Atomistic theory of mesoscopic pattern formation induced by bimolecular surface reactions between oppositely charged molecules

V. N. Kuzovkov,¹,a) E. A. Kotomin,² and G. Zvejnieks¹
¹Institute for Solid State Physics, University of Latvia, Latvia
²Max-Planck Institute for Solid State Research, Stuttgart, Germany

(Received 5 September 2011; accepted 8 November 2011; published online 8 December 2011)

The kinetics of mesoscopic pattern formation is studied for a reversible \( A + B \rightleftharpoons 0 \) reaction between mobile oppositely charged molecules at the interface. Using formalism of the joint correlation functions, non-equilibrium charge screening and reverse Monte Carlo methods, it is shown that labyrinth-like percolation structure induced by (even moderate-rate) reaction is principally non-steady-state one and is associated with permanently growing segregation of dissimilar reactants and aggregation of similar reactants into mesoscopic size domains. A role of short-range and long-range reactant interactions in pattern formation is discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3664862]

I. INTRODUCTION

Pattern formation phenomena at surfaces and interfaces¹ is area of great scientific interest. In the case of patterns formed by charged molecules²–⁴ adsorbed onto biological membranes and other neutral surfaces, periodic nanostructures were theoretically predicted, e.g., lamellar structure⁵ with the alternating domains of oppositely charged molecules. The competition between the short-range interactions (responsible for domain formation) and the electrostatics (attractive Coulomb interaction of opposite charge domains) offers route to self-assembly.⁶ Theoretical results were focused so far mainly on equilibrium state⁵ whereas adsorption/desorption to the interface and chemical reactions were neglected. However, the stability of such systems under non-equilibrium conditions is far from obvious. The proper solution to this problem has to expand language used for the analysis of equilibrium systems² for non-equilibrium ones.⁷ There exists so far a wide gap between the atomistic language used in the statistics of equilibrium systems and that commonly for mesoscopic pattern formation where particle distributions are defined by the concentration fields.⁸

In the present study, we consider mesoscopic pattern formation arising in diffusion-controlled reactions of charged molecules at surfaces/interfaces (2d) with a focus on the spatial correlations between reactants. All the kinetic parameters such as reaction rates are self-consistently calculated as a function of reactant spatial distributions. The lateral reactant (molecule) interactions include both short-range Lennard-Jones (LJ) potentials and long-range Coulomb interactions. For simplicity, we restrict ourselves to the case of bimolecular reversible annihilation, \( A + B \rightleftharpoons 0 \).

II. THEORETICAL APPROACH

We combine here two methods. (i) The first one deals with many-point densities of reactants.⁷,⁹,¹⁰ Its key point is taking into account the spatial fluctuations in reactant densities caused by reactions. Our formalism⁹,¹⁰ is similar to the well-known Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) method¹¹ in statistical theory of dense gases and liquids and based on an infinite set of the coupled equations. In both theories this is decoupled, leading to the joint correlation functions for similar and dissimilar reactants (particles). However, the problem of statistical physics is more simple since the steady-state solution of a set of integro-differential equations is sought for here, unlike our formalism of many-point densities whose time-dependence (kinetics) analysis is a very time-consuming task. We managed here to perform calculations until so long times that we could observe the pattern formation development at the mesoscopic spatial scale \( \xi(t) \), of the order of hundreds Å. We call hereafter the analytically calculated joint correlation functions for similar and dissimilar reactants (analogs of the radial distribution functions in condensed matter) as standard. (ii) At the next step, the reverse Monte Carlo (RMC) (Ref. 12) method is applied to the standard distribution functions. Using special optimization algorithms⁸ and moving tens of thousands of atoms in the system, one is searching for the particle spatial configuration giving the best fit to the standard radial distribution functions. As a result, the relevant molecular configuration snapshots are obtained, which are especially informative in the 2d case. Our study is the first attempt to use the RMC for characterization of the mesoscopic-scale patterns which require large scale computer simulations.

