

Density fingering of an exothermic autocatalytic reaction

T. Bánsági, Jr.,¹ D. Horváth,¹ Á. Tóth,¹ J. Yang,² S. Kalliadasis,² and A. De Wit³

¹*Department of Physical Chemistry, University of Szeged, P.O. Box 105, Szeged H-6701, Hungary*

²*Department of Chemical Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom*

³*Service de Chimie Physique, CP 231, Université Libre de Bruxelles, B-1050 Brussels, Belgium*

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Density fingering of exothermic autocatalytic fronts in vertically oriented porous media and Hele-Shaw cells is studied theoretically for chemical reactions where the solutal and thermal contribution to density changes have opposite signs. The competition between these two effects leads to thermal plumes for ascending fronts. The descending fronts behave strikingly differently as they can feature, for some values of the parameters, fingers of constant amplitude and wavelength. The differences between up and down going fronts are discussed in terms of dispersion curves and nonlinear dynamics. The theoretically predicted dispersion curves are experimentally evidenced with the chlorite-tetrathionate reaction.

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Fingering of interfaces between two miscible fluids of different mobility is an ubiquitous phenomenon encountered in applications such as enhanced oil recovery, combustion, and separation processes. An essential feature of fingering is the selection of a specific finger wavelength at the onset of the instability. In terms of linear stability analysis, the dispersion curves (giving the growth rate σ of the perturbations transverse to the interface as a function of their wave number k) are characterized by an unstable band $0 \leq k \leq k_c$ containing the wave number k_{\max} with the largest positive growth rate (dispersion curve of type II according to Cross and Hohenberg [1])—see Fig. 1. Experimental and numerical dispersion curves all show type-II characteristics in viscous and density fingering [2,3] and in fingering in fields as diverse as electrochemical deposition [4], non-Newtonian fluids [5], and reaction-diffusion systems [6–11]. The wavelength at onset is given by $\lambda = 2\pi/k_{\max}$ measured between subsequent tips. The resulting fingering pattern has an amplitude, i.e., a distance between tip and trough of the fingered zone, which grows in time. The nonlinear dynamics of the instability is characterized by coarsening of the fingers due to merging and shielding phenomena.

In this paper, we predict theoretically that fingers of constant amplitude and wavelength can result from the coupling of solutal and thermal buoyancy effects in the density fingering of exothermic autocatalytic fronts. In this case, as confirmed experimentally, the dispersion curves are characterized by a narrow band of unstable wave numbers bounded by two neutral modes k_1 and k_2 such that $0 < k_1 \leq k \leq k_2$ (dispersion curve of type I [1])—see Fig. 1. The fully nonlinear system demonstrates the existence of a stationary cellular structure of wave number k_{\max} such as in the case of Turing patterns [1,12] or Rayleigh-Bénard convection [13]. The thermal destabilization of chemical fronts due to the exothermicity of the reactions has already been studied in the case where no mass changes occur across the interface [14]. Solutal buoyancy driven fingering of isothermal chemical fronts has also received attention [6–11]. The competition between thermal and solutal contributions to density changes has been discussed both experimentally [15] and theoretically [16]. Nevertheless, in these studies, no dispersion curves are pre-

sented and the long-time dynamics features coarsening. Here, we study both theoretically and experimentally the density fingering of exothermic autocatalytic fronts and show that previously unreported fingering can result from the coupled solutal and thermal buoyancy effects. In particular, heat effects can change the stability properties of both ascending and descending fronts and induce a change of the dispersion curve of down going fronts from type II to type I while the nonlinear stage of the instability equilibrates at a stationary norm state. Changes from type I to type II have been obtained in the context of density/viscous fingering in the absence of chemical reactions, without, however, stationary patterns [17].

