Interaction of Reaction-Diffusion Fronts and Marangoni Flow on the Interface of a Deep Fluid

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It is shown that interfacial solitary structures (spots) generated by a bistable chemical reaction can be stabilized by Marangoni flow preventing the spread of a dynamically favorable state with a higher surface tension. The solutions are constructed using the method of matched asymptotic expansions to resolve the singularity at a sharp interface between the alternative states, and to compute the self-induced flow velocity advecting the domain boundary. [S0031-9007(96)02088-1]

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It has long been realized that chemical instabilities can both induce and be strongly affected by hydrodynamic flows. In early experiments with BZ and other oscillatory reactions, this interaction led to a transition from propagating waves in confined systems to cellular structures in systems with a free interface where Marangoni flow was excited by concentration gradients of chemical origin [1]. Strong interaction between chemical and interfacial instabilities has been the subject of a number of experimental studies [2]. A related direction was the study of chemical fronts affected by buoyancy [3]; both effects were apparently relevant in the observations of patterns of photochemical origin [4].

Following the linear analysis of chemical instability coupled with Marangoni flow [5], theoretical analysis of the nonlinear development of reaction-convection instabilities has been restricted so far either to very shallow layers enabling lubrication approximation [6] or to systems close to a bifurcation point [7]; both approaches are inapplicable to the most practical case of sharp reaction fronts. The only alternative was numerical modeling [8].

This Letter demonstrates a possibility of the formation of interfacial solitary structures generated by chemical instabilities and stabilized by Marangoni flow. A suitable basic system is a multistable chemical reaction involving an insoluble surfactant taking place on the interface of deep fluid. The analysis is based on the following assumptions: (a) The induced flow is creeping, and inertial effects can be neglected. (b) The boundary between alternative surface states is sharp, which requires that the characteristic diffusional length be much smaller than both the characteristic viscous length and the size of the emerging structures.

Both assumptions are physically realistic, and allow one to make use of the most powerful technique for constructing and analyzing nonequilibrium patterns of chemical origin, based on tracing the motion of sharp interfaces between alternative states of a bistable system interacting with a long-range field [9,10]. Marangoni flow that is induced by concentration gradients in the transitional region separating the two alternative states and, in its turn, advects this boundary, well qualifies as a long-range controlling agent; its action is, however, highly nonlocal, which poses serious analytical difficulties.

Recently, the boundary integral technique was applied to the computation of the motion of interfacial domains coupled to the creeping motion of the underlying fluid [11,12]. The effect of a sharp interface was, however, the emergence of a finite time singularity [12] that ruled out the formation of stable structures. We shall further see that the singularity can be indeed resolved when finite, though low, diffusivity is taken into account. The method of matched asymptotic expansions (akin to that used for the analysis of the motion of vortex lines [13]) will be applied to resolve the structure of the domain boundary, and to obtain a finite stationary velocity of the induced flow. It will be further shown that inward flow can stabilize a solitary spot of a dynamically prevalent state with a higher surface tension.

Consider an insoluble surfactant taking part in an autocatalytic chemical reaction. The surface concentration θ obeys the convective reaction-diffusion equation that we write in a dimensionless form

$$\theta_t = \tfrac{1}{2}\nabla^2\theta - \nabla\cdot(\mathbf{c}\theta) + f(\theta)\,. \tag{1}$$

The time scale is the characteristic reaction time τ, the coordinates are scaled by the diffusional length $\sqrt{2D\tau}$, where D is the surface diffusivity, $\mathbf{c} = \mathbf{v}\sqrt{\tau/2D}$ is the dimensionless surface velocity, and $f(\theta)$ is the dimensionless net surfactant source due to chemical reactions and exchange with the gas phase. We are interested in the case when at least two stable stationary solutions exist; therefore the function $f(\theta)$ should have three zeros, and its derivative at the smallest and largest zero should be negative. The simplest function possessing this property is a cubic. By shifting and rescaling, the two stable zeros can be placed at $\theta = 0$ and $\theta = 1$. Thus, we can assume $f(\theta) = -\theta(\theta - q)(\theta - 1)$, where $0 < q < 1$.