Single A, B reactant migration on a defect-free surface is characterized by the relevant partial diffusion coefficients \( D_A \) and \( D_B \). We assume also that dynamical interactions between reactants consist of the short-range and long-range two-particle forces. The former is classic 6–12 LJ potential \((\nu = A, B)\) characterized by two scale parameters \((U_0\) and \(r_0)\):

\[
U_{ij}^{\text{LJ}}(r) = 4U_0 \left[ \left( \frac{r}{r_0} \right)^{12} - \left( \frac{r}{r_0} \right)^6 \right].
\]
We apply this potential only to the similar reactants, to mimic their final sizes but neglect it for dissimilar reactants, to allow their close mutual approach.

The long-range Coulomb interaction has a standard form

\[ U^C_{\nu\nu}(r) = \frac{e_\nu e_{\nu'}}{er}, \]

where \( \epsilon \) is the dielectric constant and \( e_A \) and \( e_B \) are particle charges (\( e = e_A = -e_B \)).

The reversible chemical reaction \( A + B \rightleftharpoons 0 \) has two steps. This is characterized by the reaction radius \( r_a \) approaching which reactants instantly disappear.\(^3\) For simplicity, we consider here the limiting case of a small recombination rate assuming \( r_a \to 0 \) (this is possible only for low-dimensional systems,\(^13\) \( d \leq 2 \)). Another reaction step is a formation (adsorption) of reactants \( A \) and \( B \) on a free surface with the rate (per surface unit) \( p = p_A = p_B \). That is, reactant macroscopic concentrations are always equal, \( n(t) = n_A = n_B \).

The reactant is considered as successfully adsorbed at some surface place if there are no other reactants within a circle with a given reaction radius. Thus, the surface could be saturated with the maximum reactant density \( n_0, n_A + n_B < n_0 \). We also assume that rate parameter \( p \) is small. The main purpose of this paper is to demonstrate that even for small reaction rates, reaction-induced patterns are non-steady-state and have nothing in common with a relaxation to the equilibrium without reaction.\(^7,14\)

It is convenient to use dimensionless parameters: the spatial scale \( r_0 \) and time unit \( t_0 = r_0^2/D \), where \( D = D_A + D_B \) is the coefficient of a mutual diffusion. The characteristic temperature based on the LJ parameter \( U_0 \) is \( T_0 = U_0/k_B \), so that one can introduce the dimensionless temperature \( \theta = T/T_0 \). The competition between the short-range and long-range potentials is characterized by the parameter \( \delta = e_\nu r_0 k_B T_0 \).

The dimensionless maximal density of molecules reads \( n_0 = n_0 r_0^2 \), the dimensionless adsorption rate \( \xi = p r_0^2 t_0 = p r_0^4 / D \) (small parameter \( \xi \ll 1 \)), and the dimensionless diffusion asymmetry \( \mu = D_A / D_B \). That is, five control parameters are \( n_0, \theta, \delta, \xi, \mu \). In this paper two less important parameters are fixed, \( n_0 = 0.5, \xi = 10^{-3} \). We analyze below a role of three key parameters (\( \theta, \delta, \mu \) [temperature, Coulomb interaction, asymmetry of diffusion] in pattern formation.

In the many-point density method the system is characterized, along with macroscopic densities (concentrations) \( n_A = n_B \), also by three joint correlation functions: two functions for similar reactant pairs, \( X_\nu(r, t) \), and one more function for dissimilar reactants, \( Y(r, t) \). All functions strive asymptotically to unity, \( X_\nu(\infty, t) = Y(\infty, t) = 1 \) (no spatial correlations at long relative distances). If the correlation function exceeds unity value at short distances, this indicates at the reactant aggregation, if instead it goes below unity, this means depletion of the concentration.

