Properties of nano-islands formation in nonequilibrium reaction–diffusion systems with memory effects

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Abstract
We study the dynamics of the pattern formation in a class of adsorption/desorption systems described by the reaction-Cattaneo model (with memory effects of the diffusion flux). It is shown that pattern selection processes are realized in such systems due to the memory effects. We found that the oscillatory behavior of the radius of the adsorbate islands is governed by the finite propagation speed. The oscillatory dynamics of the pattern formation are studied in detail by numerical simulations.

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(Some figures may appear in colour only in the online journal)

1. Introduction

From theoretical and experimental observations it is known that reaction–diffusion systems play an important role in the study of the generic spatiotemporal behavior of nonequilibrium systems. Usually such models contain main contributions related to both local dynamics (chemical reactions of a birth-and-death type) and mass transport. In order to monitor the chemical reactions on the metal surfaces on the atomic level one can use such novel experimental methods as field ion microscopy and scanning tunneling microscopy. In adsorption–desorption processes when material can be deposited from the gaseous phase, these experimental methods allow one to investigate the formation of clusters or islands of adsorbed molecules/atoms which can have a linear size in the nanometer range [1, 2]. The occurrence of nano-patterns on a solid surface and nano-islands in adsorbed mono-atomic layers was experimentally confirmed in [3–7]. Such patterns emerge from the interplay of reactions and lateral interactions between the adsorbed particles on scales shorter than the diffusion length. The adsorbate presence can modify the local crystallographic structures of the substrate surface layer, producing long range interactions between the adsorbed atoms and their clusters (see for example, [8–10]). The experimental studies give a possibility to see that the nanometer-sized vacancy islands can be organized in a perfect triangular lattice when a single monolayer of Ag was exposed on Ru(0001) surface at room temperature [7]. The nanometer elongated islands were observed experimentally in Si/Si(100) [11], the same was found at deposition of Ge on Si [12]; the metallic elongated islands were observed at deposition of Cu on Pd(110) [13]. In these systems the elongated adsorbate clusters appear due to the formation of dimers and their reconstructions [14] representing nonequilibrium chemical reactions.

It is well known that short-range transient patterns can be observed at the initial stages of phase separation processes [15]. These transient patterns can be stabilized by nonequilibrium chemical reactions leading to an emergence of stationary patterns [16]. Adsorption and thermal desorption are ‘equilibrium reactions’ and, therefore, cannot induce the formation of the kinetic spatially modulated stationary
phases [17, 18]. In model systems with adsorption and desorption processes, additional chemical reactions should be introduced in order to freeze the patterns. A problem of the formation of stationary microstructures in such systems with irreversible nonequilibrium chemical reactions was discussed in [19, 20]; the properties of pattern formation in systems of an adsorption–desorption type with dissipative dynamics were studied in [18, 21]. From studies reported in [22–25] it follows that a stochastic contribution obeying the fluctuation–dissipation relation in pure dissipative systems can sustain the formation of stationary patterns of the nano-size range.

For adsorption/desorption systems, an evolution of the field variable $x = x(r, t)$ (the local coverage at a surface) is governed by the reaction–diffusion equation of the form

$$\partial_t x = f(x) - \nabla \cdot J. \quad (1)$$

Here $x$ is defined as the quotient between the number of adsorbed particles in a cell of the surface and the fixed number of available sites in each cell, $x \ll 1$. The term $f(x)$ stands for the local dynamics and describes birth-and-death or adsorption–desorption processes; the flux $J$ represents the mass transport.

Most theoretical studies deal with the standard Fick’s law $J = -D \nabla x$, where $D$ is the diffusion constant. It is well known that at $f = 0$ the ordinary diffusion equation $\partial_t x = \nabla \cdot D \nabla x$ has the unrealistic feature of an infinitely fast (infinite) propagation speed. Indeed, assuming that all the particles start from the origin at the initial time $t = 0$, one finds a solution in the form $x(r, t) = (4\pi D t)^{-1/2} \exp(-r^2/4Dt$).

