Infinitely fast reactions in micromixers

James P. Gleeson

Department of Applied Mathematics
University College Cork, Ireland, j.gleeson@ucc.ie

ABSTRACT

Efficient mixing to promote chemical reactions is extremely desirable in lab-on-a-chip devices, but is difficult to achieve in the typical low Reynolds-number flows. Numerical simulation of the high Peclet-number case common in microfluidics is computationally challenging, and asymptotic solutions have proved useful in understanding the interplay between convection and diffusion in particular devices. Most mixing studies to date have examined non-interacting species, so that the total concentration of each is conserved. In this paper we include the effects of chemical reaction terms to describe the infinitely fast reaction between two species. Analytical results identify two important timescales for the yield of the product species: an initial Rhines-Young shear-enhanced mixing time, and a long-time approach of the yield to its final value. The latter regime is crucial for high-efficiency microreactors, and is associated with persistent structures in the mixer flow field.

Keywords: micromixing, microchemistry, Peclet number, asymptotic analysis.

1 INFINITELY FAST REACTIONS

We consider the infinitely fast reaction $A + B \rightarrow D$, whereby one molecule of species A reacts with one molecule of species B to produce one molecule of the product species D. We assume that the molecular diffusivities of species A and B are the same, and write the convection-diffusion-reaction equations for their respective concentrations $c_A(\mathbf{x}, t)$ and $c_B(\mathbf{x}, t)$:

$$\frac{\partial c_A}{\partial t} + \mathbf{v} \cdot \nabla c_A - \kappa \nabla^2 c_A = R(c_A, c_B), \quad (1)$$

$$\frac{\partial c_B}{\partial t} + \mathbf{v} \cdot \nabla c_B - \kappa \nabla^2 c_B = R(c_A, c_B). \quad (2)$$

The convective velocity of the (incompressible) fluid is $\mathbf{v}(\mathbf{x}, t)$, and the term on the right-hand side of the equations is a nonlinear function of c_A and c_B which models the chemical reaction. The detailed form of the reaction function is not important, provided it is the same in both equations. In this case, a *linear* equation (see (4) below) is satisfied by the difference between the concentrations of the species: define $c(\mathbf{x}, t)$ by

$$c = c_A - c_B.$$

While both c_A and c_B are concentrations, and hence are necessarily non-negative, the new field c can have both positive and negative values, depending on the local excesses in concentration of species A over species B, or vice versa. Indeed, given that the infinite speed of reaction precludes the two species co-existing at any one spatial position, it is possible to identify c_A and c_B when only the field c is given:

$$c_A = \text{positive part of } c = \frac{1}{2}(|c| + c)$$

$$c_B = -(\text{negative part of } c) = \frac{1}{2}(|c| - c)$$

Note then that the absolute value of c is given by

$$|c| = c_A + c_B, \quad (3)$$

and the linear equation satisfied by c is found by subtracting equation (2) from equation (1):

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c - \kappa \nabla^2 c = 0 \quad (4)$$

Although the field $c(\mathbf{x}, t)$ can have both positive and negative values we occasionally call the solution of this linear equation the "concentration" c. Note that the reduction of the two nonlinear equations (1) and (2) to the linear equation (4) has been utilized in previous work by, e.g., Cerbelli et al. [1].

The main result of this paper is a method for calculating the total amount of the product species D as a function of time, given the initial concentrations of species A and B in a closed micromixer system. Our general result is given in equation (8) below, and we then proceed to derive an analytical formula for the product as a function of time in a specific micromixer geometry examined by us recently [2].