Equation (1) with the cubic source has a simple stationary solution in a co-moving frame that describes a straight-line front propagating with the speed $c_0 = q - \frac{1}{2}$:

$$\theta = \frac{1}{1 + e^{-x}} \equiv \frac{1}{2}\left(1 + \tanh\frac{x}{2}\right). \tag{2}$$

The x axis is directed normally to the front, and the velocity is positive when the lower state advances. The front is stationary when the interface is advected in the direction opposite to chemical propagation with the same speed. Generally, $c_0 + \mathbf{c} \cdot \mathbf{n}$ is the displacement speed of a point on a curved front along the normal $\mathbf{n}$. This speed can be corrected to account for a weak curvature effect.

The interfacial flow velocity appearing in Eq. (1) is induced by the Marangoni force due to an instantaneous distribution of surface tension $\sigma(\mathbf{x})$ that corresponds to a given instantaneous surface concentration profile. Under a realistic assumption of large Prandtl numbers $\mathrm{Pr} = \nu/D$ (ν is the kinematic viscosity), the characteristic flow relaxation time is far shorter than the characteristic diffusional time. Assuming $\sqrt{\nu\tau} \gg L$, the viscous response time can be neglected, and the stationary Stokes equation is applicable. The 2D horizontal velocity vector $\mathbf{v}$ and the vertical velocity w are expressed, assuming vanishing vertical vorticity, respectively, as $\mathbf{v} = \nabla\chi_z,\ w = -\nabla^2\chi$, where ∇ is the 2D vector differential operator. The velocity potential $\chi(\mathbf{x}, z)$ is determined by the Stokes equation

$$(\nabla^2 + \partial_z^2)^2\chi = 0\,. \tag{3}$$

We shall solve this equation in an infinitely deep and infinitely extended layer $z < 0$ with the Marangoni boundary conditions on the undeformable free boundary $z = 0$:

$$\chi(\mathbf{x}, 0) = 0, \qquad \mu\chi_{zz}(\mathbf{x}, 0) = -\nabla\sigma\,, \tag{4}$$

where μ is the dynamic viscosity.

The solution is found most readily by Fourier transform [14], yielding

$$\hat{\chi}(k) = -\frac{1}{2k\mu}\, z e^{kz}\hat{\sigma}(k)\,, \tag{5}$$

where hats denote Fourier transforms of the respective functions, dependent on the wave number $k = |\mathbf{k}|$. The only quantity relevant for our purpose is the interfacial velocity, which is computed as $\mathbf{v} = \nabla\phi(\mathbf{x})$; the interfacial flow potential $\phi(\mathbf{x}) = \chi_z(\mathbf{x}, 0)$ can be expressed as

$$\phi(\mathbf{x}) = \mu^{-1}\int G(|\mathbf{x} - \mathbf{y}|)\sigma(\mathbf{y})d^2\mathbf{y}\,, \tag{6}$$

where the integration is carried out over the entire free surface. The kernel $G(r)$ depends only on the 2D distance $r = |\mathbf{x} - \mathbf{y}|$, and is obtained as the inverse transform of $\hat{\chi}_z(0)$:

$$\begin{aligned} G(r) &= \frac{1}{8\pi^2}\int k^{-1}e^{-i\mathbf{k}\cdot\mathbf{x}}d^2\mathbf{k} \\ &= \frac{1}{4\pi}\int_0^\infty J_0(kr)dk = \frac{1}{4\pi r}\,. \end{aligned}$$

It is convenient to express the velocity through the *gradient* of surface tension. After transforming to the dimensionless variables, we obtain the expression for the surface flow velocity

$$\mathbf{c}(\mathbf{x}) = -M\int G(|\mathbf{x} - \mathbf{y}|)\nabla\theta(\mathbf{y})d^2\mathbf{y}\,, \tag{7}$$

where $M = (\Delta\sigma/\mu)\sqrt{\tau/2D}$ is the Marangoni number based on the characteristic diffusional length and $\Delta\sigma$ is the difference of surface tension between the lower ($\theta = 0$) and upper ($\theta = 1$) stationary states (it is assumed that the surface tension decreases linearly with growing concentration). This solution exists provided $\sigma(\mathbf{x}) = \mathrm{const}$ at $|\mathbf{x}| \to \infty$. Using Eq. (7) in Eq. (1) yields an integro-differential equation of the surface concentration. This equation is *nonlocal* so that the motion is dependent on the instantaneous distribution of domains occupied by the alternative states in the entire region.

