

# Density profiles around $A+B \rightarrow C$ reaction-diffusion fronts in partially miscible systems: A general classification

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Various spatial density profiles can develop in partially miscible stratifications, when a phase A dissolves with a finite solubility into a host phase containing a dissolved reactant B. We investigate theoretically the impact of an  $A+B \rightarrow C$  reaction on such density profiles in the host phase and classify them in a parameter space spanned by the ratios of relative contributions to density and diffusion coefficients of the chemical species. While the density profile is either monotonically increasing or decreasing in the non reactive case, reactions combined with differential diffusivity can create eight different types of density profiles featuring up to two extrema in density, at the reaction front or below it. We use this framework to predict various possible hydrodynamic instability scenarios inducing buoyancy-driven convection around such reaction fronts when they propagate parallel to the gravity field.

## I. INTRODUCTION

The study of partially miscible stratifications has recently gained interest due to its relevance for ground-water management [1, 2], enhanced oil recovery [3–5] or carbon dioxide ( $\text{CO}_2$ ) sequestration [5–14]. Such stratifications are typically composed of a reservoir phase A dissolving with a finite solubility into a host phase, containing chemicals that may react with A. The dissolution of A is limited by its solubility in the host phase, where most of the dynamics occurs [12–18]. Upon dissolution and reaction, various concentration profiles can develop and thereby affect the physical properties of the host phase.

In particular, dynamic changes in concentrations can induce spatio-temporal variations of the density of the solution which, in turn, can generate hydrodynamic buoyancy-driven instabilities [19]. As an example, Rayleigh-Taylor convection can develop whenever locally a denser zone overlies a less dense one in the gravity field [20] or gravity currents can also be observed because of horizontal density gradients [21, 22]. In the case of partially miscible interfaces, so-called “dissolution-driven” convection can also develop when the transfer of one phase to the other one locally changes the density of the host solution upon dissolution [23, 24]. This is for instance the case during dissolution from above of less dense  $\text{CO}_2$  into brine [12–18], or upon dissolution from below of methanol into cyclohexane [25].

We thus see that changes of density gradients by reaction-diffusion processes during dissolution in partially miscible systems can be the source of convective motions affecting mixing and the transfer from one phase to the other. Classifying the possible density profiles developing around  $A+B \rightarrow C$  reaction-diffusion fronts in such partially miscible systems is therefore crucial to understanding the onset of possible buoyancy-driven instabilities. It also helps to predict the spatial zones in which

convection can be localized in cases of non-monotonic density profiles i.e. spatial profiles featuring local extrema [26–29].

Density profiles have already been classified in the case of a miscible interface between two solutions containing solutes A and B. In the non reactive case, six different density profiles can develop depending on the relative contribution of A and B to density and their ratio of diffusion coefficients [30]. In the reactive case where an  $A+B \rightarrow C$  reaction takes place, six different profiles are also possible if all species diffuse at the same rate [31, 32]. On the contrary, if differential diffusion is taken into account, the number of possible density profiles increases up to 62 in the miscible case [33].

For partially miscible stratifications, the possible density profiles have been classified in the case where all species diffuse at the same rate [15, 16]: without reaction, only two density profiles can build up, monotonically increasing or decreasing [16]. The number of possible density profiles increases up to four when a reaction  $A+B \rightarrow C$  takes place in the host phase [15, 16]. If the non reactive profile can be buoyantly unstable, i.e. the density of the solution increases upon dissolution, a minimum of density is formed when C contributes less to density than B, which slows down the growth of buoyancy-driven fingering [15–17]. If C is sufficiently denser than B, the density profile remains monotonic and the reaction can accelerate the development of the instability [15, 16]. Chemistry can even be at the origin of the instability by creating a maximum of density when the dissolving species decreases or does not modify density [16, 34–38]. Similarly to what has been done in miscible stratifications [33], a classification of the possible density profiles is now needed for partially miscible systems in the more general case where species can diffuse at different rates.

In this context, we analyze here theoretically the reaction-diffusion (RD) density profiles building up in a partially miscible system when a species A dissolves into a host solution of B and an  $A+B \rightarrow C$  reaction takes

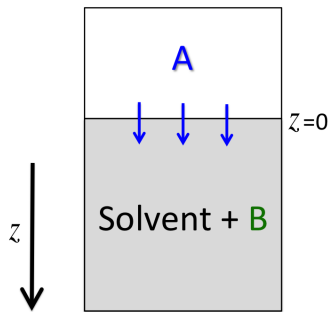


FIG. 1: Schematic of a two-layer partially miscible stratification, where the reservoir phase A dissolves with a finite solubility into the host phase (shaded) containing a dissolved reactant B.

place in the host phase. We classify these profiles in a parameter space spanned by the diffusivity and solutal expansion coefficient ratios. To do so, we derive asymptotic concentration profiles from the classical RD equations. By reconstructing the density profiles in the host solution, we show that eight different types of RD density profiles can be observed, with either zero, one or two extrema at the reaction front or below. Each type of RD density profile will lead to a different scenario for the development of buoyancy-driven convection. The classification developed here can be used as a framework to unify previous results as well as predict potential dynamics in unexplored parameter zones.

This work is structured as follows. The model and the equations are presented in Section II. We compute the asymptotic concentration profiles in Section III and construct the related RD density profiles both above and below the reaction front in Section IV. Section V gives more details about the extrema of density below the reaction front. The global density profiles are described in section VI and compared to their counterparts in miscible stratifications in Section VII. Finally, we conclude this study in Section VIII.

## II. MODEL

Let us consider an isothermal partially miscible system in which a reservoir phase A is placed in contact with a host phase along a planar interface located at  $z = 0$  with  $z$  pointing into the host phase (Fig. 1). Although this study is valid for any orientation of the  $z$  axis with regard to gravity, Fig. 1 illustrates the special case where the interface is at the top of the host phase, which is for instance the case in the convective dissolution of  $\text{CO}_2$  into brine during  $\text{CO}_2$  sequestration [6, 7, 12–14]. The host phase contains a dissolved reactant B in initial concentration  $B_0$ . Phase A dissolves in the course of time into the host phase, and reacts with B according to the  $A+B \rightarrow C$  scheme. This bimolecular reaction is considered to occur as an elementary step so that its rate is

given by  $qAB$ , with  $q$  the kinetic constant, and  $A, B$  the concentrations of species A and B, respectively.

In order to model the dynamics in the host phase, we make the following assumptions. At the interface, the concentration of A is equal to its solubility  $A_0$  in the host phase (local chemical equilibrium). This value is not limited by the concentration of A in the reservoir phase and does not evolve over time. Moreover, we suppose that  $A_0$  does not depend on the concentrations of B or C. This approximation is valid as long as the initial concentration  $B_0$  of the solute B in solution is small enough [14]. No mass transfer takes place from the host phase to the reservoir phase A.

The RD equations governing the evolution of the concentration profiles  $A, B, C$  in the host phase write

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial z^2} - qAB, \quad (1a)$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial z^2} - qAB, \quad (1b)$$

$$\frac{\partial C}{\partial t} = D_C \frac{\partial^2 C}{\partial z^2} + qAB, \quad (1c)$$

where the molecular diffusion coefficients  $D_i$  are assumed constant for each species  $i = A, B, C$ .

To describe the convective dynamics in the host phase, Eqs. (1) can be coupled to an equation for the velocity of the fluid. We explicitly do not detail the flow equation here as we aim to classify the density profiles before the onset of convection, i.e. when there is still no fluid flow. In this limit, the profiles governed by reaction and diffusion processes depend on the  $z$  direction only. Our approach is thus generic, in other words valid for any flow equation, e.g. Darcy's law in porous media and Hele-Shaw cells, Stokes or Navier-Stokes equations in other cases [20]. The buoyancy term  $\rho \mathbf{g}$  typically appears in such a flow equation, where  $\mathbf{g}$  is the gravity field and  $\rho$  is the density of the solution depending on the concentrations. In a diluted solution, this dependence is assumed to be linear [9] as

$$\rho = \rho_0(1 + \alpha_A A + \alpha_B B + \alpha_C C) \quad (2)$$

where  $\rho_0$  is the density of the solvent of the host phase and  $\alpha_i = \frac{1}{\rho_0} \frac{\partial \rho}{\partial i}$  is the solutal expansion coefficient of species  $i$ .

