1. Introduction

At thermal equilibrium, any system is found in a stationary state characterized by the maximum of its entropy. Dynamical evolution of such a system, representing relaxation towards the equilibrium state, terminates when this state is reached. A different situation is characteristic for open systems with a permanent supply of energy and its dissipation. As noted in 1944 by Schrödinger,

1 generated entropy can be exported with the flux of energy passing through a system. Therefore, open nonequilibrium systems can evolve towards a state with low entropy content, increasing the degree of their order. Moreover, the resulting states need not be stationary: persistent oscillations, wave propagation, and complex spatiotemporal regimes (turbulence) become possible. In contrast to structure formation in equilibrium systems, known as self-assembly, these processes are seen as self-organization phenomena. According to Schrödinger, self-organization should play a fundamental role in biology; it underlies all active functions of a living biological cell. In the same book, he has predicted that genetic information should be maintained inside a cell at a molecular level, in the structures of macromolecules resembling irregular crystals.

Today we know that these are the DNA molecules. Proteins are the other stable macromolecules with complex internal organization, which operate as active machines inside a cell.

While spectacular advances have been made since that time by cell biology in the studies of molecular structures, the progress in understanding the self-organization aspects of a biological cell has been much less pronounced. The phenomena of self-organization have mainly been investigated for reaction-diffusion systems, formed by reacting molecules that diffuse freely through the medium. The classical example of such a system is the Belousov–Zhabotinsky reaction in an aqueous solution, where complex travelling wave structures are observed. Reaction-diffusion systems can also exhibit the formation of nonequilibrium stationary dissipative structures, including the Turing patterns predicted a long time ago, but only relatively recently observed in chemical experiments. Reaction-diffusion models have been efficient in explaining self-organization processes in microbiology and at the level of multi-cellular organisms. Turing patterns are of principal significance for biological morphogenesis; travelling waves explain the coherent activity of cell populations, such as collective amoebae. Similar models are used to describe wave patterns of electric excitations in the heart tissue or in the brain. But self-organization phenomena, based purely on reactions and diffusion, do not seem to play the fundamental role inside individual living cells. The characteristic sizes of cells lie in the micrometer domain and the intracellular processes proceed at the submicrometer- and nanoscales. The characteristic length scale of spatiotemporal pattern formation in reaction-diffusion systems is, however, limited by the diffusion length. Essentially, it represents the mean distance passed by a diffusing molecule between two reaction events. For typical biochemical reactions, the diffusion length is about a micrometer. Therefore, self-organization based on reactions and diffusion cannot provide a basis for understanding the operation of a single cell.

To go to the nanoscale, cohesion also needs to be involved in the processes of self-organization. Attractive energetic interactions between atoms and molecules easily lead to the formation of small equilibrium structures, such as atomic clusters or polymer macromolecules. There is a broad class of condensed

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Nonequilibrium Microstructures in Reactive Monolayers as Soft Matter Systems

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systems, known as soft matter, where cohesion is present and ensures condensation, but it is weak enough to leave such systems highly labile and subject to a rich variety of structural phase transitions. Remarkably, soft matter is indeed involved in most of the processes inside a biological cell.

Chemical reactions in molecular systems with weak energetic cohesion provide an alternative to self-organization relying merely on reactions and diffusion. An interplay between reactions, diffusion and structural phase transitions in soft matter yields nonequilibrium self-organized structures in the submicrometer domain and on the nanoscale.

The aim of our Minireview is to survey the current state of research of self-organization phenomena in reactive monolayers seen as examples of soft matter systems. Herein, we omit technical details and mathematical formulations. Rather, our attention is focused on the conceptual aspects of such research.

2. Nonequilibrium Reaction-Diffusion Systems

For reactions in dilute solutions, energetic interactions between reacting molecules can be neglected. Therefore, each molecule performs an independent diffusive motion through the liquid. Such systems are like ideal gases where molecules move freely between the collisions, with the difference that the motion of the particles is not ballistic, but Brownian. Upon collision, chemical reactions take place between the molecules. This situation can also be characteristic of reactions between molecules or atoms adsorbed on solid surfaces, provided that the energetic interactions between them are not significant.

In a closed system, the state of thermal equilibrium is solely determined by the energetic properties of the constituents and is not affected by the kinetic parameters of the reaction involved. In flow reactors, where fresh reactants are pumped into the vessel and the products are continuously removed, nonequilibrium states can, however, be reached. These states need not be stationary: persistent kinetic oscillations or traveling waves can also be observed under such conditions. Even if a nonequilibrium state is stationary, it is qualitatively different from the state of thermal equilibrium. Kinetic coefficients, such as reaction and diffusion rate constants, determine its properties.

Oscillations and waves typically develop when the reaction scheme includes an (effective) autocatalytic step. The chemical species capable of autocatalytic reproduction can be called an activator. The growth of the activator concentration cannot continue indefinitely. It is terminated either through the depletion of the required substrate, or through the accumulation of a product that hinders the reproduction. The latter substance is called an inhibitor.

In a pioneering study, which has laid the foundation for the theory of nonequilibrium chemical pattern formation, Turing has shown that the uniform state of an activator–inhibitor system can become unstable and stationary nonequilibrium patterns, now known as Turing patterns, may develop. This occurs when the diffusion rate of the inhibitor is much higher than that of the activator. Subsequently, Turing patterns have indeed been observed experimentally.

In any system with reactions and diffusion, characteristic diffusion lengths play an important role. Generally, the diffusion length of a chemical species is defined as $L = \sqrt{D/\kappa}$, where $D$ is the diffusion constant of this species and $\kappa$ is its characteristic reaction rate constant. For an activator, this would be the rate of its autocatalytic reproduction. For an inhibitor, this is the rate at which it would degrade in the absence of an activator.

