Chemical Instability Induced by a Shear Flow

Desiderio A. Vasquez

Department of Physics, Indiana University Purdue University Fort Wayne, Fort Wayne, Indiana 46805, USA
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We predict a new type of instability induced by shear flow in chemical systems. A homogeneous steady state solution of a reaction-diffusion system loses stability in a Poiseuille flow. The instability appears as the speed of the flow increases beyond a certain threshold. This results in a steady pattern moving with the average fluid velocity. The chemical reaction consists of two species (activator and inhibitor) moving with identical velocities. Contrary to Turing's instability, the pattern arises when the activator has a higher diffusivity than the inhibitor.

The interaction between chemical reaction, molecular diffusion, and fluid flow has generated several mechanisms for pattern formation. Turing predicted the existence of chemical patterns in a reaction-diffusion equation requiring different diffusivities for different chemical species [1]. Forty years later experiments found these patterns confined in polyacrilamide gels [2]. In liquids, fluid motion leads to important mechanisms of pattern formation playing an important role in pattern selection [3]. Convection increases the speed and curves reaction fronts in the iodate-arsenous acid reaction [4,5]. Rovinsky and Menzinger found a pattern-forming mechanism where a pattern arises in an activator-inhibitor kinetics requiring each chemical to flow with different speed [6,7]. Further research also found patterns in fluid flow with oscillatory kinetics [8,9]. Recent results on chemical fronts in the iodate-arsenous acid reaction under shear flow showed that the distribution of fluid velocity produces different effects on the speed and shape of the front depending on whether the front propagates with or against the fluid flow [10,11]. These effects cannot be explained by replacing the distributed flow with an average fluid velocity since this will result in an identical front propagation in a reference frame comoving with the average fluid speed. Neither can be fully explained by introducing an effective diffusion coefficient that depends only on the magnitude of the average fluid speed as in Taylor dispersion [12], since the observed behavior also depends on the direction of the fluid velocity. These experiments indicate the averaging methods are not enough to fully understand pattern-forming mechanisms in shear flow; therefore, we need to carry out a complete analysis of the complete reaction-diffusion-advection system. In this Letter we carry out such an analysis presenting a novel pattern-forming mechanism that does not require a different flow for each of the chemical species, does not require an oscillatory chemical reaction, and contrary to Turing's mechanism leads to pattern formation when the diffusion coefficient of the activator is larger than the diffusion coefficient of the inhibitor.

We chose the Brusselator kinetics coupled to molecular diffusion in the presence of fluid flow as our model of chemical pattern formation [13]. This results in a set of reaction-diffusion-advection equations:

$$\frac{\partial X}{\partial t} + \vec{V} \cdot \vec{\nabla} X = D_X \nabla^2 X + A - (B+1)X + X^2 Y, \quad (1)$$

$$\frac{\partial Y}{\partial t} + \vec{V} \cdot \vec{\nabla} Y = D_Y \nabla^2 Y + BX - X^2 Y. \quad (2)$$

Here X and Y are chemical concentrations, D_X and D_Y are their corresponding diffusivities, A and B are external parameters, and $\vec{V}(x, z)$ is the local fluid velocity. The chemical kinetics corresponds to an autocatalytic production of an activator (X) which is limited by an inhibitor (Y). We solve the equations in a rectangular domain in the x-z plane. The domain is confined in the z direction with $-a/2 < z < a/2$. The fluid flow $\vec{V}$ consists of a Poiseuille flow parallel to the x direction with

$$\vec{V}(x, z) = V(z)\hat{x} = \frac{3}{2}\bar{V}\left(1 - 4\frac{z^2}{a^2}\right)\hat{x}. \quad (3)$$

Here $\bar{V}$ corresponds to the average fluid velocity and $\hat{x}$ is a unit vector along the x direction. The fluid velocity vanishes at the walls $z = \pm a/2$ in agreement with viscous boundary conditions. The equations admit a homogeneous steady solution with $X_0 = A$ and $Y_0 = B/A$. We focus on the deviations from this state $X' = X - X_0$, and $Y' = Y - Y_0$. Since our study investigates the instability caused by the fluid flow, we set $A = 10$ and $B = 100$, which corresponds to a stable homogeneous steady state without fluid velocity and equal diffusivities. The steady state is also stable for uniform flow or fluid velocities that are not distributed across the rectangular tube (z direction). In our study, we set the width of the tube a to 0.1. For all parameters A and B, a necessary condition for Turing pattern formation is $d = D_Y/D_X > 1$. For our chosen parameters, the homogeneous steady state undergoes a Turing instability as the ratio d becomes greater than a critical ratio $d_c = 1.235$.