Formally it means that for any small $t$ at a large $r$ the quantity $x$ will be nonzero, though exponentially small. The obtained result leads to an unphysical effect: the particles move with infinite speed (more than sound speed in solids). To avoid such pathology the diffusion flux can be obtained result leads to an unphysical effect: the particles move with infinite speed (more than sound speed in solids). To avoid such pathology the diffusion flux can be governed by the reaction–diffusion equation of the form

$$J(r, t) = -D \nabla x(r, t), \quad (2)$$

where $\mathcal{M}(t, t')$ is the memory kernel. The delay time $\tau_J$ is related to the correlated (persistent) random walk. In the case of $f(x) = 0$ one gets the finite propagation speed $\sqrt{D/\tau_J}$. At $\tau_J \to 0$, the asymptotic $\mathcal{M}(t, t') \to \delta(t-t')$ leads to the classic Fick law $J = -D \nabla x$ with the infinite propagation speed. Thus, in order to describe real systems (molecules, atoms) which have a finite propagation speed one should use equation (2) or an equivalent equation: $\tau_J \partial_t x = -J - D \nabla x$ [27]. Equations (1) and (2) can be combined into one reaction-Cattaneo equation of the form

$$\tau_J \partial_x^2 x + (1 - \tau_J f'(x)) \partial_t x = f(x) + \nabla \cdot D \nabla x, \quad (3)$$

where prime denotes the derivative with respect to the argument. In the absence of the reaction term ($f = 0$) the corresponding telegraph equation has a solution of the form

$$x(r, t) = \begin{cases} \frac{1}{N} \exp \left( -\frac{t}{2\tau_J} \right) I_0 \left( \frac{\sqrt{D}}{\tau_J} \right), & \text{for } |r| < \sqrt{\frac{D}{\tau_J}}, \\ 0, & \text{otherwise}, \end{cases}$$

where $N = \sqrt{4\pi D \tau_J}$, $\chi = (D/\tau_J) r - r^2$, $I_0(\cdot)$ is the modified Bessel function. As was pointed out in [27] this equation has some restrictions: (i) it typically does not preserve the positivity of the solution $x(r, t)$; (ii) the damping coefficient must be positive, i.e. $f'(x) < \tau_J^{-1}$.

Therefore, equation (3) can be used for more realistic models where particles have finite speed at smaller time scales and attain diffusion motion on larger time scales. The reaction-Cattaneo equation (3) can have oscillatory solutions [27]. An application of such formalism to the investigation of the phase separation processes with finite $\tau_J$ allows one to describe the pattern selection processes at the early stages of decomposition in binary systems (see [28, 29]) and the oscillatory formation of the ordered phase in crystalline systems [30, 31]. The oscillatory solutions in a class of reaction-Cattaneo systems with fluctuating quantity $\tau_J$ were previously considered in [32].

In this study we aim to describe the dynamics of pattern formation and selection processes in a class of reaction-Cattaneo systems described by equation (3). The novelty of our approach lies in studying the oscillatory dynamics of pattern formation in a class of models where the chemical reactions are governed by the adsorption/desorption processes. Following the formalism proposed in [20, 22, 23] we compare the behavior of both the overdamped reaction–diffusion dissipative system and the system belonging to the reaction-Cattaneo model. It is revealed that for the last class of models the pattern selection processes are realized. Studying the behavior of islands as clusters of a dense phase we show that their average size behaves in the oscillatory manner. Considering the formation of islands of adsorbed particles we discuss the properties of the island’s size distribution during the system evolution.

The paper is organized as follows. In section 2 we formulate the reaction-Cattaneo model for adsorption/desorption systems generalized by the introduction of nonequilibrium chemical reactions. The linear stability analysis and the properties of the pattern selection processes are given in section 3. The discussion of the obtained results by numerical simulation is presented in section 4. Finally, in section 5, we draw conclusions from our study.

## 2. Model

Let us consider a model where there is just one class of particles. Following [18–23, 33] one assumes that the particles can be adsorbed/desorbed, can diffuse and interact among themselves. Therefore, we introduce the scalar field describing the dynamics of the local coverage $x(r, t) \in [0, 1]$. The reaction term incorporating the adsorption and desorption terms together with nonequilibrium chemical reactions is as follows: $f(x) = k_a p (1 - x) - k_d x \exp (U(r)/T) - k_d x^n$. Here, $k_a$ and $k_d$ are the adsorption and desorption rates, respectively; $p$ is the partial pressure of the gaseous phase; $U(r)$ is the interaction potential, the Boltzmann factor is absorbed into $T$. The term $-k_d x^n$ corresponds to the nonequilibrium chemical reaction of the order $n \geq 1$ with the rate constant $k_d$. It estimates the islands/dimers formation or the associative desorption [14]. In further consideration we put $n = 2$. 

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The total flux $J$ is a sum of both ordinary diffusion flux ($-D \nabla x$) and a flow of the adsorbate ($-(D/T)x(1-x)\nabla U$). Here the multiplier $x(1-x)$ denotes that the flux is possible only to the $(1-x)$ free sites. Hence, the total flux is

$$J = -D \nabla x - \frac{D}{T}x(1-x)\nabla U,$$  \hspace{1cm} (4)$$

it can be rewritten in an equivalent form

$$J = -DM(x)\left[ \frac{\nabla x}{x(1-x)} + \frac{1}{T} \nabla U \right].$$  \hspace{1cm} (5)$$

Here $M(x) = x(1-x)$ is the Cahn mobility.