To solve Eqs. (1), we use the initial conditions

$$A = A_0 \text{ for } z = 0, \quad A = 0 \text{ for } z > 0, \quad (3a)$$

$$B = B_0, \quad C = 0 \quad \forall z, \quad (3b)$$

and the boundary conditions

$$A = A_0, \quad \frac{\partial B}{\partial z} = 0, \quad \frac{\partial C}{\partial z} = 0 \text{ for } z = 0, \quad (4a)$$

$$A \rightarrow 0, \quad B \rightarrow B_0, \quad C \rightarrow 0 \text{ for } z \rightarrow \infty. \quad (4b)$$

We nondimensionalize Eqs. (1) by introducing the dimensionless time  $\hat{t} = t/t_c$ , space coordinate  $\hat{z} = z/l_c$ ,

concentrations  $[\tilde{A}, \tilde{B}, \tilde{C}] = [A, B, C]/A_0$ , and density  $\tilde{\rho} = (\rho - \rho_0)/\rho_c$ , with  $t_c = 1/(qA_0)$  and  $l_c = \sqrt{D_A t_c}$  the characteristic RD time and length scales [15, 16, 31, 32], and  $\rho_c$  a characteristic density whose expression depends on the flow equation. For example, if Darcy's law is used,  $\rho_c = \mu D_A / (\kappa l_c g)$ , with  $\mu$  the viscosity of the solvent,  $\kappa$  the permeability of the porous medium and  $g$  the norm of the gravity field.

Substituting these dimensionless variables into Eqs. (1)-(2) and dropping tildes for convenience leads to the dimensionless equations:

$$\frac{\partial A}{\partial t} = \frac{\partial^2 A}{\partial z^2} - AB, \quad (5a)$$

$$\frac{\partial B}{\partial t} = \delta_B \frac{\partial^2 A}{\partial z^2} - AB, \quad (5b)$$

$$\frac{\partial C}{\partial t} = \delta_C \frac{\partial^2 A}{\partial z^2} + AB, \quad (5c)$$

$$\rho = R_A A + R_B B + R_C C. \quad (5d)$$

$\delta_i = D_i/D_A$  is the ratio of diffusion coefficient of species  $i$  with that of the dissolving species A. The Rayleigh number  $R_i = \alpha_i A_0 \rho_0 / \rho_c$  of species  $i$  quantifies the relative contribution of  $i$  to density.  $R_i$  can be positive, zero or negative, depending on whether species  $i$  increases ( $\alpha_i \geq 0$ ), does not modify ( $\alpha_i = 0$ ) or decreases ( $\alpha_i \leq 0$ ) the density of the solution.

The initial conditions (3) are nondimensionalized as:

$$A = 1 \text{ for } z = 0, \quad A = 0 \text{ for } z > 0, \quad (6a)$$

$$B = \beta, \quad C = 0 \quad \forall z, \quad (6b)$$

where  $\beta = B_0/A_0$  is the ratio of the initial concentration of B and the solubility of A in the host phase. Similarly, boundary conditions (4) become

$$A = 1, \quad \frac{\partial B}{\partial z} = 0, \quad \frac{\partial C}{\partial z} = 0 \text{ for } z = 0, \quad (7a)$$

$$A \rightarrow 0, \quad B \rightarrow \beta, \quad C \rightarrow 0 \text{ for } z \rightarrow \infty. \quad (7b)$$

The dynamics in this reactive partially miscible stratification depends thus on six dimensionless parameters: the diffusivity ratios  $\delta_B$  and  $\delta_C$ , the Rayleigh numbers  $R_A$ ,  $R_B$  and  $R_C$ , and the ratio  $\beta$  of the initial concentration of B and solubility of A.

### III. REACTION-DIFFUSION CONCENTRATION PROFILES

To understand the dynamics in the host phase and reconstruct the density profiles therein, we compute the RD concentration profiles solutions of Eqs. (5a)-(5c) with the initial (6) and boundary (7) conditions specific to the partially miscible case, and compare them to their non reactive counterpart.

#### A. Non reactive case ( $\beta = 0$ )

We first recall the dynamics in the non reactive case upon dissolution of A into the host phase [12–14]. The only species present in solution is A, and its diffusive concentration profile is a solution of Fick's law  $\frac{\partial A}{\partial t} = \frac{\partial^2 A}{\partial z^2}$  with initial conditions (6) and boundary conditions (7) where  $B = 0$  and  $C = 0$ . We introduce the self-similar variable  $\eta = z/(2\sqrt{t})$  and thus solve  $A'' + 2\eta A' = 0$ , with the notation  $A' = \frac{dA}{d\eta}$  and  $A'' = \frac{d^2 A}{d\eta^2}$ . The solution, illustrated in Fig. 2a, is

$$A = 1 - \text{erf}(\eta), \quad (8)$$

where  $\text{erf}(\eta)$  is the error function. Species A dissolves from the boundary  $\eta = 0$  and spreads towards the bulk of the host solution. The flux  $J_{NR}$  of A dissolving through the interface into the host phase is evaluated as  $J_{NR} = -\frac{\partial A}{\partial z} \Big|_{z=0}$  and reads

$$J_{NR} = \frac{1}{\sqrt{\pi t}}, \quad (9)$$

where ‘‘NR’’ stands for ‘‘non reactive’’. This flux decreases in time as diffusion smoothes the concentration gradient.

#### B. Reactive case ( $\beta \neq 0$ )

In the reactive case, all three species A, B and C contribute to the density of the host phase. The dimensionless density (5d) therefore evolves in space and time depending on the dynamic changes of the concentration profiles  $A$ ,  $B$  and  $C$ .

##### 1. Asymptotic solutions

An analytical solution of Eqs. (5a)-(5c) can be obtained by assuming that the reaction takes place only at a reaction front that moves on a diffusive time scale. The position of the reaction front is defined as  $z_f = 2\eta_f \sqrt{t}$  where  $\eta_f > 0$  is a constant [39–42]. This assumption is valid in the asymptotic regime when the reaction is limited by the diffusive transport of A and B towards each other, i.e. for sufficiently large times compared to the characteristic chemical reaction time ( $t \gg 1$ ). In this limit, species A and B are immediately and entirely consumed at the reaction front. Outside the reaction front, no reaction takes place and the concentration fields  $j$  are solutions of the diffusive equations  $\delta_j j'' + 2\eta j' = 0$  with the following boundary conditions

$$\eta = 0: \quad A = 1, \quad B' = 0, \quad C' = 0, \quad (10a)$$

$$\eta = \eta_f: \quad A = 0, \quad B = 0, \quad C = \gamma, \quad (10b)$$

$$\eta \rightarrow \infty: \quad A = 0, \quad B = \beta, \quad C = 0, \quad (10c)$$

where  $\gamma$  is the maximum concentration possible for C, which will be computed below (Eq.(13b)). The asymptotic concentration fields in the region above the reaction front  $0 \leq \eta \leq \eta_f$  denoted by “U” (short for “Upper”) are

$$A_U = 1 - \frac{\text{erf}(\eta)}{\text{erf}(\eta_f)}, \quad (11a)$$

$$B_U = 0, \quad (11b)$$

$$C_U = \gamma. \quad (11c)$$

The asymptotic concentration fields in the region below the reaction front  $\eta \geq \eta_f$  denoted by “L” (short for “Lower”) are

$$A_L = 0, \quad (12a)$$

$$B_L = \beta \left( 1 - \frac{\text{erfc}(\eta/\sqrt{\delta_B})}{\text{erfc}(\eta_f/\sqrt{\delta_B})} \right), \quad (12b)$$

$$C_L = \gamma \frac{\text{erfc}(\eta/\sqrt{\delta_C})}{\text{erfc}(\eta_f/\sqrt{\delta_C})}, \quad (12c)$$

where  $\text{erfc}(\eta) = 1 - \text{erf}(\eta)$  is the complementary error function.

## 2. Concentration profiles

Let us analyze the shape of the concentration profiles (11)-(12), shown in Figs. 2 for different values of parameters  $\beta$ ,  $\delta_B$ ,  $\delta_C$ .

$A_U$  is like an error function, decreasing monotonically from the interface like the non reactive concentration profile (8). The consumption of A by the reaction is reflected by the denominator  $\text{erf}(\eta_f) \leq 1$  in (11a): at the same coordinate  $\eta$ ,  $A_U$  is smaller than its non reactive counterpart (Fig. 2a). This difference grows when  $\beta$  or  $\delta_B$  increase (Figs. 2b-2c), due to a larger flux of reactant B towards the reaction front.

Below the reaction front,  $B_L$  given by (12b) increases from 0 at the front towards its initial value  $\beta$  in the bulk of the solution (Fig. 2b). This profile becomes sharper when  $\delta_B$  decreases (Fig. 2c) as then weaker diffusion acts less efficiently at smoothing the concentration gradient. Neither  $A$  nor  $B$  depend on  $\delta_C$  (Fig. 2d). The concentration profiles  $A$  and  $B$  are monotonic, like their counterparts in miscible systems.

