Multiscale methods and modelling for chemical reactions on oscillating surfaces

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Abstract

We study the dynamics of simple reactions where the chemical species reside on a non-uniform, oscillating surface, and are subject to externally-imposed stirring. We derive a model for this based on a reaction-advection-diffusion equation. We first of all focus on the autocatalytic reaction, and determine whether stirring and surface oscillation can stabilise a particular homogeneous state. To do this, we use homogenisation methods: we show that the influence of the surface oscillation on the concentration field can be parametrised by an effective-diffusion operator. In practice, our criterion for extinction is difficult to interpret, and we therefore carry out numerical simulations. We focus on a chemical reaction occurring on the surface of a thin liquid film, and show that the surface oscillation can enhance the reaction yield. In this numerical context, we demonstrate that the extinction of the catalyst is unlikely. Qualitatively similar results arise when we consider purely homogeneous motion; here we consider both autocatalytic and bistable reaction kinetics. Fisher-KPP equation; Advection; Multiscale methods; Manifolds

1 Introduction

We investigate the dynamics of the logistic and bistable reactions on a non-uniform, oscillating surface, with flow. Such spatially inhomogeneous problems call for the solution of a reaction-advection-diffusion equation, and much chemical and biological activity in fluid flow can be modelled by such equations. In particular, problems concerning autocatalytic chemical reactions [Strogatz, 1994] and population dynamics [Skellam, 1951, Murray, 1993] possess a logistic growth function as a reaction term, and thus satisfy a Fisher-KPP type of equation. Other, more complicated growth functions can be used to model a variety of phenomena, including the spread of insect populations, or the propagation of electro-chemical waves in organisms [Murray, 1993].

Before deriving and analysing our model, we place our work in context by examining several streams of work that are relevant. It is known that a growing domain can modify biological pattern formation, as evidenced by the work of Newman and Frisch [1979]. This has given impetus to the study of reaction-diffusion equations on growing, one-dimensional domains [Kondon and Asal, 1995, Crampin et al., 1999].

Logically, this has led to the study of such problems on manifolds embedded in three dimensions. In multiple dimensions, Gomatam and Amdjadi [1997], Varea et al. [1999], and Chaplain et al. [2001] have considered the effects of curvature, while Plaza et al. [2004] and Gjorgjieva and Jacobsen [2007] have examined the twin effects of domain growth and curvature. The paper of Plaza et al. [2004] is particularly relevant to the present work. In it, the authors derive the reaction-diffusion equation for a class of manifolds, and then study pattern formation on growing domains. We re-work their derivation to include the most general two-dimensional (differentiable) manifold possible, and then shift the focus from pattern formation to reactions in the presence of stirring. The geometric formalism of Aris [1962] is central to our derivation. These references [Plaza et al., 2004, Gjorgjieva and Jacobsen, 2007] consider the 'geometric sink', that is, the notion that a growing domain can act as a sink for the chemical reaction. We extend this idea to oscillating domains and examine the effects of the sink through numerical simulation.

The notion of flow-driven reactions is not new. Neufeld [2001] has considered the effects of chaotic advection on the FitzHugh–Nagumo model. The flow produces a coherent global excitation of the system, for a certain range of stirring rates. The effects of flow can also induce distinctive spatial structure in the chemical concentration; this is studied by Neufeld et al. [1999]. Neufeld [2001] has also examined the single-component logistic or Fisher-KPP model. There the focus is on regime-change, namely how the rate of chaotic advection affects the spatial structure of the concentration. For slow stirring / fast reactions, a spatially inhomogeneous perturbation decays rapidly, and the equilibrium state is reached rapidly. On the other hand, for fast stirring / slow reactions, the perturbation persists, and a filament structure propagates throughout the domain. Nevertheless, the asymptotic state is still a stable homogeneous one. A similar problem has been considered by Cox and Gottwald [2006], who used a bifurcation analysis to estimate the parameter regimes for which a chaotic flow inhibits a chemical reaction in a bistable system. Also, Birch et al. [2007] examine the averaged effect of a non-constant growth rate on the dynamics of the stirred Fisher-KPP equation, wherein they use the theory of estimates to obtain bounds on the reaction yield, as a function of the stirring and the non-constant growth rate. When the mean growth rate is negative, the previously-unstable zero state of the Fisher-KPP equation can become stable; then the catalyst fails to propagate the reaction. In the Birch paper, the inhomogeneous growth rate is the consequence of an inhomogeneous distribution of nutrient in a plankton population. It could, however, be the result of placing the population or chemical species on an oscillating surface, which is the subject of our report. Indeed, our results demonstrate the possibility of increasing the reaction yield by placing the chemical species on a moving surface.