Since one molecule of species A is used to generate each molecule of the product species D, the total amount of product in the mixer (assuming none at time $t = 0$) must equal the reduction in the amount of species A at that time, i.e.,

$$p_D(t) = \int \int [c_A(\mathbf{x}, 0) - c_A(\mathbf{x}, t)] \, d\mathbf{x}. \quad (5)$$

Here the spatial integration is over the entire mixer, and $p_D(t)$ denotes the total amount of species D in the mixer at time t. Equivalently, p_D can be written in terms of the reduction in species B:

$$p_D(t) = \int\int \left[c_B(\mathbf{x}, 0) - c_B(\mathbf{x}, t) \right] d\mathbf{x}, \qquad (6)$$

and by adding equations (5) and (6), and using equation (3), the product may be calculated from the field c as:

$$p_D(t) = \frac{1}{2} \int\int \left[|c(\mathbf{x}, 0)| - |c(\mathbf{x}, t)| \right] d\mathbf{x}. \qquad (7)$$

This form is especially convenient as it allows the calculation of the total product from the solution of the linear equation (4), rather than from the coupled nonlinear equations (1) and (2).

We normalize $p_D(t)$ by dividing by $\frac{1}{2} \int\int |c(\mathbf{x}, 0| \, d\mathbf{x}$ to define the normalized total product $p(t)$:

$$p(t) = 1 - \frac{\int\int |c(\mathbf{x}, t)| \, d\mathbf{x}}{\int\int |c(\mathbf{x}, 0)| \, d\mathbf{x}} \qquad (8)$$

Note that $p(0) = 0$, and (assuming that equal amounts of species A and B are reacted) $p \to 1$ as $t \to \infty$. Equation (8) allows us to calculate the total amount of product species in the system by solving the linear convection-diffusion equation (4). As an example, in the next section we use an asymptotic solution for annular micromixers to explicitly calculate $c(\mathbf{x}, t)$, and hence find the product $p(t)$ as a function of time.

2   EXAMPLE: ANNULAR MICROMIXER

The annular micromixer described in [2] uses magnetohydrodynamic forcing to pump liquids around the annulus (Figure 1) . The two-dimensional analysis of [2] is simplified in the case of high Peclet number and when the channel width is much smaller than the mixer diameter. Under the latter condition, the channel is modelled as locally straight, and the full convection-diffusion equation is reduced to

$$\frac{\partial c}{\partial \tilde{t}} + \frac{3}{2}\left(1 - \tilde{r}^2\right)\frac{\partial c}{\partial \phi} - \epsilon \frac{\partial^2 c}{\partial \tilde{r}^2} = 0, \qquad (9)$$

(see [2] for details). This reduction is equivalent to modelling a Poiseuille flow in a straight channel, with the spanwise coordinate $\tilde{r}$ equal to ± 1 at the channel walls, and $\tilde{r} = 0$ in the center of the channel. The concentration is 2π-periodic in the streamwise coordinate ϕ, analogous to flow out of one end of the channel reappearing at the other end. The variable $\tilde{t}$ is a dimensionless time ωt, where ω is the convective rotation frequency of the mixer. Finally, ϵ is a small parameter, inversely proportional to the Peclet number Pe.
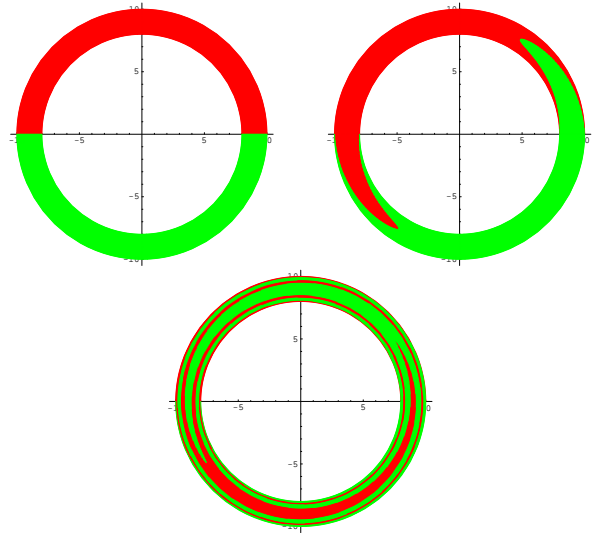

Figure 1: Operation of the annular micromixer at three times (neglecting diffusion).