Formally the right hand side of equation (5) can be rewritten as follows:

$$J = -DM(x)\nabla \frac{\delta F}{\delta x},$$

where $F = F_0 + F_{\text{int}}$ is the total mesoscopic free energy functional. Its noninteracting part takes the form

$$F_0 = \int dr \left[ x(r) \ln(x(r)) + (1-x(r)) \ln(1-x(r)) \right],$$

whereas $F_{\text{int}}$ is governed by the interaction potential $U$ which we assume in the standard form [18]

$$U(r) = -\int dr' u(r-r')x(r').$$ \hspace{1cm} (8)$$

Here $-u(r)$ is the binary attraction potential of the symmetrical form, i.e. $\int dr^{2n}u(r) = 0$, $n = 1, \ldots, \infty$. Therefore, one can rewrite the total mesoscopic free energy as

$$F = \int dr \left[ x \ln(x) + (1-x) \ln(1-x) \right] - \frac{1}{2T} \int \int \! drdr' x(u(r-r')x(r')).$$ \hspace{1cm} (9)$$

Following [20], we choose the Gaussian profile as a simple approximation for the interaction potential

$$u(r) = \frac{2\epsilon}{\sqrt{4\pi r_0^2}} \exp(-r^2/4r_0^2),$$ \hspace{1cm} (10)$$

where $\epsilon$ is the interaction strength and $r_0$ is the interaction radius. Assuming that $x$ does not vary significantly within the interaction radius, one gets

$$\int \! drdr' x(r-r')x(r') \simeq \int \! drdr' u(r-r') \sum_n \frac{(r-r')^n}{n!} \nabla^n x(r).$$ \hspace{1cm} (11)$$

Substituting equation (10) into equation (11) up to terms of the fourth order one has $\int u(r) x(r) \, dr = 2\epsilon x$, $\frac{1}{2\epsilon} (\int u(r)^2 \, dr) \nabla^2 x(r) = 2\epsilon r_0^2 \nabla^2 x$, and $\frac{1}{4\epsilon} (\int u(r)^4 \, dr) \nabla^4 x(r) = \epsilon r_0^4 \nabla^4 x$. Therefore, using notation $\epsilon = \epsilon / T$ we arrive at the expression

$$\frac{1}{T} \int \! drdr' x(r-r') x(r') \simeq \epsilon x(r) + \epsilon (1 + r_0^2 \nabla^2)^2 x(r).$$ \hspace{1cm} (12)$$

Hence, the total free energy functional takes the form

$$F = \int dr \left[ -\frac{\epsilon}{2} x^2 + x \ln x + (1-x) \ln(1-x) \right]$$

$$-\frac{\epsilon}{2}(1 + r_0^2 \nabla^2)^2 x \right].$$ \hspace{1cm} (13)$$

Therefore, the total flux can be written as

$$J = -DM(x)\nabla \left[ \frac{\delta F_{\text{loc}}}{\delta x} - \epsilon (1 + r_0^2 \nabla^2)^2 x \right].$$ \hspace{1cm} (14)$$

where $F_{\text{loc}}$ is defined through the local part of the free energy density (first three terms in equation (13)).

Next, it will be more convenient to introduce the diffusion length $L_d = \sqrt{D/T}$ and dimensionless rates $\alpha = k_d p / k_d$ and $\beta = k_d / k_f$; the dimensionless time is $t / k_d$. Then, the reaction term takes the form $f(x) = \alpha (1-x) - x e^{-2\gamma x} - \beta x^2$ and the system is described by two length scales, where $r_0 \ll L_d$.

As far as real systems (molecules, atoms) have a finite propagation speed one should take into account the memory (correlation) effects, assuming

$$J = -L_d \int_0^t \! dt' M(t, t'; \tau) \nabla \frac{\delta F}{\delta x} \left|_{x(r', t')} \right.$$

Taking the memory kernel in the exponential decaying form $M(t, t') = \gamma f(t; t') \exp(-|t - t'| / \tau_f)$, where $\tau_f$ is the flux relaxation time we get a system of two equations:

$$\frac{\partial x}{\partial t} = f(x) - L_d \nabla \cdot J,$$ \hspace{1cm} (15)$$

$$\tau \frac{\partial \gamma}{\partial t} = -J - L_d M(x) \nabla \frac{\delta F_{\text{loc}}}{\delta x}, \hspace{1cm} \tau = \tau_f k_d.$$ \hspace{1cm} (16)$$

In the limit $\tau_f \to 0$ the Fick law $J = -L_d M(x) \nabla \delta F_{\text{loc}} / \delta x$ with an infinite propagation speed is revealed.

