Phase Separation in the Wake of Moving Fronts

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The formation of precipitate stripes in the wake of moving reaction-diffusion fronts is investigated. The $NaOH + CuCl_2$ reaction in poly(vinyl alcohol) hydrogel yield stripes parallel or slightly oblique to the front that supplies the precursor of the precipitate. The pattern formation was modeled by phase separation described by the Cahn-Hilliard equation and reproduced by computer simulations. Pattern formation in the wake of quenching fronts has also been investigated computationally. It has been shown that below a certain front speed stripes perpendicular to the front will appear. Moreover, they will bend so that their growing end will be kept perpendicular even if the front changes its direction.

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Introduction.—Recently, there has been growing interest in spontaneous pattern-forming processes that can yield regular microscopic textures. A widely studied example is phase separation, shown by various chemical and physical processes [1–6]. Most of the experiments are concerned with initially homogeneous systems, but a new stream of research is being defined by studies on those processes where phase separation takes place in the wake of moving fronts.

Two mechanisms are known to yield spinodal phase separation behind traveling fronts. In the first, the concentration of the phase-separating compound lies between the spinodal points, but the temperature drops below the critical value, required for the instability to occur, only behind a quenching front. Alternatively, when the concentration is initially in the stable regime, a source front shifting it in between the spinodal points can switch the system into the unstable, pattern-forming range. Some important aspects on these mechanisms are listed as follows.

Computational studies on phase separation under *directional quenching* are presented in [7,8]. The phase separation was studied in the framework of the Cahn-Hilliard equation. At high velocities of the cooling front, irregular morphology emerged. At decreasing front velocities, stripes parallel to the quenching front, termed lamellar morphology, and stripes perpendicular to the front, termed columnar morphology, were found. Although little attention has been paid to the textures when the stripes were oblique to the front, we will consider these kind of patterns, referring to them as oblique morphology.

The examination of phase separation in the wake of *source fronts* has been motivated by the desire to set up a minimal model of the Liesegang phenomenon, in which a series of precipitate stripes emerge in the wake of the diffusion front of a reagent, referred to as the "outer electrolyte," that penetrates into a hydrogel containing an "inner electrolyte" [9,10]. Modeling the formation of the one-dimensional Liesegang patterns has also been achieved by assuming that the reaction of the electrolytes yields an intermediary compound first, which separates into high and low density regions according to the Cahn-Hilliard equation [11,12].

In this Letter we investigate the formation of the striped patterns with an oblique morphology emerging in the $NaOH + CuCl_2$ reaction running in poly(vinyl alcohol) (PVA) hydrogel sheets [13].

Experiment.—The $NaOH + CuCl_2$ reaction has been studied in a "Liesegang-like" setup, with NaOH as the outer electrolyte and $CuCl_2$ as the inner electrolyte homogenized in PVA hydrogel [13,14]. The NaOH penetrates into the gel by diffusion, and its reaction with the inner electrolyte leads to a great variety of precipitate structures [13,15–18].

The $NaOH + CuCl_2$ reaction-diffusion front that sweeps through the gel is assumed to be the source front [19]. Although the source front is not visible, it is followed by a sharp border where a blue-green compound is formed that can easily be observed even by the naked eye. The character of pattern formation is correlated with the front speed. At front velocities above about 0.6–0.9 μ/s only uniform precipitation occurs. When the velocity is smaller, a regular structure of parallel stripes of colloidal precipitate appears, which is interpreted as the result of a phase separation. Decreasing front velocities leads to longer stripe wavelengths [13].

The first emerging stripes will be parallel to the source front. When the source front does not change its shape and orientation, the subsequent stripes will form parallel to the previous stripes and the front as well, giving rise to *lamellar morphology.* In some cases *oblique morphology* has also been observed, which can be identified by an intrinsic characteristic: the stripes have growing end points in the wake of the source front, and they form an angle with the envelope of their terminal points [20]. A possible scenario for the formation of the oblique stripes is the following: When the source front suddenly changes its shape or orientation, e.g., as a result of an influx of the outer electrolyte from a novel direction, the newly formed stripes cannot follow the front's altered orientation, but form more or less parallel to the previous ones. The stripes elongate only up to the limit of the region already visited by the source front, with the envelope of their growing end points being parallel to the actual position of the front (Fig. 1).