If the flow field or the oscillations have small length scales compared to the domain size, then homogenisation theory naturally presents itself as a tool for understanding the effects of flow and surface oscillation in an averaged sense [Pavliotis and Stuart, 2008]. The small scales are bundled up into an effective-diffusion constant, and the model reduces to a more manageable equation involving a diffusion operator. Such methods have been applied to the linear advection-diffusion equation by McLaughlin et al. [1985], McCarty and Horsthemke [1988], and Rosencrans

[1997]. Some differences in the formal treatment of the problem arise depending on whether the transport equation models a passive tracer [Pavliotis and Stuart, 2008], or a scalar density [Vergassola and Avellaneda, 1997, Goudon and Poupaud, 2004]. Further techniques to estimate the magnitude of the effective diffusivity have involved variational methods [Fannjiang and Papanicolaou, 1994].

The same methods have been applied to linear reaction-advection-diffusion equations. In particular, Mauri [1990] has examined the behaviour of a passive scalar in a porous medium, where the chemical reaction occurs only at the boundary. Appropriate scaling laws for the Damköhler and Péclet numbers are prescribed, and the effective-diffusion operator is derived. Papanicolaou [1995] has studied a similar problem in the same scaling limit, and has shown in detail how to construct the homogenised solution. The convergence of the solution of the basic equation to the solution of the homogenised equation in a singular limit has been proved rigorously by Allaire and Raphael [2007], while Allaire and Piatnitski [2010] have recently examined strongly nonlinear reaction-diffusion equations, in the process deriving the formal asymptotics for the effective diffusion. We propose and justify the application of this theory to a linearised, advective Fisher-KPP equation on a time-varying manifold. In this way, we determine the stability characteristics of the steady homogeneous state and, if unstable, the speed at which the system departs from this state.

This paper is organised as follows. In Sec. 2 we formulate the reaction-advection-diffusion equation for chemical reactions on a time-varying surface. In Sec. 3 we outline a separation-of-scales technique that enables us to compute the spatial distribution of concentration as the solution of a diffusion equation, and write down criteria for the extinction of the catalyst. In Sec. 4 we consider reaction kinetics on the surface of a thin film under flow. We show that oscillating surfaces can increase the reaction yield. In Sec. 5 we demonstrate a similar effect for homogeneous systems, and extend our findings to the bistable reaction. Finally, in Sec. 6 we present our conclusions.

2 Theoretical formulation

In this section we introduce the mass-action law for the autocatalytic reaction, and generalise to spatially-varying concentrations on oscillating two-dimensional surfaces. The basic autocatalytic reaction is standard [Murray, 1993], while the generalisation to time-varying manifolds is based on the treatment Aris [1962] (but see also the works of Stone [1990] and Pereira and Kalliadasis [2008]); these last three papers focus on a similar problem, albeit one in which the chemical species are non-reacting.

In the homogeneous case, the evolution of two chemical species undergoing the autocatalytic reaction reaction $c_1 + c_2 \to 2c_2$ is given by the equation pair

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = -\lambda_0 c_1 c_2, \qquad \frac{\mathrm{d}c_2}{\mathrm{d}t} = \lambda_0 c_1 c_2, \tag{1}$$

where $\lambda_0 > 0$ is the reaction rate. The implied equation $\mathrm{d}(c_1 + c_2)/\mathrm{d}t = 0$ is a statement of molecular conservation. This system is reduced to a single equation by defining a new variable $c = c_2/\left(c_1 + c_2\right)$, giving rise to the logistic growth law

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \lambda c(1-c), \tag{2}$$

where $F(c) = \lambda c(1-c)$ is the reaction function and $\lambda = \lambda_0(c_1 + c_2) > 0$ is the associated rate. The evolution of this relative concentration is a contest between linear creation and quadratic destruction, which manifests itself through the sigmoid solution

$$c = \frac{c(0)\mathrm{e}^{\lambda t}}{1 + c(0)(\mathrm{e}^{\lambda t} - 1)}, \tag{3}$$

where $c(0) > 0$ is the initial concentration. The states $c = 0$ and $c = 1$ are equilibria, because $\mathrm{d}c/\mathrm{d}t = 0$ there. Moreover, since $F'(c) = \lambda(1-2c)$, $c = 0$ is unstable and $c = 1$ is stable.