The product C accumulates in the zone  $0 \leq \eta \leq \eta_f$  between the interface and the reaction front and its concentration decreases monotonically beyond  $\eta > \eta_f$ . The amount of C produced increases with  $\beta$  and  $\delta_B$  following a larger consumption of A (Figs. 2b-2c). Increasing  $\delta_C$  does not affect the total amount of C produced but smoothes its concentration profile because of faster diffusion (Fig. 2d).

## 3. Position of the reaction front and maximum concentration of C

We now examine  $\eta_f$ , the position of the reaction front in self-similar coordinates, and  $\gamma$ , the maximum dimensionless concentration of product C.

To compute  $\eta_f$  and  $\gamma$ , we invoke the fact that the reaction is diffusion-limited. According to the stoichiometry of the reaction, the fluxes must be equal at the reaction front, i.e.  $A'_U|_{\eta_f} = -\delta_B B'_L|_{\eta_f} = \delta_C C'_L|_{\eta_f}$ , which after rearrangement gives

$$\text{erfc}(\eta_f/\sqrt{\delta_B}) = \beta \sqrt{\delta_B} \text{erf}(\eta_f) \exp \left[ -\eta_f^2 \left( \frac{1}{\delta_B} - 1 \right) \right], \quad (13a)$$

$$\gamma = \frac{\text{erfc}(\eta_f/\sqrt{\delta_C})}{\sqrt{\delta_C} \text{erf}(\eta_f)} \exp \left[ \eta_f^2 \left( \frac{1}{\delta_C} - 1 \right) \right]. \quad (13b)$$

We use a Newton-Raphson iterative method [43] to obtain  $\eta_f$  as a function of  $\delta_B$  and  $\beta$  from the implicit Eq. (13a). Once  $\eta_f$  is known,  $\gamma$  can be explicitly computed as a function of  $\delta_C$  and  $\eta_f$  using Eq. (13b).

Let us analyze how  $\eta_f$  and  $\gamma$  depend on the parameters  $\beta$ ,  $\delta_B$  and  $\delta_C$ .

In the case of contact between miscible solutions of A and B,  $\eta_f$  can be of either sign, i.e. the reaction front can move in either direction with regard to its initial position or stay immobile, depending on the diffusivity and initial concentration ratios [31, 32, 39–42]. Here, A progressively invades the host solution from the interface where it dissolves. Therefore the reaction front always moves in the same direction towards positive  $\eta$  ( $\eta_f > 0$ ).

The value of  $\eta_f$  depends on  $\beta$  and  $\delta_B$ , and determines the rate the front moves forward. When  $\delta_B = 1$ , the dependence of  $\eta_f$  on  $\beta$  is given by  $\text{erf}(\eta_f) = \frac{1}{\beta+1}$  [16]. More generally,  $\eta_f$  decreases, i.e. the motion of the reaction front slows down, when  $\beta$  or  $\delta_B$  increases (Figs. 2b-2c and 3). Note that for small  $\eta_f$  and short time, the reaction front can be assumed to be at the interface, so that only the lower concentration profiles are considered [44, 45]. Increasing  $\beta$  or  $\delta_B$  amplifies the flux of fresh reactant B towards the reaction zone. This enhances the consumption of the dissolving species A, slowing down its invasion of the host phase and increasing the amount of C produced (Figs. 2b-2c and 4a).

$\gamma$  increases thus when  $\beta$  and  $\delta_B$  increase. In particular when  $\delta_B = \delta_C$ ,  $\gamma$  is equal to  $\beta$  [15, 16]. In addition,  $\gamma$  decreases when  $\delta_C$  increases (Figs. 2d and 4b) because then the product diffuses faster away from its production zone.

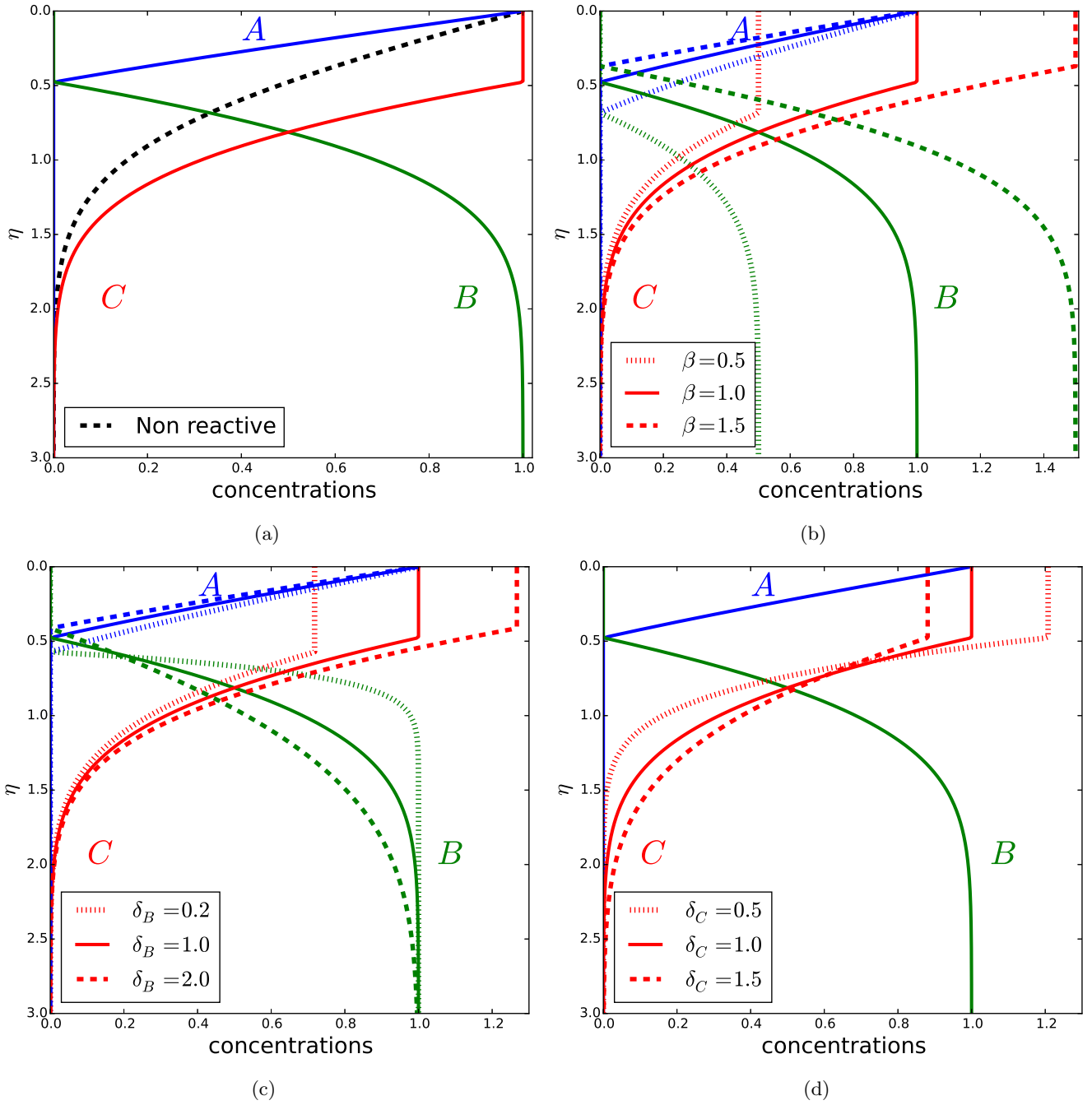


FIG. 2: (Color online) Asymptotic concentration profiles (11)-(12) of A, B and C for (a)  $\delta_B = \delta_C = 1$ ,  $\beta = 1$  compared to the non reactive profile (8) of A (dashed black), (b)  $\delta_B = \delta_C = 1$  and different  $\beta$ , (c)  $\beta = 1$ ,  $\delta_C = 1$  and different  $\delta_B$ , (d)  $\beta = 1$ ,  $\delta_B = 1$  and different  $\delta_C$ .