We introduce perturbations to the homogeneous steady state of the form $X' = X_1(z)e^{ikx}e^{\sigma t}$ and $Y' = Y_1(z)e^{ikx}e^{\sigma t}$ neglecting all quadratic terms. This leads to a boundary eigenvalue problem on the z direction with the growth rate σ as the eigenvalue:

$$\sigma X_1 = D_X\left(\frac{d^2 X_1}{dz^2} - k^2 X_1\right) - ikV(z)X_1 + (B-1)X_1 + A^2 Y_1,$$
(4)

$$\sigma Y_1 = D_Y\left(\frac{d^2 Y_1}{dz^2} - k^2 Y_1\right) - ikV(z)Y_1 - BX_1 - A^2 Y_1.$$
(5)

We impose no flow boundary conditions on the variables X_1 and Y_1 so their derivatives vanish at $z = \pm a/2$. The eigenvalue problem is solved by discretizing the z direction. We use a mesh of 400 equally spaced points for a given wave number k. This leads to a linear eigenvalue system that can be calculated using standard techniques. We chose the EISPACK package to obtain the eigenvalues of the resulting matrix [14].

The stability of the steady state is determined by the real part of the growth rate σ. If all the real parts are negative, then the steady state is stable; if there is one eigenvalue with a positive real part, it is unstable to a small perturbation. To investigate the effects of the fluid flow on the stability of the homogeneous steady state, we chose the diffusion coefficients equal to $D_X = 1$ and $D_Y = 0.5$, which provide the condition for stability in the absence of fluid flow. In Fig. 1, we show the largest real part of the growth rate ($\text{Re}\,\sigma$) as a function of the wave number k for different values of the average fluid velocity. Each curve defines a dispersion relation $\text{Re}\,\sigma$ vs k. We find that without fluid flow all growth rates have a negative real part; therefore, the steady state is stable. The maximum in this dispersion curve corresponds to the wave number $k = 0$. Imposing a Poiseuille flow changes the characteristics of the dispersion relations. We observe the development of a local maximum away from $k = 0$ as we increase the average flow speed. For $\bar{V} = 130$, the maximum is clearly negative, resulting in a stable steady state. For $\bar{V} = 150$, we find that the maximum increases and becomes positive, leading to a range of wave numbers with a positive real part of the growth rate, thus resulting in an unstable steady state. The transition for the instability occurs at $\bar{V} = 145.0$ where the real part of the growth rate is zero. In Fig. 2 we show the transition to the instability as the fluid speed increases by plotting the wave number where the real part of the growth rate is maximum. We also display the wave numbers for $\text{Re}\,\sigma = 0$. Both lines intersect at the transition speed. For fluid speeds above the transition speed we find a band of wave numbers with $\text{Re}\,\sigma$ positive. For fluid speeds below the transition speed, there is no wave number with zero real part of the growth rate, and all wave numbers lead to perturbations with $\text{Re}\,\sigma < 0$. We notice in Figs. 1 and 2 that the wave number for the maximum real part of
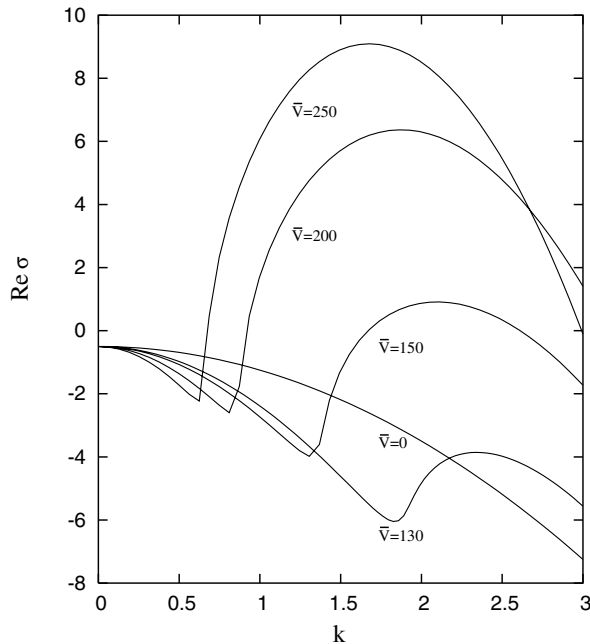