We extend the mass-action law to the inhomogeneous case: we consider the effects of diffusion and externally-enforced stirring. Thus, we assume that the chemical reaction takes place on a curved surface $\mathcal{M}$, which varies in time in a prescribed fashion. We assume that the surface $\mathcal{M}$ can be given coordinates that are independent of time, such that time-dependence enters into the geometry only through the metric tensor. This assumption is not necessary for this derivation [Aris, 1962]; however, such coordinates are the most natural ones for the applications we have in mind (e.g. Secs. 3 and 4). To introduce flow into the problem, we use Lagrangian coordinates: at time $t = 0$ the manifold is endowed with coordinates $\boldsymbol{a}$, such that

$$\mathcal{M}\left(0\right) = \{\boldsymbol{x} \in \mathbb{R}^3 | \boldsymbol{x} = \boldsymbol{x}\left(a^1, a^2\right)\}.$$

These coordinates can be used to label the fluid particles at time $t = 0$. As time evolves, the fluid particles are advected by an imposed flow $\boldsymbol{U}$, and the particles move along trajectories with coordinates $\boldsymbol{q}\left(t\right)$ on the manifold, such that

$$\boldsymbol{U}\left(\boldsymbol{q}, t\right) = \left(\frac{\partial \boldsymbol{q}}{\partial t}\right)_a \equiv \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t},$$

where the time derivative is taken at fixed particle label $\boldsymbol{a}$. Since the manifold varies smoothly in time, there is a set of transformations connecting the $\boldsymbol{a}$ and the $\boldsymbol{q}$ coordinate systems:

$$\boldsymbol{q} = \boldsymbol{q}\left(\boldsymbol{a}, t\right), \qquad \boldsymbol{a} = \boldsymbol{a}\left(\boldsymbol{q}, t\right). \tag{4}$$

We prescribe a metric tensor:

$$g_{ij}\left(\boldsymbol{q}, t\right) = \frac{\partial \boldsymbol{x}}{\partial q^i} \cdot \frac{\partial \boldsymbol{x}}{\partial q^j}, \qquad \Gamma = \sqrt{\det\left(g_{ij}\right)}. \tag{5}$$

Thus, by using (4) and the metric tensor (5), we obtain a definition of area, either as an integral over a fixed domain, or a time-varying one:

$$\int_{S(t)} \mathrm{d}S = \int_{S(t)} \Gamma \mathrm{d}q^1 \mathrm{d}q^2 = \int_{S(0)} \Gamma J \, \mathrm{d}a^1 \mathrm{d}a^2,$$

where $S\left(0\right)$ is the pre-advected domain and

$$J=\frac{\partial\left(q^1,q^2\right)}{\partial\left(a^1,a^2\right)}$$

is the Jacobian of the transformation. This formalism facilitates the derivation of an analogue of the Reynolds transport theorem for a concentration field $c\left(\boldsymbol{q}\left(t\right),t\right)$ [Aris, 1962, Bicak and Schmidt, 1999, Hu and Zhang, 2007]:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{S(t)}c\,\mathrm{d}S &= \int_{S(t)}\left[\left(\frac{\partial c}{\partial t}\right)_a+\frac{c}{\Gamma}\left(\frac{\partial\Gamma}{\partial t}\right)_a\right]\mathrm{d}S,\\ &= \int_{S(t)}\left[\left(\frac{\partial c}{\partial t}\right)_q+\operatorname{div}\left(\boldsymbol{U}c\right)+\frac{c}{\Gamma}\left(\frac{\partial\Gamma}{\partial t}\right)_q\right]\mathrm{d}S. \qquad (6)\end{aligned}$$