The reduced equation (9) was shown in [2] to closely match numerical simulations of the full convection-diffusion equation; moreover its relatively simple form permits an analytical solution. We assume that the initial concentration is independent of the radial variable $\tilde{r}$, and depends only on the periodic variable ϕ. The initial condition may thus be expressed as a Fourier series in ϕ:

$$c\left(\tilde{r}, \phi, 0\right) = \mathrm{Re} \sum_{n=1}^{N} a_n e^{in\phi}, \qquad (10)$$

for complex Fourier coefficients a_n, with N being the number of Fourier modes. Here Re denotes the real part of the complex sum. It was shown in [2] that a solution of equation (9) with initial condition (10) is given by

$$
\begin{aligned}
c\left(\tilde{r}, \phi, \tilde{t}\right) &= \mathrm{Re} \sum_{n=1}^{N} a_n g\left(\sqrt{n}\tilde{t}\right) \times \\
&\times \exp\left[in\phi - \frac{3}{2}in\tilde{t} - i\sqrt{n}f\left(\sqrt{n}\tilde{t}\right) \right], \quad (11)
\end{aligned}
$$

with

$$
\begin{aligned}
f(\tilde{t}) &= \frac{3(1+i)}{2}\frac{1}{\mu}\tanh\left(\frac{-1+i}{2}\mu\tilde{t}\right), \\
g(\tilde{t}) &= \left[\cosh\left(\frac{-1+i}{2}\mu\tilde{t}\right) \right]^{-\frac{1}{2}}, \qquad (12)
\end{aligned}
$$

and we have written $\mu = 2\sqrt{3\epsilon}$ for clarity. Unfortunately the solution (11) does not satisfy the physical no-flux boundary conditions at $\tilde{r} = \pm 1$, but the numerical simulations presented in [2] show that this does not appreciably affect the mixing measure. Consequently we proceed to examine the prediction of equation (8) for this case.
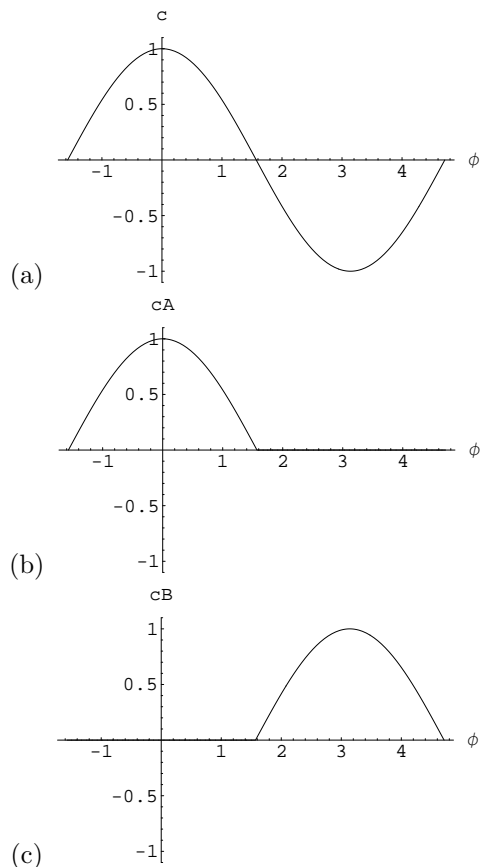
Figure 2: Single harmonic initial condition as a function of ϕ: (a) The initial field $c = \cos\phi$ for equation (4); (b) initial concentration c_A of species A; (c) initial concentration c_B of species B.

