# Turing pattern formation in a two-layer system: Superposition and superlattice patterns

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Turing patterns in the chlorine dioxide–iodine–malonic acid reaction are studied in a system consisting of two coupled gel layers. Patterns with two wavelengths are observed. Changing the strength of the interlayer coupling causes a transition between a superposition of Turing patterns and a superlattice pattern. The effects of the reactant concentrations on the pattern wavelengths are delineated.

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## I. INTRODUCTION

There has been much recent interest in superlattices, the complex patterns that emerge when several Fourier modes interact to give rise to a spatially periodic structure. Superlattice patterns occur in a variety of systems, including surface waves [1], vertically oscillated Rayleigh-Benard convection [2], forced Faraday waves [3] and nonlinear optics [4]. Typically, a second wavelength is introduced by external forcing [2,3], though it is possible for the superlattice structure to arise from interaction between bistable modes intrinsic to the system [5]. Another possibility, closer to the reciprocal interaction in bistable systems than to the one-way interaction in forced systems, is to introduce symmetric coupling between pattern-forming systems with different intrinsic wavelengths.

We study here the case of pattern formation in a coupled reaction-diffusion system. Zhou *et al.* [6] recently demonstrated the formation of "black-eye" superlattice Turing patterns in the chlorine dioxide–iodine–malonic acid (CDIMA) reaction in a system containing porous glass and a polyvinyl alcohol gel. A black-eye pattern consists of a hexagonal lattice of black spots surrounded by white rings; Fourier analysis reveals that it contains two simple hexagonal lattices rotated by 30° with respect to one another. Recent experiments in our laboratory [7] showed that superlattice patterns can be generated by photochemically imposing a simple pattern on this reaction if the wavelengths of the intrinsic Turing pattern and the imposed pattern are appropriately related. Simulations [8] suggest that a rich variety of superlattice and other patterns can be obtained if layers containing reaction-diffusion systems with different kinetic and/or transport properties are diffusively coupled. We report here experiments in which two layers containing the ingredients of the CDIMA reaction in the Turing pattern region of the parameter space are coupled by diffusion. When the coupling is weak, we obtain patterns corresponding to superposition of the patterns in the individual layers. On increasing the coupling strength, we find superlattice patterns. We also observe the stabilization of traveling waves due to coupling between layers.

## II. EXPERIMENTAL ARRANGEMENT

The reaction takes place in a one-sided continuously fed unstirred reactor (CFUR) [7]. Above the feeding chamber we place two membranes: an Anapore membrane (Whatman, 0.2 $\mu$m pore size) impregnated with 4% agarose gel to eliminate stirring effects, and a cellulose nitrate membrane (Whatman, 0.45 $\mu$m pore size) to improve contrast. The membranes are 0.1 mm thick. The two gels are located above the membranes.

There are two arrangements for the gels: In the first (shown as System I in Fig. 1), a 0.3 mm thick polyacrylamide (PAA, Bio-Rad) gel containing 1 g/l starch (Aldrich), which is immobilized in the gel, is placed in contact with the membranes. Above this first gel layer, we place a 0.3 mm thick 2% agarose (Fluka) gel loaded with 10 g/l polyvinyl alcohol (PVA, Aldrich, average molecular weight 9000–10 000). In the second arrangement (System II in Fig. 1), the 2% agarose gel is placed immediately above the membranes, and a PAA gel with 10 g/l of starch is situated above the agarose gel.

The feed to the reactor consists of three solutions, one containing chlorine dioxide [9], another iodine (Aldrich), and the third malonic acid (MA, Aldrich) and PVA, all in 10 m*M* sulfuric acid.

The temperature is kept at 4 °C and the residence time in the reactor is 230 s.