Turing patterns develop when the diffusion length $L_{\text{act}}$ of the activator is much shorter than the diffusion length $L_{\text{inh}}$ of the inhibitor species. The patterns spontaneously emerge as a result of the instability of the uniform state towards the growth of a periodic spatial mode. The characteristic wavelength $\lambda$ of these periodic stationary patterns is roughly $\lambda \propto \sqrt{L_{\text{act}}/L_{\text{inh}}}$, thus, it lies between the diffusion lengths of the activator and the inhibitor species.

The example of the Turing patterns reveals typical features of nonequilibrium patterns in reaction-diffusion systems: 1) these patterns are purely kinetic in origin and their properties are determined by the kinetic constants of the system, 2) the characteristic length scales of such patterns are set by the diffusion lengths of the reactants.

For biochemical reactions, rate constants are typically of the order of milliseconds$^{-1}$. Combining this with the typical diffusion constant in water (of about $10^{-5}$ cm s$^{-1}$), one obtains a characteristic diffusion length of the order of a micrometer. This puts a limit on spatiotemporal pattern formation in such reactions, implying that no pattern details can be much shorter than a micrometer.


Energetic interactions between molecules in a solution are always present, but they become important only when concentrations are sufficiently high. A binary solution of two kinds of molecules A and B, with attractive forces acting between particles A, undergoes spontaneous separation into A- and B-rich phases, provided that temperature is low enough and the relative concentration of molecules A is sufficiently high. This process, known as spinodal decomposition, begins with the appearance of a short-scale lamellar structure. As time goes on, the characteristic wavelength of this structure gradually increases until eventually large macroscopic domains, occupied predominantly by A- or B-type molecules, are formed. Near the boundaries of the spinodal decomposition region in the phase diagram, spontaneous instability of the uniform state is absent and a sufficiently strong local perturbation (a supercritical nucleus) may be needed to initiate the phase-separation transition.

Phase-separating mixtures represent the simplest example of systems considered as soft matter. In this example, interactions between particles A suffice to produce phase separation of the mixture. However, they are not so strong that the solidification transition takes place and a rigid crystal consisting of A is formed.

Generally, soft matter represents a class of weakly condensed systems. In addition to phase-separating mixtures, it in-
cludes polymers, gels, biomembranes, and Langmuir monolayers formed by organic lipid or amphiphilic molecules at water–air interfaces. Such systems typically exhibit a variety of structural phase transitions. Because of weak cohesion, they are highly labile and can easily be moved from one phase into another.

Soft matter can form equilibrium spatially modulated phases. Returning to the binary solution of A and B, suppose that, in addition to short-range attractive interactions, long-range repulsive interactions between particles A are present. Because of such interactions, the uniform A-rich phase can become destabilized, so that phase separation into macroscopic A and B domains is no longer possible. Instead, spatially modulated phases characterized by periodic alteration of A- and B-rich micro-domains form.

Microphase separation is frequently found in polymer systems. A polymer molecule is an elastic chain where individual particles (monomers) are chemically bonded to one another. In addition to chemical bonds, energetic interactions between the monomers are usually present. Diblock polymers are made by linking two subchains consisting exclusively of monomers A and B. If monomers A attract each another, this would favour their phase separation. However, the formation of macroscopic A-rich domains is prohibited because of the geometrical constraints, since particles A are linked in the chains to particles B. Therefore, a microscopic lamellar phase with periodic alterations of A- and B-domains is formed.\(^\text{[13]}\)

Protein molecules are heteropolymers whose chains are made by irregular sequences of several kinds of monomers A, B, C, ... . Additionally, attractive and repulsive interactions between these monomers are present. Folding of a protein into its native equilibrium conformation can be viewed, as a rough approximation, as a process of microphase separation into a complex, but still highly ordered, spatial state.

Microphase separation phenomena is also possible in other kinds of soft matter.\(^\text{[14]}\) The developing equilibrium microstructures are typically in the nanoscale range. Their characteristic length scales are determined only by the energetic properties of the system.

4. Reactive Phase-Separating Mixtures

What happens if particles A and B, forming a phase-separating binary mixture, are additionally involved in the reactions A → B and B → A, converting them into one another? Obviously, such reactions would prevent the formation of macroscopic domains filled exclusively with particles A or B. The analysis reveals that, instead, periodically modulated nonequilibrium stationary phases are established.\(^\text{[15]}\) Figures 1 a and b show two successive snapshots of spinodal decomposition patterns in a binary mixture in the absence of a reaction. As expected, the characteristic wavelength of the pattern increases with time and macroscopic phase domains are gradually formed. With additional reaction, the initial development is the same as under the spinodal decomposition. However, the process of phase separation is chemically terminated before the macroscopic domains are reached. As a result, nonequilibrium stationary lamellar patterns, whose characteristic wavelength is controlled by the reaction rate, are produced. Two examples of such final patterns are shown in Figures 1 c and d.

In mathematical terms, the formation of such nonequilibrium structures is equivalent to the problem of microphase separation in diblock polymers.\(^\text{[16]}\) Physically, however, there is a principal difference between these phenomena. Both kinetic processes (reaction and diffusion) and energetic interactions are involved in the genesis of lamellar structures in reactive phase-separating mixtures. Therefore, their characteristic wavelength is determined by a combination of the diffusion length \(L_d \propto \sqrt{D/\Gamma}\) of the considered reaction (where \(\Gamma\) is the rate constant of the reaction) and of the radius \(r_0\) of attractive interactions between the particles, responsible for the phase-separation instability. This wavelength \(\lambda\) tends to infinity for vanishing reaction rate constants. Note that these nonequilibrium structures are different from Turing patterns, which have a purely kinetic origin and whose characteristic lengths are therefore only determined by the kinetic properties (i.e. the characteristic diffusion lengths) of the system.

