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ABSTRACT

Chemical reactions can induce Marangoni flows by changing the surface tension of a solution open to the air, either by changing the composition and/or by modifying the temperature. We consider the case of a simple $A + B \rightarrow C$ reaction front propagating in a thin horizontal system open to air. The effect of the three chemical species on the surface tension of the aqueous solution is quantified by three solutal Marangoni numbers, while the effect of temperature changes is determined by the thermal Marangoni number. By integrating numerically the incompressible Navier–Stokes equations coupled to reaction-diffusion-convection equations for the chemical concentrations and temperature taking into account the Lewis number (ratio between heat and mass diffusivities), we emphasize the importance of thermal changes occurring due to the heat of reaction on the dynamics of chemically induced Marangoni convection. Based on the reaction-diffusion profiles of concentrations and temperature, asymptotic analytical solutions for the surface tension profiles are obtained and classified as a function of the Marangoni numbers and the Lewis number. This new classification allows for the prediction of the convective patterns in thermo-solutal Marangoni flows. The analytical predictions are further confirmed by numerical results and additional extrema in surface tension profiles induced by the thermal effects are found to affect the nonlinear dynamics.

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I. INTRODUCTION

Bimolecular A + B \rightarrow C reactions can sustain a reactiondiffusion (RD) front provided that the miscible pool solutions of reactants are initially separated in space. The properties of such fronts were first studied in Ref. 1 showing, among other results, that the position of the front scales with time as $\sim t^{1/2}$. This work was later extended to the case of unequal diffusivities of the species involved.^{2–9} Numerous experimental studies conducted in gels to avoid convection are in exceptional agreement with the RD theoretical predictions mentioned above.^{10–13}

However, in the absence of gels, spontaneous motions of the fluid arise from local gradients in physical properties (such as density, surface tension, and viscosity) that are induced by changes in the composition and/or temperature of the system.¹⁴ The nonlinear dynamics of these reaction-diffusion fronts coupled with natural solutal convection have been comprehensively studied in the past for autocatalytic and bimolecular reactions.^{14–43}

In horizontal systems, studies of pure buoyancy-driven flows induced in bimolecular reactive systems by changes in composition, for equal initial concentrations and diffusion coefficients of the reactant solutions, showed that the dynamics of the front can be exclusively predicted from the one-dimensional RD density profiles. The front propagation was shown to be determined by the density gradients, with a motion toward the region with the smallest density gradients.¹⁷ For unequal initial concentrations of reactant solutions, the front propagation is more complex due to a competition between diffusive and convective effects.¹⁹

Studies of A + B \rightarrow C reactions in vertically oriented systems, where a miscible pool of reactant solution A overlies a reactant solution B in the gravity field, showed that buoyancy-driven instabilities can arise along the horizontal interface.²⁰ Various instability scenarios have been highlighted and further classified as a function of the relevant parameters (ratio of initial concentrations, ratio of diffusion coefficients, etc.).²¹

Similar to the buoyancy-driven case, the propagation of chemical fronts has been studied in thin horizontal layers of solution in contact with air. In this case, the reaction, which takes place in the bulk, produces a surface-active species, which, in turn, induces

surface tension gradients. Tiani and Rongy²² did an extensive analytical and numerical study of the isothermal Marangoni convection driven by a bimolecular reaction $A + B \rightarrow C$ with equal initial concentrations and diffusion coefficient of the reactant solutions. They classified the surface tension profiles based on the solutal Marangoni numbers of the three species involved, A, B, and C, and related the position of the reaction front on the surface to the existence of a single or no extremum in surface tension profiles.

This classification was further adapted to account for unequal initial concentrations⁴⁴ or diffusivities.⁴⁵ By varying the initial concentrations of species A and B, the speed of the front is affected as well as the time scales at which diffusion takes over convection, and some specific dynamics (e.g. front reversal) were no longer observed. When differential diffusion, chemical reaction, and Marangoni effects were at play, oscillatory dynamics were reported.⁴⁵

Recent studies^{46–49} focused on systems where both buoyancyand Marangoni-driven solutal flows are acting antagonistically in bimolecular reactions. It was shown that autonomous self-organized complex behaviors can arise from the competition between both effects, leading to sustained spatio-temporal oscillations.

Up to now, $A + B \rightarrow C$ reactions have been investigated under the assumption that temperature remains constant throughout the solution, hence neglecting the effects of the heat of reaction on the surface tension gradients. However, it was shown numerically¹⁸ that taking into account the heat of reaction led to the observation of new unsteady spatio-temporal dynamics of autocatalytic fronts propagating in the presence of chemically induced Marangoni convection.

In this context, the aim of this paper is to study thermochemically induced Marangoni convective patterns that can develop in the presence of a simple $A + B \rightarrow C$ reaction. In strong agreement with numerical results, we further propose a classification of surface tension profiles as a function of the physical properties of the chemical species and the reaction, which are based on an analytical solution for concentrations and temperature obtained in RD conditions. However, the mathematical properties of the surface tension profiles governing the structure of the flow are shown to be independent of the presence of convection.

This paper is organized as follows. In Sec. II, we introduce the governing equations of the study and briefly review the numerical technique used to compute the solutions followed by our results (Sec. III), which highlight the classification of surface tension profiles and the dynamics of chemically induced Marangoni convection when coupled to thermal effects. Finally, the work is concluded in Sec. IV.