The system (16) can be transformed into one equation of the second order for the coverage. Indeed, taking the time derivative from the first equation of the system (16) and using the time derivative of the flux from the second equation, and, at last, expressing the flux from the first equation we obtain

$$\tau \frac{\partial x}{\partial \gamma} + \gamma \frac{\partial x}{\partial t} = f(x) + L_d^2 \nabla \cdot \left[ \nabla x - \epsilon M(x) \left( \nabla x + \nabla \mathcal{L}_{\text{SH}} x \right) \right],$$ \hspace{1cm} (17)$$

$$\mathcal{L}_{\text{SH}} = (1 + r_0^2 \nabla^2)^2.$$$$

Let us consider stationary homogeneous system states. The considered system undergoes the first order phase transition. In the case of $\beta = 0$ the corresponding stationary uniform states are given by $\alpha (1-x) = x exp(-2\gamma x)$. The critical point of this equilibrium phase transition $\gamma_c = 1/2$ is located at $\epsilon_c = 2$. $\epsilon_c = \exp(-2)$. A coexistence line of diluted $(x < 1/2)$ and dense $(x > 1/2)$ phases is given by the relation $\alpha = \exp(-\epsilon)$. The introduction of the nonequilibrium chemical reactions governed by the rate $\beta$ shifts the whole phase diagram and shrinks the domain where the system is

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4 Here we deal with the mesoscopic free energy functional $F[x]$, not the true thermodynamic free energy $F = -T \ln \int dx \exp(-F[x]) / T$. From the methodological viewpoint one can note that the interaction part in $F$ has a sign different to the phase field crystals approach prediction (see [34–36]).

5 For $r_0$ one has the estimation $r_0 \sim 1 \text{ nm}$, whereas $L_d \sim 1 \mu \text{m}$ [19, 20].
bistable. Here possible values of $\alpha$ related to the uniform states decrease, whereas the critical values of $\varepsilon$ become larger; if $\beta$ grows then critical values for $\alpha$ decrease. The corresponding phase diagram is shown in figure 1. Outside the cusp the system is monostable: at $\alpha < \alpha b_1$ the system is in a low density state $x_{LD}$, whereas at $\alpha > \alpha b_1$ the high density state $x_{HD}$ is realized (see insertion in figure 1). In the cusp ($\alpha b_1 < \alpha < \alpha b_2$) the system is bistable. Analytical relations between the corresponding critical values are: $\varepsilon_c = (1 + \sqrt{5 - 2\alpha_c})/(2\alpha_c(2 - \alpha_c))$, $\alpha_c = 2\varepsilon_c^2\lambda_1^3\exp(-2\varepsilon_c\alpha_c)$, $\beta_c = 2\varepsilon_c(1 - \varepsilon_c\alpha_c)\exp(-2\varepsilon_c\alpha_c)$.

3. Linear stability analysis

It is known that systems with memory effects exhibit the pattern selection processes at a fixed set of the system parameters [28–30]. These processes can be observed at early stages of the system evolution where linear effects are essential. Therefore, pattern selection can be studied considering the stability of statistical moments reduced to the average field and/or the structure function which is the Fourier transform of a two-point correlation function for the coverage. As far as the fourth order contribution to the interaction potential $u(r)$ is not essential at small $r_0 \ll L_d$, next we consider a case when $\int u(r)x(r)dr \simeq 2\alpha(1 + r_0^2\nabla^2)x$.

Averaging equation (17) over initial conditions and taking $\langle x \rangle - x_0 \propto e^{i\omega t - \varepsilon \tau}$ one gets the dispersion relation in the form

$$
\omega(k)_{+} = -\frac{i\gamma(x_0)}{2\tau} \quad \left[ \frac{L_d^2k^2(1 - 2\varepsilon M(x_0)(1 - r_0^2k^2)) - f'(x_0) - \gamma^2(x_0)}{4\tau^2} \right]^{1/2}.
$$

(18)