Modeling the pattern formation in the wake of source fronts.—The process of phase separation, occurring in the wake of the NaOH + $CuCl_2$ reaction-diffusion front, has been modeled by the Cahn-Hilliard equation with a Ginzburg-Landau–like free energy [6] having minima at -1 and $+1$. In order to focus our attention on the pattern formation, the reaction-diffusion system that produces the phase-separating chemical has not been included in our model. Instead, a Gaussian-type source term $S(x, t; v)$ has been added to the Cahn-Hilliard equation [11]:

$$\frac{\partial c(x, y, t)}{\partial t} = -\Delta[c(x, y, t) - c(x, y, t)^3 + \epsilon \Delta c(x, y, t)] + S(x, y, t; v), \quad (1)$$

where

$$S(x, y, t; v) = A \exp[-\alpha(x + \beta - vt)^2]. \quad (2)$$

Initially, the concentration of the compound c is set to the stable magnitude $c_0(x, y, 0) = -1 + \eta$ in the whole rectangular simulation area, where η is a random uniform deviate distributed between ± 0.0005 [8].

The value c_0 is increased by the source, moving with constant speed v to the constant value c_f [22]. The speed v of the source as well as the concentration c_f next to the source front are considered as independent simulation parameters. Having the speed v fixed, the value of c_f is determined by the amplitude A and the width α of the Gaussian source. If c_f lies in between the spinodal points, the system will be unstable against linear perturbations, and phase separation will take place in the wake of the front.

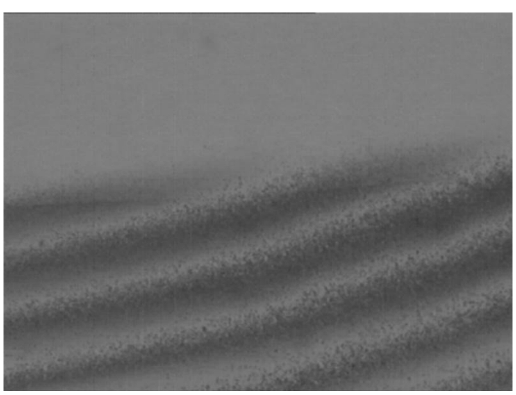

FIG. 1. Stripes of colloidal CuO grains of oblique morphology. The precipitate structures form as a result of $8.0M$ NaOH + $0.586M CuCl_2$ reaction in a thin PVA gel sheet of about 0.2 mm thickness, located between a microscope slide and a cover glass. The width of the figure is 0.58 mm. The sharp straight line shortly below the end points of the stripes represents the border where the nongrainy blue-green precipitate appears.

Equation (1) was solved on a rectangular grid using the finite difference method. The parameter β was introduced to fix the initial position of the front. Time evolution of the system was computed by explicit simple time marching on a rectangular grid. Periodic boundary conditions have been used in both directions. It is important to mention that the effect of the grid anisotropy on the simulation results was also of minor importance. This has been checked by comparing pattern formation in the wake of source fronts with different orientations.

Simulation results: Source fronts traveling with constant speed.—The speed of the source front as well as the initial conditions play a decisive role in determining the character of the pattern formation. Similar effects have been observed in other chemical systems as well [23,24].

Initially, the concentration was set to $c_0(x, y, 0) = -1 + \eta$ in the simulation area. In our simulations this value was increased by the front to $c_f = 0$, which is in the middle of the pattern-forming parameter region. The source front was parallel to the Y axis of the rectangular grid.

Depending on the front speed, two characteristic morphologies were observed. If the front speed is higher than $v \approx 5$, an irregular morphology builds up in the wake of the front. The explanation is straightforward: the relatively slow phase separation drops behind the rapidly progressing front, and the scenario will essentially be the same as the phase separation in a field with a homogeneous concentration in the unstable regime.

At front speeds below $v \approx 2$, stripes parallel to the front are formed [Fig. 2(a)]. This pattern is referred to as a lamellar morphology. Regular lamellar morphology appears at much lower front speeds as well, but the wavelength of the stripes is increased. This effect is reminiscent of the results encountered in modeling the Liesegang phenomenon [11].

The form and orientation of the preceding stripes will strongly influence the location of the subsequent stripes. In order to show this, in the $x \in (5, 30)$ space units region of the simulation area a regular structure of tilted stripes with $c(x, y, 0) = 0$ was introduced before starting the front with a constant speed around $v = 1$. When the front sweeps through this "prepatterned" region, its contribution will quickly accumulate on the stripes with the unstable concentration $c = 0$. Since the growth of a stripe depletes its surrounding, the source front will recover the concentration necessary for the emergence of a new stripe only above a certain distance from the old one. In this way, a stable striped structure, oblique to the front, will develop [Fig. 2(b)].