II. MODEL

The model system, as shown in Fig. 1, is a thin two-dimensional solution layer of length L'_x and height L'_z with $L'_x \gg L'_z$ to avoid any boundary effects in *x*-direction. The system consists of two miscible solutions of species A and B, initially separated horizontally that react to form a third species C. The coupling of this kinetics with molecular diffusion gives rise to the propagation of a planar reaction-diffusion front, with the product (C) invading the reactant solutions (A and B) and causing changes in the physical properties of the solution. In addition, the reaction can be endothermic or exothermic and, hence, modify the temperature of the system.



FIG. 1. Sketch of the dimensionless A + B \rightarrow C system. The two miscible solutions of reactants A and B, of surface tension γ_a and γ_b , respectively, are initially separated in space at an initial temperature T_0 and react upon contact to form C in the reactive zone modifying the local surface tension, γ_p . The temperature of the solution, T, also varies due to the heat of the reaction, ΔH , further changing the surface tension.

Due to these changes in composition and temperature, gradients in surface tension are created, inducing Marangoni-driven convection that couples back with reaction and diffusion. To focus on Marangoni convection, the dependence of density on temperature or solutal changes is neglected. Therefore, the density of the solution, ρ_0 , is assumed to remain constant. This is a theoretical limiting case expected to be observed typically in very thin layers⁵⁰ or microgravity conditions. ^{51,52} Surface tension, γ' , is a function of a', b', c', the concentrations of the chemical species A, B, C, respectively, and of temperature T'. To describe the system dynamics, the incompressible Navier–Stokes equations for the fluid velocity $\underline{\nu'}$ = (u', w') are coupled to the reaction-diffusion-convection (RDC) equations for a', b', c' and T'. The 2D model equations are given as

$$\frac{\partial \underline{v'}}{\partial t'} + \underline{v'} \cdot \underline{\nabla} \underline{v'} = v \nabla^2 \underline{v'} - \frac{1}{\rho_0} \underline{\nabla} p', \qquad (1)$$

$$\underline{\nabla}.\underline{\nu}'=0, \tag{2}$$

$$\frac{\partial a'}{\partial t'} + \underline{v'} \cdot \underline{\nabla} a' = D \nabla^2 a' - k a' b', \qquad (3)$$

$$\frac{\partial b'}{\partial t'} + \underline{\nu'} \cdot \underline{\nabla} b' = D \nabla^2 b' - ka'b', \qquad (4)$$

$$\frac{\partial c'}{\partial t'} + \underline{\nu'} \cdot \underline{\nabla} c' = D \nabla^2 c' + k a' b', \qquad (5)$$

$$\rho_0 c_p \left(\frac{\partial T'}{\partial t'} + \underline{\nu'} \cdot \underline{\nabla} T' \right) = \kappa_T \nabla^2 T' - \Delta H \ ka'b', \tag{6}$$

where p' is the dynamic pressure, v is the kinematic viscosity given by $v = \mu/\rho_0$, μ is the dynamic viscosity, and D is the molecular diffusion coefficients assumed to be constant and equal for all species. The initial concentrations of the reactant solutions A and B are also assumed equal $(a_0 = b_0)$. In such conditions, the reactiondiffusion profiles develop symmetrically, and the position of the maximum production rate $a'b'_{max}$ remains at the point of initial contact between A and B. c_p is the specific heat capacity of the solution, κ_T is the thermal conductivity, and ΔH is the molar enthalpy of the reaction (positive or negative depending on whether the reaction is endothermic or exothermic, respectively). The kinetic constant k is assumed to be constant since the dependence of k on temperature has negligible effect on the surface tension profiles (see the Appendix).

The air-liquid interface at $z' = L'_z$ is assumed to be nondeformable so that w' = 0 at $z' = L'_z$. At the free surface, a Marangoni boundary condition is applied for the horizontal component of the velocity [Eq. (8)]. This boundary condition takes into account the changes in horizontal surface velocity due to the variations in surface tension caused by gradients in temperature and chemical concentrations. The dependence of surface tension on chemical concentrations and temperature is assumed linear, i.e.,

$$\gamma' = \gamma_0 + \sum_{I=a',b',c'} I(\partial \gamma'/\partial I) + (T' - T_0)\partial \gamma'/\partial T',$$
(7)

where the solutal and thermal coefficients, $\partial \gamma' / \partial I$ and $\partial \gamma' / \partial T'$, are assumed to be constant. T_0 is the initial temperature in the system, and γ_0 is the surface tension of the solvent. Hence, the Marangoni boundary condition at the free surface $(z' = L'_z)$ is given by⁵⁰

$$\mu \frac{\partial u'}{\partial z'} = \frac{\partial \gamma'}{\partial x'} = \sum_{I=q',b',c'} \frac{\partial \gamma'}{\partial I} \frac{\partial I}{\partial x'} + \frac{\partial \gamma'}{\partial T'} \frac{\partial T'}{\partial x'}.$$
(8)