It is seen that $\omega(k)$ can have both real and imaginary parts, i.e. $\omega(k) = \Re \omega(k) + i\Im \omega(k)$. The component $\Re \omega(k)$ is responsible for the oscillatory solutions, whereas $\Im \omega(k)$ describes the stability of solution $\langle \delta x_k(\omega) \rangle$. The analysis of both $\Re \omega(k)$ and $\Im \omega(k)$ allows one to get a threshold for a wave-number where oscillatory solutions are possible. Moreover, it gives a wave-number for the first unstable mode. From the obtained dispersion relation it follows that at $k = k_0$ two branches of the dispersion relation (18) degenerate. The corresponding value $k_0$ is defined as the solution of the equation

$$
k_0^0(1 - 2\varepsilon M(x_0)(1 - r_0^2k_0^2)) = \frac{1}{L_d^2} \left[ f'(x_0) + \frac{\gamma^2(x_0)}{4\tau} \right].
$$

(19)

The unstable mode appears at $k = k_c$, where $k_c$ satisfies the equation

$$
L_d^2k_c^2(1 - 2\varepsilon M(x_0)(1 - r_0^2k_c^2)) = f'(x_0).
$$

(20)

From the dispersion relation (18) one can find the most unstable mode $k_m$ as a solution of the equation $d\omega/dk = 0$. It coincides with the first unstable mode when only one nonzero solution of the equation $\Im \omega(k) = 0$ emerges.

Using the obtained relations we calculate a diagram indicating the spatial stability of all homogeneous states to the inhomogeneous perturbations shown in figure 2. Here the domain of unstable modes with respect to the inhomogeneous perturbations is limited by solid and dash thick lines. The solid curve relates to a high density phase, whereas the dash line corresponds to a low density phase; the dot line addresses the unstable homogeneous stationary state. Increasing the adsorption rate $\alpha$ from zero one can find that the first unstable mode related to the high density phase emerges at large $k$. There is a small domain for values of $\alpha$ where spatial instability of the low density phase is possible (see magnified insertion of $\alpha(k)$ at small $\alpha$ and $k$). It should be noted that the wave numbers related to these unstable modes in both low- and high density phases are observed in a fixed interval $k \in [k_c, k_0]$. The thin solid line in figure 2 denotes critical values $k_0$ when the oscillatory solutions $\langle x(k, t) \rangle$ are possible. The domain of unstable modes with respect to inhomogeneous perturbations is limited by large values of $\alpha$. It means that instability of the high density phase is possible only in the fixed interval for adsorption rate values.

According to the obtained dependences of $\alpha(k)$, the critical values of $\alpha$ and $\varepsilon$ related to the formation of spatially modulated phases are shown in figure 3, where the solid lines denote binodals and the dash lines bound the spatially modulated phases. In the case of $\beta = 0$ one has only the existence of binodal bounding domains of one uniform phase and the domain of two uniform phases. Here no spatially modulated stationary phases are possible. For the case $\beta \neq 0$ an increase in the adsorption rate results in the formation of the uniform low density state (uLD) only at small $\alpha$; at large $\alpha$ one has the uniform high density state (uHD) only. In the cusp, depending on the values of $\alpha$, one has: (i) the uniform low density state and the modulated high density phase (uLD&mHD) at small $\alpha$; (ii) the modulated low density and high density phases (mLD&mHD) are possible at elevated $\alpha$. With the further increase in the adsorption rate only the mHD is realized. Controlling the rate $\beta$ one can govern the size of domain where both mLD&mHD emerge; when $\beta$ grows, the domain of the mHD increases and the can emerge before the first binodal.
It is well known that pattern selection processes can be studied considering the dynamics of the structure function $S(k, t)$ as the Fourier transform of the two-point correlation function $\langle \delta x(r, t) \delta x(r', t) \rangle$. The corresponding dynamical equation for $S(k, t)$ takes the form

$$
\tau \frac{\partial}{\partial t} S(k, t) + \gamma(x_0) \partial_t S(k, t) = 2 \left\{ f'(x_0) - L^2 k^2 (1 - 2\epsilon M(x_0)) \times (1 - r_0^2 k^2) \right\} S(k, t), \quad (21)
$$

The analytical solution can be found assuming $S(k, t) - S_0 \propto \exp(-i\omega(k)t)$, where

$$
\omega(k) = \frac{\gamma(x_0)}{2\tau} \pm \sqrt{\frac{2 (L^2 k^2 (1 - 2\epsilon M(x_0)(1 - r_0^2 k^2)) - f'(x_0)) - \frac{\gamma^2(x_0)}{4\tau^2}}{4\tau^2}}.
$$

As in the previous case $\Im\sigma$ is responsible for the stability of the system, whereas $\Re\sigma$ relates to the pattern selection processes.