We consider two different initial conditions for c: the first is a single Fourier mode, $c(\tilde{r}, \phi, 0) = \cos\phi$; the second is a step-function form for $c(\tilde{r}, \phi, 0)$. Recall from section 1 that the concentration of species A is given by the positive part of c, while the concentration of species B is given by (minus) the negative part of c. Thus the cosine initial condition for c corresponds to identical concentrations of A and B situated in opposite halves of the annulus, with each having zero concentration at the initial interface between species, see Figure 2. We show below that a closed form solution for $p(t)$, the total amount of produce in the mixer at time t, may be derived in this case. The second initial condition corresponds to (nearly) uniform concentrations of species A and B in separate halves of the annular mixer, as in Figure 3. In section 2.2 below we calculate $p(t)$ from equation (8) for this case also, and show it exhibits similar scaling to the analytically-solvable single harmonic case.

2.1 $N = 1$: an analytic formula for $p(t)$

When the angular dependence of c can be described using just one Fourier mode ($N = 1$ in equation (11)), the integral defining the total product $p(t)$ in equation (8)) may be evaluated in closed form, yielding

$$
\begin{aligned}
p(\tilde{t}) &= 1 - \sqrt{\frac{\pi\mu}{3}} \left[\frac{\cosh(\mu\tilde{t}) + \cos(\mu\tilde{t})}{2\left(\sinh(\mu\tilde{t}) - \sin(\mu\tilde{t})\right)^2} \right]^{\frac{1}{4}} \times \\
&\quad \times \operatorname{erf}\left[\sqrt{\frac{3}{2\mu}} \sqrt{\frac{\sinh(\mu\tilde{t}) - \sin(\mu\tilde{t})}{\cosh(\mu\tilde{t}) + \cos(\mu\tilde{t})}} \right].
\end{aligned} \quad (13)
$$

(Here erf denotes the error function). This is plotted as a function of $\tilde{t}$ with the dashed (for $\epsilon = 2 \times 10^{-2}$) and solid ($\epsilon = 8.3 \times 10^{-4}$) lines in Figure 4. The short-time behaviour of $p(\tilde{t})$ is

$$
p(\tilde{t}) \approx \frac{\mu^2\tilde{t}^3}{12} \text{ for } \mu\tilde{t} \ll 1 \quad (14)
$$

and so the initial timescale for product formation depends on the Rhines-Young shear-enhanced mixing of lamellae in the mixer — this time scales as $\epsilon^{-\frac{1}{3}}$, i.e. as $Pe^{\frac{1}{3}}$ with the Peclet number (see [2]). However the long-time approach of $p(\tilde{t})$ to 1 as given by (13) is on a timescale proportional to $\epsilon^{-\frac{1}{2}}$, i.e., $Pe^{\frac{1}{2}}$. This longer timescale becomes important because of the lack of shear-enhanced mixing at the centre of the channel as discussed in [2] — the longer mixing time for this 'persistent structure' [3] limits the formation of the product species, and becomes relevant when high efficiency of reactions is important.

2.2 $N > 1$: numerical integration

The initial condition in Figure 3 is generated using $N = 50$ Fourier modes. In this case the integral in equation (8) defining the total product $p(t)$ must be calculated numerically. Results of such numerical integrations are shown with triangles (for $\epsilon = 2 \times 10^{-2}$) and squares ($\epsilon = 8.3 \times 10^{-4}$) in Figure 4. While the initial evolution of $p(\tilde{t})$ is different to the single mode case (solid and dashed lines), the long-term behaviour closely mirrors that discussed following equation (13) above. In particular, the comments regarding the timescales scaling with $Pe^{\frac{1}{3}}$ (for early times) and the longer timescale $Pe^{\frac{1}{2}}$ (for completion of the reaction) also appear to be relevant in this case.