The reactions under consideration may also take place in a closed volume, without a supply of energy or fresh reactants and in the absence of energy dissipation or evacuation of products. However, the laws of thermodynamics forbid the formation of kinetically controlled patterns in closed systems. Therefore, the equilibrium (i.e. thermally activated) reactions A → B and B → A do not change the outcome of the spinodal decomposition process.\(^\text{[17]}\)

The reaction A → B can be considered as a transition between two different states A and B of the same particle. The rate constant of this reaction depends on the energetic barrier separating state B from state A. When the energy of state A is changed, this affects the barrier height and thus the transition rate. In the presence of attractive interactions, the energy of a particle in state A is lower if it is surrounded by particles in the
same state A. Therefore, the rate constant for the reaction $A \rightarrow B$ must depend on the local density of molecules $A$ and is different for the $A$- and $B$-rich phases. When this dependence is taken into account, reactions indeed do not influence the equilibrium state of the system.

In the original analysis, rate constants for both reactions were fixed and independent of local concentrations. This assumption is not correct for thermally activated reactions. It does however hold if one of these reactions is energetically activated (e.g. photo-induced). The energy brought with a photon may be much higher than the energy differences due to interactions between the molecules, so that the rate constants are not sensitive to such interactions.

Effects of photochemical reactions on spinodal decomposition have been investigated experimentally for polymer mixtures.\(^{18, 19}\)

5. Inorganic Soft Matter: Adsorbates on Metal Surfaces

The presence of weakly condensed matter is not only characteristic of organic systems. Atoms adsorbed on metal surfaces show similar behaviour, which may be even easier to observe and understand.

At sufficiently high temperatures, adsorbed atoms or molecules remain mobile on the surface and can diffuse over it, forming a 2D gas. Additionally, lateral interactions between adsorbed particles are typically present. Such lateral interactions are often mediated through the substrate. They arise because the adsorbed particles locally modify electronic wave functions of the metal, thus affecting adsorption energies of other particles in the neighbourhood. A similar role is played by elastic deformations of the metal lattice, locally induced by an adsorbed particle. The lateral interactions can be attractive or repulsive; their range extends from several Ångstroms to several nanometers.\(^{20}\)

Attractive lateral interactions between adsorbed atoms can be so strong that a condensation transition takes place. Modern microscopy methods allow monitoring such phase transitions in real time down to atomic resolution. In an experimental study, spinodal decomposition of Au adatom gas on a Au(111) surface was observed in situ by scanning tunnelling microscopy (STM). The 2D gas of adsorbed gold atoms was produced by quick electrochemical dissolution of the top layer of the metal, thus creating the initial thermodynamically unstable state. The concentration of the adatoms could be controlled by the duration of the applied voltage pulse. Figure 2 shows a typical STM observation. Immediately after the pulse, a labyrinthine pattern of monoatomic high Au islands appears on the surface, which coarsens slightly while image scanning proceeds.

In the theory of equilibrium phase transitions, one traditionally distinguishes situations where the order parameter of the phase transition is conserved or not conserved. If the transition takes place only through a redistribution of the material originally present, the total amount of this material must be conserved. In the vicinity of a critical point of a first-order phase transition, such systems are described by the phenomenological Cahn–Hilliard equation.\(^{21}\) On the other hand, there are also phase transitions, such as the paramagnetic–ferromagnetic transition, where the structural change is local and no conservation law is involved. The kinetics of such transitions with the non-conserved order parameter is described by the Ginzburg–Landau equation.

Phase separation in adsorbates during the occurrence of both adsorption and desorption does not belong to any of such two classes. It combines both the processes that do and do not conserve the total number of the adsorbed particles. To investigate such phenomena, a special theoretical description was proposed.\(^{22}\) In addition to standard kinetic terms, corresponding to adsorption, desorption and diffusion, the proposed mean-field equation for adsorbate coverages includes a surface flow term. This term takes into account the viscous flow of the adsorbate induced by the lateral forces generated in interactions with the surrounding adsorbed particles. The forces are given by the local gradient of the interaction potential for an adsorbed particle which, in turn, is obtained by summing all binary interaction potentials within the interaction radius. Therefore, the resulting kinetic equation is integro-differential.\(^{23}\) Similar mean-field descriptions have been used for classical binary mixtures\(^{24}\) and in the studies of microfluidics problems.\(^{25}\)

In microscopic imaging, moving phase boundaries look similar to travelling fronts. However, in contrast to such fronts, they are much narrower, with a width of only a few Ångstroms (see Figure 2), which is determined by the energetic interaction radius.

Thus, the emerging structures may be so small that a single phase domain contains only hundreds of atoms. On such scales, the atomistic stochastic nature of diffusion and of adsorption and desorption becomes important. Stochastic effects may be taken into account in kinetic Monte-Carlo simulations of surface processes. Such simulations are essentially numerical experiments and their analytical interpretation is not straightforward. Alternatively, fluctuations can be taken into account by introducing appropriate “internal noise” terms into the ki-
nentic equations. The mesoscopic kinetic equations for fluctuating local concentrations have been derived by coarse-graining from the corresponding master equation of the full stochastic lattice model, explicitly determining the magnitude and the functional form of the noise terms related to diffusion and other kinetic processes. Numerical integration of mesoscopic stochastic equations is much faster than the kinetic Monte-Carlo simulations; it allows one to see the stochastic nucleation effects directly, as well as seeing the fluctuations at the earliest stages of spinodal decomposition. Similar approaches are currently used to take into account intrinsic fluctuations in processes of genetic expression in biological cells.

6. Phase Separation in Reactive Adsorbates

An adsorbate can be viewed as a binary mixture formed by adsorbed atoms (A) and empty lattice sites (*) on the metal surface. The condensation transition, caused by attractive lateral interactions between adsorbed particles, then represents a process of phase separation in this binary mixture. Moreover, adsorption and desorption processes can formally be considered as the reactions * + A → A * and A → *. When two kinds of particles (A and B) are present on the surface, further chemical reactions are possible between them. If the reaction product immediately leaves the surface, the reaction scheme is A + B → 2*.