#### 4. Flux of A through the interface

The reactive flux  $J = -\frac{\partial A_V}{\partial z}\bigg|_{z=0}$  of A through the interface is evaluated as

$$J = \frac{1}{\text{erf}(\eta_f) \sqrt{\pi t}} = \frac{J_{NR}}{\text{erf}(\eta_f)}, \quad (14)$$

which shows that the flux decreases with time. As  $\text{erf}(\eta_f) \leq 1$ , the reactive flux is always larger than its non reactive counterpart (9). The difference between the reactive and non reactive cases increases with  $\beta$  and  $\delta_B$ , as shown in Figs. 5. When the host solution is more concentrated in B and when this species diffuses faster, the consumption of A by the reaction is indeed amplified, which accelerates the transfer of A towards the host

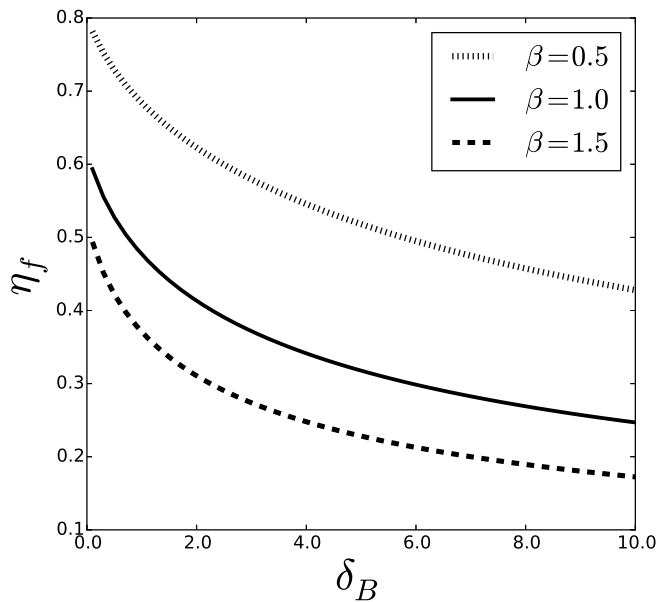


FIG. 3: The position  $\eta_f$  of the reaction front with regard to the interface at  $\eta_f = 0$ , computed with Eq. (13a), decreases when  $\delta_B$  or  $\beta$  increases.

solution.

#### IV. CLASSIFICATION OF THE REACTION-DIFFUSION DENSITY PROFILES

As the presence of extrema in the density profile  $\rho$  is known to affect the convective stability of the system [15, 16, 31, 32], we search for the region in the parameter space where  $\rho$  is non monotonic, i.e. for which its derivative  $\rho'$  changes sign at a given location  $\eta_m$ .

##### A. Non reactive case ( $\beta = 0$ )

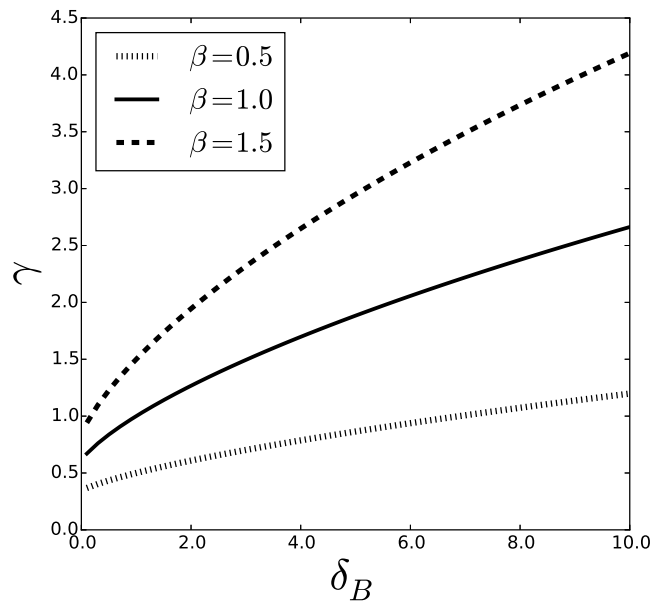
We first consider the density profile in the non reactive case, where  $\rho$  depends only on the concentration profile (8) of species A as [15, 16]

$$\rho = R_A A = R_A [1 - \text{erf}(\eta)]. \quad (15)$$

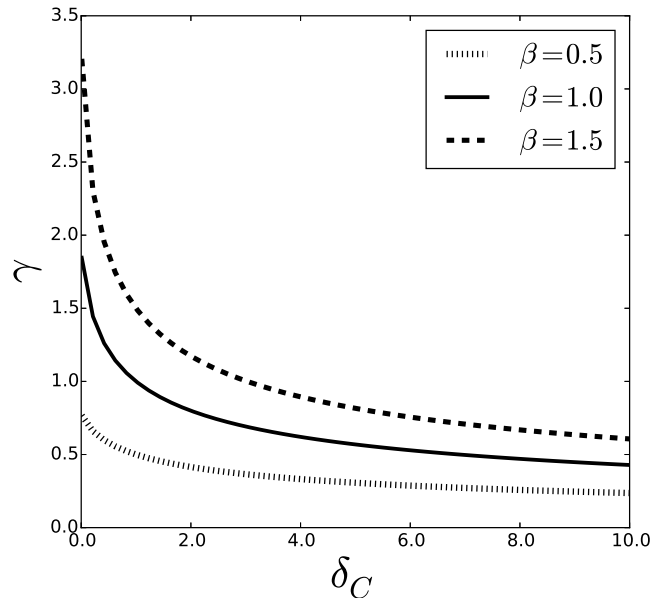
The derivative  $\rho'$  is given by

$$\rho' = R_A A' = -\frac{2}{\sqrt{\pi}} R_A e^{-\eta^2}. \quad (16)$$

The sign of  $\rho'$ , depending on  $R_A$  only, is constant over its domain.  $\rho$  is thus monotonic increasing along  $z$  when  $R_A > 0$ , decreasing along  $z$  when  $R_A < 0$  and constant when  $R_A = 0$ .



(a)



(b)

FIG. 4: The maximum product concentration  $\gamma$  given by (13b) is amplified when  $\beta$  increases or (a)  $\delta_B$  increases ( $\delta_C = 1$ ), or (b)  $\delta_C$  decreases ( $\delta_B = 1$ ).

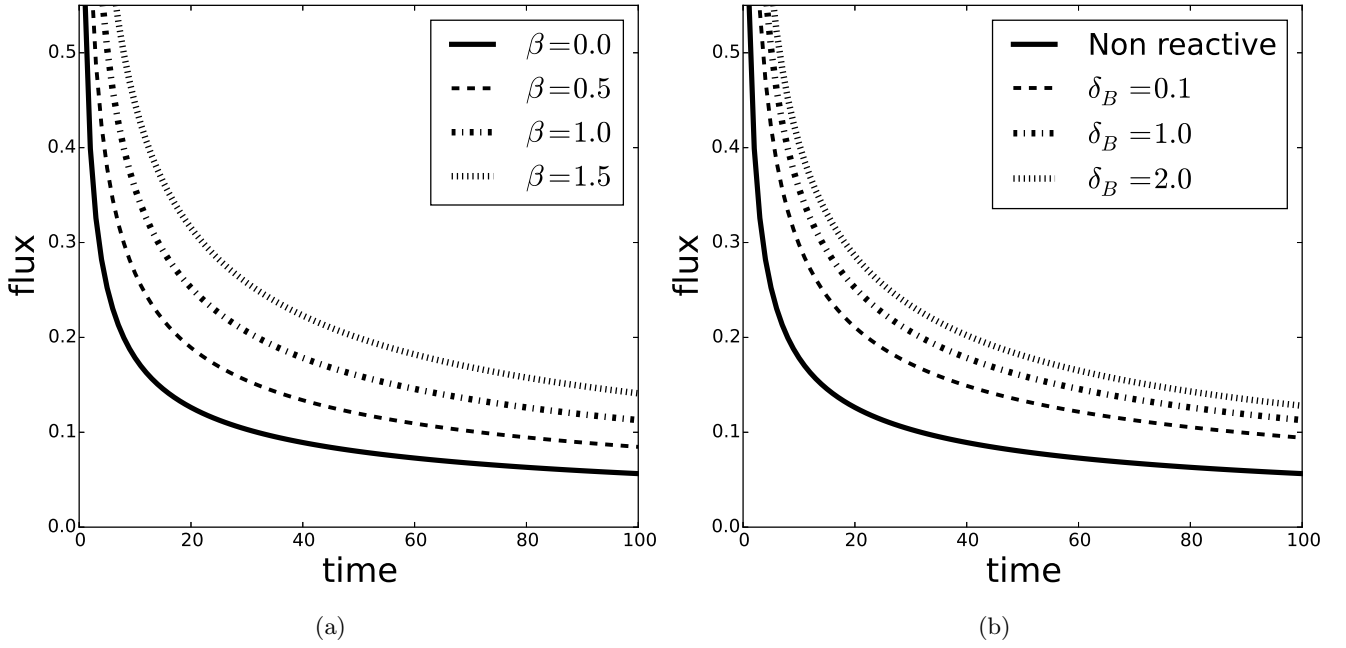


FIG. 5: The flux (14) of A through the interface decreases with time, and at a given time increases with (a)  $\beta$  ( $\delta_B = 1$ ) and (b)  $\delta_B$  ( $\beta = 1$ ). The full curve represents the flux in the non reactive case (9).

