or-Guil, M. Bode, C. P. Schenk, and H.-G. Purwins, Phys. Rev. E **57**, 6432 (1998).

[4] A. S. Mikhailov and G. Ertl, Chem. Phys. Lett. **238**, 104 (1995); Science **272**, 1596 (1996).

[5] S. C. Glotzer, E. A. Di Marzio, and M. Muthukumar, Phys. Rev. Lett. **74**, 2034 (1995); Q. Tran-Cong and A. Harada, Phys. Rev. Lett. **76**, 1162 (1996); M. Motoyama and T. Ohta, J. Phys. Soc. Jpn. **66**, 2715 (1997).

[6] M. Hildebrand, A. S. Mikhailov, and G. Ertl, Phys. Rev. E **58**, 5483 (1998), and references therein.

[7] M. Hildebrand, A. S. Mikhailov, and G. Ertl, Phys. Rev. Lett. **81**, 2602 (1998).

[8] J. Wintterlin, S. Völkening, T. V. W. Janssens, T. Zambelli, and G. Ertl, Science **278**, 1931 (1997); V. Gorodetskii, J. Lauterbach, H. H. Rotermund, J. H. Block, and G. Ertl, Nature (London) **370**, 276 (1994).

[9] Ch. D. Zangmeister and J. E. Pemberton, J. Phys. Chem. B **102**, 8950 (1998).

[10] M. D. Graham, I. G. Kevrekidis, K. Asakura, J. Lauterbach, K. Krischer, H. H. Rotermund, and G. Ertl, Science **264**, 80 (1994).

[11] T. Gritsch, D. Coulman, R. J. Behm, and G. Ertl, Phys. Rev. Lett. **63**, 1086 (1989); G. Ertl, Science **254**, 1750 (1991).

[12] T. Fink, J.-P. Dath, R. Imbihl, and G. Ertl, J. Chem. Phys. **95**, 2109 (1991).

[13] A. Hopkinson, J. M. Bradley, X.-C. Guo, and D. A. King, Phys. Rev. Lett. **71**, 1597 (1993).

[14] N. Khrustova, G. Veser, A. S. Mikhailov, and R. Imbihl, Phys. Rev. Lett. **75**, 3564 (1995); N. Khrustova, A. S. Mikhailov, and R. Imbihl, J. Chem. Phys. **107**, 2096 (1997).

[15] R. F. S. Andrade, G. Dewel, and P. Borckmans, J. Chem. Phys. **91**, 2675 (1989).

[16] A. J. Bray, Adv. Phys. **43**, 357 (1994).

[17] G. Giacomin and J. L. Lebowitz, Phys. Rev. Lett. **76**, 1094 (1996).

[18] M. Hildebrand and A. S. Mikhailov, J. Phys. Chem. **100**, 19 089 (1996).

[19] E. Bauer, in *Structure and Dynamics of Surfaces II*, edited by W. Schommers and P. v. Blanckenhagen, Topics in Current Physics Vol. 43 (Springer-Verlag, Berlin, 1987).