Almost simultaneously with the publication of ref. [15], it has been suggested that reactive phase separation may be observed in surface chemical reactions. [20] The “reactions” considered in that study were the processes of thermal adsorption and desorption. Such thermally activated processes should not, however, change the equilibrium state of the system.

In our theoretical investigation, [30] we have shown that thermal adsorption and desorption processes do not prevent macroscopic phase separation. If, on the other hand, an energetically activated process A → * (such as photo-desorption) is present, kinetic freezing of phase separation, leading to the formation of stationary nonequilibrium structures, can occur. Lamellae and labyrinthine structures generally develop in the parameter regions with spinodal decomposition taking place in the absence of the reaction. Arrays of dense islands or voids tend to appear on the wings of the phase separation diagram, where critical nucleation takes place instead.

The wavelength of the developing structures at the instability boundary of the uniform state was estimated [30] as \( \lambda \propto \sqrt{L_d K_d} \), where \( r_a \) is the characteristic radius of attractive lateral interactions and \( L_d \) is the diffusion length with respect to the energetically activated reaction (or desorption) process, that is, \( L_d = \sqrt{D/K_d} \), with \( D \) being the rate constant of surface diffusion and \( K_d \) representing the rate constant of the energetically activated process. Remarkably, this resembles the result \( \lambda \propto \sqrt{K_a \gamma} \) for the Turing instability in reaction-diffusion systems. The principal difference is, however, that the characteristic wavelength is given by a combination of the kinetic \( (L_d) \) and energetic \( (r_a) \) properties.

Using the mesoscopic description, [24] stochastic simulations of phase separation in reactive adsorbates have been performed. It was found that, despite their small sizes, emerging microstructures are not destroyed by internal statistical fluctuations. Figure 3 shows irregular lamellar structures in a system with linear size of about 500 lattice lengths, corresponding to roughly 59 nanometers. Four successive snapshots of the same system at time intervals equal to 15 characteristic thermal desorption times are shown. Although the fluctuations are relatively strong, the basic morphology of the pattern is retained.

These theoretical predictions can be tested in experiments with an energetically activated desorption process (such as photo-induced desorption).

7. Surface Reactions with Co-Adsorbed Non-Reactive Species

Surface reactions often take place in the presence of passive co-adsorbed species. While not directly participating in a catalytic reaction, such substances can significantly increase or decrease its rate, thus acting as promoters or poisons. Alkali metals are a well-known example of a promoter species finding use in a number of technologically important catalytic reactions.

Theoretical investigations have been performed [32, 33] for a model three-component system (A, B and C) with adsorption and desorption of species A and B, involved in the reaction A + B → 2*. In this system, the adsorbed species C is not involved in the reaction, but has strong interactions with one of the reactants (B). In absence of the other reactant, the homogeneous binary mixture B-C is unstable and undergoes spinoidal decomposition. For such surface reactions, the theory predicts the formation of stationary nonequilibrium microstructures whose characteristic length scale is directly controlled by the reaction rate [32, 33].

Figure 3. Nonequilibrium nanostructures in a reactive adsorbate in numerical mesoscopic simulations. Four successive snapshots are shown. From ref. [30]. Reprinted with permission from the American Physical Society.
Experimentally, this situation was realized in the reaction of catalytic water formation on a Rh(110) surface in the presence of co-adsorbed potassium.\(^{[32]}\) Both gases, O\(_2\) and H\(_2\), adsorb dissociatively and the atomic adsorbates then recombine, forming water, which rapidly desorbs. Potassium is highly mobile on the rhodium surface. It has a high affinity to oxygen, with which it forms a number of well-ordered two-dimensional coadsorbate phases. When hydrogen was added, initiating the reaction, development of stationary lamellar patterns was reported.\(^{[32]}\) These patterns, observed with photoemission electron microscopy (PEEM), had characteristic wavelengths of the order of tens of micrometers.

A systematic investigation of reaction-induced patterns in the same reaction, but in the presence of coadsorbed Au and Pd atoms, has been performed as well.\(^{[34]}\) These coadsorbed atoms are characterized by repulsive interactions with the adsorbed oxygen. They block adsorption sites and can therefore be viewed as an inhibitor of the catalytic water formation reaction. These experiments were carried out at Synchrotron Trieste where high-resolution microscopy methods, such as LEEM (low-energy electron microscopy) and XPEEM (X-ray photoemission electron microscopy), are available.

The LEEM images in Figure 4 show the temporal evolution of the patterns for two different experimental conditions. Before introducing H\(_2\) and O\(_2\) reactants in the gas phase, the metal adatoms are uniformly distributed and only the step bunches of the Rh surface are seen (\(t = 0\) s). When the reaction starts, lamellae begin to form. Later on, the wavelengths of these structures increase until a stationary state is reached. The last two images in each column of Figure 4 demonstrate that the phase separation is “frozen” and that the patterns do not change further. The local composition of the structures was probed by imaging the Au 4f\(_{7/2}\), Pd 3d\(_{3/2}\), and O 2p core emission using XPEEM. Bright regions in LEEM are the areas where adsorbed Au and Pd atoms are found; dark regions are filled with oxygen.

Figure 5 shows the experimental phase diagram of this nonequilibrium system, together with typical examples of the observed patterns. At high temperatures (\(T > 860\) K), spontaneous pattern formation is absent and microscopic rearrangement of metal atoms that decorate substrate steps and step bunches is seen. At lower temperatures, the behavior depends on the metal coverage (Au or AuPd). If the coverage is small, no patterns are observed and the system remains homogeneous. However, the homogeneous state becomes unstable as the metal coverage is increased and first gives rise to a pattern of small metal islands (c), followed by a lamellar structure (d). At even lower temperatures, large islands (a) and voids (b) are observed.

