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

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Abstract

We consider a bistable reaction-diffusion system on the interface of deep fluid interacting with Marangoni flow. The method of matched asymptotic expansions is used to resolve the singularity at a sharp interface between the alternative states, and to compute the self-induced flow velocity advecting the domain boundary. It is shown that Marangoni flow serves as an efficient mechanism preventing the spread of the state with a higher surface tension when it is dynamically favorable.
It has been long 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 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 other alternative was numerical modeling \[8\].

The most powerful technique for constructing and analysing non-equilibrium patterns of chemical origin is 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 due to concentration gradients in the transitional region separating the two alternative states and, in its turn, advecting this boundary, well qualifies as a long-range controlling agent; its action is, however, highly nonlocal, which poses serious analytical difficulties.

Recently, boundary integral technique was applied to computation of the motion of interfacial domains coupled to 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 formation of stable structures. I shall show in this Letter 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 motion of vortex lines \[14\]) will be applied to resolve the structure of the domain boundary, and to obtain a finite stationary
velocity of the induced flow. I shall further show that inward flow can stabilize a solitary spot of a dynamically prevalent state with a higher surface tension.

Consider creeping motion of a viscous incompressible fluid in an infinitely deep and infinitely extended layer $z < 0$ induced by the Marangoni force due to a given stationary distribution of surface tension $\sigma(\mathbf{x})$ on the undeformable free boundary $z = 0$. Since the vertical vorticity vanishes, the 2d horizontal velocity vector $\mathbf{v}$ and the vertical velocity $w$ are expressed, respectively, as $\mathbf{v} = \nabla \chi_z$, $w = -\nabla^2 \chi$, where $\nabla$ is the 2d vector differential operator. The velocity potential $\chi(\mathbf{x}, z)$ is determined by solving the Stokes equation

$$
(\nabla^2 + \partial_z^2)^2 \chi = 0
$$

with the Marangoni boundary conditions at the free surface $z = 0$:

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

where $\mu$ is dynamic viscosity.

The solution is found most readily by Fourier transform [13], yielding

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

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

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

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

$$
G(r) = \frac{1}{8\pi^2} \int k^{-1} e^{-ik \cdot \mathbf{x}} d^2 \mathbf{x} = \frac{1}{4\pi} \int_0^\infty J_0(kr) dk = \frac{1}{4\pi r}. \tag{5}
$$

It is convenient to express the velocity through the gradient of surface tension:

$$
\mathbf{v}(\mathbf{x}) = \mu^{-1} \int G(\mathbf{x} - \xi) \nabla \sigma(\xi) d\xi. \tag{6}
$$
The solution exists provided $\sigma(x) = \text{const}$ at $|x| \to \infty$.

The distribution of the surface concentration $\theta$ of an insoluble surfactant on the free surface obeys the convective reaction-diffusion equation, which we shall write in a dimensionless form

$$\theta_t = \frac{1}{2} \nabla^2 \theta - \nabla \cdot (c \theta) + f(\theta).$$

(7)

Here $f(\theta)$ is the dimensionless net surfactant source due to chemical reactions and exchange with the gas phase; the time scale is the characteristic reaction time $\tau$; the coordinates are scaled by the diffusional length $\sqrt{2D\tau}$, where $D$ is the surface diffusivity; $c = v\sqrt{\tau/2D}$ is the dimensionless velocity. We are interested in the case when at least two stable stationary solutions exist; therefore the function $f(\theta)$ should have three zeroes, 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 zeroes can be placed at $\theta = 0$ and $\theta = 1$. Thus, we can assume $f(\theta) = -\theta(\theta - q)(\theta - 1)$, where $0 < q < 1$.

If $c = \text{const}$, Eq. (7) with the cubic source has a simple stationary solution

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

(8)

corresponding to the velocity $c = -c_0 = \frac{1}{2} - q$ directed along the $x$ axis. The front translates normally to itself towards the upper state with the “chemical” speed $c_0$ in the coordinate frame comoving with the local interface flow velocity $c$. Hence, $c_0 - c \cdot n$ is the displacement speed of a point on the front along the normal $n$. This speed can be corrected to account for the curvature effect. The front is stationary when the interface is advected in the direction opposite to chemical propagation with the same speed.