## III. RESULTS AND DISCUSSION

Before discussing coupled layer systems, we consider the case of a single layer. Under the same feeding conditions used for coupled layers, single layer systems show Turing patterns. For the agarose gel [Fig. 2(a)] the wavelength of the pattern is 0.32 mm. Experiments under similar conditions in a single agarose layer but with 10 g/l of PVA in the feed

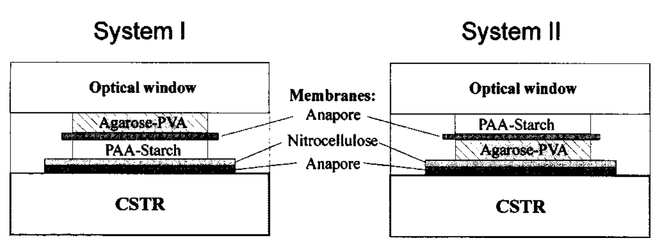


FIG. 1. The two coupled layer systems. Weak coupling is shown.

 

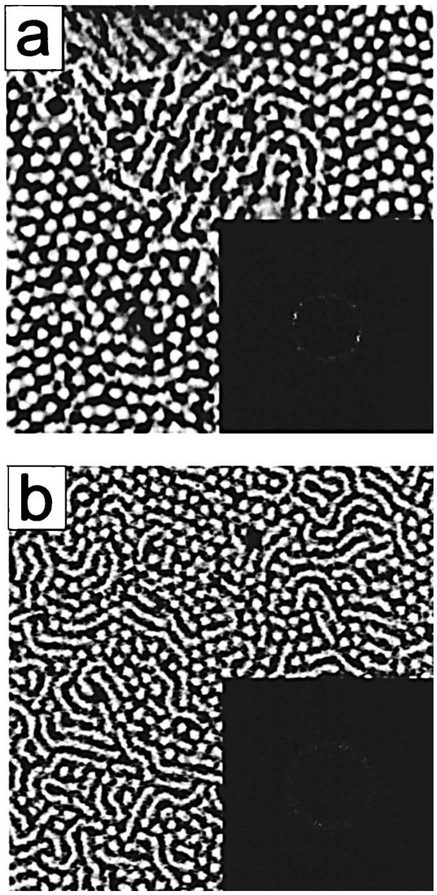


FIG. 2. Turing patterns obtained in single layer experiments. (a) Pattern obtained using agarose gel. $[I_2]_0 = 0.37$ m*M*, $[MA]_0 = 1.80$ m*M*, $[ClO_2]_0 = 0.136$ m*M*. PVA 1 g/l. (b) Pattern obtained in PAA-starch (1 g/l) gel. $[I_2]_0 = 0.35$ m*M*, $[MA]_0 = 1.91$ m*M*, $[ClO_2]_0 = 0.156$ m*M*, PVA 1 g/l. Image sizes, $10 \times 10$ mm$^2$. Fourier spectra are shown as insets.

yielded striped Turing patterns with a wavelength of 0.45 mm [11].

For the PAA-starch system [Fig. 2(b)] the wavelength is 0.25 mm, consistent with studies with a single layer of PAA-starch, which show wavelengths in the range 0.2–0.33 mm [12,13].

We attribute the difference in wavelengths between the two layers to the different diffusive behavior of the complexing agents. In the PAA gel matrix, the starch is essentially immobilized, while PVA is still able to move, though slowly, through the agarose gel [10].

One of the most important parameters in determining the behavior of the coupled system is the strength of the coupling between the two layers. This quantity is easily varied in simulations, and as it moves from weak to strong, a model system undergoes a variety of transitions among several types of patterns [8]. In an actual experimental system, controlling the strength of the coupling is considerably more difficult. In the experiments described here, we consider only two cases: weak coupling, in which a single Anapore membrane (thickness 0.1 mm) is placed between the two gels, and strong coupling, in which the gels are in direct contact with one another.