The thickness of the front region where the change of the surfactant concentration occurs is determined by the characteristic diffusional length $\sqrt{2D/\tau}$. On distances far exceeding this scale, the concentration distribution can be considered as stepwise. Using the discontinuous function $\theta(\mathbf{x})$ that assumes two alternative values $\theta = 0$ and $\theta = 1$ in the domains separated by a boundary Γ (presumed smooth but not necessarily simply connected) brings Eq. (7) to the form

$$\mathbf{c}(\mathbf{x}) = -\frac{M}{4\pi}\oint_\Gamma \frac{\mathbf{n}}{r(s)}\,ds\,, \tag{8}$$

where the contour is parametrized by the arc length s, and $r(s) = |\mathbf{x} - \mathbf{y}(s)|$ is the distance from the reference point to a point on the contour; by convention, the normal is directed towards the domain occupied by the upper state.

Equation (8) is quite adequate for computing the flow velocity far from the fronts but cannot be applied to the problem of front dynamics, since the integral diverges on the front location. To compute the velocity induced within the front region, one has to remove a short arc segment from the integral (8). On the removed segment, the finite diffusional length has to be taken into account by applying Eq. (7) containing a smooth concentration profile. Both parts of the contour are further matched as in Ref. [13].

We presume that the local curvature radius of the front is of the same order of magnitude as the characteristic macroscopic scale L, and far exceeds the diffusional length. Then the concentration gradient is directed normally to the front, and the contour segments are almost rectilinear on distances $s \ll L$. In accordance with a common procedure of the theory of front dynamics [9,10], we transform to a local coordinate frame co-moving with the front, and take a certain contour, say, $\theta = q$, as the origin of the normal coordinate ξ. The origin of the tangential coordinate η is taken at the foot of the normal drawn from the reference point. Consider a point with a normal coordinate $\xi \ll L$, and cut from the contour integral in Eq. (8) a small arc of the length 2δ, where $\xi \ll \delta \ll L$. On the remaining part of the contour, ξ can be neglected; thus, the velocity induced at the reference point by the "far" contour is determined by Eq. (8). The normal velocity computed in this way diverges logarithmically at $\delta \longrightarrow 0$, and can be expressed as

$$c^{(o)} \asymp -\frac{M}{2\pi} \ln \frac{C}{\delta}, \tag{9}$$

where C is a constant dependent on the shape of the contour in the far region. In the near region, we introduce a stretched coordinate $\eta = s/\xi$, and compute the inner integral as

$$\begin{aligned} c^{(i)}(\xi) &= -\frac{M}{2\pi} \lim_{\delta/\xi \to \infty} \int_{-\infty}^{\infty} \theta'(\xi - \zeta) d\zeta \int_0^{\delta/\zeta} \\ &\quad \times \frac{d\eta}{\sqrt{\zeta^2 + \eta^2}} \\ &= -\frac{M}{2\pi} \left[\ln(2\delta) - \int_{-\infty}^{\infty} \ln|\zeta| \theta'(\xi - \zeta) d\zeta \right]. \end{aligned} \tag{10}$$

The auxiliary value δ falls out when both integrals are added up. The resulting finite expression for the flow velocity in the front region is

$$c(\xi) = -\frac{M}{2\pi} \ln \frac{C}{\beta(\xi)},$$
$$\ln \beta(\xi) = \int_{-\infty}^{\infty} \ln|\xi - \zeta| \theta'(\zeta) d\zeta. \tag{11}$$

Since $\theta'(\zeta) \rightarrow 0$ at $\zeta \rightarrow \infty$, $\beta(\xi) \asymp \xi$ at $\xi \gg 1$. The function $\beta(\xi)$ computed numerically using the analytical solution $\theta'(\xi) = \frac{1}{4} \operatorname{sech}^2 \frac{\xi}{2}$ corresponding to Eq. (2) is plotted in Fig. 1.