FIG. 1. The real part of the growth rate ($\text{Re}\,\sigma$) as a function of the wave number k for different average fluid velocities ($\bar{V}$). The curves with $\bar{V} = 0$ and 130 have all $\text{Re}\,\sigma$ negative, while for $\bar{V} = 150$, 200, and 250 there is a band of wave numbers with positive $\text{Re}\,\sigma$ corresponding to an unstable homogeneous steady state.
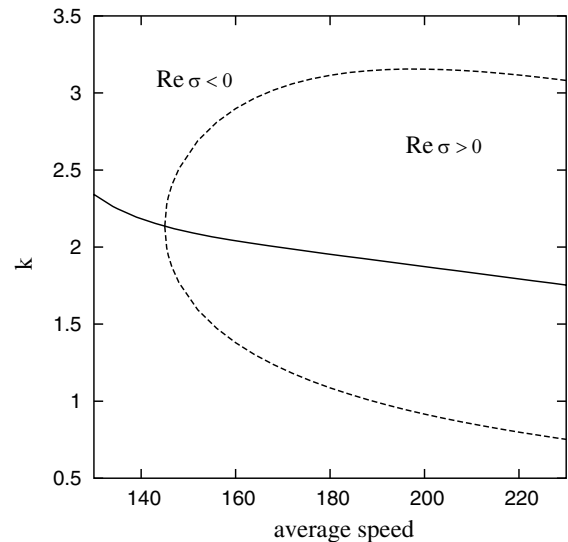

FIG. 2. The solid line represents the wave number with the maximum real part of the growth rate as a function of the average fluid velocity. The broken line represents the wave numbers with zero growth rate defining a region where $\text{Re}\,\sigma$ is positive.

the growth rate decreases with increasing speed. The band of unstable wave numbers becomes wider with increasing fluid speed. Our calculations also show that the imaginary part of the growth rate is nonzero for all unstable perturbations.

In Fig. 3 we show the effects of the diffusivity on the shear flow instability. We choose $D_X = 1$, fix $\bar{V}$ to 240, and vary D_Y; therefore, the ratio for the diffusion coefficients d corresponds to D_Y. In this figure we display the dispersion relations for different values of d. We observe that for $d = 0.75$, all growth rates have negative real parts with the curve having a local maximum away from $k = 0$. As we decrease the ratio d we observe that the local maximum increases and the corresponding wave number for this maximum decreases. As we switch to $d = 0.5$ we observe that some growth rates have positive real parts, indicating perturbations with wave numbers that correspond to instabilities. The transition to instability occurs at $d = 0.69$. Contrary to Turing pattern formation, we find not only that the critical ratio is less than one, but even smaller ratios are more favorable to the shear flow chemical instability. We observe the instability even when $d = 0$, which corresponds to a nondiffusive inhibitor. We emphasize that without fluid flow there is no instability, regardless of the value of d.

To explore the instability beyond the linear regime, we also carried out a numerical solution of the full reaction-diffusion-advection system. The numerical method consists of a finite difference discretization over a rectan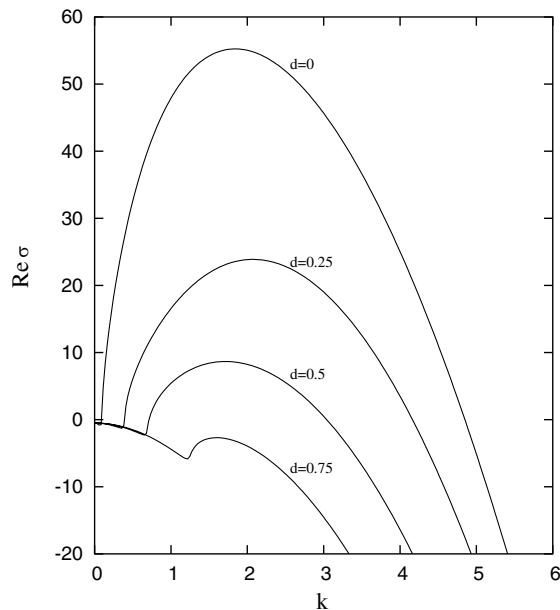gular domain. The spatial partial derivatives are replaced with finite increments over a two-dimensional mesh. We chose a rectangle of length equal to 20 and the corresponding tube width equal to 0.1 as before. The mesh consists of 25 points along the width of the tube and 300 points along its length. We set the average fluid speed to $\bar{V} = 200$, and the diffusivities to $D_X = 1$ and $D_Y = 0.5$. This choice of parameters provide wavelengths that correspond to unstable perturbations as shown in Fig. 1. The boundary conditions for the chemicals X and Y are chosen as no flow in the z direction ($\partial X/\partial z|_{z=\pm a/2} = \partial Y/\partial z|_{z=\pm a/2} = 0$), and periodic boundary conditions along the x direction. The time evolution of the system was carried out by a simple discretization with a very small time step in order to avoid numerical instabilities. The initial condition corresponds to a small random perturbation to the steady state. Having a finite length means that the wavelength of the perturbations $\lambda = 2\pi/k$ is limited by the length of the domain. Our choice of domain size ensures the inclusion of unstable wavelengths. We show the results of the numerical solution in Fig. 4. A well-defined pattern evolves from the initial state. The pattern is stationary in a reference frame comoving with the average fluid velocity. The figure represents the concentration of the chemical X on a gray scale. The dark bands correspond to high concentrations: completely dark represents a maximum concentration of 14.2, while completely white represents a minimum concentration of 0.6. The figure shows that regions of higher concentration alternate with regions of lower concentration. Although the shape of the pattern in the figure appears flat along the z direction, it is slightly parabolic resembling the distribution of the fluid flow. The reason for this apparent flatness is that the position of the chemical interface (defined as $X = A = 10$) at the center of the tube is only 0.05 units above the interface at the limiting wall $z = \pm a/2$.