Rotating source fronts.—The oblique morphology in the NaOH + $CuCl_2$ reactions in PVA gel sheets usually appears when the traveling reaction-diffusion front changes its direction, while the newly forming stripes keep the orientation of previous stripes. This process was computationally modeled by a rotating source front segment having

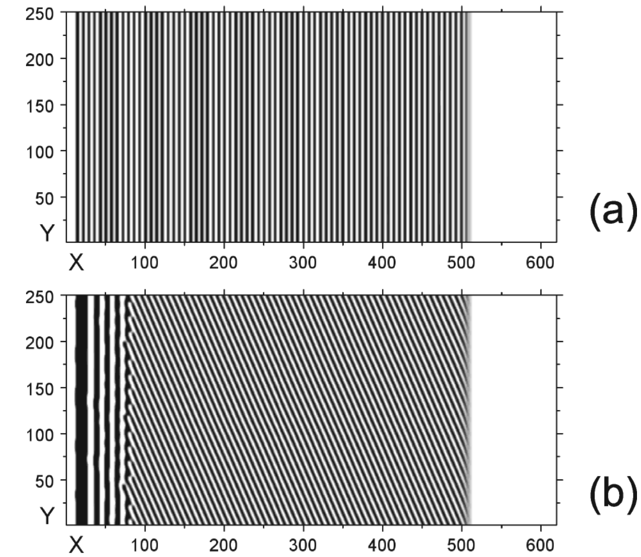

FIG. 2. Pattern formation in the wake of source fronts traveling with constant speed. The dimensions of the simulation area are 250×620 space units. $\epsilon = 0.5$, $\alpha = 0.1$, and $\beta = 10$ in both subfigures. Gray scale has been used, with white as $c = -1$ and black as $c = +1$. (a) Regular lamellar patterns; $v = 1$, $A = 0.178$ ($c_f = 0$), and $t = 500$. (b) Oblique morphology formed when the $x \in (5, 30)$ space units region was "prepatterned" with tilted stripes forming an angle of about 30° with the Y axis and having a wavelength of about 8 space units. Note the coarsening that turns out in the wake of the oblique morphology. $v = 1$, $A = 0.178$ ($c_f = 0$), and $t = 500$.

a length of 570 space units. The initial concentration in the whole simulation area was set to $c_0(x, y, 0) = -1 + \eta$. The source term added to the Cahn-Hilliard equation takes the form

$$S(x, y, t; \omega) = A\sqrt{(x - x_0)^2 + (y - y_0)^2} \times \exp\{-\alpha[(x - x_0)\sin(\omega t + \theta_0) + (y - y_0)\cos(\omega t + \theta_0)]^2\}. \quad (3)$$

The character of the pattern formation is a function of the front speed. The front speed depends on the angular velocity, as well as the position along the radius. In our simulations, having a front length of 570 space units, striped patterns just behind the front appeared around the angular velocity interval $\omega \in (0.002–0.02)$. The dynamics of the pattern formation was as follows: The first stripe forms roughly along the initial position of the front. Although the orientation of the front is continuously altered, the newly formed stripes will "try" to form along the old ones, parallel with them, roughly due to the reasons presented in the previous section. Since the front changes its orientation in the meanwhile, the above scenario will lead to an oblique morphology (Fig. 3).

However, the simulations showed that the stripes cannot grow perpendicular to the front. Their elongation becomes unstable when the angle of the stripes formed to the source front reaches about 70°–90° [Fig. 3(b)]. At this stage, in some domains just behind the front oblique stripes with a small angle or irregular morphology appear. Later, the above scenario may repeat itself.