The prime notations correspond to the dimensional variables, and the system is cast in its dimensionless form using the reactiondiffusion scales for concentration a_0 , time $\tau_c = 1/(ka_0)$, length $L_c = \sqrt{D\tau_c}$, the derived scale for velocity $u_c = L_c/\tau_c = \sqrt{D/\tau_c}$, and pressure $p = p'/p_c$, where $p_c = \mu/\tau_c$. The dimensionless surface tension is given by $\gamma = (\gamma' - \gamma_0)/\gamma_c$ with $\gamma_c = \mu\sqrt{D/\tau_c}$. The adiabatic rise or drop in temperature resulting from the heat of the reaction, ΔT , is used to scale the temperature of the solution. The dimensionless temperature is given by $T = (T' - T_0)/\Delta T$, where $\Delta T = -\Delta H a_0/(\rho_0 c_p)$. ΔT will be negative (positive) for an endothermic (exothermic) reaction with a positive (negative) enthalpy, ΔH . We obtain the system of equations for the dimensionless variables (without primes) as

$$\frac{\partial \underline{\nu}}{\partial t} + (\underline{\nu} \cdot \underline{\nabla}) \underline{\nu} = S_c (\nabla^2 \underline{\nu} - \underline{\nabla} p), \tag{9}$$

$$\underline{\nabla}.\underline{\nu}=0, \tag{10}$$

$$\frac{\partial a}{\partial t} + \underline{v} \cdot \underline{\nabla} a = \nabla^2 a - ab, \tag{11}$$

$$\frac{\partial b}{\partial t} + \underline{v} \cdot \underline{\nabla} b = \nabla^2 b - ab, \tag{12}$$

$$\frac{\partial c}{\partial t} + \underline{v} \cdot \underline{\nabla} c = \nabla^2 c + ab, \tag{13}$$

$$\frac{\partial T}{\partial t} + \underline{v} \cdot \underline{\nabla} T = Le \nabla^2 T + ab, \tag{14}$$

where $S_c = v/D$ is the Schmidt number, and $Le = D_T/D$ is the Lewis number, with D_T the thermal diffusivity given by $D_T = \kappa_T/(\rho_0 c_p)$.

Typically,¹⁴ for an aqueous solution and small molecules, $S_c = 1000$, which is kept fixed in the remainder of this paper. In addition, the thermal diffusivity is usually one or two orders of magnitude greater than the solutal diffusivity as heat travels faster than mass. Hence, unless otherwise mentioned, *Le* is fixed equal to 10 in the remainder of this paper. Using these scales in Eq. (7), the dimensionless surface tension writes

$$\gamma(x,t) = -\sum_{i=a,b,c} M_i i(x,L_z,t) - M_T T(x,L_z,t),$$
(15)

where the solutal, M_i , and thermal, M_T , Marangoni numbers are defined as

$$M_i = \frac{-1}{\mu} \sqrt{\frac{a_0}{Dk}} \frac{\partial \gamma'}{\partial I},$$
(16)

$$M_T = \frac{-\Delta T}{\mu \sqrt{Dka_0}} \frac{\partial \gamma'}{\partial T'} = \frac{\Delta H}{\mu \rho_0 c_p} \sqrt{\frac{a_0}{Dk}} \frac{\partial \gamma'}{\partial T'}.$$
 (17)

Species with higher positive Marangoni number imply a higher surface activity, meaning a higher decrease in surface tension due to an increase in concentration. $\partial y'/\partial T'$ is negative for most solutions so that exothermic reaction ($\Delta T > 0$, $M_T > 0$) will result in a decrease in surface tension, while an endothermic reaction ($\Delta T < 0$, $M_T < 0$) results in an increase in surface tension. The dimensionless Marangoni boundary condition along the free surface ($z = L_z$) becomes

$$\partial_z u = \partial_x \gamma = -\sum_{i=a,b,c} M_i \partial_x i - M_T \partial_x T.$$
 (18)

It should be noted that only positive values of solutal Marangoni numbers (M_i) will be considered in the remainder of this paper, while the thermal Marangoni number, M_T , can attain both positive or negative values depending on the reaction being exothermic or endothermic, respectively. Thus, the changes in surface tension during a reaction depend on the respective values of M_a, M_b, M_c , and M_T .

No-slip boundary conditions are assumed at all solid boundaries, i.e., u = w = 0 at $x = \pm L_x/2$ and z = 0, and no-flux is assumed for both concentration and temperature on all four insulating boundaries of the system, i.e.,

$$\partial_x a, b, c = 0 = \partial_x T$$
 for $x = \pm L_x/2$, (19)

$$\partial_z a, b, c = 0 = \partial_z T \quad \text{for} \quad z = 0, L_z.$$
 (20)

At t = 0, the reactants A and B are separated such that the concentrations and temperature are defined as

$$a = 1, b = 0, c = 0, T = 0, \forall z, x \le 0,$$
 (21)

$$a = 0, b = 1, c = 0, T = 0, \forall z, x > 0.$$
 (22)

The spatial discretization of the system is performed by decomposing the mesh into N_x and N_z grid points, and hence, the size of each rectangular grid cell is $dx = L_x/N_x$ and $dz = L_z/N_z$. Unless mentioned, the size of the system is fixed in the remainder of this paper, with $L_x = 512$ and $L_z = 10$. The grid cell size is fixed at dx = 0.5 and dz = 0.25. The time stepping is performed in increments of the order of 10^{-5} , and Eqs. (9)–(22) are integrated for each time step using the method described in Ref. 18.