The basic equation for the reactant concentrations look very simple,

\[ \frac{dn(t)}{dt} = p^{eff}(t) - K(t)n^2(t). \]

However, in general the effective adsorption rate \( p^{eff}(t) \) and reaction rate \( K(t) \) are non-steady-state and depend on the spatial correlation of reactants (which are not necessarily well stirred in the system as typically assumed in standard chemical kinetics). For instance, the effective reaction rate \( K(t) \) is defined by the flux of particles through the surface of the recombination sphere of radius \( r_a \),\(^13\)

\[ K(t) = 2\pi r_a \left| j(r_a, t) \right|. \]

To calculate the particle flux, the set of equations for the correlation functions should be solved. Let us write here for simplicity only first two equations,

\[ \dot{Y}(r, t)/\dot{t} = \nabla \cdot \left( \frac{D}{k_B T} \nabla Y(r, t) \right), \]

\[ \dot{Y}(r, t) = D \left( \nabla Y(r, t) + \frac{Y(r, t)}{k_B T} \nabla W_{AB}(r, t) \right). \]

The (kinetic) adsorption parameters \( p^{eff}(t) \) and \( p^{eff}_{AB}(r, t) \) are functionals of densities and correlation functions, \( W_{AB}(r, t) \) the mean force potentials, whose calculations were discussed in Refs.\(^9\) and\(^10\) (see also study\(^7\) of systems with both the short-range and long-range interactions). Note that for the \( d = 2 \) case under study saturation of the macroscopic densities (concentrations), \( n_A + n_B \approx n_0 \), does not means that the joint correlation functions became steady-state;\(^9,10\) their continuous time evolution reflects the nonequilibrium pattern formation process.

The inhomogeneous reactant spatial distribution could be analyzed in terms of the so-called charge screening factors.\(^11,14\) Any charged particle (molecule) \( v = A, B \) in the infinitely diluted system produces at the distance \( r \) the standard potential \( \phi^0(r) = e_\nu/\epsilon r \). Due to many-particle effects, this standard potential is transformed into the effective potential \( \phi(r, t) \), which could be time-dependent (through dynamical spatial inhomogeneous redistribution of reactants). Despite the fact that the effective potential calculation\(^14\) could be based on ideas of the Debye–Hückel (DH) theory,\(^11\) the charge screening turns out to be nonequilibrium and the results obtained could differ considerably from the standard DH theory. Let us introduce (and discussed below) two screening factors, \( Q_A(r, t) \) and \( Q_B(r, t) \), via the simple relation: \( \phi(r, t) = Q_A(r, t)\phi^0(r) \).

III. RESULTS

The present study has led us to unexpected results: mesoscopic pattern formation in this system is completely determined by the chemical reaction whereas three parameters (\( \theta, \delta, \mu \)) affect only the size of the domains, their compactness (density) and presence/absence of a short-range reactant ordering. Thus, we consider below, one by one, the cases without Coulomb interactions, those with the Coulomb interactions and finally, diffusion asymmetry.

Let us first neglect Coulomb interactions (\( \delta \to 0 \)) and consider the case of high temperatures (\( \theta = 100 \)) and equal diffusion coefficients, Fig. 1. The radial distribution functions for similar reactants are plotted on the left side, top, whereas that for dissimilar reactants is shown below it. Symbols (open circles) are obtained using the RMC at \( t = 2^{15} \). The charge
screening factors are plotted on the right-hand side, at the top and the effective reaction rate \( K(t) \) below it. The effects of a short-range repulsion of similar reactants is well observed as a sharp decrease (down to zero) of the joint correlation functions of similar reactants, \( X_\nu(r,t) \to 0 \), as \( r < r_0 \).

All other peculiarities of the correlation functions in Fig. 1 arise due to chemical reaction. Thus, a strong negative correlation (concentration depletion) occurs due to recombination of dissimilar reactants, \( Y(r,t) \ll 1 \), as \( r < \xi(t) \), where \( \xi(t) \) is time-dependent characteristic spatial scale. (Note that we neglect the short-range interaction for dissimilar reactants.) In other words, dissimilar reactants show a trend to segregate in space\(^9,10\) which induces strong aggregation of similar reactants (positive correlation), \( X_\nu(r,t) > 1 \) in the same coordinate range \( r < \xi(t) \). Thus, similar reactants form a kind of local domains. This is accompanied with a drastic reduction of the effective reaction rate \( K(t) \) with time.