In the presence of Marangoni flow, Eq. (7) becomes an integro-differential equation, where $c$ is expressed with the help of Eq. (6) as

$$c(x) = -M \int G(x - \xi) \nabla \theta(\xi) d\xi,$$

(9)

where $M = (\Delta \sigma / \mu) \sqrt{\tau/2D}$ is the Marangoni number based on the characteristic diffusional length; $\Delta \sigma$ 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).

If the front motion is sufficiently slow, so that the flow field remains quasistationary, Eq. (9) applies, which gives a closed equation of the front displacement. 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 $\theta(x)$ that assumes the two alternative values $\theta = 0$ and $\theta = 1$ in the domains separated by a boundary $\Gamma$ (presumed smooth but not necessarily simply connected) brings Eq. (9) to the form

$$c(x) = -\frac{M}{4\pi} \oint_{\Gamma} \frac{n}{r(s)} ds,$$  \hspace{1cm} (10)

where the contour is parametrized by the arc length $s$, and $r(s) = |x - \xi(s)|$ 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.

Eq. (10) 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 Eq. (10), and apply on the rest of the contour Eq. (9) containing a smooth concentration profile. On the removed segment, the finite diffusional length has taken into account, and both parts of the contour matched as in Ref [14].

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 to a common procedure of the theory of front dynamics [9,10], we transform to a local coordinate frame comoving with the front, and take
a certain contour, say, \( \theta = q \) as the origin of the normal coordinate \( \xi \). The origin of the tangential coordinate \( \eta \) 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. (10) a small arc of the length \( 2\delta \), where \( \xi \ll \delta \ll L \). On the remaining part of the contour, \( \xi \) can be neglected; thus, the velocity induced at the reference point by the “far” contour is determined by Eq. (10). The normal velocity computed in this way diverges logarithmically at \( \delta \to 0 \), and can be expressed as

\[
c^{(\alpha)} \approx -\frac{M^2}{2\pi} \ln \frac{C}{\delta}, \tag{11}
\]

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

\[
c^{(i)}(\xi) = -\frac{M}{2\pi} \lim_{\delta/\xi \to \infty} \int_{-\infty}^{\infty} \theta'(\xi - \zeta) d\zeta \int_{0}^{\delta/\zeta} d\eta \sqrt{\zeta^2 + \eta^2}
= -\frac{M}{2\pi} \left[ \ln(2\delta) - \int_{-\infty}^{\infty} \ln |\zeta| \theta'(\xi - \zeta) d\zeta \right]. \tag{12}
\]

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

\[
c(\xi) = -\frac{M}{2\pi} \ln \frac{C}{\beta(\xi)}, \quad \ln \beta(\xi) = \int_{-\infty}^{\infty} \ln |\xi - \zeta| \theta'(\zeta) d\zeta. \tag{13}
\]

Since \( \theta'(\zeta) \to 0 \) at \( \zeta \to \infty \), \( \beta(\xi) \propto \xi \) at \( \xi \gg 1 \). The function \( \beta(\xi) \) computed numerically using the analytical solution \( \theta'(\xi) = \frac{1}{\xi} \text{sech}^2 \frac{\xi}{2} \) corresponding to Eq. (8) 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. (11) as

\[
c(\rho) = -\frac{M}{2\pi} \int_{0}^{\pi} \cos \alpha d\alpha \frac{\cos \alpha}{\sqrt{1 + (\rho/l)^2 - 2(\rho/l) \cos \alpha}}
\]
\[
\frac{-M}{\pi} \left[ K \left( \frac{l}{\rho} \right) - E \left( \frac{l}{\rho} \right) \right] \text{ at } \rho > l, \\
\frac{-ML}{\pi \rho} \left[ K \left( \frac{\rho}{l} \right) - E \left( \frac{\rho}{l} \right) \right] \text{ at } \rho < l.
\]

where \( \rho, \alpha \) are polar coordinates, and \( K, E \) are complete elliptic integrals. The radial flow velocity vanishes at \( r = 0 \) and decreases \( \propto \frac{1}{r} \) at \( r \to \infty \) (Fig. 2).