In view of the nonlocal character of the induced motion, only a symmetric configuration may be stationary. Consider a spot of the radius L occupied by the lower state on the infinite interface occupied by the upper state. We presume that the spot radius is large when measured on the diffusional scale, so that the dimensionless radius $l = L/\sqrt{2D\tau} \gg 1$. The induced surface flow velocity is computed using Eq. (8) as

$$\begin{aligned} c(\rho) &= -\frac{M}{2\pi} \int_0^{\pi} \frac{\cos \alpha \, d\alpha}{\sqrt{1 + (\rho/l)^2 - 2(\rho/l)\cos\alpha}} \\ &= \begin{cases} -\frac{M}{\pi}[\mathbf{K}(\frac{l}{\rho}) - \mathbf{E}(\frac{l}{\rho})], & \text{at } \rho > l, \\ -\frac{Ml}{\pi\rho}[\mathbf{K}(\frac{\rho}{l}) - \mathbf{E}(\frac{\rho}{l})], & \text{at } \rho < l, \end{cases} \end{aligned} \tag{12}$$

where ρ, α are polar coordinates, and $\mathbf{K}, \mathbf{E}$ are complete elliptic integrals. The radial flow velocity vanishes at $r = 0$ and decreases $\propto 1/r$ at $r \longrightarrow \infty$ (Fig. 2).

As expected, there is a divergence in the vicinity of the front:

$$c \asymp -\frac{M}{2\pi} \ln \left| \frac{8l}{e^2 \xi} \right| \quad \text{at } \xi \longrightarrow 0, \tag{13}$$

where $\xi = \rho - l$ and $l \gg \xi = O(1)$. The divergence is resolved using the asymptotic procedure described above. The resulting finite expression for the flow velocity at distances $\xi = O(1)$ from the spot circumference coincides with Eq. (11), where $C = 8l/e^2$. In the outer limit $x \longrightarrow \infty$, Eq. (11) coincides with the inner limit (13) of the outer solution. The uniformly valid composite expansion can be obtained by adding up Eqs. (11) and (12), and extracting their common limit (13).

For the purpose of semiquantitative estimation, one can assume that the front propagation is affected mostly by the maximum advection velocity in the front region, which is observed at the location where the concentration gradient is also at its maximum. Using the numerical value $\beta(0) = 0.882$, the maximum velocity is computed as $c_m = -(M/2\pi)\ln(0.955l)$. Since the dependence on l is logarithmical, this velocity may be of $O(1)$ on the diffusional scale and balance the intrinsic front velocity $c_0 = q - \frac{1}{2}$ when $M \leq O(1)$ and $l \gg 1$, but $\ln l$ is not exceedingly large. The curvature correction to the intrinsic speed of the chemical front is of $O(l^{-1})$, and can be neglected. The radius of a stationary spot is computed as

$$l_s = L/\sqrt{2D\tau} = 1.047 \exp \frac{\pi(2q - 1)}{M}. \tag{14}$$

Since the variable flow velocity is actually smaller than its maximal value, a somewhat larger radius might be actually necessary to induce the flow counterbalancing the speed of the chemical front; thus, the above expression gives a lower estimate of the spot size; the correction would only amount, however, to modifying the numerical coefficient. The above analysis is applicable if the spot radius is bounded by the conditions $\sqrt{D\tau} \ll L \ll \sqrt{\nu\tau}$.

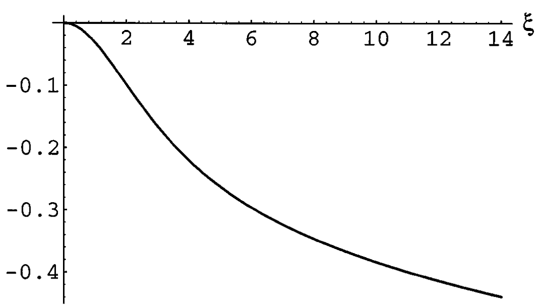

FIG. 1. The velocity profile in the vicinity of the front (the maximum velocity is taken as zero level).