This change in the amount of concentration in the control patch must be matched by the diffusive flux through the boundary of the patch, and by the amount of matter created or destroyed by the reaction, that is,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{S(t)}c\left(\boldsymbol{q},t\right)\mathrm{d}S=-\int_{\partial S(t)}\kappa\,\operatorname{grad}c\cdot\mathrm{d}\boldsymbol{\ell}+\int_{S(t)}F\left(c\right)\mathrm{d}S,$$

where κ is the (constant) diffusion coefficient and ∂S is the boundary of S. A simple application of Gauss's law then gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{S(t)}c\left(\boldsymbol{q},t\right)\mathrm{d}S=\int_{S(t)}\kappa\Delta c\,\mathrm{d}S+\int_{S(t)}F\left(c\right)\mathrm{d}S,\qquad \Delta=\operatorname{div}\operatorname{grad}. \qquad (7)$$

Combining Eqs. (6) and (7) gives the following local conservation law:

$$\frac{\partial c}{\partial t}+\operatorname{div}\left(\boldsymbol{U}c\right)=\kappa\Delta c+F\left(c\right)-\frac{c}{\Gamma}\frac{\partial\Gamma}{\partial t}. \qquad (8)$$

Note that in coordinate form,

$$\operatorname{div}\left(\boldsymbol{U}c\right)=\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma U^i c\right),\qquad \Delta c=\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma g^{ij}\frac{\partial c}{\partial q^j}\right),$$

where (g^{ij}) is the inverse of (g_{ij}).

The appearance of the term $-(c/\Gamma)\partial_t\Gamma$ in Eq. (8) has interesting ramifications. We call it the *geometric sink*: its inclusion is necessary to conserve the total number of particles on a time-varying substrate. In previous applications [Gjorgjieva and Jacobsen, 2007, Plaza et al., 2004], this extra term was negative-definite, and was indeed a sink; here we consider the general case, and this term can therefore act also as a source. The presence of this added term means that the state $c=1$ is no longer a solution for the autocatalytic system; however, the state $c=0$ is still a solution. Moreover, the geometric sink necessitates a modification of the mathematical condition for incompressible flow: we call a flow $\boldsymbol{U}$ on a manifold $\mathcal{M}$ with coordinates q^i incompressible if

$$\frac{\partial\Gamma}{\partial t}+\frac{\partial}{\partial q^i}\left(\Gamma U^i\right)=0. \qquad (9)$$

For such flows, Eq. (8) reduces to a standard type of reaction-diffusion equation:

$$\frac{\partial c}{\partial t} + U^i \frac{\partial c}{\partial q^i} = \kappa \Delta c + F\left(c\right). \tag{10}$$

However, we focus on fully compressible flows throughout this paper. We now turn to homogenisation theory to investigate further implications of this geometric sink.

3 Scale separation with stirring and surface oscillation

In this section, we continue to focus on the autocatalytic reaction. Previously, in Sec. 2, we noted that the state $c = 0$ remains a solution of the autocatalytic system in the presence of the geometric sink. Here, we linearise the system about the state $c = 0$ and use homogenisation theory to determine whether surface oscillations can stabilise an otherwise unstable uniform state $c = 0$. This approach applies equally to other reaction functions ($F(c)$-functions) for which $c = 0$ is an unstable equilibrium. The scope of this section is limited deliberately to the linear regime, and the associated question of the stabilisation of the $c = 0$ state; the nonlinear regime is treated numerically in Secs. 4–5. Our calculations demonstrate that small-scale oscillations fail to stabilise the state $c = 0$, although the results for large-scale oscillations are not so clear-cut.

The macroscopic behaviour of a system with phenomena occurring at various length- and time-scales is described by homogenisation theory, wherein the partial differential equation that describes the system is regarded as having rapidly oscillating differential operators corresponding to the different scales of the phenomena. Taking the appropriate limit of infinite scale separation, the solution of the homogenised partial differential equation describes the large-scale behavior induced by the small-scale dynamics. Solving the full logistic model (8) in this way is problematic, as it is a non-linear equation. However, the linearised solution

$$c(\boldsymbol{q}, t) = C_0 + \delta\psi(\boldsymbol{q}, t), \qquad C_0 = 0, \qquad |\delta| \ll 1 \tag{11}$$

provides important information, since it enables us to predict whether the twin effects of stirring and surface oscillation can stabilise the state $c = 0$, and extinguish the reaction.