III. THERMO-CHEMICALLY INDUCED MARANGONI CONVECTION

A. Isothermal and thermal flows

Under certain physical conditions, no convection is induced ($\underline{\nu} = 0$) even with non-zero Marangoni numbers. Tiani and Rongy²² showed in their classification of surface tension profiles that, for isothermal Marangoni convection, no flow can be achieved under the condition, $2M_a = 2M_b = M_c$.

In physical terms, assuming A, B, and C contribute to a decrease in surface tension, it means that as the concentrations of A and B diminish in the reaction zone, the production of species C balances the difference in surface tension, resulting in a uniform surface tension throughout the free surface. In the case of thermal Marangoni convection, temperature can be considered as a pseudo product affecting the surface tension alongside A, B, and C.

When Le = 1, the RDC equations for concentration c (13) and temperature T (14) can be added together to give an RDC equation for an effective product of concentration ($c^* = c + T$) with an effective Marangoni number $M_c^* = M_c + M_T$. In this scenario, the entire classification of surface tension profiles in thermo-chemically induced Marangoni convection can be derived directly from Tiani and Rongy²² (Fig. 2).

Hence, according to this classification, a no-flow situation can be obtained when $2M_a = 2M_b = M_c^*$. When integrating Eqs. (9)–(22) with $M_a = 20$; $M_b = 20$; $M_c = 60$; $M_T = -20$, the surface tension profiles depend on the Lewis number, as shown in Fig. 3. Only the blue line, for Le = 1, corresponds to a no-flow condition where the decrease in surface tension by solutal effects is exactly compensated by its increase during the endothermic reaction. Nevertheless, as the Lewis number is increased (Le > 1), the surface tension profiles are no longer uniform and exhibit extrema. The patterns and dynamics of Marangoni convection are characterized by the number of convective rolls formed due to the forces acting at the surface, where



FIG. 2. Classification of surface tension profiles under isothermal Marangonidriven convection,²² which can be adapted to thermal conditions only if Le = 1. Sketches of the expected convection rolls are depicted for the six regions.



FIG. 3. Surface tension profiles for different Lewis numbers at t = 50: $M_a = 20$, $M_b = 20$, $M_c = 60$, and $M_T = -20$. The isothermal no-flow condition, $2M_a = 2M_b = M_c + M_T = 40$, is only valid for Le = 1.

the flow is initiated toward the regions of higher surface tension and induces, by continuity, a convective roll across the whole layer.

Consequently, a flow can be generated exclusively by the difference in thermal and solutal diffusivities, and the intensity of the flow is further enhanced by increasing the Lewis number, as shown in Fig. 4. As a result of the two main counter-rotating vortices induced by the surface tension gradients, the production rate is maximum at the bottom of the system at x = 0, and its value



FIG. 4. Patterns of Marangoni convection at t = 50 for various Lewis numbers. The fluid velocity field is superimposed on a 2D field of the production rate (*ab*). The system has been magnified to see the details of the velocity field. All examples shown here have common $M_a = 20$, $M_b = 20$, $M_c = 60$, and $M_T = -20$: (a) Le = 1, (b) Le = 10, and (c) Le = 100.

increases when increasing *Le*. Since the forces acting on the surface dictate the flow patterns in the bulk,²² it is crucial to revisit the classification of surface tension profiles when $Le \neq 1$. A new classification based on the solutal and thermal Marangoni numbers and the Lewis number can be performed analytically by using the long-time asymptotic solutions of the reaction-diffusion profiles as presented below.

B. Classification of surface tension profiles

To understand when and how many convective rolls are formed, one needs to understand the forces acting on the surface of the fluid. Therefore, it is necessary to study surface tension profiles and their number of extrema.

One extremum generally results in the formation of two counter-rotating convective rolls.

1. Long-time asymptotic solution

In the diffusion-limited regime (equivalent to the long-time limit), $A + B \rightarrow C$ systems with initially separated reactants possess analytical solutions for the concentration profiles. Those RD solutions were obtained analytically^{1–3,21} by neglecting the convective term in Eqs. (11)–(13).

In Ref. 1, they showed that when the diffusion coefficients of all species are equal, the position of the reaction front (x_f) scales with \sqrt{t} , and the width of the reaction front scales with $t^{1/6}$. Hence, on the diffusive length scale, which scales with \sqrt{t} , the width of the reaction front tends to zero. This allowed them to construct a solution outside the reaction zone in which no reaction takes place and set the two reactant concentrations to zero at the position of the reaction front. Furthermore, Koza² continued their work by obtaining the long-time asymptotic solutions for reactants with unequal diffusion coefficients, while Sinder and Pelleg³ obtained the solution for the product.