Our model system is a two-dimensional porous medium or Hele-Shaw cell (two glass plates separated by a thin gap width a) oriented vertically in the gravity field $g\mathbf{i}_x$ and filled with the reactants of an exothermic reaction generating fronts. Traveling fronts separating reactants and products are

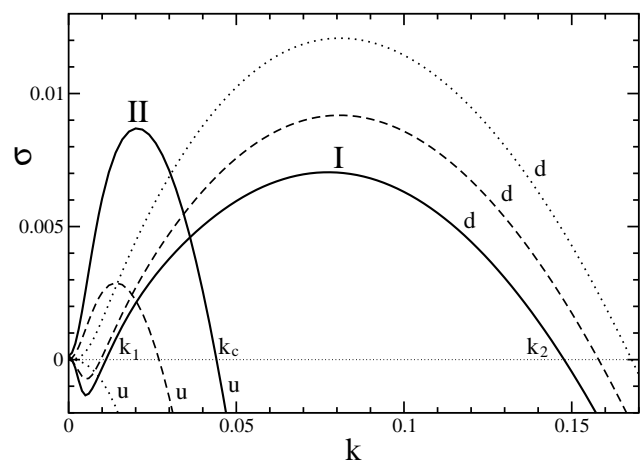


FIG. 1. Theoretical dimensionless dispersion curves for both up (u) and down (d) going fronts for $Da=0.001$, $\kappa=1$, $Le=10$, and $\gamma_T' = -3$ (plain); -2 (dashed); -1 (dotted). Type-I dispersion curves have a band of unstable modes such that $k_1 \leq k \leq k_2$ while type-II dispersion curves have modes with positive growth rates in the range $0 \leq k \leq k_c$.

initiated at both the top and the bottom of the cell. We consider here reactions for which the solutal contribution to the density increases in the course of the reaction as the products are heavier than the reactants. The reaction is exothermic so that the thermal contribution to the density decreases when the front passes by and thermal effects are thus opposite to the solutal effects. Darcy's law, used to describe the flow, is coupled to the reaction-diffusion-advection equation for the concentration α of the chemical species that controls the density of the solution as well as to the energy equation for the temperature T . T is nondimensionalized as $T \rightarrow (T - T_0)/T_0$, where T_0 is the initial temperature. Following Ref. [10] velocities, lengths, and time are scaled by $U = \Delta\rho_S g \kappa / \nu$, $L_h = D_\alpha / U$, and $\tau_h = D_\alpha / U^2$, respectively, with D_α the molecular diffusivity of species α , $\Delta\rho_S = (\rho_2 - \rho_1)_S / \rho_0$, the solutal contribution to the density, with $\rho_{0,1,2}$ the density of water and of the reactant and product solutions, respectively. Density and concentrations are scaled by $(\rho_2 - \rho_1)_S$ and α_0 , the initial concentration of α . Pressure is normalized by $\mu D_\alpha / K$, with $K = a^2 / 12$ the permeability, and contains the constant hydrostatic pressure gradient. Using the Boussinesq approximation, the dimensionless equations are then

$$\nabla p = -\mathbf{u} + (\gamma_T T - \alpha) \mathbf{i}_x, \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (2)$$

$$\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T = \text{Le} \nabla^2 T + \phi \text{Daf}(\alpha), \quad (3)$$

$$\frac{\partial \alpha}{\partial t} + \mathbf{u} \cdot \nabla \alpha = \nabla^2 \alpha - \text{Daf}(\alpha), \quad (4)$$

where $\text{Da} = D_\alpha q \alpha_0^3 / U^2$ is the Damköhler number and q the kinetic constant. For the chlorite-tetrathionate (CT) reaction, $f(\alpha) = 36\alpha(1 - \alpha)^2(\kappa + 7\alpha)$, with $\kappa = 2[\text{ClO}_2^-]_0 / \alpha_0 - 7$ [10,11]. In this reaction, the solutal $\Delta\rho_S$ and thermal $\Delta\rho_T$ components of the density jump across the front are of opposite signs where $\Delta\rho_T = (\rho_2 - \rho_1)_T / \rho_0$. The contribution of heat effects depends on three dimensionless parameters: the Lewis number, $\text{Le} = D_T / D_\alpha$, which is the ratio of the thermal and molecular diffusivities, the volumetric thermal expansion coefficient $\gamma_T = \Delta\rho_T T_0 / \Delta T_b \Delta\rho_S$, and the exothermicity $\phi = \Delta H \alpha_0 / \rho_0 c_p T_0 \equiv \Delta T_b / T_0$, where ΔH is the heat of reaction and c_p the heat capacity of water. $\Delta T_b = T_b - T_0$ is the adiabatic temperature rise with T_b the adiabatic temperature. Here, ΔH , ν , D_T , and c_p are considered constant. We further suppose that the kinetics of the reaction does not depend on T as $\Delta T_b \sim 2-3$ K for the CT reaction. Notice that for $\phi = 0$ the hydrodynamic and thermal problems are decoupled. We recover in this limit the isothermal density fingering of the CT system as studied in Refs. [10,11].