In this linearised regime, the initial-value problem to study reads

$$\left(\frac{\partial}{\partial t} - \lambda\right)\psi = -\mathrm{div}\left(\boldsymbol{U}\psi\right) + \kappa\Delta\psi - \frac{\psi}{\Gamma}\frac{\partial \Gamma}{\partial t}, \tag{12}$$

where κ and λ are positive constants, and the spatio-temporal domain is

$$\mathcal{M}_t = \{(\boldsymbol{x}, t) | \boldsymbol{x} = (x, y, h(x, y, t)), (x, y) \in \Omega, t > 0\}. \tag{13}$$

Note that the linearisation approach (12) pertains also to other reaction functions for which $c = 0$ is an unstable equilibrium. We take $\Omega = [0, L]^2$ (Fig. 1); we also take $h(x, y, \cdot)$ to be a smooth, periodic function:

$$h(x + L, y, \cdot) = h(x, y, \cdot), \qquad h(x, y + L, \cdot) = h(x, y, \cdot), \tag{14}$$

Also, the solution $\psi(\boldsymbol{q},t)$ is assumed to inherit this periodicity (here $\boldsymbol{q}=(x,y)$):

$$\psi(q^1+L,q^2,\cdot)=\psi(q^1,q^2,\cdot),\qquad \psi(q^1,q^2+L,\cdot)=\psi(q^1,q^2,\cdot).$$

The function $\boldsymbol{U}(\boldsymbol{q},t)$ is taken to be smooth and periodic in each of the variables (see Eqs. (18) and (27) for the precise details) and finally, the initial condition is given by

$$\psi=\psi_{\text{in}}\text{ for }(\boldsymbol{x},t)\in\mathcal{M}_0=\{(\boldsymbol{x},t)|\boldsymbol{x}=(x,y,h(x,y,0))\,,(x,y)\in\Omega,t=0\}.$$

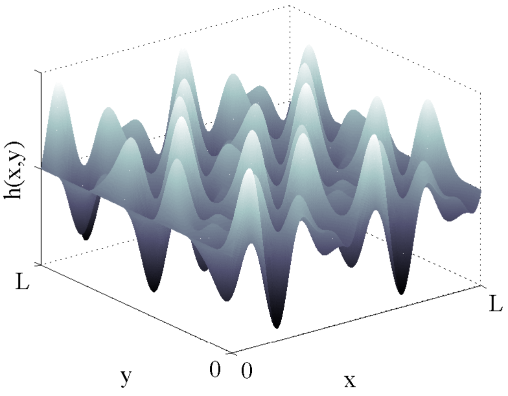


Figure 1: Schematic description of the manifold on which the chemical species are confined.

Next, we re-write Eq. (12) in coordinate form:

$$\left(\frac{\partial}{\partial t}-\lambda\right)\psi=-\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(U^i\Gamma\psi\right)+\frac{\kappa}{\Gamma}\frac{\partial}{\partial q^i}\left(g^{ij}\Gamma\frac{\partial\psi}{\partial q^j}\right)-\frac{\psi}{\Gamma}\frac{\partial\Gamma}{\partial t},\tag{15}$$

where $\Gamma=\sqrt{\det(g_{ij})}$. We non-dimensionalise Eq. (15) according to the patch size L and the diffusive timescale L^2/κ. The result is the following equation:

$$\left(\frac{\partial}{\partial\tilde{t}}-DaPe\right)\psi=-\frac{Pe}{\Gamma}\frac{\partial}{\partial\tilde{q}^i}\left(\tilde{U}^i\Gamma\psi\right)+\frac{1}{\Gamma}\frac{\partial}{\partial\tilde{q}^i}\left(g^{ij}\Gamma\frac{\partial\psi}{\partial\tilde{q}^j}\right)-\frac{\psi}{\Gamma}\frac{\partial\Gamma}{\partial\tilde{t}},\tag{16}$$

where $Pe=U_0L/\kappa$ (U_0 is the velocity scale) and $Da=\lambda L/U_0$, and where the quantities with the tilde denote non-dimensional variables; the metric tensor and the scale factor are inherently non-dimensional. Following standard practice, we henceforth omit the tilde over the variables and work exclusively with non-dimensional quantities.