The calculated correlation functions could be illustrated by snapshots, Figs. 2(a) and 2(b), obtained using RMC for different times, as in curves (2, 3), Fig. 1 for obtained different times, curves (2, 3), Fig. 1, using the RMC. High accuracy of the RMC is well seen from the symbols (circles) in curve 3, Fig. 1, which fit perfectly to the standard radial functions. The snapshot (b) shows that at long times distribution density of molecules in domains is inhomogeneous: there are areas with dense and loose areas.

As known for systems with irreversible chemical reaction \( A + B \to 0 \), Refs. 9 and 10, the above-mentioned spatial scale characterizing arising patterns is diffusion-controlled, \( \xi(t) = \xi_D(t) = \sqrt{D t} \). The scaling analysis of the correlation functions in our problem shows that the exponent \( \alpha \) in the spatial scale growth \( \xi(t) \propto t^\alpha \) exceeds unity, \( \alpha > 1 \). Therefore, the domains grow not due to the diffusion but mostly through percolation, i.e., formation of bridges between pre-existing domains. As a result, the labyrinth-like complex structure is created where network containing reactants \( A \) is interconnected with that of reactants \( B \). As time increases, these two networks rapidly cover a whole space. The labyrinth-like structure is dynamical, some bridges disappear but new bridges arise at other positions.

![FIG. 1. Development of non-equilibrium reactant structure in a system with short-range interactions only and at high temperatures. Reaction time: \( t = 2^{13} \) (1), \( t = 2^{14} \) (2), and \( t = 2^{15} \) (3).](image)

![FIG. 2. Calculated labyrinth-like structures (RMC snapshots) for systems without Coulomb interaction, \( \delta = 0 \). Reactants A are shown in red, B in blue.](image)
The effective reaction rate $K(t)$ shown in Fig. 1 rapidly decreases in time, almost down to zero. This effect is typical for fluctuation-controlled kinetics\(^9\),\(^10\) and demonstrates how much reaction rate depends on inhomogeneous spatial distribution of reactants (note that $K(t)$ is defined by $Y(r, t)$, Fig. 4), which is coupled, in its turn, to $X_\nu(r, t)$. A sharp reaction rate reduction has a simple physical meaning - since domain sizes increase in time, more and more reactants inside them are immobile and cannot take part in reaction, whereas a fraction of mobile reactants within a narrow area between domains is diminishing.

The basic assumption of the standard DH theory is a rapid spatial rearrangement of reactants so that each charge $A$ is surrounded by a cloud of oppositely charged particles $B$ which compensates the charge $A$, and vice versa. However, as one can see from Fig. 1, the calculated screening factors $Q_\nu(r, t)$ are increasing with the distance, up to quite large values, in a complete contrast to the DH theory. At high temperatures under study, the LJ attraction between similar particles could be neglected, nevertheless, as we discussed above, the reaction induces formation of similar (say, $A$) reactant aggregates (domains). In these $A$-domains each particle $A$ is surrounded by similar particles whereas dissimilar particles $B$ exist only outside it (in $B$-domains). All this makes the standard DH theory invalid.

The reaction-induced statistical aggregation of similar reactants is well observed in Fig. 2(c), which emphasizes a role of diffusion asymmetry $\mu$ at high temperatures ($\theta = 100$, $\mu = 0.1$, $t = 2^{15}$). Fast particles $B$ form here the percolation network whereas slow particles $A$ form a set of isolated dense domains. The correlation functions for slowly mobile similar reactants $X_\nu(r, t)$ reveal strong oscillations at short distances which indicate at their quite dense packing in domains. All screening factors $Q_A(r, t)$ and $Q_B(r, t)$ calculated for different mobilities are very close. That is, the screening factors are integral insensitive to the detailed structure of the correlation functions (note that all $Y(r, t)$ also coincide). The same is true for the effective reaction rate $K(t)$.