### B. Reactive case ( $\beta \neq 0$ )

The asymptotic RD density profiles computed by inserting solutions (11)-(12) into Eq. (5d) are

$$\rho_U = R_A \left( 1 - \frac{\text{erf}(\eta)}{\text{erf}(\eta_f)} \right) + R_C \gamma, \quad (17a)$$

$$\rho_L = R_B \beta \left( 1 - \frac{\text{erfc}(\eta/\sqrt{\delta_B})}{\text{erfc}(\eta_f/\sqrt{\delta_B})} \right) + R_C \gamma \frac{\text{erfc}(\eta/\sqrt{\delta_C})}{\text{erfc}(\eta_f/\sqrt{\delta_C})}. \quad (17b)$$

Equations (17) show that in the bulk solution ( $\eta \rightarrow \infty$ ), where B is the only species contributing to the density,  $\rho$  tends to its initial value  $R_B \beta$ . At the reaction front  $\eta_f$  where A and B are entirely consumed by the reaction and C is the only species present at concentration  $\gamma$ , the density is given by  $\rho = R_C \gamma$ . At the interface A and C are present in amount  $A = 1$  and  $C = \gamma$  and the density is equal to  $R_A + R_C \gamma$ .

We now analyze the density profiles above and below the reaction front separately.

#### 1. Above the reaction front ( $0 \leq \eta \leq \eta_f$ )

Above the reaction front, the reactant B is not present because it has been consumed by the reaction. Only A and C contribute to the density profile. The derivative

$\rho'_U$  is written as

$$\rho'_U = R_A A'_U = -\frac{2}{\sqrt{\pi}} \frac{R_A}{\text{erf}(\eta_f)} e^{-\eta^2}. \quad (18)$$

Similarly to its non reactive counterpart (see subsection IV A),  $\rho_U$  is a monotonic function with two possibilities: if A decreases or does not change the density of the solution ( $R_A \leq 0$ ),  $\rho$  increases or remains constant from the interface towards the reaction front ( $\rho'_U \geq 0$ , zone II<sub>U</sub> in Fig. 6). In the other case ( $R_A > 0$ ), the density decreases from the interface towards the reaction front ( $\rho'_U < 0$ , zone I<sub>U</sub> in Fig. 6). Note that in this study, “II” will always correspond to monotonic increasing and “I” to monotonic decreasing profiles. This classification does not depend on the magnitude of  $R_A$  but only on its sign.

#### 2. Below the reaction front ( $\eta \geq \eta_f$ )

Below the reaction front, two species contribute to the density profile: the dissolved reactant B and the product C, so that  $\rho'_L$  reads

$$\begin{aligned} \rho'_L &= R_B B'_L + R_C C'_L \\ &= \frac{2}{\sqrt{\pi}} \left( R_B \frac{\beta e^{-\frac{\eta^2}{\delta_B}}}{\text{erfc}(\eta_f/\sqrt{\delta_B})\sqrt{\delta_B}} - R_C \frac{\gamma e^{-\frac{\eta^2}{\delta_C}}}{\text{erfc}(\eta_f/\sqrt{\delta_C})\sqrt{\delta_C}} \right). \end{aligned} \quad (19)$$

Therefore, the balance between both contributions  $R_B B'_L$  and  $R_C C'_L$  to the slope of the density profile determines whether  $\rho_L$  has an extremum or not.

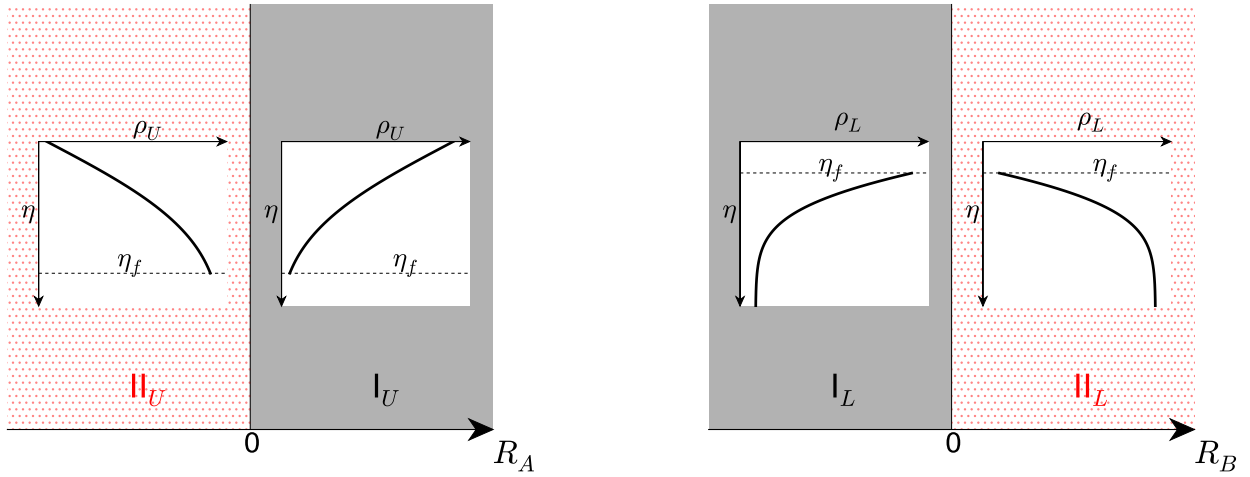


FIG. 6: Classification of the density profiles  $\rho_U$  above the reaction front ( $0 \leq \eta \leq \eta_f$ ): monotonic increasing in zone  $\text{II}_U$  (dot-hatched), constant on the boundary  $R_A = 0$ , and monotonic decreasing in zone  $\text{I}_U$  (shaded). The dashed line in the plots  $\rho_U(\eta)$  indicates the position  $\eta_f$  of the reaction front.

Let us first mention a few trivial cases before moving to the more complex case where both species B and C increase the density of the solution.

When C does not contribute to the density of the solution ( $R_C = 0$ , Fig. 7a), the density profile trivially follows the B profile and  $\rho'_L = R_B B'_L$ . As B increases from zero at the reaction front to its bulk value  $\beta$  ( $B'_L > 0$ , Figs. 2),  $\rho_L$  increases along  $z$  when B increases the density of the solution ( $R_B > 0$ , zone  $\text{II}_L$ ). Conversely, when B decreases the density ( $R_B < 0$ , zone  $\text{I}_L$ ),  $\rho_L$  decreases along  $z$  ( $\rho'_L < 0$ ), and when neither B nor C contributes to the density (boundary  $R_B = 0$  in Fig. 7a),  $\rho_L$  is a constant ( $\rho'_L = 0$ ).

Similarly, when  $R_B = 0$ , the density profile follows the C profile, with C decreasing from  $\gamma$  at the reaction front to zero in the bulk ( $C'_L < 0$ , Figs. 2).  $\rho_L$  decreases thus towards the bulk when C increases the density of the solution ( $R_C > 0$ , in zone  $\text{I}_L$  of Fig. 7b), and vice versa (not shown here).

Finally, the trivial case when  $R_B$  and  $R_C$  are of opposite sign can be understood as follows. As  $B'_L > 0$  and  $C'_L < 0$ , the density gradients  $R_B B'_L$  and  $R_C C'_L$  are of the same sign and the density profile is monotonic (Eq. (19)). More specifically, the density profile decreases along  $z$  when C increases the density and B decreases it ( $R_C > 0$  and  $R_B < 0$ , in zone  $\text{I}_L$  of Fig. 7b) and vice versa (not shown here).

Let us now restrict our analysis to cases where B and C increase the density of the solution ( $R_B$  and  $R_C$  positive) without loss of generality. The sign of  $\rho'_L$  can straightforwardly be deduced when  $R_B$  and  $R_C$  are negative with the relation  $\rho'_L(-R_B, -R_C) = -\rho'_L(R_B, R_C)$  derived from Eq. (19).

The case  $\delta_B = \delta_C$  has already been analyzed [15, 16].