The phase diagram in Figure 5 has an apparent similarity to the classical phase diagram of a binary mixture, with lamellae formed in the spinodal decomposition region and islands or holes in the area where critical nucleation occurs. Now, however, the lamellar structure and the islands are stationary and do not represent only the transients, as in the classical process of Ostwald ripening.

Interesting results were found when the influence of the reaction rate on the morphology of the developing stationary microstructures was investigated. As shown in Figure 6 (top), the wavelength of the lamellar structure decreases upon increasing the reactants’ pressures and, hence, the reaction rate. At high pressures, lamellae disappear and are replaced by large metal islands. The characteristic wavelength of the lamellae was determined by Fourier analysis of the LEEM images. As seen in Figure 6 (bottom), the dependence of the wavenumber (proportional to the inverse wavelength) on the reactant pressure follows a power law. The power-law dependence holds over two decades of variation of the reactants’ pressure and the smallest lamellae formed have wavelengths of less than a micrometer. The best fit, shown by the straight line in Figure 6, yields an exponent of \(0.18 \pm 0.02\).

We see that the morphology and wavelength of the nonequilibrium microstructures in reactive adsorbates can be tuned over a wide range by varying the reaction conditions. Generally, such microstructures exist only as long as the reaction continues. In the experimental system considered, however, they remain on the surface after the reaction is terminated. This is because the surface mobility of adsorbed oxygen is very low. When hydrogen is no longer supplied and the reaction

Figure 4. Development of lamellar structures on a Rh(110) under different experimental conditions (a, b). From ref. [34]. Reprinted with permission from the American Chemical Society.
stops, the surface distribution of oxygen atoms becomes kinetically frozen. Although the adsorbed gold atoms are mobile, in a lamellar pattern they are confined between the stripes formed by adsorbed oxygen. Thus, in the absence of hydrogen, the gold and palladium microstructures, created under reaction conditions on the surface of Rh crystal, remain stable. They can however be further modified by placing the sample into a reaction chamber. This opens the possibility of creating micro-templates with tunable morphology, which may be important for applications.

8. Travelling Surface Nanostructures

In contrast to thermal equilibrium, nonequilibrium systems may exhibit persistent oscillations and show actively propagating waves. These phenomena are well documented for reaction-diffusion systems, such as the Belousov–Zhabotinsky reaction. Oscillations and travelling structures should also be possible in the nonequilibrium soft matter, where they can be very small, with the characteristic sizes going down to the nanoscale.

Patterns formed by travelling waves are often observed in surface reactions. Such patterns, seen using low-resolution PEEM (photo-emission electron microscopy) or optical microscopy methods, are typically on the scale of tens of micrometers and are well described by kinetic reaction-diffusion models. Theoretical analysis, however, predicts the existence of very small, nanoscale travelling structures when reactions and diffusion are coupled to the phase transitions caused by lateral interactions between the adsorbed particles.

In our studies, a hypothetical system with two adsorbed chemical species A and B was investigated. They participate in the reaction \( A + B \rightarrow 2^* \), in which the product immediately leaves the surface and two lattice sites become free. Both species arrive by adsorption from the gas phase. The particles B are strongly chemisorbed, they do not desorb thermally and cannot move across the surface laterally. The particles A are only weakly bound to the substrate, they are highly mobile and can desorb. An essential property of the system is the exis-

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**Figure 5.** Morphology of the reaction-induced microstructures. LEEM images of selected structures (top) and the phase diagram (bottom). (a) indicate the pure Au adlayers and (b) the mixed Au–Pd adlayers. LEEM images correspond to selected points (a–d). From ref. [34]. Reprinted with permission from the American Chemical Society.

**Figure 6.** Top: LEEM images of stationary nonequilibrium microstructures formed at different gas pressures of reactants; \( T = 820 \text{ K}, P[H_2]/P[O_2] = 0.8 \). Bottom: Log–log plot of the structures wavenumber as a function of the reactants pressure. From ref. [34]. Reprinted with permission from the American Chemical Society.
tence of interactions between the particles. Particles A attract each other strongly and, in absence of the reactant B, this adsorbate undergoes a phase separation transition. The particles B are attracted to A, but do not interact among themselves.

Theoretical analysis reveals that the uniform state of the system is unstable and spinodal decomposition in the system of adsorbed A particles begins. Because reaction between A and B does occur, this process does not lead to macroscopic phase separation and a lamellar structure is formed. However, this lamellar structure is not stationary—it travels across the surface at a constant speed.

The travelling structures can be much smaller than the characteristic diffusion length, which itself may be in the submicrometer domain. In such a situation, only a relatively small number of adsorbed particles contributes to the formation of a specific pattern and, hence, internal fluctuations have to be taken into account. Numerical simulations were therefore performed by using the stochastic mesoscopic description.[36]

Figure 7 shows the fluctuation coverage distributions obtained in a numerical simulation. Here, the total size of the system is only 555 atomic lattice lengths and the diffusion length is 327 lattice lengths, so that the characteristic sizes of the microstructures are in the nanodomain and each of them includes only hundreds of adsorbed particles. At these small scales, the internal noises of the diffusion, adsorption, desorption and reaction processes exhibit a strong influence on the patterns. The lamellae are broken into many short fragments that form irregular spatial patterns, as seen in the snapshots of Figures 7a, b and c. Nonetheless, examining the time evolution in the central cross section (Figure 7d), one sees that these fragments do not just fluctuate. They travel across the surface while undergoing irregular variations of their shapes. The directions of the translational motion of the fragments are different and the fragments can collide. Merging of travelling fragments, as well as splitting events, were observed. Remarkably, the magnitude of the propagation velocity of different fragments did not differ significantly.