For $\Delta T_b = 3$ K and $T_0 \sim 300$ K, we find $\phi \sim 0.01$ while $D_T = 1.43 \times 10^{-3}$ cm²/s and $D_\alpha \sim 1.2 \times 10^{-4}$ cm²/s gives $\text{Le} \sim 10$. As $\Delta\rho_T \sim -5.9 \times 10^{-4}$ while the isothermal density change measured by a digital density meter is $\Delta\rho_S = (4.5 \pm 0.1) \times 10^{-4}$, we have $\gamma_T \sim -130$. Finally, other typical values are $\kappa = 1$ and $\text{Da} = 0.001$ [10]. Notice that the

transformation $T \rightarrow \phi T$ scales away ϕ from the energy equation and introduces a *modified* expansion coefficient $\gamma'_T = \gamma_T \phi (\sim O(1))$. This implies that for given Da and κ the behavior of the system is universal for all ϕ and depends on two parameters only: Le and γ'_T .

In the absence of convection ($\mathbf{u}_s = 0$), system (1)–(4) admits a base state traveling front solution (α_s, T_s, p_s) obtained numerically by shooting methods [10]. A linear stability analysis of this base state yields the growth rate curves in Fig. 1. The translational invariance of the system in the streamwise direction implies that $\sigma = 0$ for $k = 0$. The most striking result is that the dispersion curves are different depending on whether the base state corresponds to an up going or down going front. In the absence of thermal effects, the up going front is stable as the isothermal density increases in the course of the CT reaction. However, for a nonzero reaction exothermicity, the hot products lie under the cold reactants which can lead to a thermal destabilization of the up going front. As can be seen from Fig. 1 when γ'_T is varied, the dispersion curves of the thermally unstable up going front always feature type-II dispersion curves. All variations of parameters leading to an increase of the temperature effects across the front contribute to the thermal destabilizing density stratification. In that respect, the system becomes more unstable when the Lewis number is decreased which corresponds to sharpening the thermal front by decreasing the thermal diffusivity. In this case the temperature front is very localized around the concentration front which then strongly feels the destabilizing thermal effect. At the same time, increasing the exothermicity ϕ which leads to larger $|\gamma'_T|$ for a given Lewis number generates more heat per mole of α and thus destabilizes the front. Similarly, increasing $|\gamma'_T|$ means increasing the density difference across the front for a given temperature gradient which also destabilizes the front. We notice that, for either Le or γ'_T fixed, there exists a critical value of the other parameter at which the flat front becomes unstable with respect to fingering instabilities. The dispersion curves for the up going fronts are always of type II.

Solutal and thermal effects compete the other way round for the downward moving front. When the reaction is triggered at the top of the system, the denser products lie on top of the lighter reactants and the front is buoyantly unstable because of solutal unfavorable stratification. The dispersion curves of such solutal destabilization in the absence of any heat effect are of type II [10,11] as in standard Rayleigh-Taylor fingering. If the stabilizing heat effects are strong (small Le , large γ'_T , i.e., high ϕ and/or high γ_T) the system is completely stabilized and the down going front is uniform in the spanwise direction without any fingering. There exists, however, for each of these parameters, a critical value beyond which competition between the solutal and thermal effects drastically changes the dispersion curves leading to stabilization of long waves and destabilization of a band of modes centered around a most unstable mode k_{max} and hence to dispersion curves of type I with one of the neutral modes always at zero wave number. The role of the energy equation