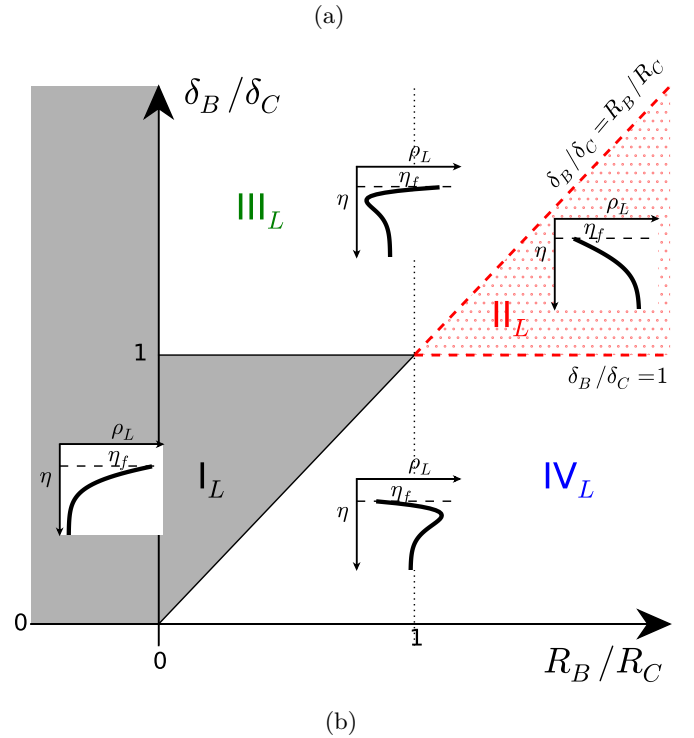


FIG. 7: Classification of the density profiles  $\rho_L$  below the reaction front ( $\eta \geq \eta_f$ ) for (a)  $R_C = 0$  and (b)  $R_C > 0$ : monotonic decreasing in zone  $\text{I}_L$  (shaded), monotonic increasing in zone  $\text{II}_L$  (dot-hatched), with a minimum in zone  $\text{III}_L$ , with a maximum in zone  $\text{IV}_L$ , and constant for  $R_B = R_C = 0$  or  $R_B/R_C = \delta_B/\delta_C = 1$ . The dashed line in the plots  $\rho_L(\eta)$  indicates the position  $\eta_f$  of the reaction front.

$\rho_L$  decreases if  $R_B < R_C$ , is constant if  $R_B = R_C$  and else increases. We now consider the most general case where B and C diffuse at different rates ( $\delta_B \neq \delta_C$ ).

With the conditions  $R_B, R_C > 0$  and  $\delta_B \neq \delta_C$ , we



insert Eqs. (13a)-(13b) into Eq. (19) and rewrite it as:

$$\rho'_L = \frac{2}{\sqrt{\pi}} \frac{e^{-\eta_f^2}}{\text{erf}(\eta_f)} \frac{R_C}{\delta_B} \left( \frac{R_B}{R_C} e^{-\frac{\eta^2 - \eta_f^2}{\delta_B}} - \frac{\delta_B}{\delta_C} e^{-\frac{\eta^2 - \eta_f^2}{\delta_C}} \right). \quad (20)$$

$\rho_L$  admits thus an extremum at  $\eta = \eta_m$  if the following equality is satisfied:

$$\rho'_L|_{\eta_m} = 0 \Leftrightarrow \eta_m^2 - \eta_f^2 = \frac{\ln\left(\frac{R_B \delta_C}{R_C \delta_B}\right)}{\frac{1}{\delta_B} - \frac{1}{\delta_C}}, \quad (21)$$

which is equivalent to

$$\left(\frac{\delta_B}{\delta_C} - \frac{R_B}{R_C}\right) \left(\frac{\delta_B}{\delta_C} - 1\right) > 0, \quad (22)$$

and if

$$\rho''_L|_{\eta_m} = \frac{4\eta_m e^{-\eta_f^2}}{\sqrt{\pi} \text{erf}(\eta_f)} \left(\frac{R_B \delta_C}{R_C \delta_B}\right)^{\frac{\delta_B/\delta_C}{\delta_B/\delta_C - 1}} \frac{R_C}{\delta_B} \left(\frac{\delta_B}{\delta_C} - 1\right) \neq 0. \quad (23)$$

As a consequence,  $\rho_L$  has a minimum ( $\rho'_L|_{\eta_m} = 0$  and  $\rho''_L|_{\eta_m} > 0$ ) if  $\delta_B/\delta_C > \max(1, R_B/R_C)$  (zone III<sub>L</sub> in Figs. 7b-8a), and else a maximum if  $\delta_B/\delta_C < \min(1, R_B/R_C)$  (zone IV<sub>L</sub> in Figs. 7b-8a).

Therefore, when (22) or (23) is not satisfied,  $\rho_L$  is monotonic. As the sign of its derivative  $\rho'_L$  does not change, we determine whether  $\rho_L$  increases or decreases by looking at the sign of  $\rho'_L$  close to the reaction front:

$$\rho'_L|_{\eta \rightarrow \eta_f} \rightarrow \frac{2}{\sqrt{\pi}} \frac{e^{-\eta_f^2}}{\text{erf}(\eta_f)} \frac{R_C}{\delta_B} \left(\frac{R_B}{R_C} - \frac{\delta_B}{\delta_C}\right), \quad (24)$$

and, when (24)=0 (i.e. when  $\delta_B/\delta_C = R_B/R_C$ ), at the sign of  $\rho''_L|_{\eta \rightarrow \eta_f}$ :

$$\rho''_L|_{\eta \rightarrow \eta_f, \frac{\delta_B}{\delta_C} = \frac{R_B}{R_C}} \rightarrow \frac{4\eta_f e^{-\eta_f^2}}{\sqrt{\pi} \text{erf}(\eta_f)} \frac{R_C}{\delta_C \delta_B} \left(\frac{\delta_B}{\delta_C} - 1\right) \quad (25)$$

From the possible signs of (24) and (25), we deduce that  $\rho_L$  is monotonic decreasing if  $0 < R_B/R_C \leq \delta_B/\delta_C < 1$  (in zone I<sub>L</sub> of Fig. 7b), and monotonic increasing if  $1 < \delta_B/\delta_C \leq R_B/R_C$  (zone II<sub>L</sub> of Fig. 7b).

In conclusion, Figs. 7 summarize the classification of the four possible lower density profiles  $\rho_L$  in the reactive system: monotonic decreasing (zone I<sub>L</sub>), monotonic increasing (zone II<sub>L</sub>), with a minimum (zone III<sub>L</sub>) or with a maximum (zone IV<sub>L</sub>), corresponding to

$$\text{zone I}_L: \frac{R_B}{R_C} \leq \frac{\delta_B}{\delta_C} \leq 1 \text{ for } R_C > 0; R_B < 0 \text{ for } R_C = 0, \quad (26a)$$

$$\text{zone II}_L: 1 \leq \frac{\delta_B}{\delta_C} \leq \frac{R_B}{R_C} \text{ for } R_C > 0; R_B > 0 \text{ for } R_C = 0, \quad (26b)$$

$$\text{zone III}_L: \frac{\delta_B}{\delta_C} > \max\left(1, \frac{R_B}{R_C}\right) \text{ for } R_C > 0, \quad (26c)$$

$$\text{zone IV}_L: \frac{\delta_B}{\delta_C} < \min\left(1, \frac{R_B}{R_C}\right) \text{ for } R_C > 0. \quad (26d)$$

## V. EXTREMA BELOW THE REACTION FRONT

In zones III<sub>L</sub> and IV<sub>L</sub> of Fig. 7b, the density profiles  $\rho_L$  below the reaction front have extrema because of differential diffusivity ( $\delta_B \neq \delta_C$ ). We now analyze these extrema in detail, and in particular how their characteristics depend on the diffusivity ratio.

Figure 8a illustrates the transition from zone IV<sub>L</sub> to zone III<sub>L</sub> of Fig. 7b when  $\delta_B/\delta_C$  is increased along the line  $R_B/R_C = 1$ , i.e. if B and C contribute equally to the density of the solution and only differential diffusivity effects are at play. This allows one to understand the switch from a maximum to a minimum in the density profile when  $\delta_B/\delta_C$  is varied. The relative value of the extremum is defined as  $(\rho_m - \rho_\infty)/\rho_\infty$ , where  $\rho_m = \rho(\eta_m)$  is the extremum of density and  $\rho_\infty = \rho(\eta \rightarrow \infty) = R_B \beta$  is the density in the bulk solution. This relative value is positive in zone IV<sub>L</sub>, as the maximum  $\rho_m$  is larger than  $\rho_\infty$ , and conversely negative in zone III<sub>L</sub> where  $\rho_m$  is a minimum. The transition between these two zones occurs when B and C diffuse at the same rate ( $\delta_B = \delta_C$ ). The density profile is then constant and equal to  $\rho_\infty = R_B \beta$  everywhere.