Trevelyan *et al.*²¹ performed a theoretical analysis exclusively for density-driven flows in vertical systems. They reconstructed and classified density profiles based on the individual contributions of each species to the density, initial concentrations of the reactants, and ratios of solutal diffusion coefficients. They formed two sets of analytical long-time asymptotic solutions for concentrations with unequal diffusion coefficients for the regions on the top and bottom of the reaction front. Following that work, the temperature will be considered as a pseudo product, and the solutions adapted to account for the ratio of thermal diffusivity to solutal diffusivity. If δ_i is defined as the ratio of diffusivity between species i and A, then $\delta_B = \delta_C = 1$ and $\delta_T = Le$. The position of the reaction front is located at²¹

$$x_f = 2\alpha\sqrt{t},\tag{23}$$

where α is the solution of Eq. (24) [corresponding to Eq. (10d) in Trevelyan *et al.*²¹] depending on δ_B and the ratio of initial reactant concentrations $\beta = b_0/a_0$,

$$e^{\alpha^{2}(\delta_{B}^{-1}-1)}\operatorname{erfc}(\alpha/\sqrt{\delta_{B}}) = \beta\sqrt{\delta_{B}}\operatorname{erfc}(-\alpha).$$
(24)

Substituting $\delta_B = 1$, we can simplify the equation as

$$\operatorname{erf}(\alpha) = \frac{1-\beta}{(1+\beta)}.$$
 (25)

The large-time asymptotic base-state solutions [Eqs. (10a) and (10b) in Trevelyan *et al.*²¹] are here given on the right (R) and left (L) sides of the reaction front by

$$\overline{a}^R = 0 = \overline{b}^L, \tag{26}$$

$$\overline{a}^{L} = 1 - \frac{\operatorname{erfc}(-\eta)}{\operatorname{erfc}(-\alpha)}, \quad \frac{\overline{b}^{R}}{\beta} = 1 - \frac{\operatorname{erfc}(\eta)}{\operatorname{erfc}(\alpha)}, \quad (27)$$

$$\frac{\overline{c}^{L}}{\theta_{c}} = \frac{\operatorname{erfc}(-\eta)}{\operatorname{erfc}(-\alpha)}, \quad \frac{\overline{c}^{R}}{\theta_{c}} = \frac{\operatorname{erfc}(\eta)}{\operatorname{erfc}(\alpha)}, \quad (28)$$

$$\frac{\overline{T}^{L}}{\theta_{T}} = \frac{\operatorname{erfc}(-\eta/\sqrt{Le})}{\operatorname{erfc}(-\alpha/\sqrt{Le})}, \quad \frac{\overline{T}^{R}}{\theta_{T}} = \frac{\operatorname{erfc}(\eta/\sqrt{Le})}{\operatorname{erfc}(\alpha/\sqrt{Le})}, \quad (29)$$

where $\eta = x/(2\sqrt{t})$ and the constants θ_c and θ_T are given by

$$\theta_T = e^{\alpha^2 (Le^{-1}-1)} \frac{\operatorname{erfc}(\alpha/\sqrt{Le})\operatorname{erfc}(-\alpha/\sqrt{Le})}{2\sqrt{Le}\operatorname{erfc}(-\alpha)},$$
(30)

$$\theta_c = \operatorname{erfc}(\alpha)/2.$$

We note that θ_c and θ_T correspond to Eq. (10c) of Ref. 21 for the solution of *c* and *T*, respectively. Since we have considered equal initial concentrations of A and B ($a_0 = b_0$), $\beta = 1$ and, hence, $\alpha = 0$. When $\alpha = 0$, the front remains localized at the point of initial contact between the solutions of A and B. By substituting θ_c and θ_T with α = 0 in Eqs. (28) and (29), we obtain the simplest form of the longtime solutions as

$$\overline{a}^{L} = 1 - \operatorname{erfc}(-\eta), \quad \overline{b}^{R} = 1 - \operatorname{erfc}(\eta), \quad (31)$$

$$\bar{c}^L = \frac{\operatorname{erfc}(-\eta)}{2}, \quad \bar{c}^R = \frac{\operatorname{erfc}(\eta)}{2}, \quad (32)$$

$$\overline{T}^{L} = \frac{\operatorname{erfc}(-\eta/\sqrt{Le})}{2\sqrt{Le}}, \quad \overline{T}^{R} = \frac{\operatorname{erfc}(\eta/\sqrt{Le})}{2\sqrt{Le}}.$$
(33)



FIG. 5. Case of a maximum on the left side of the reaction front (red dashed line): two types of surface tension profiles are possible (a) when surface tension at the front is larger than in the pure reactant solution A ($\gamma_F > \gamma_a$) and (b) when surface tension at the front is smaller than in the pure reactant solution A ($\gamma_F < \gamma_a$).

Using those asymptotic solutions for non-isothermal A + B \rightarrow C reactions, the surface tension profiles can be reconstructed using Eq. (15). Hence, two solutions for the surface tension profile are obtained, i.e., one for the left side, γ^L , and the other one for the right side of the reaction front, γ^R , given by

$$\gamma^{L} = -M_{a}(1 - \operatorname{erfc}(-\eta)) - M_{c} \frac{\operatorname{erfc}(-\eta)}{2} - M_{T} \frac{\operatorname{erfc}(-\eta/\sqrt{Le})}{2\sqrt{Le}}, \quad (34)$$

$$\gamma^{R} = -M_{b}(1 - \operatorname{erfc}(\eta)) - M_{c} \frac{\operatorname{erfc}(\eta)}{2} - M_{T} \frac{\operatorname{erfc}(\eta/\sqrt{Le})}{2\sqrt{Le}}.$$
 (35)