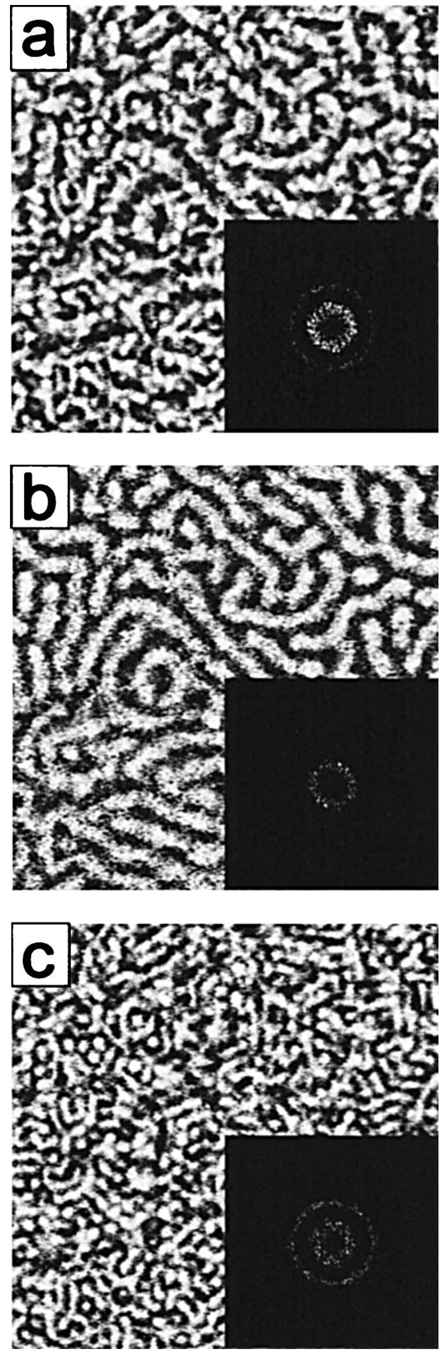


FIG. 3. Superposition patterns obtained with weak coupling in System I. (a) Unfiltered image (summation of both layers). (b) Same pattern seen through a filter transparent to blue light. (c) Same pattern seen through a filter transparent to red light. Image sizes, $10 \times 10$ mm$^2$. Fourier spectra are shown as insets. $[I_2]_0 = 0.37$ m*M*, $[MA]_0 = 1.80$ m*M*, $[ClO_2]_0 = 0.145$ m*M*. PVA 1 g/l.

### A. Weak coupling in System I

For our first gel configuration, a typical pattern obtained in the weak coupling case is shown in Fig. 3(a). It consists of a superposition of the patterns found in the uncoupled systems. The Fourier spectrum, presented in the inset, clearly shows two wavelengths, 0.54 mm and 0.23 mm. To determine the origin of these wavelengths, we examined the sys-

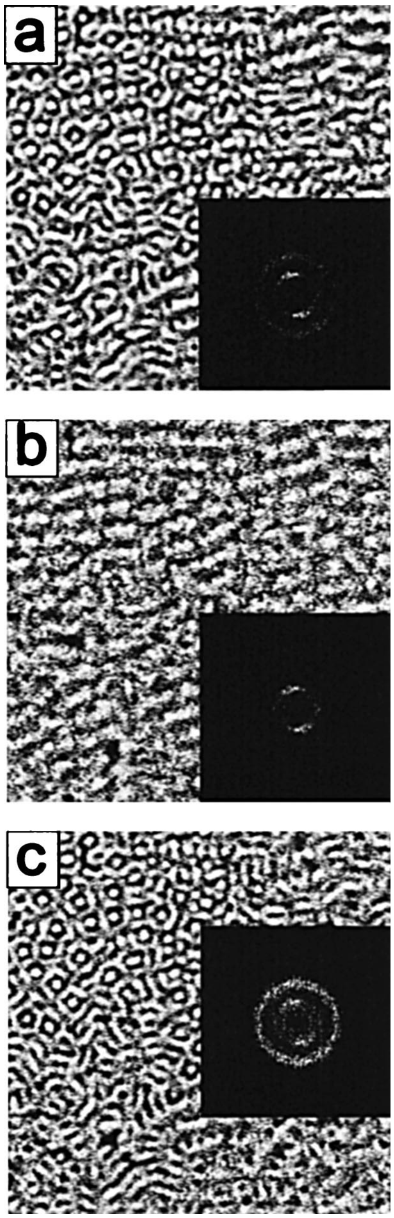

FIG. 4. Superlattice Turing patterns obtained with strong coupling in System I. (a) Unfiltered image (summation of both layers). (b) Same pattern seen through a filter transparent to blue light. (c) Same pattern seen through a filter transparent to red light. Image sizes, $10\times10$ mm$^2$. Fourier spectra are shown as insets. $[I_2]_0 = 0.37$ m$M$, $[MA]_0 = 1.80$ m$M$, $[ClO_2]_0 = 0.144$ m$M$. PVA 1 g/l.