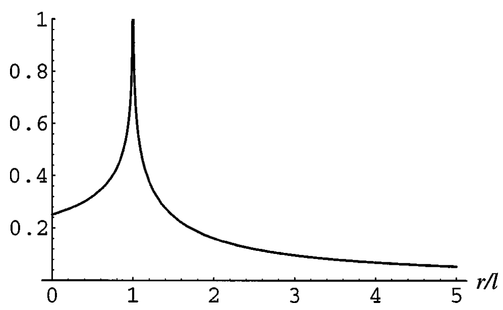

FIG. 2. The interfacial radial velocity in and around a solitary spot.

The dynamic equation for the dimensionless radius of a circular spot is $dl/dt = c_0 + c_m(l)$. Since $c_m'(l) < 0$, the spot should be stable to homogeneous perturbations; indeed, an increase of the radius would cause (at $M > 0$) an increased inward flow restoring the stationary state.

Stability to perturbations breaking the circular symmetry can be checked with the help of the method of boundary perturbations similar to that of Ref. [10]. Integrating Eq. (8) over a weakly distorted circle with the radius $l(\phi) = l_s + \tilde{l} e^{in(\phi - \phi_0)}$, $\tilde{l} \ll l_s$, proves that the spot is stable at $M > 0$ also to inhomogeneous boundary perturbations. A reverse setup, with a spot occupied by the upper state (with a lower surface tension), is treated formally in the same way, but, as the flow in this case is outward, the stationary state is evidently unstable. A similar instability was observed in experiment with radial spreading of a surfactant [15].

A rational expansion can be carried out for the case when the Marangoni number is small, and the two alternative states are close to the Maxwell construction. The most interesting situation arises when front curvature effects are also of the same order of magnitude. Thus, we can take l^{-1} as the small parameter of the expansion, and set $q = \frac{1}{2} + q_1/l$, $M = M_1/l$. Expanding $\theta = \theta_0 + l^{-1}\theta_1 + \ldots$, $c = l^{-1}c_1 + \ldots$, yields in the zero order θ_0 defined by Eq. (2). The homogeneous part of the first-order equation valid in the vicinity of the boundary of a circular spot with the radius l has a zero eigenvalue corresponding to the translational symmetry of the zero-order equation. The solvability condition of the first-order equation requires that its inhomogeneous part be orthogonal to the corresponding eigenfunction $\theta_0'(\rho) = \frac{1}{2}\,\mathrm{sech}^2 \frac{\xi}{2}$; $\xi = \rho - l$. Since the eigenfunction falls off sharply at $\xi \gg 1$, the asymptotic expression for the velocity valid in the front region, Eq. (11) with M replaced by M_1 can be used for c_1. This yields a relation between q_1 and M_1 that has to be satisfied at a stationary front:

$$\frac{1}{2} - q_1 + \frac{M_1}{2\pi} \ln \frac{l}{l_0} = 0\,, \tag{15}$$

where

$$\ln l_0 = 6 \int_{-\infty}^{\infty} \theta_0''(\xi)\theta_0(\xi)d\xi \times \int_{-\infty}^{\infty} \ln|\xi - \zeta|\theta_0'(\zeta)d\zeta = 1.344\,.$$

The first term in Eq. (15) describes the curvature effect. If it is neglected, Eq. (14) is recovered, but with a larger numerical coefficient $\exp(l_0) = 1.969$.

If there are a number of spots removed at distances far exceeding the diffusional length, the induced flow is additive, since the Stokes problem is linear. Separate spots are attracted one to the other by the induced inward flow; clearly, the system shows a tendency to aggregation but coalescing spots should shrink again to the same stable radius at which the inward flow is compensated by the chemical propagation speed. Thus, Marangoni flow serves as an efficient mechanism for preventing the spread of the state with a higher surface tension when it is dynamically favorable.

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