2. Extrema in surface tension profiles

To investigate the number of extrema in the surface tension profile and their position on the surface, the analytically obtained surface tension, γ , is differentiated with respect to η . The positions of the extrema, η_L and η_R , are defined as $(\partial \gamma^L / \partial \eta)_{\eta_L} = 0$ and $(\partial \gamma^R / \partial \eta)_{\eta_R} = 0$, and the primary conditions to have extrema are, thus, acquired as a function of the Marangoni and Lewis numbers,

$$\eta_L^2 = \frac{Le}{(Le-1)} \ln\left\{\frac{Le(2M_a - M_c)}{M_T}\right\},\tag{36}$$



FIG. 6. Classification of surface tension profiles on the left and right sides of the reaction front. The reaction can be either exothermic ($M_T > 0$) or endothermic ($M_T < 0$).

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$$\eta_R^2 = \frac{Le}{(Le-1)} \ln \left\{ \frac{Le(2M_b - M_c)}{M_T} \right\}.$$
 (37)

To have real solutions for η_L and η_R (when Le > 1), the logarithmic term must be greater than 1, i.e., $Le(2M_a - M_c)/M_T > 1$ and $Le(2M_b - M_c)/M_T > 1$. According to equations,

$$M_c Le + M_T = 2M_a Le, \tag{38}$$

$$M_c Le + M_T = 2M_b Le, \tag{39}$$

extrema are, thus, observed for positive (negative) values of M_T when the right-hand side terms are higher (lower) than the left-hand side terms. Each extremum found in the surface tension profile is

responsible for the creation of two convective rolls on either side of it. To find which one of these rolls is the largest, we look for the largest surface tension gradient. For example, assuming that there is one maximum on the left side of the reaction front, there can be two possibilities. Figure 5 describes these two possible surface tension profiles with a maximum on the left side of the reaction front, i.e., when $\gamma_a < \gamma_F$ [Fig. 5(a)] or $\gamma_a > \gamma_F$ [Fig. 5(b)], where γ_F is the surface tension at the reaction front ($x = x_F = 0$). It can be obtained from the long-time asymptotic solution by substituting $\eta = 0$ in Eqs. (34) and (35),

$$\gamma_F = -\frac{M_c}{2} - \frac{M_T}{2\sqrt{Le}}.$$
(40)





We recall that γ_a and γ_b are the surface tensions of the initial reactant solutions A and B, respectively. The set of conditions to distinguish the size of the convective rolls, for the left and right sides of the reaction front, respectively, is obtained using Eqs. (15) and (40),

$$\gamma_a = \gamma_F \Rightarrow 2M_a \sqrt{Le} = M_c \sqrt{Le} + M_T,$$
 (41)

$$\gamma_b = \gamma_F \Rightarrow 2M_b \sqrt{Le} = M_c \sqrt{Le} + M_T.$$
 (42)

All the conditions above [Eqs. (38), (39), (41), and (42)] can be represented on a $M_c - M_T$ plane as shown in Fig. 6 to showcase the surface tension profiles on each side of the reaction front.

By further merging the profiles on the left and right sides of the reaction front, nine surface tension profiles can be generated for each case (endothermic and exothermic), giving a total of 18 combinations possible. Among those, only 12 give rise to surface tension profiles with different properties, as represented in Fig. 7 for $M_a < M_b$. The non-monotonic properties of the surface tension profiles are unchanged when $M_a \leftrightarrow M_b$ in Fig. 7. Thus, the front dynamics for $M_a > M_b$ can be inferred from the first case, and 12 symmetric surface tension profiles are found with respect to x = 0. The analytical surface tension profiles defined by Eqs. (34) and (35) were verified with the ones reconstructed from the numerical solutions of the RD equations, emphasizing that the analytical solutions are excellent approximations for the RD dynamics (see Fig. SF1 in the supplementary material).

C. Interpretation

The surface tension profiles in Fig. 7 can be interpreted based on the isothermal profiles in Fig. 2. The explanation below is provided for a reaction where $M_a < M_b$ but can trivially be extended to the case $M_a > M_b$.

If $M_c < 2M_a$, then the surface tension profile obtained in isothermal conditions corresponds to region III of Fig. 2, and the surface tension is maximal at the front position. By adding an endothermic contribution $(M_T < 0)$, we increase the domain in the parameter space $(M_c < 2M_a - M_T/Le)$, where a local maximum exists (region IV_L + IV_R). On the other hand, if an exothermic contribution $(M_T > 0)$ is considered, the local maximum remains due to solutal effects, but two additional local minima emerge due to thermal effect, as heat diffuses faster than mass (region III_L + III_R). As