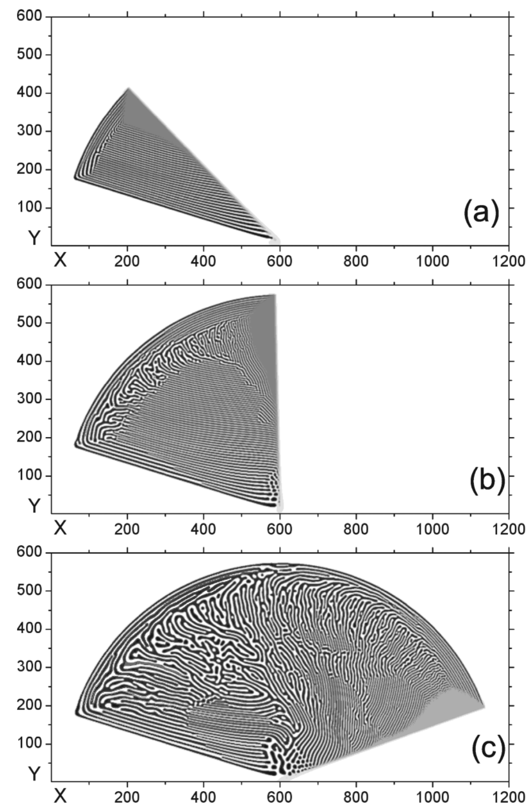

FIG. 3. Pattern formation in the wake of rotating source fronts. The angular velocity is $\omega = 0.005$; the dimensions of the simulation area are 1200×600 space units. The parameter $\theta_0 = 0.3$ was introduced to prevent the first stripes from being parallel to one of the grid lines. $\epsilon = 0.5$, $x_0 = 600$, $y_0 = 5$, $A = 0.00089$, $\alpha = 0.1$ ($c_f = 1$), and $c_0 = -1 + \eta$. Attention should be paid to the regions just behind the wake of the fronts; after this, coarsening will restructure the patterns. (a) Oblique striping at $t = 100$. (b) The critical angle is reached; the growth of the stripes becomes unstable. $t = 250$. (c) Oblique morphology with new angles builds up in the wake of the front. $t = 500$.

Note that in the vicinity of the outer end point of the rotating front, where the speed is relatively high, the source front may not immediately be followed by the phase separation. The outer core of the circular region may be patterned by a different mechanism, namely, the striping initiated by the arclike edge where the concentration changes from $c = 0$ to $c = -1$.

Quenching fronts revisited.—Pattern formation in the wake of quenching fronts has been studied by similar computational analyzes. The quenching in our simulations has been realized by changing the sign of the second-order term in the Cahn-Hilliard equation. The initial concentration in the whole simulation area was set to $c_0(x, y, 0) = \eta$.

The main difference with respect to the pattern formation in the wake of the source fronts is the appearance of

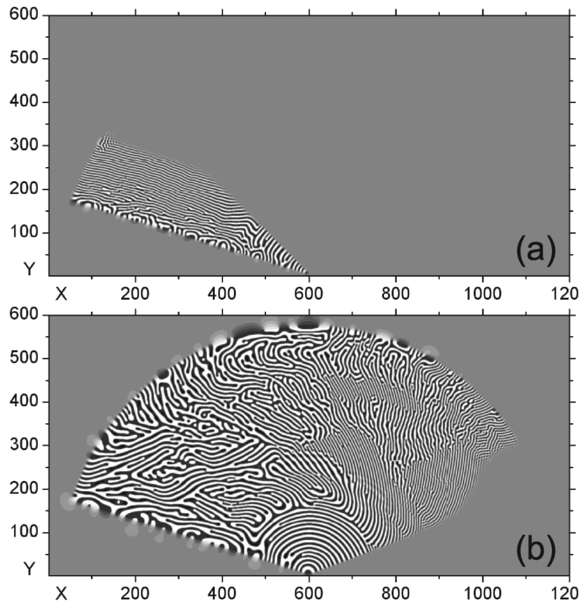

FIG. 4. Pattern formation in the wake of a rotating quenching front. The dimensions of the simulation area are 600×1200 space units. The parameter $\theta_0 = 0.3$ was introduced to prevent the stripes from being parallel to the grid lines. $\omega = 0.005$, $\epsilon = 0.5$, $x_0 = 600$, $y_0 = 5$, and $c_0 = 0$; $t = 100$ (a) and $t = 500$ (b). Note the continuous arc-shaped stripes in the vicinity of the rotation center, where the local velocity is small. The growing end points of these stripes are always perpendicular to the radial quenching front.

the columnar morphology at low front speeds, in agreement with Furukawa's results [7]. The most interesting characteristics of the pattern formation in a growing quenched area were found in the computational investigation of rotating fronts. Moving outwards along the radius, that is, reaching front segments with higher velocities, bent columnar structures, oblique patterns forming different angles to the front, and, near the border of the quenched region, lamellar morphologies have been observed. It is remarkable that the growing ends of the bent columnar stripes always remain perpendicular to the rotating radial front (Fig. 4). As a consequence, in the case of a front rotating with an appropriate speed, bent columnar structures build up, which develop into regular arc-shaped stripes. This result can be of major importance in various nanotechnological processes, since it makes possible the ''wiring'' of a surface upon a previously given curve. By moving a quenching front, having an appropriate speed, along an arbitrary nonintersecting path, a columnar structure of high and low density regions builds up behind it.

Conclusion.—The formation of striped microscopic patterns in the NaOH + $CuCl_2$ chemical system has been investigated. The scenario was modeled by the terms of phase separation described by the Cahn-Hilliard equation with a traveling Gaussian source term. The formation of the stripes, being parallel or oblique to the reaction-diffusion front, has been reproduced by computer simulations.

Computational studies on directional quenching resulted in a method that enables one to ''draw'' on a surface regular stripes following an arbitrary curve. Such a patterning could be of major importance in nanotechnology and lithography.

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