Let us consider now the system with a strong Coulomb interactions (and high temperature as before). The results plotted in Fig. 3 correspond to the same time, $t = 2^{15}$. The Coulomb parameter $\delta$ is known to define the size of the recombination area where dissimilarly charged particles instantly recombine:\(^9\),\(^10\) the larger this parameter, the faster reaction. As one can see, the correlation functions and screening factors remain qualitatively similar when the parameter $\delta$ changes in a wide range – from negligibly weak to a strong Coulomb interactions. The main difference is only the rate of the spatial scale $\xi(t)$ change (being controlled by the $\delta$ parameter). Note also that this parameter affects the reaction rate only at short times when domains are small, at long times $K(t)$ becomes independent on the $\delta$ and is close to the value characteristic for the system without Coulomb interaction (curves 1).

In order to understand better this situation, we complemented the screening factors with the analysis of the dimensionless effective potentials $\phi_\nu(r, t)$. In the range of coordinates where the correlation functions $X_\nu(r, t)$ show a plateau (within similar-particle domains), the same behavior is observed for the potentials. In other words, molecules inside domains behave as they would have no charge. (The Coulomb repulsion at short distances $r < r_0$ could be neglected since the LJ repulsion is stronger.) However, at even longer distances where $X_\nu(r, t)$ fall down to the asymptotic value $X_\nu(\infty$,?
Fig. 4. The diagram similar to Fig. 1: the formation of nonequilibrium structure in a system without Coulomb interactions, $\delta = 0$, at low temperature, $\theta = 2$, and symmetrical diffusion. Time: (1) $t = 2^{13}$, (2) $t = 2^{14}$, and (3) $t = 2^{15}$. Symbols (circles) correspond to the RMC calculations, Fig. 2(d).

t) = 1 \ (\text{domain boundary}), \text{ potentials also rapidly decrease which indicates that the forces acting on particles are directed towards the domain boundaries. These forces correlate with the parameter } \delta. \text{ As a result, domains are expanding in size through making bridges with other similar domains and destroying dissimilar domains.}

Let us consider now the low-temperature case, Fig. 4, when attractive part of the LJ potential at $r \sim r_0$ is important. This leads to the formation of dense domains with well-observed short-range ordering, see Fig. 2(d) ($\theta = 2$, $\mu = 0.5, t = 2^{15}$). These domains coexist side by side with voids where newly created particles predominantly are adsorbed. Mutual particle attraction makes the labyrinth-like structure stable and well-pronounced. Incorporation of the Coulomb interaction at low temperatures produces no qualitatively new effects. The general trend remains the same, only the spreading rate of the labyrinth-like structure increases.

IV. CONCLUSIONS

Summing up, based on the formalism of joint correlation functions, we demonstrated the formation of labyrinth-like percolation structures containing interpenetrating different-charge domains, each of them containing similar-type molecules. This structure is induced due to the reversible reaction $A + B \rightleftharpoons 0$ at 2d interface. The continuous aggregation of similar reactants and segregation of dissimilar ones occur, despite saturation in the total reactant concentrations and quite low rates for reactant creation and recombination. The obtained reactant patterns and the relevant kinetic parameters (e.g., effective reaction rate $K(t)$) are fundamentally non-steady-state (time-dependent). The similar reactant short-range attraction makes their aggregates (domains) more compact and stable at low temperatures. On the other hand, the long-range Coulomb interactions do not affect the labyrinth-like pattern structure but determine the time development of its spreading.

ACKNOWLEDGMENTS

Authors are greatly indebted to M. Olvera de la Cruz for numerous fruitful discussions. The work has been supported by an ESF through Grant No. 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141.