4. Numerical results

Next, we study a morphology change and the dynamics of pattern formation by numerical simulations on a two dimensional grid with $256 \times 256$ sites and periodic boundary conditions. We solve numerically equation (17) by the Verlet method with double precision [37]. The spatial operators were calculated according to the standard finite difference scheme [38]. In our simulations the time step was set to $\Delta t = 2.5 \times 10^{-4}$ and we considered a case when $L_d = 40r_0$. The total size of the system is $L = 12.8L_d$. In order to avoid a formation of metastable structures, we consider a statistical system taking random initial conditions with the
A typical evolution of the system with different values of $\tau$, $\varepsilon$ and $\alpha$ is shown in figure 4. In the case of a pure dissipative system ($\tau = 0$) at $\alpha = 0.1$ the adsorbate is organized into separated islands with a small difference in the linear size (see the first column). For the case $\tau = 0.5$ (see second column) at the same other system parameters we get the pattern where all islands at a large time interval are combined into one percolating cluster. At small $\alpha$ one gets a set of adsorbate islands with a large difference in linear size (see third column). For large $\alpha$ the islands of vacancies are formed (see fourth column). Such islands have the same structure as islands of adsorbate at the small adsorption rate.

In figure 5 we present the dynamics of the average field $\langle x(\mathbf{r},0) \rangle$ and its dispersion $\langle (\delta x)^2 \rangle$. It is known that the growth of $\langle (\delta x)^2 \rangle$ corresponds to the ordering of the system (an increase in concentration fluctuations). Following the obtained dependences, one can find that in the absence of nonequilibrium reactions ($\beta = 0$) the system passes toward an equilibrium thermodynamic state where no stationary patterns can be realized. Here all possible patterns appearing during the system evolution are transient; at the final stages the system becomes totally homogeneous. According to the behavior of both $\langle x \rangle$ and $\langle (\delta x)^2 \rangle$, one can say that the average $\langle x \rangle$ goes toward the uniform stationary value $x_{HD}$, whereas dispersion increases at the early stages (formation of transient patterns) and decreases further toward zero (no dispersion in adatoms concentration field is realized). Therefore, the system moves into the homogeneous state. The situation is crucially changed when nonequilibrium chemical reactions are introduced. Such reactions freeze the patterns formed at the coarsening stage and the patterns develop very slowly. As a result of competing chemical reactions and potential interactions between atoms, such patterns are stable in time and, following the results from [17–21], they can be considered as the stationary ones (see figure 4).

Following the standard approach for a numerical analysis of statistical systems (see [38]) we identify stationary states as states when all statistical moments take a stationary value during a long time interval. As far as we deal with an ergodic system, the averages over the statistical ensemble coincide with the corresponding averages over time. Here the average $\langle x \rangle$ take lower values than the ones related to $\beta = 0$ and the dispersion $\langle (\delta x)^2 \rangle$ does not decrease in time at late stages. The quantity $\langle (\delta x)^2 \rangle$ can be used as the effective order parameter. Indeed, if it decreases in time toward zero, then the system moves into the homogeneous
state, whereas nonzero values of the dispersion mean that the modulated spatial patterns are realized. From figure 5 one can see that at \( \beta \neq 0 \) and at the large adsorption rate \( \alpha \) the system is in the high density state, whereas at the elevated interaction strength of the adsorbate the small islands of the dense phase are possible. Here due to large interactions between adsorbates, evaporation/dissolution processes are less probable. Comparing the curves related to the two cases, \( \tau = 0 \) and \( \tau \neq 0 \), one can find that at \( \tau \neq 0 \) both \( \langle x \rangle \) and \( \langle (\delta x)^2 \rangle \) exhibit nonmonotonic behavior with oscillations of a small amplitude. It agrees well with the results of the linear stability analysis. Moreover, it is worth mentioning that in the case \( \tau = 0 \), most of the islands of the dense phase have an equiaxial symmetry, whereas at \( \tau \neq 0 \) such islands are elongated in one of two possible equivalent directions.