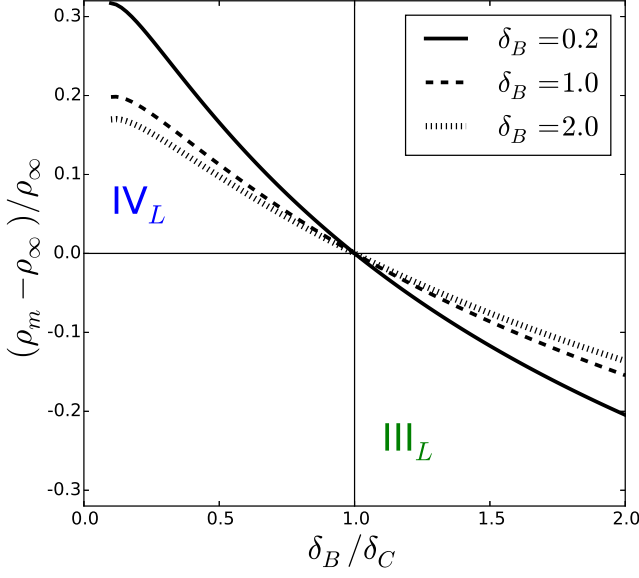
The maximum of density in zone IV<sub>L</sub> can be understood as follows. When the reactant B diffuses more slowly than the product C ( $\delta_B < \delta_C$ ), its concentration just below the reaction front becomes larger than in the case of equal diffusivities (see Fig. 2c). This can induce a maximum of density if B is sufficiently denser than C ( $R_B > R_C \delta_B/\delta_C$ ). If this is not the case ( $R_B \leq R_C \delta_B/\delta_C$ ), the density decreases monotonically (zone II<sub>L</sub>).

Similarly, the minimum of density in zone III<sub>L</sub> can be explained by the slower diffusion ( $\delta_C < \delta_B$ ) and sufficiently large contribution to density of C ( $R_C > R_B \delta_C/\delta_B$ ). The faster escape of B towards the reaction front is not compensated by the diffusion of C, as C lags behind in the upper part of the solution (see Fig. 2d).

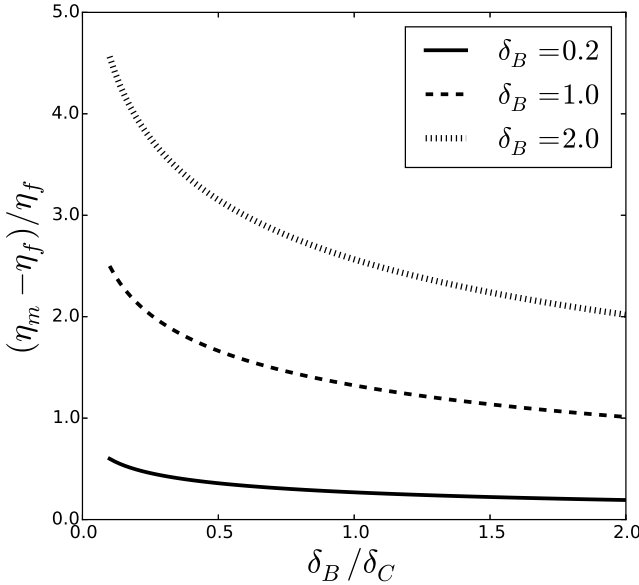
In both zones III<sub>L</sub> and IV<sub>L</sub>, the absolute value of the extremum increases when the differential diffusivity effect becomes more important, i.e. when  $|1 - \delta_B/\delta_C|$  increases. This increase is amplified with smaller  $\delta_B$  (Fig. 8a) and  $\delta_C$  (not shown here) as the concentration profiles are then sharper. Furthermore, the relative distance between the extremum and the reaction front increases when  $\delta_B/\delta_C$  decreases (Fig. 8b), and when  $\delta_B$  (Fig. 8b) or  $\delta_C$  (not shown here) increases.

## VI. GLOBAL DENSITY PROFILES AND POSSIBLE DYNAMICS

In order to have an idea of the global density profiles in the host phase, the two types of density profiles  $\rho_U$  ( $0 \leq \eta \leq \eta_f$ , Fig. 6) must be combined with the four possible lower density profiles  $\rho_L$  ( $\eta \geq \eta_f$ , Figs. 7), leading to eight different possible types of density profiles:



(a)

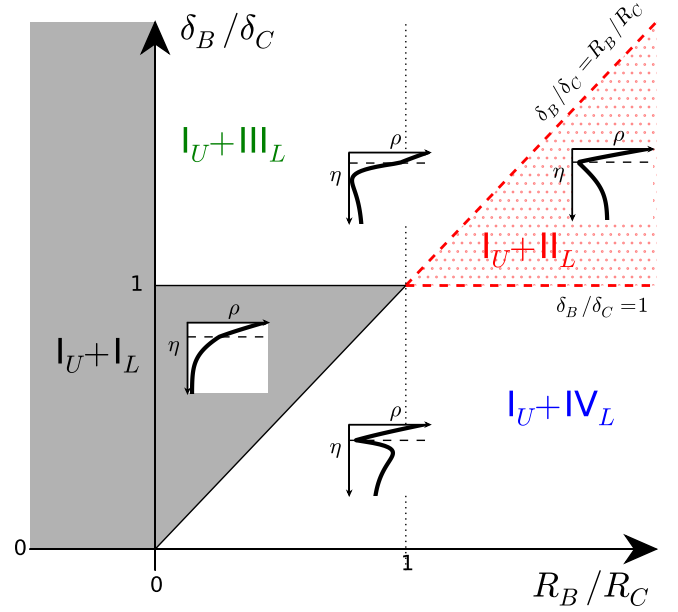


(b)

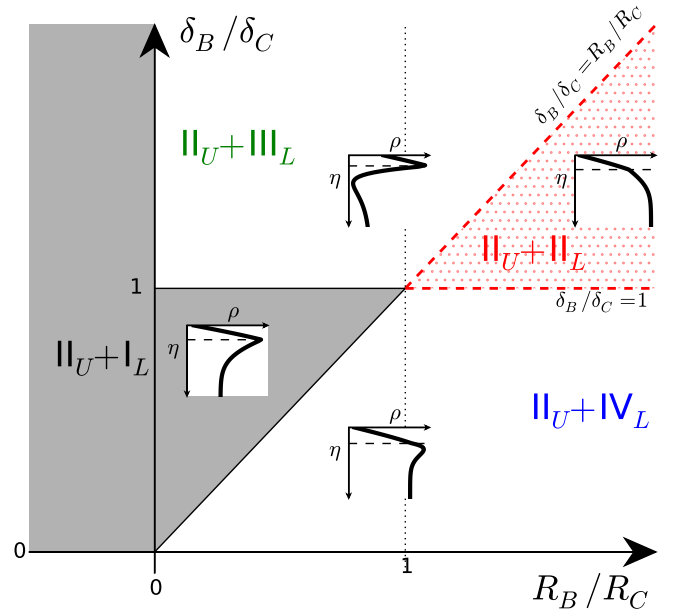
FIG. 8: Characteristics of the extremum  $\rho_m$  of density for  $R_B = R_C = 1$ : (a) for any value of  $\delta_B$ , the relative density extremum  $(\rho_m - \rho_\infty)/\rho_\infty$  becomes negative when  $\delta_B/\delta_C > 1$ , illustrating the transition from zone  $IV_L$  to zone  $III_L$ ; (b) the relative distance  $(\eta_m - \eta_f)/\eta_f$  between the extremum and the reaction front increases when  $\delta_B/\delta_C$  decreases or  $\delta_B$  increases.

monotonic (increasing or decreasing), with one extremum (minimum or maximum, at the reaction front or below) or two extrema (minimum followed by maximum or the opposite). All these profiles are shown in Figs. 9.

Further quantitative studies such as linear stability analyses or non linear simulations are necessary to an-



(a)



(b)

FIG. 9: Classification of the global density profiles  $\rho$  for  $R_C > 0$  and (a)  $R_A < 0$ , or (b)  $R_A > 0$ . Typical plots of  $\rho(\eta)$  are included, with a dashed line showing the position of the reaction front  $\eta_f$ .

alyze the temporal dynamics and assess the convective stability of these density profiles for a given initial angle between the interface and gravity. The density profiles presented here are valid at large times and could thus become unstable with regard to convection before this asymptotic limit. However, their spatial dependence, i.e. the type and number of extrema, typically remains the

same over time as shown previously for specific zones [15, 16, 46]. Therefore, we can analyze the shape of the density profiles to predict possible scenarios for the development of buoyancy-driven instabilities.