tem through color filters. The PVA-triiodide complex is red (absorbing light at 490 nm), while the PAA-starch-triiodide complex is blue (absorbing at 600 nm). Therefore, with a filter that is transparent to blue light, having low absorption at 490 nm and high absorption at 600 nm, we can focus on the pattern in the agarose-PVA layer [Fig. 3(b)], while a filter transparent to red light, absorbing at 490 nm and not at 600 nm, highlights the pattern in the PAA-starch layer [Fig. 3(c)]. The Fourier spectrum [inset of Fig. 3(b)] suggests that the pattern in the agarose-PVA layer, which exhibits only a single wavelength, is unaffected by the pattern in the PAA-starch layer. On the other hand, the pattern in the PAA-starch layer is modulated by the pattern in the agarose-PVA layer; the long wavelength of the upper pattern is seen along with the short wavelength in the Fourier spectrum of Fig. 3(c).

The larger wavelength in the agarose-PVA layer compared with single layer experiments can be explained in the following way: The presence of the PAA gel between the CSTR and the agarose-PVA gel retards the arrival of reactants to the second gel, which is equivalent to having a longer residence time. In experiments in which we varied the residence time, we found that the wavelength of the pattern increases with the residence time.

### B. Strong coupling in System I

When the coupling is strong enough, the interaction of the patterns in the two layers results in a superlattice structure [8]. An example is shown in Fig. 4. The superlattice pattern is formed in the PAA-starch layer, which can sustain the short wavelength, while the agarose layer only shows the long wavelength. The wavelengths obtained from the Fourier spectrum (inset) are 0.46 mm and 0.25 mm, i.e., the wavelengths found in the weak coupling case have now been "pulled" slightly toward one another. The ratio of wavelengths, 1.84, is close to 2, the ideal value for obtaining black-eye patterns [7]. The patterns seen here are "white-eyes," which are the inversion of the black-eye patterns observed earlier in single layer experiments [7].

At other wavelength ratios, such as 3, it is possible to obtain other superlattice patterns. In order to assess whether such patterns are accessible with our one-sided CFUR, we varied the reactant concentrations over as broad a range as possible while still remaining in the Turing pattern region of the parameter space and maintaining sufficient contrast for the patterns to be visible. The results, shown in Table I,

TABLE I. Wavelengths of patterns observed in System I with weak coupling. $\lambda_1$ is wavelength in the agarose-PVA layer, $\lambda_2$ in the PAA-starch layer.

| $[I_2]=0.37$ m$M$, $[MA]=1.8$ m$M$ | | | | $[I_2]=0.37$ m$M$, $[ClO_2]=0.157$ m$M$ | | | | $[MA]=1.8$ m$M$, $[ClO_2]=0.155$ m$M$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $[ClO_2]$(m$M$) | $\lambda_1$(mm) | $\lambda_2$(mm) | Ratio $\lambda_1/\lambda_2$ | $[MA]$(m$M$) | $\lambda_1$(mm) | $\lambda_2$(mm) | Ratio $\lambda_1/\lambda_2$ | $[I_2]$(m$M$) | $\lambda_1$(mm) | $\lambda_2$(mm) | Ratio $\lambda_1/\lambda_2$ |
| 0.135 | 0.74 | 0.31 | 2.4 | 1.8 | 0.47 | 0.22 | 2.1 | 0.42 | 0.59 | 0.27 | 2.2 |
| 0.145 | 0.54 | 0.23 | 2.3 | 1.6 | 0.47 | 0.22 | 2.1 | 0.40 | 0.54 | 0.24 | 2.3 |
| 0.157 | 0.47 | 0.22 | 2.1 | 1.4 | 0.47 | 0.22 | 2.1 | 0.38 | 0.54 | 0.24 | 2.3 |
| | | | | 1.2 | 0.47 | 0.21 | 2.2 | 0.36 | 0.54 | 0.24 | 2.3 |