Let us consider the structure function dynamics at different values of \( \tau \) and different time intervals (see figure 6). To calculate \( S(k, t) \) we used the fast Fourier transformation procedure. Let us start with the simplest case of \( \tau = 0 \) (see solid lines in figures 6(a) and (b)). Here, only a major peak of \( S(k, t) \) is realized, which is related to the period of islands. One should note that there is a smooth behavior of the structure function tails. During the system evolution the peak is shifted toward the stationary value of the island’s size; its height increases (islands become well defined and boundaries between dense and diluted phases become less diffusive). In the case \( \tau \neq 0 \) we get one major peak at the small wave number and additional peaks at the large \( k \). The emergence of such minor peaks reflects the formation of other patterns (patterns with other periods). In the course of time an amplitude of such satellite peaks decreases, indicating the pattern selection processes. In this case the system selects the most unstable mode characterized by the major peak whose height increases. Such oscillatory behavior of the structure function at large wave numbers was well predicted by the linear stability analysis. At large times the structure function state, whereas nonzero values of the dispersion mean that the modulated spatial patterns are realized. From figure 5 one can see that at \( \beta \neq 0 \) and at the large adsorption rate \( \alpha \) the system is in the high density state, whereas at the elevated interaction strength of the adsorbate the small islands of the dense phase are possible. Here due to large interactions between adsorbates, evaporation/dissolution processes are less probable. Comparing the curves related to the two cases, \( \tau = 0 \) and \( \tau \neq 0 \), one can find that at \( \tau \neq 0 \) both \( \langle x \rangle \) and \( \langle (\delta x)^2 \rangle \) exhibit nonmonotonic behavior with oscillations of a small amplitude. It agrees well with the results of the linear stability analysis. Moreover, it is worth mentioning that in the case \( \tau = 0 \), most of the islands of the dense phase have an equiaxial symmetry, whereas at \( \tau \neq 0 \) such islands are elongated in one of two possible equivalent directions.

Let us consider the structure function dynamics at different values of \( \tau \) and different time intervals (see figure 6). To calculate \( S(k, t) \) we used the fast Fourier transformation procedure. Let us start with the simplest case of \( \tau = 0 \) (see solid lines in figures 6(a) and (b)). Here, only a major peak of \( S(k, t) \) is realized, which is related to the period of islands. One should note that there is a smooth behavior of the structure function tails. During the system evolution the peak is shifted toward the stationary value of the island’s size; its height increases (islands become well defined and boundaries between dense and diluted phases become less diffusive). In the case \( \tau \neq 0 \) we get one major peak at the small wave number and additional peaks at the large \( k \). The emergence of such minor peaks reflects the formation of other patterns (patterns with other periods). In the course of time an amplitude of such satellite peaks decreases, indicating the pattern selection processes. In this case the system selects the most unstable mode characterized by the major peak whose height increases. Such oscillatory behavior of the structure function at large wave numbers was well predicted by the linear stability analysis. At large times the structure function
does not change the shape: the position of the main peak and its height. This means a formation of stationary structures.

Next, we study the behavior of the average radius of islands. In our computations we have calculated a number of sites related to the one island (the corresponding area). Assuming that an island with spherical symmetry has the same square we have computed the mean radius $\langle R \rangle$ of the corresponding spherical island. In figure 7(a) we plot the dynamics of the number of islands at different values of $\tau$ and $\alpha$. The dynamics of $\langle R \rangle$ (measured in units of diffusion length $\ell$) are shown in figure 7(b). It follows that the system attains the stationary state with the finite number of islands. Comparing the curves obtained at different $\tau$, one can find that nonequilibrium effects related to $\tau \neq 0$ decrease essentially the number of islands (but stationary islands have a large size). At small $\alpha$ the number of small sized islands is large. From figure 7(b) it is seen that in the simplest case of a pure dissipative system characterized by $\tau = 0$ the average radius is a monotonically increasing quantity. At the large time interval it attains a stationary value. This means that the coarsening procedure is finished and the stationary patterns are obtained. It follows that the islands of the adsorbate have the average length $\langle R \rangle \sim (0.15 \div 0.9) \ell$. Following [39, 40] one can estimate $\langle R \rangle$ considering the deposition of Al on TiN(100): at room temperature one has the lattice constant $a_{Al} = 4.05 \times 10^{-10}$ m, the pair interaction energy $\varepsilon_0 = -0.22$ eV with the coordination number $Z = 4$ gives $\varepsilon_0 \simeq 1.6 \times 10^{-9}$ m, the diffusion constant $D = 10^{-10}$ cm$^2$ s$^{-1}$. Hence the patterns have the size $\langle R \rangle \sim (10 \div 60) \times 10^{-9}$ m.

Figure 7. Dynamics of the number of islands (a) averaged island size (b) and the corresponding averaged aspect ratio (c) at $\beta = 0.1$, $\varepsilon = 4$. Values for the dynamical exponent $z$ related to the scaling law $\langle R \rangle \propto t^z$ are shown near the approximate lines. In (c) snapshot of pieces of the system obtained at $t = 200$, 220, 240, 280, 300 illustrate a change of $R_t/R_s$; other parameters are: $\varepsilon = 4$, $\beta = 0.1$, $\alpha = 0.1$.