As the convective dynamics depend on the orientation of the interface with regard to gravity, we fix ideas by considering a horizontal interface. The reservoir A is on top of the denser host phase containing B and gravity points downwards along  $z$ , so that the initial density stratification is statically stable. We discuss which part(s) of the profile can evidently be buoyantly unstable and associate each zone to dynamics previously observed in quantitative studies (e.g. [15–17, 34–38, 44, 45]).

#### A. $R_A > 0$ : Chemistry can modify the characteristics of the buoyancy-driven instability

If the density of the host solution increases upon dissolution of A ( $R_A > 0$ ), the density profile in the non reactive case can be buoyantly unstable, as a boundary layer of denser fluid rich in A grows on top of the solution. More specifically, buoyancy-driven convection does not develop immediately but after an onset time depending on the experimental conditions [12–14]. This is the case e.g. of alkyl formate [17] or gaseous  $\text{CO}_2$  [44–46] dissolving into an aqueous solution. Even when a reaction takes place in the host phase, it is not possible to observe a stratification statically stable everywhere: at least above the reaction front, the density of the solution decreases downwards due to the contribution of the dissolving species to density (Fig. 9a).

When the upper and lower density profiles are of the same type I (zone  $\text{I}_U + \text{I}_L$  in Fig. 9a), global density profiles are monotonic decreasing like their non reactive counterpart (Section IV A). This case has been illustrated by experiments of  $\text{CO}_2$  dissolving into a solution of monoethanolamine ( $\delta_B/\delta_C \approx 1$ ,  $R_B/R_C \approx 0.45$ ) [44]. The instability develops faster than in the non reactive case because the contribution of the product C to density adds to that of the dissolving species [15, 16].

Density profiles of other zones in Fig. 9a have at least one minimum, at the reaction front or below, which can lead to different dynamics.

In zone  $\text{I}_U + \text{II}_L$ , the minimum forms at the reaction front even without differential diffusivity if the product is less dense than the initially dissolved reactant ( $R_C < R_B$ ) [15, 16]. In that case, this minimum acts as a stabilizing barrier because locally less dense fluid lies on top of denser one. The instability and thus the fingering pattern observed experimentally develop more slowly than in the non reactive case [15–17].

By contrast, the minimum of density in zone  $\text{I}_U + \text{III}_L$ , below the reaction front, can build up only if the product and initially dissolved reactant diffuse at different rates. This zone has been illustrated by the experiments of  $\text{CO}_2$  dissolving into aqueous solutions of alkalis ( $\delta_B/\delta_C \approx 2$ ,  $R_B/R_C \approx 0.4$ ). In that case, the instability develops

faster than without reaction [15, 46]. The concentration of C above and at the reaction front is larger than in the equal diffusivities case (Figs. 2d and 4), which increases the density jump at the origin of convection and thus opposes the stabilizing effect of the minimum [46].

In zone  $\text{I}_U + \text{IV}_L$ , the minimum of density at the reaction front is followed by a maximum where denser fluid lies on top of less dense one. We expect that this local unstable density stratification can generate buoyancy-driven convection. This type of density profile can build up during the dissolution of  $\text{CO}_2$  into a solution of sodium carbonate and bicarbonate ( $\delta_B/\delta_C \approx 0.8$ ,  $R_B/R_C \approx 1.11$ ) [44, 45].

#### B. $R_A \leq 0$ : Chemistry can be at the origin of buoyancy-driven instability

When the density of the host solution decreases or remains constant upon dissolution of A ( $R_A \leq 0$ ), the corresponding non reactive case is buoyantly stable. This is usually the case when a gas, e.g. oxygen [34–38], dissolves into an aqueous solution, except when that gas is  $\text{CO}_2$  [8]. The dissolution of  $\text{CO}_2$  can nevertheless decrease the density of some organic solvents, for example nitrobenzene or chlorobenzene [47]. Studying the case  $R_A \leq 0$  is also relevant in the context of  $\text{CO}_2$  sequestration, because the density of the brine decreases upon dissolution of  $\text{CO}_2$  with a sufficiently large fraction of hydrogen sulfide ( $\text{H}_2\text{S}$ ) impurities [48].

If the upper and lower density profiles are both of type II “increasing” (zone  $\text{II}_U + \text{II}_L$  in Fig. 9b), they combine in a global profile statically stable as everywhere less dense fluid lies on top of denser one. Despite this statically stable stratification, this profile can still be unstable with regard to double diffusive instabilities if species B and C diffuse at different rates ( $\delta_B \neq \delta_C$ ) [19, 30, 33].

Outside this zone, reactions create a maximum in the density profile, and as discussed above, this localized unstable density stratification can be at the origin of buoyancy-driven convection. This is indeed the case in the methylene-blue-glucose system corresponding to zone  $\text{II}_U + \text{I}_L$  ( $R_A = R_B = 0$ ,  $R_C > 0$ ) [34–38]. Unlike zones  $\text{I}_U + \text{IV}_L$  and  $\text{II}_U + \text{IV}_L$ , the maximum is here located exactly at the reaction front. The location of the density maximum seems to affect the development of fingering as the periodic birth of fingers described by Wylock *et al.* [44, 45] has not been reported in the methylene-blue-glucose system [34–38].

To the best of our knowledge, no experiment illustrates the development of the fingering pattern in zones  $\text{II}_U + \text{III}_L$  and  $\text{II}_U + \text{IV}_L$ . We expect that the dynamics in these zones will look like those in zones  $\text{I}_U + \text{III}_L$  and  $\text{I}_U + \text{IV}_L$ , respectively, although the instability could grow more slowly due to the stable density gradient above the reaction front.

## VII. COMPARISON WITH MISCIBLE STRATIFICATIONS

The density profiles classified here for partially miscible systems bear some similarities and differences with their counterparts in miscible stratifications [33].

In both cases, the theoretical framework used to compute the density profiles is similar. The same RD equations can be solved to compute the concentration fields in both systems. The main difference lies in the initial and boundary conditions with a constant concentration of A imposed at the top boundary, equal to the solubility  $A_0$  of A in the host solution for the partially miscible stratification. By contrast, for miscible stratifications, no-flux boundary conditions are imposed at  $\eta \rightarrow \pm\infty$  as the system is typically isolated while the miscible interface expands diffusively in both directions around  $\eta = 0$ , the initial contact line. This completely changes the picture, as discussed below.

Although the expressions for the concentration profiles below the reaction front (12) have the same form in both systems, the maximum concentration  $\gamma$  of the product and the coordinate  $\eta_f$  of the reaction front are different. Moreover, the number of possible profiles is much larger in miscible fluids, where 62 profiles can be obtained [33]. Indeed, the situation above the reaction front is more complex: density profiles with zero, one or two extrema can develop because of the combination of the two opposing concentration gradients  $A'_U$  and  $C'_U$  [33]. By contrast, here only  $A'_U$  affects the type of upper density profile. Furthermore, in miscible stratifications the front can remain at the same location or move towards positive or negative  $\eta$ , amplifying the number of possibilities. On the contrary, here there is only one direction possible for the movement of the reaction front: species A can only invade the host phase from the interface towards positive  $\eta$  where it dissolves.

## VIII. CONCLUSION

We have theoretically computed reaction-diffusion (RD) density profiles in partially miscible stratifications where a solute A dissolves into a host phase containing a solute B and an  $A+B \rightarrow C$  reaction takes place. While only two different types of density profiles can develop in the non reactive case, eight different types of profiles can be observed in the reactive case, depending on the solutal and diffusivity ratios, each potentially associated to a different type of convective dynamics. The coupling between dissolution and diffusion on the one hand, and chemistry on the other hand, multiplies the number of possible scenarios for the development of buoyancy-driven instabilities. This enlarged complexity can be explained by the increased number of parameters as three species A, B and C are involved in the dynamics instead of only one in the non reactive case.

This work opens up new horizons for further research. We have proposed a general framework, independent on the chosen flow equation, in order to guide future quantitative experiments, linear stability analyses or non linear simulations. The present study also represents a first step towards a similar classification of density profiles in immiscible stratifications where the transfer of solutes between phases can be diffusion-limited and complex dynamics can appear in both phases. Further, we note that our results can easily be extended to any property of the fluid depending linearly on the concentrations of the solutes, such as e.g. surface tension. Understanding the coupling of chemistry, differential diffusivity and fluid flow helps clarifying the development of convection, for instance in industrial setups (chemical extraction,...) or geological formations ( $\text{CO}_2$  sequestration, enhanced oil recovery, natural convection in aquifers beneath saline lakes,...) to name but a few.

## ACKNOWLEDGMENTS

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