FIG. 8. Patterns of chemically induced Marangoni convection at t = 50. The fluid velocity field is superimposed on a 2D field of the production rate (*ab*). The system has been magnified to see the details of the velocity field. All examples shown here have common $M_a = 20$, $M_b = 40$, and Le = 10, and they correspond to (a) an isothermal reaction and four various endothermic reactions with negative thermal Marangoni numbers (i) $M_c = 25$, $M_T = 0$, (ii) $M_c = 10$, $M_T = -300$, (iii) $M_c = 80$, $M_T = -300$, (iv) $M_c = 100$, $M_T = -100$, and (v) $M_c = 300$, $M_T = -300$ and (b) an isothermal reaction and four various exothermic reactions with positive thermal Marangoni numbers, (i) $M_c = 25$, $M_T = 0$, (ii) $M_c = 40$, $M_T = 100$, (iii) $M_c = 100$, $M_T = 100$, (iv) $M_c = 5$, $M_T = 50$, and (v) $M_c = 25$, $M_T = 60$. The eight sets of M_c and M_T correspond to eight different regimes described in Fig. 7.

the exothermicity is further increased $(M_T \gg 0)$, the solutal contribution is counterbalanced, and the surface tension at the front decreases (regions II_L + III_R and II_L + II_R).

In region I of the isothermal classification, $M_c > 2M_b$, and the surface tension is minimal at the front position. In the presence of heat effects, the interpretation is the same as above. By adding an exothermic contribution ($M_T > 0$), we increase the domain in the parameter space ($M_c > 2M_b - M_T/Le$) in which a local minimum exists (region $I_L + I_R$). If the reaction is endothermic, then two local maxima due to thermal effects emerge, alongside the initial solutally induced minimum (region $VI_L + VI_R$) that can be modulated by increasing the endothermicity (region $VI_L + V_R$ and $V_L + V_R$).

Finally, if $2M_a < M_c < 2M_b$, the isothermal surface tension profile is monotonous (region II of Fig. 2). In this case, the addition of an endothermic effect results in the emergence of a local maximum on the left side of the front (region VI_L + IV_R), and the surface tension at the front increases with endothermicity, i.e., when M_T decreases (region V_L + IV_R). For exothermic effects, a minimum on the right side of the reaction front is observed (region I_L + III_R), and the surface tension at the front decreases as the thermal effects are strengthened, i.e., when M_T increases (region I_L + II_R).

D. Convective dynamics

In this section, the analytical predictions are compared to an isothermal and several exothermic/endothermic reactions that have been numerically investigated. Figure 8 highlights the 2D production rate fields as well as the fluid velocity fields for different values of M_c and M_T .

In isothermal conditions for $M_a = 20$, $M_b = 40$, and $M_c = 25$ [Fig. 8(i)], an increase in the surface tension is observed as the reaction occurs, giving rise to a maximum in surface tension, as well



FIG. 9. Numerical RDC surface tension profiles corresponding to the (a) endothermic and (b) exothermic reactions studied in Fig. 8.

as two counter-rotating convective rolls, one on each side of the reaction front.

The flow at the surface is directed toward the front, and the convective roll on the right of the front is the largest one following the highest surface tension gradient (Region III of Fig. 2). As discussed previously, when thermal effects are at play, the surface tension gradients change, thereby affecting the flow patterns in the bulk. One or three extrema in the surface tension profiles are found analytically in the exothermic/endothermic cases. This leads to the emergence of up to two or four convective rolls, respectively.

The impact of thermal effects on the velocity field is shown in Figs. 8(a-ii)–8(a-v) for endothermic systems and in Figs. 8(b-ii)–8(b-v) for exothermic systems. The number of convective rolls observed numerically is matching with analytical predictions [Fig. 7(b)], and we note that the position of the reaction front, the number, relative size, and orientation of convective rolls are all influenced by the combination of M_c and M_T .

Thus, it appears that completely different convection patterns can be achieved in the bulk depending on the extent of endothermicity $(M_T < 0)$ or exothermicity $(M_T > 0)$ of the reaction. The creation of new extrema in the surface tension profile due to the addition of thermal effects is furthermore emphasized in Fig. 9 for both endothermic (a) and exothermic (b) reactions. It shows that systems composed of two convective rolls are characterized by one extremum in the surface tension profile, whereas three extrema are observed for systems presenting four convective rolls, confirming the analytical predictions. Interestingly, no case of zero extremum (monotonous surface tension profiles) has been observed as soon as $Le \neq 1$, as opposed to the same system in isothermal conditions (regions II and V of Fig. 2).²² We note that the values of M_c and M_T in Fig. 8 were chosen arbitrarily to illustrate different convective dynamics with one or three extrema in the surface tension profiles.

All the surface tension profiles predicted in Fig. 7 were successfully recovered numerically in RDC systems with consistent values of M_a , M_b , and M_c at Le = 10, except for one (region II_L + II_R). However, this particular profile was obtained for a higher Lewis number (Le = 500, see Fig. SF1 in the supplementary material).

Finally, the effect of height (L_z) on the surface tension profiles was studied and showed to be merely quantitative and not qualitative when L_z is varied over an order of magnitude (Fig. 10). As the thickness increases, the flow field intensity increases because of a smaller



FIG. 10. Influence of the height of the solution layer (L_z) on the numerically obtained reaction-diffusion-convection surface tension profiles for $M_a = 20$, $M_b = 40$, $M_c = 25$, $M_T = 25$, and Le = 10 at t = 50, corresponding to region $\|I\|_{\ell} + \|I\|_{\mathcal{B}}$.

influence of the bottom drag, but the number of extrema in the surface tension profiles remains equal for all the values of L_z studied in this paper.