Studying scaling properties of the island growth processes we have estimated a scaling exponent $z$ in the islands’ size growth law $\langle R \rangle \propto t^z$. Fitting the data related to the growth stage, we have obtained $z = 0.08$ for a pure dissipative system with $\varepsilon = 4$. Taking $\tau \neq 0$, one can find that at small $\varepsilon$ the average radius of islands increases in a nonmonotonic manner. Fitting the scaling regime, we have found that at $\tau = 0.5$ the scaling exponent takes a large value, in our case one has $z = 0.34$. A decrease in the adsorption rate leads to a delay of the growth processes characterized by the small dynamical exponent $z$ (at $\alpha = 0.06$ we get $z = 0.19$). Therefore, the nonequilibrium effects related to the relaxation of the diffusion flux accelerate the growth processes; the same is observed at large $\alpha$. It is interesting to note that at $\tau \neq 0$ the oscillations predicted for both the average field and the structure function are also possible for $\langle R(t) \rangle$. It means that the islands can change their size during the system evolution.
Figure 8. Evolution of the probability density function of the dimensionless radius of the islands size at different $\tau$ at $\beta = 0.1$: (a) $\tau = 0$, $\epsilon = 4$, $\alpha = 0.06$; (b) $\tau = 0$, $\epsilon = 3$, $\alpha = 0.25$; (c) $\tau = 0.5$, $\epsilon = 4$, $\alpha = 0.06$; (d) $\tau = 0.5$, $\epsilon = 3$, $\alpha = 0.25$.

in the oscillating manner. The amplitude of oscillations is well pronounced for large $\alpha$ and small $\epsilon$ (see figure 7(b)).

To prove that islands can change their sizes by oscillating, we compute an average aspect ratio $\langle AR \rangle = \langle R_x / R_y \rangle$, where $R_x$ and $R_y$ measures the size of the island in the $x$- and $y$-directions, respectively. From the obtained dependences shown in figure 7(c) it follows that for a pure dissipative system, deviations from the straight line are small and may be considered as fluctuations in both $R_x$ and $R_y$. At $\tau \neq 0$ and small $\epsilon$ the oscillations in $\langle AR \rangle$ are well pronounced. Such oscillations in the lateral and longitudinal sizes of islands mean that at some fixed time interval, most islands grow in one direction whereas in the other direction their size decreases; in the next time interval these two directions are changed. When this scenario is repeated one gets the oscillation picture of island size growth. In figure 7(c) we present snapshots showing the change of the growth orientation during the system evolution.

In our study we are also interested in the behavior of the probability density functions (PDF) of the island sizes distribution. Let us initially consider the PDF for a pure dissipative system. As figures 8(a) and (b) show, the islands of different sizes formed at initial stages continue to evolve in such a manner that the most probable value for $R$ is located
around \( \langle R \rangle \). The islands of other sizes are possible with small probabilities. In the stationary limit the PDF has a unique well pronounced peak, the small fluctuations of island size distribution are possible and are shown as satellite peaks around the major one. In the case of \( \tau \neq 0 \) (see figures 8(c) and (d)) the transport related to the inertial effects in the reaction-Cattaneo model promotes the formation of islands with different sizes. The principal difference comparing to the case of a pure dissipative system is in a bimodal form of the PDF observed at large times. Here at early stages the different sized islands of are formed and during the system evolution small islands dissolve and large islands reduce their size following the Ostwald ripening mechanism. In such a case two well pronounced major peaks of the PDF indicate that there are two most probable sizes of islands related to \( R > \langle R \rangle \) and \( R < \langle R \rangle \).

5. Conclusions

We have studied the dynamics of island formation of the adsorbate using the generalized approach including the persistent motion of particles having the finite speed at initial stages and the diffusion kinetics at final ones. It was found that the stabilization of nano-patterns in such a class of reaction-Cattaneo models is achieved by nonequilibrium chemical reactions. It was found that during system evolution, pattern selection processes are realized. We have shown that the possible oscillatory regimes for islands formation are realized at a finite propagation speed related to the nonzero relaxation time for the diffusion flux.

Our results can be used to describe the formation of nano-islands at processes of condensation from the gaseous phase. Even though we have considered a general model where the relaxation time \( \tau_j \) for the diffusion flux is small, but a nonzero value, one can say that the condensation processes with the formation of metallic islands can be described in the limit \( \tau_j/\omega_D^{-1} \lesssim 10^{-3} \) (here \( \omega_D \) is the Debye frequency), whereas the nano-islands formation with \( \tau_j/\omega_D^{-1} \sim 10^{-1} \div 10^{-2} \) is possible for soft matter condensation (semiconductors, polymers, etc).

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