In this Letter we have shown that the effects of shear flow can lead to chemical pattern formation by causing the instability of the homogeneous steady state. One way to understand qualitatively this instability is by using the formula for the effective diffusivity under a Poiseuille flow [12,15]. Taylor showed that molecular diffusion in a pipe with a moving fluid can be approximated with an effective diffusion coefficient. The velocity of the fluid has to vary over the cross-section of the pipe. The result

FIG. 3. The real part of the growth rate (Re σ) as a function of the wave number k for different diffusivity ratio $d = D_Y/D_X$. The curves with $d = 0.75$ have all negative Re σ, while the curves with $d \leq 0.5$ show positive Re σ.

FIG. 4. A chemical pattern moving with the speed of the average fluid velocity $\bar{V} = 200$. The width of the rectangular tube is 0.1, while its length is equal to 20.

for Poiseuille flow in a two-dimensional pipe corresponds to an effective diffusivity $D_{\mathrm{eff}} = D + a^2 \bar{V}^2/(210D)$. This implies that under Poiseuille flow the ratio of the effective diffusivities between the inhibitor and the activator can become greater than one even if $d < 1$. This opens the possibility of a pattern-forming instability. Experiments to test this prediction can be carried out in capillary tubes, as it was done for the iodate-arsenous acid reaction under Poiseuille flow. The shear flow chemical instability presents a nonoscillatory state without fluid flow, developing a pattern after the average speed increases beyond a certain threshold. New experiments are required to unveil this new mechanism. The effects of shear flow are of importance in understanding pattern formation inside gels. Liquids penetrating gels are subject to shear flow as they move into a confining space. Therefore, the development of a chemical pattern may be influenced by the fluid flow. One important characteristic of this mechanism is the dependence on d, the ratio of the diffusivities for the two chemical species. We have found that patterns develop with $d < 1$, contrary to the Turing instability that requires $d > 1$.

[1] A. M. Turing, Philos. Trans. R. Soc. London B **327**, 37 (1952).
[2] V. Cassets, E. Dulos, J. Boissonade, and P. De Kepper, Phys. Rev. Lett. **64**, 2953 (1990).
[3] D. A. Vasquez, J. W. Wilder, and B. F. Edwards, Phys. Rev. Lett. **71**, 1538 (1993).
[4] J. Masere, D. A. Vasquez, B. F. Edwards, J. W. Wilder, and K. Showalter, J. Phys. Chem. **98**, 6505 (1994).
[5] D. A. Vasquez and C. Lengacher, Phys. Rev. E **58**, 6865 (1998).
[6] A. B. Rovinsky and M. Menzinger, Phys. Rev. Lett. **69**, 1193 (1992).
[7] A. B. Rovinsky and M. Menzinger, Phys. Rev. Lett. **70**, 778 (1993).
[8] M. Kaern and M. Menzinger, Phys. Rev. E **60**, 3471 (1999).
[9] P. N. McGraw and M. Menzinger, Phys. Rev. E **68**, 066122 (2003).
[10] B. F. Edwards, Phys. Rev. Lett. **89**, 104501 (2002).
[11] M. Leconte, J. Martin, N. Rakotomalala, and D. Salin, Phys. Rev. Lett. **90**, 128302 (2003).
[12] G. I. Taylor, Proc. R. Soc. London A **219**, 186 (1953).
[13] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Chemical Systems* (Wiley, New York, 1977).
[14] B. T. Smith *et al.*, *Matrix Eigensystem Routines-EISPACK Guide* (Springer, Berlin, 1976), 2nd ed.
[15] R. Aris, Proc. R. Soc. London A **252**, 538 (1959).