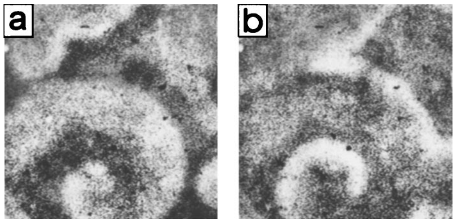


FIG. 5. Traveling waves obtained in System II with starch concentration 1 g/l in PAA layer. Images obtained with blue filter. Image sizes, $10\times 10$ mm$^2$. Image in (b) taken 50 s after (a). $[I_2]_0 = 0.35$ m*M*, $[MA]_0 = 1.90$ m*M*, $[ClO_2]_0 = 0.157$ m*M*. PVA 1 g/l.

indicate that it will be difficult in the current configuration to reach other resonant wavelength ratios. Although varying $[ClO_2]$ has a pronounced effect on the individual wavelengths, their ratio remains well below 3, and further decreasing the chlorine dioxide concentration causes the disappearance of the pattern in the agarose layer. Changing the malonic acid concentration has essentially no effect on the wavelengths, nor does changing the iodine concentration. These behaviors, in particular the decrease in wavelength with $[ClO_2]$ and the near-independence of [MA], mirror what has been observed in CFURs with a single gel layer [10,14]. These results are consistent with the longer wavelength patterns obtained at longer residence times, since longer residence time is equivalent to a lower effective concentration of $ClO_2$.

### C. System II

When we reverse the order of the gels, the weak coupling case leads to traveling waves rather than Turing structures in the agarose-PVA gel (Fig. 5), while the PAA-starch layer remains colorless, suggesting that $I_3^-$ binds more strongly to PVA than to starch.

If we increase the starch concentration to 10 g/l in the PAA gel with weak coupling, there is better competition for $I_3^-$, allowing Turing patterns to form. Now the coupling with the layer closer to the feeding chamber produces superlattice Turing structures (Fig. 6) in the starch-PAA layer. The wavelengths observed are 0.43 mm and 0.27 mm.

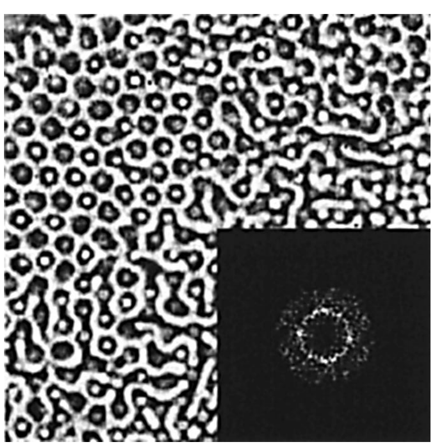

FIG. 6. Superlattice Turing pattern obtained with weak coupling in System II with starch concentration 10 g/l. Image sizes, $10\times 10$ mm$^2$. Fourier spectrum shown as inset. $[I_2]_0 = 0.36$ m*M*, $[MA]_0 = 1.87$ m*M*, $[ClO_2]_0 = 0.155$ m*M*. PVA 1 g/l.