Travelling waves have also been discussed for three-component mixtures with the nonequilibrium cyclic reaction A → B → C → A, where components A and B undergo phase separation in absence of the reaction.[38]

9. Self-Organized Surface Nanoreactors

Permanent microreactors for the engineering of surface reactions can be fabricated by microlithography, where defined patterns of an inert material are deposited onto an active surface.[39] The resulting structures exhibit typical sizes in the range of tens of micrometers. Such permanent microreactors cannot be made much smaller, due to the intrinsic limitations of the optical manufacturing method. On the other hand, localized stationary structures with sizes down to the nanoscale domain may spontaneously emerge on a surface as a result of nonequilibrium self-organization processes and play the role of chemical reactors.

In addition to phase transitions that are caused by lateral energetic interactions between the adsorbed particles, surface chemical reactions are often accompanied by structural phase transitions in the top layer of the metal substrate. When the metal surface is covered by an adsorbate, this affects interactions between the metal atoms in the top substrate layer and can lead to the rearrangement of these atoms, so that the crystallographic symmetry of the top layer becomes different from that of the bulk crystal. This is known as adsorbate-induced surface reconstruction. Thus, without the adsorbate, the surface is found in one state, but the presence of the former triggers a structural transformation into the reconstructed state. The driving force is the gain in adsorption energy and hence, the reconstructed surface region is attractive for the adsorbed molecules, representing a potential well for them (Figure 8).

Molecules diffusing across the surface are trapped by such regions and growing adsorbate islands are formed.

In absence of reactions, this process continues until the reconstructed regions become macroscopic or the whole surface becomes reconstructed. The situation is different if an energetically activated surface reaction (or the process of photo-induced desorption) is present. As a result of this reaction, adsorbed particles are removed from the surface. Because the reaction is activated, the differences in the local chemadsorption
energy between the reconstructed and nonreconstructed areas may play no role in determining the reaction rate constant.

An island grows due to the diffusion flux of molecules into it from the surrounding surface region. 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.\[40, 41\]

The total diffusion flux of adsorbed particles into an island is proportional to its perimeter. However, 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 should grow. On the other hand, 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 therefore gives the size of the stationary localized structure.

Such localized structures represent small self-organized chemical reactors. Indeed, the reaction essentially takes place only inside these reconstructed regions, where the adsorbate coverage is high. Their radii are controlled by the reaction and they decrease when the reaction gets faster. The smallest size of the stable self-organized reactors is of the order \(\sqrt{r_0 L_{\text{diff}}}\) where \(L_{\text{diff}}\) is the characteristic diffusion length with respect to the reaction and \(r_0\) is the atomic lattice length. Therefore, they can persist down to the nanoscale.

Large islands (on the scale of micrometers) are unstable with respect to the transverse deformations of their boundary (Figure 9), giving rise to extended labyrinthine and other complex structures.

10. Multicomponent Langmuir Monolayers

Langmuir monolayers are a kind of organic soft matter related to adsorbates on solid surfaces. They are formed by molecules disposed at a water–air interface. The molecules have hydrophilic heads, drawn inside the water, and hydrophobic tails which stay in the air.

At low densities, such systems represent a two-dimensional gas with only weak interactions between the particles (Figure 10). Under lateral compression, the expanded phase, similar to a 2D liquid, is formed first. Upon further increase in the density, transitions to the tilted condensed phase and then to the untitled condensed phase are observed. Both these phases are characterized by orientational ordering, but the translational ordering is absent. Therefore, they are the 2D analogs of liquid crystals. In the untitled phase, the molecules are oriented orthogonally to the interface plane. In the other phase, they are tilted with respect to the normal direction. Thus, their local orientational ordering is characterized by two variables: the tilt and the local azimuthal orientation. At still higher densities, translational symmetry is broken and various solid 2D states are formed. For a review of equilibrium properties of Langmuir monolayers, see ref. [43].

Multicomponent Langmuir monolayers represent a 2D surface solution of two or several species. In such systems, lateral energetic interactions between the different kinds of molecules are important. If they are repulsive and sufficiently strong, phase separation can take place inside a monolayer, leading to the formation of surface domains predominantly occupied by one of them.

In mixed states, the so-called splay coupling between local concentrations and the orientation field is important.\[44\] If this coupling is sufficiently strong, it leads to an equilibrium phase transition into a spatially modulated stripe phase.\[45\] This phase is characterized by periodic modulation of the local chemical composition of the monolayer accompanied by periodic changes in the local azimuthal orientation of molecules.

11. Travelling Structures in Illuminated Langmuir Monolayers

Two components, forming a monolayer, may actually represent different conformations of the same molecule. This situation is specifically characteristic of the derivatives of azobenzene where \(\text{trans}\) and \(\text{cis}\) isomers have largely different conformations and can be viewed as two different physical species. The shapes of the two isomers are largely different: the \(\text{trans}\) isomer has an elongated shape with a tail, whereas the \(\text{cis}\) isomer is more compact. Transitions between these two con-
formations can be photo-induced. Thus, by applying illumination, such systems can be brought away from the state of thermal equilibrium.

In the experiments by Y. Tabe and H. Yokoyama,[46, 47] steadily travelling orientation waves have been observed in illuminated Langmuir monolayers (Figure 11). The waves travel steadily at a velocity of about 50 μm s⁻¹ and have a characteristic wavelength in the range of tens of micrometers.

Aiming to explain these experimental observations, a theoretical model of a nonequilibrium two-component Langmuir monolayer has been developed.[48, 49] In this model, the monolayer represents a mixture of two components A and B. Because of the repulsion between the two species, the system undergoes phase separation at equilibrium. The energetically activated (e.g. photoinduced) reactions continuously convert A into B and back.

An important aspect of the model is that only one of the molecules (A) has an elongated shape and can undergo orientational ordering. These molecules form the tilted condensed phase and show a phase transition to the untitled condensed phase when their concentration is increased. The other molecules (B) have compact shapes. They do not undergo orientational ordering and act as a surface solvent with respect to particles A. The reaction converting A into B therefore leads to the local loss of orientational ordering. In the reverse reaction B → A, new elongated molecules with random initial orientations are created.