IV. CONCLUSIONS

The nonlinear dynamics of $A + B \rightarrow C$ chemical fronts in horizontal solution layers can be influenced by both thermal and solutal Marangoni-driven convection. We have studied the dynamics of such fronts both theoretically and numerically by integrating the 2D incompressible Navier–Stokes equations coupled with reaction-diffusion-convection equations for the concentrations of the three chemical species and the temperature in the bulk. We have performed these studies for equal initial concentrations and solutal diffusion coefficients. The thermal diffusion coefficient was considered to be ten times larger than the solutal diffusivity coefficient, corresponding to a Lewis number, *Le*, equal to 10.

We have assumed that all three components A, B, and C contribute to a decrease in surface tension. The heat of reaction can result in either an increase or decrease in surface tension depending if the reaction is endothermic or exothermic, respectively. When Le = 1, the temperature can be treated as a pseudo product, and the surface tension profiles can be classified simply using the isothermal surface tension profile classification.²² In particular, a no-flow ($\underline{v} = \underline{0}$) situation can be attained under the condition $2M_a = 2M_b$ $= M_c + M_T$. Under the same condition, when $Le \neq 1$, the difference in heat and mass diffusivities creates extrema in the surface tension profile, and the convection is always present.

We have shown that the enthalpy of the reaction has a pivotal role in controlling the dynamics of chemically induced Marangoni convection. Primarily, additional extrema in the surface tension profiles can be observed. The heat of reaction and its effect on the flow, represented by the thermal Marangoni number (M_T) , are able to create more than just one extremum or two associated convective rolls as is the case in isothermal system with Marangoni-driven convection.²² Here, up to three extrema in the surface tension profiles were observed implying four convective rolls in the bulk. Both exothermic and endothermic reactions were studied for a wide range of values of M_T . The higher the exo/endothermicity of the reaction, the greater the impact on the direction, strength, and size of the convective rolls. In some cases, the entire dynamics were reversed with respect to the isothermal case just due to thermal effects.

Therefore, the heat of reaction can dramatically affect the dynamics of Marangoni-induced convection and induce more complex behaviors by creating additional convective rolls.

To understand the physics behind those observations, the surface tension profiles have been classified. To do this, we have used the long-time asymptotic solutions^{1-3,21} for the corresponding reaction-diffusion (RD) profiles. Temperature was assumed to be a pseudo product with a diffusion coefficient different from the chemical species and equal to the Lewis number. Those asymptotic solutions were used to reconstruct the analytical surface tension profiles as a function of the Marangoni numbers, M_a , M_b , M_c , and M_T , and of the Lewis number, *Le*. Those analytical profiles are in good agreement qualitatively with both the reaction-diffusion and reaction-diffusion-convection numerical surface tension profiles reconstructed from the concentrations and temperature profiles obtained with numerical integrations.

The extrema in the surface tension profiles are of utmost importance while studying Marangoni-driven flows. Using the asymptotic solutions, the conditions to observe extrema can be identified theoretically as a function of the Lewis number, thermal number, and solutal Marangoni number. Thus, we have proposed a state-ofthe-art classification of the surface tension profiles for exothermic $(M_T > 0)$ and endothermic $(M_T < 0)$ reactions (see Figs. 6 and 7). A total of 12 different profiles could be reconstructed from the proposed classification. One can predict the shape of surface tension profiles and the number, relative size, and direction of these convective rolls in a Marangoni convection solely from this classification.

Furthermore, this work could be extended to thermochemically induced Marangoni systems presenting different solutal diffusion coefficients for A, B, and C, hence making the flow patterns and classification even more complex.

SUPPLEMENTARY MATERIAL

See supplementary material for the comparison between analytical and numerical reaction-diffusion surface tension profiles as well as the numerical reaction-diffusion-convection surface tension profiles at Le = 500.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

A. Bigaj: Formal analysis (lead); Investigation (equal); Methodology (equal); Validation (lead); Visualization (lead); Writing – review & editing (lead). V. Upadhyay: Formal analysis (equal); Software (lead); Visualization (equal); Writing – original draft (lead).
L. Rongy: Conceptualization (lead); Formal analysis (equal); Funding acquisition (lead); Methodology (equal); Project administration (lead); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX: TEMPERATURE DEPENDENCE OF RATE CONSTANT

Applying the Arrhenius law for the temperature dependence of rate constants as a function of activation energy, E_a , and initial temperature, T_0 , we obtain

$$\ln\left(\frac{k}{k_0}\right) = \frac{E_a}{RT_0} \left(1 - \frac{T_0}{T}\right),\tag{A1}$$

where R = 8.314 J/(mol K) is the universal gas constant, and k_0 is the rate constant at $T = T_0$. Equations (11)–(14) can then be modified using this rate constant, and new RDC equations are obtained where the reaction term is

$$\pm a b e^{e_a \left(\frac{\Delta T}{\Delta T + T_0/T}\right)}, \qquad (A2)$$

where the activation energy is scaled by RT_0 as $e_a = E_a/RT_0$. For e_a up to 10 and adiabatic increase in temperature of the system up to $\Delta T = 0.2T_0$, the maximum difference in dimensionless surface tension profiles was of the order of 10^{-4} .

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