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

\[
c \approx -\frac{M}{2\pi} \ln \left| \frac{8l}{e^\xi} \right| \text{ at } \xi \to 0,
\]

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. (13) where \( C = 8l/e^2 \). In the outer limit \( x \to \infty \), Eq. (13) coincides with the inner limit (15) of the outer solution. The uniformly valid composite expansion can be obtained by adding up Eqs. (13), (14) and extracting their common limit (15):

\[
c(\rho) = \begin{cases} 
-\frac{M}{\pi} \left[ K \left( \frac{l}{\rho} \right) - E \left( \frac{l}{\rho} \right) \right] + \frac{1}{2} \ln \frac{\rho - l}{\beta(l - \rho)} & \text{ at } \rho > l, \\
-\frac{ML}{\pi \rho} \left[ K \left( \frac{\rho}{l} \right) - E \left( \frac{\rho}{l} \right) \right] + \frac{1}{2} \ln \frac{l - \rho}{\beta(l - \rho)} & \text{ at } \rho < l.
\end{cases}
\]

For the purpose of semi-quantitative estimation, one can assume that the front propagation is mostly affected 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 \( l \gg 1 \) but \( \ln l \) is not exceedingly large. The radius of a stationary spot is computed then as

\[
L = 1.047 \sqrt{2D\tau} \exp \frac{\pi(2q - 1)}{M}.
\]

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 spot should be stable to homogeneous perturbations, since an increase of the radius would cause an increased inward flow restoring the stationary state. The curvature correction to the intrinsic speed of the chemical front is of $O(l^{-1})$, and can be neglected. I checked the stability using the method of boundary perturbations similar to that of Ref. [10]. A reverse set-up, 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 $\theta_0$ defined by Eq. (8).

The stationary first order equation valid in the vicinity of the boundary of a circular spot with the radius $l$ is

$$\frac{1}{2}\theta_1''(\rho) + f'(\theta_0)\theta_1 + \frac{1}{2}\theta_0'(\rho) - q_1\theta_0(1 - \theta_0) - (c_1\theta_0)' = 0. \quad (18)$$

The homogeneous part of this equation has a zero eigenvalue corresponding to the translational symmetry of the zero-order equation; the corresponding eigenfunction is $\theta'_0(\rho) = \frac{1}{2}\text{sech}^2\xi$; $\xi = \rho - l$. The solvability condition of Eq. (18) requires that its inhomogeneous part be orthogonal to this eigenfunction. This yields a relation between $q_1$ and $M_1$ that has to be satisfied at a stationary front. Since the eigenfunction falls off sharply at $\xi \gg 1$, the asymptotic expression for the velocity valid in the front region, Eq. (13) with $M$ replaced by $M_1$ can be used for $c_1$. Computing the integrals, we express the solvability condition as

$$\frac{1}{2} - q_1 + \frac{M_1}{2\pi} \ln \frac{l}{l_0} = 0, \quad (19)$$
where

\[
\ln l_0 = 6 \int_{-\infty}^{\infty} \theta_0''(\xi)\theta_0(\xi) \, d\xi \int_{-\infty}^{\infty} \ln |\xi - \zeta|\theta_0'(\zeta) \, d\zeta = 1.344. \tag{20}
\]

The first term in Eq. (19) describes the curvature effect. If it is neglected, Eq. (17) is recovered, but with a larger numerical coefficient \(\exp(l_0) = 1,969\).

If there is 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 preventing the spread of the state with a higher surface tension when it is dynamically favorable.

Acknowledgement. This research has been supported by the Fund for Promotion of Research at the Technion.
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for acquainting me with an extended version of this paper (preprint, 1996) prior to
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FIG. 1. The velocity profile in the vicinity of the front (the maximum velocity is taken as the zero level).

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