3 CONCLUSION

In summary, we have shown that the amount of product species D generated by the infinitely fast reaction $A + B \rightarrow D$ in a closed micromixer may be calculated by solving the linear convection-diffusion equation (4), and calculating the integrals in (8). (Note that the assumption that the diffusivities of the species A and B
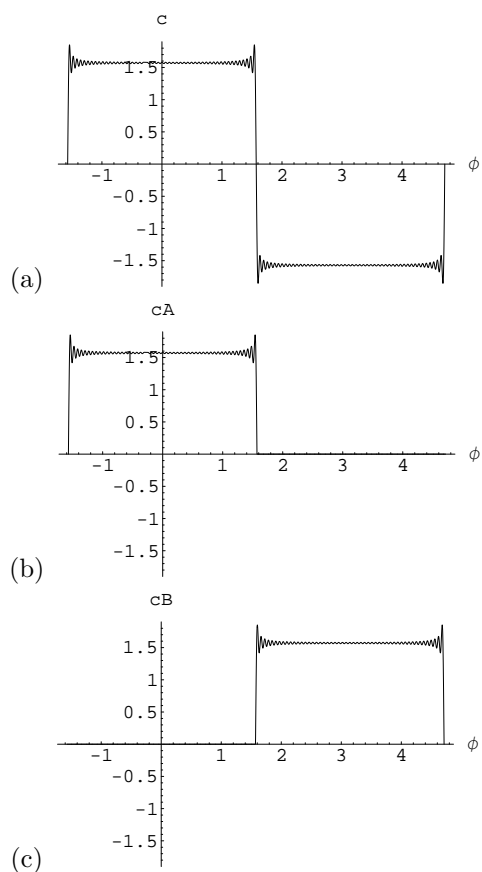
(a)

(b)

(c)

Figure 3: Step function initial condition (approximated using $N = 50$ Fourier harmonics) as a function of ϕ: (a) The initial field c for equation (4); (b) initial concentration c_A of species A; (c) initial concentration c_B of species B.
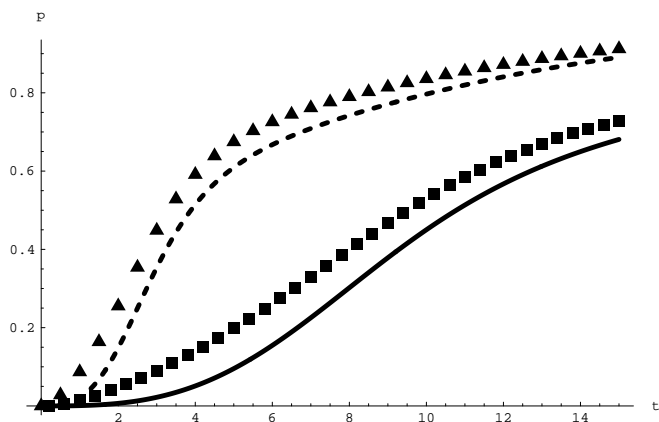

Figure 4: Total product $p(\tilde{t})$ as a function of dimensionless time $\tilde{t}$ in the annular micromixer, using equations (8) and (11). Dashed line ($N = 1$ single harmonic initial condition) and triangles (step function initial condition, $N = 50$) give $p(\tilde{t})$ for $\epsilon = 2 \times 10^{-2}$. Solid line (single harmonic initial condition) and squares (step function initial condition) are for $\epsilon = 8.3 \times 10^{-4}$.

are equal is crucial here). For a model of an annular micromixer considered previously [2], we use an asymptotic closed form solution of the convection-diffusion equation to calculate the amount $p(\tilde{t})$ of product species D in the mixer. For a simple initial condition (Fig. 2) we find the analytical formula (13) for $p(\tilde{t})$ and demonstrate the importance of short- and long- timescales. Numerical integration for a different initial condition (Fig. 3) indicates that this behaviour of $p(\tilde{t})$ may be quite typical.

Further work may examine the result of calculating p from equation (8) for other micromixers, e.g. the chaotic pulsed-diffusion model of [4], [5]. Of particular interest would be the identification of multiple timescales for the evolution of $p(\tilde{t})$ in such models or in experiments.

4 Acknowledgements

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