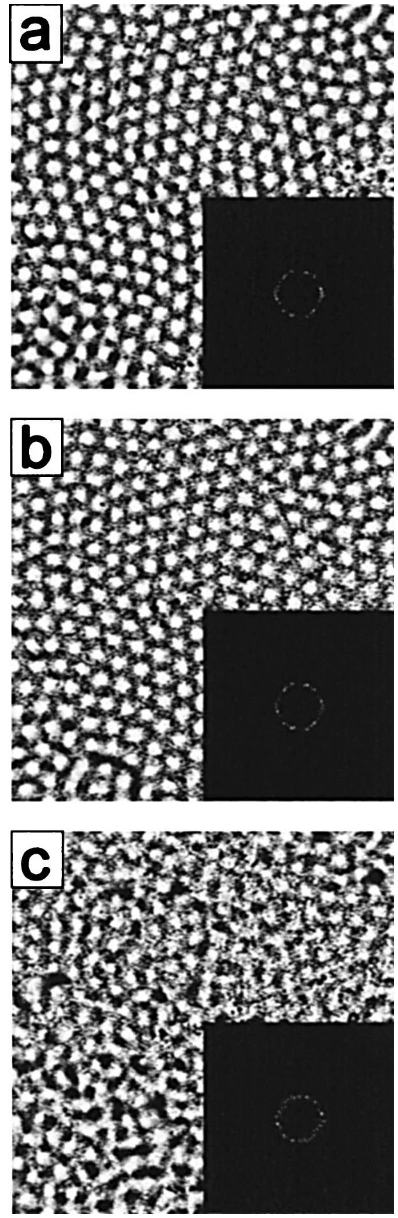


FIG. 7. Pattern obtained with strong coupling in System II with starch concentration 10 g/l. Image sizes, $10\times 10$ mm$^2$. Fourier spectrum shown as inset. $[I_2]_0 = 0.37$ m*M*, $[MA]_0 = 1.80$ m*M*, $[ClO_2]_0 = 0.150$ m*M*. PVA 1 g/l. Image sequence and sizes as in Fig. 3.

In this configuration, strong coupling results in Turing patterns with the same wavelength (0.43 mm) in both layers (Fig. 7).

We thus observe superlattice patterns in System II with weak coupling, while strong coupling is required to obtain superlattice behavior in System I. These observations suggest that the layer placed closer to the feeding chamber exerts a greater influence on the upper layer than *vice versa*, as it is easier to force a pattern with a longer intrinsic wavelength (as in System II) than with a short wavelength [15].

### D. Strength of coupling

In order to quantify the coupling between the layers, we measured the kinetics of formation of the starch-triiodide complex. The experiment is carried out by putting a PAA-starch gel (with 10 g/l of starch) in contact with an agarose gel previously loaded with a triiodide solution, with and without an Anapore membrane between them. We then follow the absorbance at 600 nm. The data thus obtained are fitted to a curve of the form

$$(x_t - x_{eq}) = (x_0 - x_{eq})e^{-kt}, \tag{1}$$

where $x_t$ is the absorbance at time $t$, $x_{eq}$ is the absorbance at equilibrium $(t \to \infty)$, $x_0$ is the initial absorbance, and $k$ is the rate constant for transfer between the gels. For each run, we obtain $x_{eq}$ with a nonlinear least squares method. We then rewrite Eq. (1) in the form

$$\ln(x_{eq} - x_t) = \ln(x_{eq} - x_0) - kt \tag{2}$$

and obtain $k$ by a linear least squares fit.

Our results are $k=(1.02\pm0.16)\times10^{-2}\ \mathrm{s}^{-1}$ with no membrane and $k=(5.04\pm0.82)\times10^{-3}\ \mathrm{s}^{-1}$ with the membrane present. The $x_0$ values obtained in all cases were zero to within the calculated error. These data suggest that the presence of a membrane between the gels reduces the coupling by about a factor of 2.

A simple argument suggests that the coupling should be proportional to $D/L^2$, where $D$ is the diffusion constant of the relevant species and $L$ is the distance between the centers of the two gel layers. Since the gels are 0.3 mm thick and the membrane thickness is 0.1 mm, this purely geometric analysis suggests that inserting the membrane between the gels should reduce the coupling by a factor of $[0.3/(0.3+0.1)]^2 = 0.56$, which is consistent with our measured results.

## IV. CONCLUSIONS

We have demonstrated experimentally, in agreement with theoretical predictions [8], that superlattice patterns consisting of two resonantly coupled Turing modes can be obtained in a system consisting of two coupled layers. If the coupling is too weak (System I), only superposition patterns result, though the pattern in one layer is modulated by that in the other. With coupling that is too strong (System II), the result, as one would expect, is identical patterns in both layers. Our one-sided feed yields a configuration intermediate in nature between externally forced [2,3] and symmetrically coupled [8] systems.

It appears unlikely that higher order superlattice patterns can be generated in this particular system, because the range of accessible wavelength ratios between the patterns in the two gels remains close to 2 over the entire experimentally attainable range. It is conceivable that, either by using a different reaction or by employing a two-sided CFUR [6,12], one might be able to obtain other wavelength ratios and hence other superlattices in such a coupled layer system.

## ACKNOWLEDGMENT

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