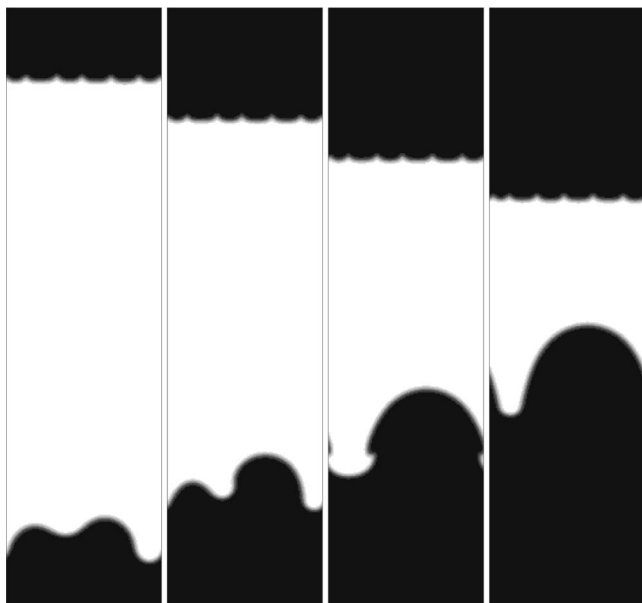


FIG. 2. Numerical nonlinear dynamics of buoyantly unstable exothermic CT fronts shown at four successive times (from left to right). The parameters are $Da=0.001$, $\kappa=1$, $Le=6$, $\gamma_T'=-2$. The up going front features thermal plumes and coarsening typical of type-II dispersion curves. The down going front develops stationary norm fingers of constant amplitude and wavelength characteristic of type-I dispersion curves. Their small amplitude results from small growth rates for these values of parameters.

in this case is not to introduce a new mode of instability but to alter the isothermal mode. Variation of one of the parameters Le or γ_T' , keeping the other one constant can lead from stable fronts, to type-I and finally type-II instabilities. This is true even if $Le=1$ which shows that no double diffusion [15] is involved here and that the dynamics results rather from a complex interplay between solutal and thermal effects through the kinetic term $f(\alpha)$ and the buoyancy term $\gamma_T T - \alpha$ (the chemistry increases T which then decreases ρ). The effect of γ_T' is shown in Fig. 1 where we see that when solutal and thermal effects are of the same order, both up going and down going fronts can be unstable but with different wavelengths and growth rates. This is evident from Fig. 2 which depicts the long-time nonlinear dynamics when two counterpropagating fronts are initiated at the top and bottom of the system, respectively. Type-I dispersion curves do not necessarily imply saturation of the instability [13]. However, our nonlinear simulations show that indeed this is the case: after a transient which depends on the noise added on the initial planar front and during which the amplitude of the fingers grows, the down going pattern saturates to a stationary norm cellular front with an amplitude and wavelength constant in time. This amplitude results from the nonlinear balance between convection, reaction, and diffusion and is independent of the initial condition. The constant wavelength is that of the most unstable mode, i.e., $\lambda = 2\pi/k_{max}$.

Motivated by these theoretical predictions, such differences between up and down going fronts and, in particular, the new type-I dispersion curve for down going front have been subsequently evidenced experimentally. The reactants

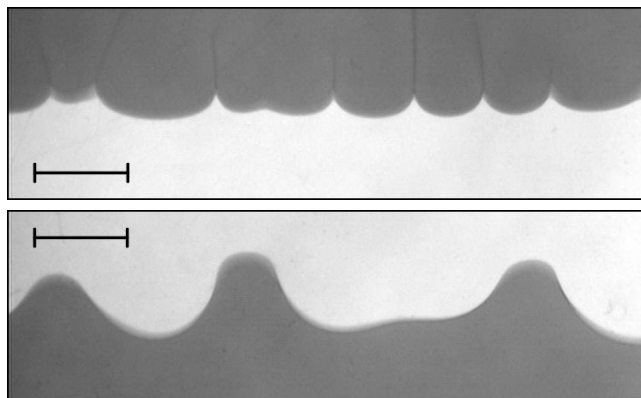


FIG. 3. Experimental fronts propagating downwards at $t=36$ s (top) and upwards at $t=55$ s (bottom). Darker regions represent the product solution. The bars are 5 mm long. The solution was prepared at a temperature of (25 ± 1) °C with reagent-grade materials of composition: $[K_2S_4O_6]=7.5$ mM, $[NaClO_2]=30$ mM, $[NaOH]=2$ mM, and Congored indicator in 0.4 mg cm^{-3} concentration.

of the exothermic CT reaction [11] are contained in a vertical Hele-Shaw cell of $(16 \times 12 \times 0.2)$ cm^3 consisting of 8-mm-thick Plexiglass wall. Planar fronts are initiated electrochemically by applying a 3 V potential difference between a pair of thin Pt-wire electrodes (0.4 mm in diameter) positioned either at the top or the bottom of the cell for 2–3 s. The front evolution is monitored through a broadband filter ($\lambda=509$ nm) [18] by a monochrome charge-coupled device camera and digitized in 0.2 s intervals. To determine the dispersion curve, a one-dimensional Fourier transform is applied on the front profiles with a Hann window. The growth rates are calculated for all Fourier modes from the slopes of the linear initial time evolution of the logarithm of the Fourier amplitudes.