Theoretical analysis and numerical simulations of the model have shown[48, 49] that phase separation in these systems leads to the spontaneous formation of travelling concentration stripe structures with definite wavelength and propagation velocity. When coupling between the orientational field and local concentration of particles A is taken into account, travelling orientation patterns (Figure 12) are observed.

It was subsequently shown[50] that polarization asymmetry must be taken into account as well to reproduce the experimental results. In the experiments,[46] the applied light had linear polarization and, therefore, the rate constant of the photoinduced trans–cis isomerization was strongly sensitive to the planar orientation of trans molecules. When this anisotropy effect is included into the model, it describes the experimental results well and, particularly, the experimental behaviour seen after changing the light’s polarization direction. Phase separation in trans–cis mixtures has, however, also been observed experimentally.[51] A detailed discussion of the experiments and of theoretical modelling of such phenomena is given in ref. [52].

12. Waves in Chiral Langmuir Monolayers with Transmembrane Flows

In different experiments, Tabe and Yokoyama have demonstrated[53] another possibility of perturbing the thermal equilibrium of Langmuir monolayers and initiating travelling waves in such systems. They have considered monolayers including a fraction (about 10%) of chiral molecules. These monolayers were at an interface between air and glycerol. Inside the glycerol, water was dissolved and water vapor was also present in the atmosphere. The concentration of water molecules in the liquid was higher than in the air and therefore water was evaporating from the liquid through the surface monolayer into the air.
The compounds used in the experiments have a rod-like molecular structure with a chiral group attached, thus they look like molecular propellers (Figure 13). Under experimental conditions, these molecules were in the orientationally ordered, tilted condensed phase. Their collective orientation was characterized by the azimuthal angle $\phi$. When a gradient of water concentration across the surface monolayer was applied, steady rotation of the azimuthal orientation was observed by using the reflected-type polarizing microscope. It could be interpreted as coherent precession of the orientationally ordered molecules in the monolayer.

The precession was very slow, with characteristic periods of several minutes. Its frequency was directly proportional to the gradient of water across the layer (Figure 14). The rotation direction was reverted when the opposite gradient (with a higher concentration of water molecules in the atmosphere than in the liquid) was applied. The authors examined 23 different compounds, 14 chiral and 9 nonchiral, that form surface layers on glycerol. All the chiral compounds exhibited similar precession behavior. It was, however, never observed in achiral films. The precession was never uniform and various spatio-temporal patterns were observed. In the example shown in Figure 15, the central region acts as the periodic source of a wave that propagates towards the outer boundaries of the system. Examining the pacemaker pattern, one can see that the wavelength gets shorter as the waves propagate away from the centre. Patterns formed by several pacemakers with colliding wavefronts, making the system look "like a pond surface hit by falling raindrops", have been observed. Complex wave patterns, including rotating spiral waves, have also been found.

The proposed theoretical explanations attributed these phenomena to the pinning of the orientational field on the lateral boundaries of the Langmuir monolayer. Indeed, if the orientation field rotates in the center, but is pinned at the boundaries, one should observe concentric waves which are regularly emitted in the central region and propagate outwards. This theory does not, however, explain why more complex wave patterns, including multiple coexisting pacemakers, are also possible.

In the experiments, the Langmuir monolayers were binary mixtures of chiral and achiral components, with the chiral molecules present only at a relatively low concentration of about 10%. Therefore, if coupling between the orientational field and the local concentration is present, the propagation of orientation waves should be accompanied by surface concentration flows which, in turn, changes in the concentration patterns would have an effect on the orientation fields.

Such coupling can be provided by splay interactions, which contribute significantly to the free energy of a Langmuir monolayer if, in addition to local orientation, it is characterized by some scalar or pseudo-scalar field. At thermal equilibrium, splay coupling leads to a phase transition into a spatially modulated stripe phase. This transition takes place when the intensity of splay coupling is increased.

A model of nonequilibrium chiral Langmuir monolayers with transmembrane flows, taking into account splay coupling with...
the chiral concentration component, has been proposed.\textsuperscript{[57]} Numerical investigations of this model revealed\textsuperscript{[57,58]} that it describes spontaneous formation of complex wave patterns.

Such self-organized wave patterns emerge when an evolution with random initial conditions is started, including many topological defects of the orientational field. At the early evolution stage, many defects disappear through annihilation processes. However, the remaining defects slowly start to aggregate in some spatial regions. At the same time, regions free from defects gradually appear, where almost uniform oscillations are observed. These regions periodically emit waves, which slow down and decrease their wavelength as the peripheral regions with the defects are approached. This process results in the formation of wave patterns with pacemakers, an example of which is shown in Figure 16. Complex wave patterns (Figure 17) with multiple pacemakers and several dense regions, where defects are present, are also often observed in the simulations. Remarkably, these self-organized structures are only weakly sensitive to the boundary conditions. They can also be seen when periodic boundary conditions are employed.

To understand the mechanisms underlying spatiotemporal pattern formation in such systems, one should take into account that, as numerical simulations show, it is accompanied by the redistribution of chiral molecules inside the monolayer.\textsuperscript{[57,58]} On average, these molecules tend to leave the central wave-emitting regions and accumulate in peripheral regions where slowly travelling tight stripe structures are observed. The local increase in the concentration of chiral molecules strengthens splay interactions and brings the system closer to the equilibrium phase transition point where the spatially modulated stripe phase is formed.

13. Related Systems

Biomembranes play a fundamental role in cell biology. Like Langmuir monolayers, they are also formed by molecules with hydrophilic heads and hydrophobic tails. If there is no water-air interface where such molecules can form a monolayer, these molecules find another way of reducing the free energy by producing bilayers inside the liquid phase. Inside a bilayer, water is expelled and hydrophobic tails of the molecules are located. Hydrophilic heads sit inside the water on both sides of the bilayer. In contrast to Langmuir monolayers, biomembranes are usually not flat, but curved. They can form spherical vesicles and, generally, nonequilibrium processes in such systems are accompanied by shape variations.