We use higher concentrations of reactants and thicker cells than in previous isothermal experiments [11] to enhance thermal effects by decreasing the contribution of heat loss to the walls on the time scale of the experiments (a few minutes). This has two main effects (Fig. 3): (i) the upward propagating fronts become unstable; (ii) the downward propagating fronts, which develop regular cellular structures with an initial wavelength of the order of 3–4 mm, are characterized by a different type of dispersion curve (Fig. 4). The long wavelength modes, which become unstable for the upward propagating fronts, are now stable for downward propagating fronts. For the values of parameters of Fig. 3, the upward propagating front evolves, with a speed slightly smaller than the downward one, towards a structure with highly curved tips and larger wave length, suggesting that—for upward fronts—the temperature destabilizes smaller wave numbers with smaller growth rates than for the downward fronts.

The stabilization by heat of the down going front leads to a new neutral wave number close to the origin below which the modes are stable. To compare quantitatively experimental and theoretical growth rates, we note in Fig. 1 that, for down going fronts, $k_{max} \sim 0.08$ roughly independently of ϕ . For a net $\Delta\rho = \Delta\rho_S + \Delta\rho_T = -1.4 \times 10^{-4}$, $D_\alpha = 1.2 \times 10^{-4}$ $cm^2 s^{-1}$, and fluid parameters of water, the di-

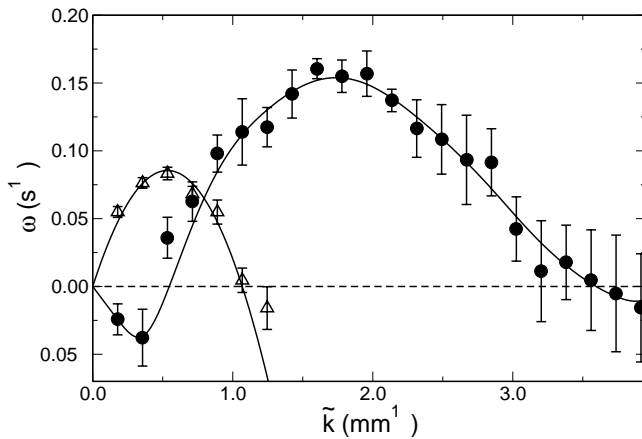


FIG. 4. Experimental dispersion curves for the dimensional growth rate ω vs dimensional wave number \tilde{k} for upward (Δ) and downward (\circ) propagating fronts. The results are the average of eight experiments. The solid lines are drawn to guide the eye.

mensional $\tilde{k}_{max} = 3 \text{ mm}^{-1}$, the correct order of magnitude of dimensional experimental values (Fig. 4). Further experimental studies on the effect of concentration changes as well as characterization of the nonlinear dynamics of the fingers are currently under way.

To summarize, we have provided the evidence of different type of fingering phenomena resulting from the coupling between solutal and thermal buoyancy-driven instability of chemical CT fronts. The dispersion curves characterizing these fingers are of type I for certain values of the parameters. The nonlinear dynamics of the unstable down going front saturates to fingers of constant amplitude and wavelength which should also be observed in other exothermic autocatalytic reaction-diffusion fronts [6–8,15]. The fact that these important properties of fingers do not vary in time should allow the use of tools from nonlinear dynamics to characterize them. Finally, notice that our analysis is based on two-dimensional (2D) Darcy's law, a good description for flows in Hele-Shaw cells with small gapwidths [2,7–9], and on a one variable model for the CT reaction [10]. This demonstrates that the new dynamics described here results solely from the coupling between solutal and thermal density changes and not from a 3D flow along the gap or from differential molecular diffusion. Further work on the influence of such effects might be of interest in the future.

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