Biomembranes often represent a mixture of several chemical components and phase separation can occur in such systems. When it takes place, membrane regions rich in a particular component appear. Since the surface tension coefficient of a membrane is sensitive to the local chemical composition, phase separation usually leads to pronounced shape changes. Budding of new vesicles can thus occur. When phase-separating components participate in a chemical reaction, formation of stationary spatially modulated (wrinkled) patterns becomes possible.\textsuperscript{[59]}

Another important class of soft matter is constituted by polymers. Individual macromolecules in homopolymers represent long chains of identical atomic groups. As a result of attractive interactions between different groups, such macromolecules can form compact globular structures. Interactions between different macromolecules of the same kind in a solution lead to the formation of weakly condensed phases, such as gels.

Gels behave as viscous elastic media, which maintain their physical shapes and respond to the application of external forces by deformation. However, they contain a large amount of water, which can include various chemical species. Reactions between them are possible and when they take place, they modify local properties of the solution, which can induce shape changes in a gel. In turn, shape changes can affect local concentrations of chemicals, thus introducing a physical feedback loop.

Periodic shape changes in gels containing a solution with the Belousov–Zhabotinsky reaction have been observed experimentally.\textsuperscript{[60]} Figure 18 shows an example of a theoretical simulation of a similar phenomenon.\textsuperscript{[61]} A stripe of gel with the Belousov–Zhabotinsky reaction is modeled. The figure shows temporal variation of the stripe thickness at two cross sections (\textit{ab} and \textit{cd}), together with the evolution of the local fraction of
Active macromolecules may be incorporated into the monolayers. For solid-supported monolayers, this can be done by adsorbing proteins on the solid surface. When molecular motors are adsorbed, active motility arrays are formed. Using such motor arrays, active directed transport of micro-cargo over the surface can be engineered.\cite{66, 67}

Alternatively, molecular machines and motors can be deposited at liquid–air interfaces. To enable them to float, such protein molecules need to be modified through the attachment of a separate hydrophobic group. When energy is supplied (with ATP molecules) to the floating motors, they behave as active surfactants, generating local mechanical pressure applied at the interface. This pressure is proportional to the concentration of the motors. Their local concentration may change because such biomolecules can move laterally, together with the liquid flows or diffusively. It has recently been shown that, if the surface density of floating motors is high enough and sufficient energy is provided, the flat liquid–air interface becomes unstable.\cite{68} As a result of this instability, a dynamic regime of surface turbulence, accompanied by irregular variations in the local height of the surface and of the local concentration of active surfactants, develops. In this regime, bumps of molecular motors are moving in various directions over the liquid surface.

Molecular machines, adsorbed on a solid surface or floating over a liquid, can furthermore interact chemically. The cycles of many protein machines can be regulated allosterically (i.e. activated or inhibited) by small organic molecules that bind to them. For machines operating as enzymes, regulatory molecules often represent the products of the same enzymatic reaction, so that allosteric product activation or inhibition takes place. Thus, chemical communication between the machines develops. As a result of such communication, synchronous dynamical regimes, characterized by coherent intramolecular dynamics, can emerge spontaneously. In these regimes, individual turnover cycles of active biomolecules become synchronous. Complex dynamical synchronization patterns and travelling waves have been seen in numerical simulations.\cite{69}

14. Outlook

Nonequilibrium soft matter is the main component of living cells and investigations of its properties are essential for the understanding of various cell functions. Therefore, theoretical and experimental research in this direction is often performed in the framework of biophysics. However, working with biological systems has intrinsic difficulties. The soft matter in a living cell is a product of a long evolution and it is usually optimized for simultaneous execution of various biological functions. Hence, its properties are complex and multi-faceted.

With this in mind, it may be more efficient first to consider the phenomenon of nonequilibrium self-organization in reactive soft matter of non-biological origin and to study them in the general context of physical chemistry. By choosing simple model systems, principal aspects of nonequilibrium microstructures in reactive soft matter can better be investigated.
Nonequilibrium Microstructures in Reactive Monolayers

The knowledge gained can then be applied to the analysis of processes in real biological systems. Beyond that, there is the fundamental challenge of designing next-generation technological systems that could employ nonequilibrium soft matter and artificially engineered nanoscale machines.

Herein, we have given examples of nonequilibrium self-organization phenomena in reactive monolayers, in situations where they behave as soft-matter systems. Working with monolayers has several experimental advantages. Such systems are intrinsically flat, following the geometry of the underlying solid or liquid support. Therefore, different microscopy surface imaging methods can be applied noninvasively to monitor the dynamics of patterns in the monolayers. On the other hand, pattern formation processes in these systems can easily be controlled. This can be done by applying external illumination or by varying the reaction parameters (e.g. through temporal modulation of the reactants’ concentration in the gas phase).

One can also introduce feedback loops in such systems, coupling illumination intensity or reaction parameters to the dynamical processes on the monitored surface. We have previously demonstrated how such global feedbacks can be used to control nonequilibrium pattern formation in oscillatory surface reactions, albeit in the regimes where the soft-matter aspects of a reaction were not important and where the characteristic length scales of the patterns were in the range of tens or hundreds of micrometers. Similar methods can be used to control the dynamics and evolution of nonequilibrium surface-supported structures on submicrometer- and nanoscale. Finally, the properties of monolayer systems can easily be handled by modifying the chemical composition of the monolayers and by introducing inclusions, which may also represent large biomolecules and molecular motors.

We did not provide a complete survey of current advances in the investigations of reactive soft-matter monolayers and we have mostly focused on our own research. Taking into account the rapid progress in this field and its importance in applications, a broader review is definitely desirable.

Keywords: kinetics · Langmuir–Blodgett films · nonequilibrium processes · phase transitions · surfaces

[33] Y. Takebe, private communication.


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