In this work, we assume that a separation of scales exists: the non-dimensional correlation length ℓ of the velocity $\boldsymbol{U}$ is assumed to be small, such that $\varepsilon=\ell/L\ll 1$. Moreover, we assume that the fluid mixing is dominated by transport rather than diffusion, and we take $Pe=1/\varepsilon\gg 1$. For definiteness, we assume that the reaction and diffusive timescales are comparable ($DaPe=O(1)$). On flat surfaces, other authors have examined alternative orderings for the group $DaPe$ – see Mauri [1990], Papanicolaou [1995], Allaire and Raphael [2007], Pavliotis and Stuart [2008]. We assume that the velocity field has the following structure:

$$\boldsymbol{U}=\boldsymbol{U}(\boldsymbol{q}/\varepsilon,t/\varepsilon^2),$$

such that the velocity varies rapidly in space and time. Here, the choice of temporal scaling is called *diffusive scaling*, and is appropriate when the effects of velocity are expected to 'average out'. The equation we study is therefore

$$\left(\frac{\partial}{\partial t}-\alpha\right)\psi=-\frac{1}{\varepsilon}\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(U^i\Gamma\psi\right)+\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(g^{ij}\Gamma\frac{\partial\psi}{\partial q^j}\right)-\frac{\psi}{\Gamma}\frac{\partial\Gamma}{\partial t},\tag{17}$$

with $\alpha:=DaPe=O(1)$. Finally, we assume that the initial condition varies only on the large scales:

$$\psi_{\mathrm{in}}=f(\boldsymbol{q}).$$

Since the initial data are slowly varying and so is the solution, it is natural to look at how small-scale motions affect the concentration described by Eq. (17) 'on average'. Indeed, if the vector field $\boldsymbol{U}$ averages to zero in an appropriate sense, we expect the 'averaged-out' behaviour of ψ to be characterised by the reaction and by an 'effective' diffusion process. Our goal is to use homogenisation methods to reduce Eq. (17) to an equation that is valid at length and time scales that are large compared to the period of oscillations of the velocity field and/or the metric tensor in space and time. We need to distinguish between two cases: when the metric tensor varies on small space and time scales, and when it varies on large scales.

3.1 The metric has small-scale variations (Case 1)

Here, both the metric tensor g^{ij} and the flow $\boldsymbol{U}$ are explicit functions of the small scales only, and we take

$$g^{ij}=g^{ij}(\boldsymbol{q}/\varepsilon,t/\varepsilon^2),\qquad \boldsymbol{U}=\boldsymbol{U}(\boldsymbol{q}/\varepsilon,t/\varepsilon^2).$$

We take $DaPe:=\alpha=O(1)$. We also introduce auxiliary independent variables $\boldsymbol{Q}=\boldsymbol{q}/\varepsilon$ and $\tau_2=t/\varepsilon^2$. We assume that the metric tensor and the flow are periodic in space and time, in the sense that

$$g^{ij}(Q^1{+}1,\cdot,\cdot)=g^{ij}(Q^1,\cdot,\cdot),\ g^{ij}(\cdot,Q^2{+}1,\cdot)=g^{ij}(\cdot,Q^2,\cdot),\ g^{ij}(\cdot,\cdot,\tau_2{+}T_{02})=g^{ij}(\cdot,\cdot,\tau_2),\tag{18}$$

and similarly for $\boldsymbol{U}$. The scale factor Γ also inherits this structure from the metric tensor. We treat the large-scale variable $\boldsymbol{q}$ and the small-scale variable $\boldsymbol{Q}$ as though they were independent. Similarly, we treat the two time variables $\tau_2=t/\varepsilon^2$ and $\tau_1=t$ as independent. We also derive the Laplace operator, treating $\boldsymbol{q}$ and $\boldsymbol{Q}$ as independent variables. Let $\phi(\boldsymbol{q},\boldsymbol{Q})$ be a scalar field. Then, by the chain rule,

$$\begin{aligned}\Delta\phi &= g^{ij}\frac{\partial^2\phi}{\partial q^i\partial q^j}+\frac{1}{\varepsilon}\frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left(\Gamma g^{ij}\frac{\partial\phi}{\partial q^j}\right)+\frac{1}{\varepsilon}g^{ij}\frac{\partial}{\partial q^i}\frac{\partial\phi}{\partial Q^j}+\frac{1}{\varepsilon^2}\frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left(\Gamma g^{ij}\frac{\partial\phi}{\partial Q^j}\right),\\ &:= \Delta_q\phi+\frac{1}{\varepsilon}\Delta_{Qq}\phi+\frac{1}{\varepsilon^2}\Delta_Q\phi.\end{aligned}$$

Similarly, the time derivative now also has two components:

$$\frac{\partial}{\partial \tau_1} + \frac{1}{\varepsilon^2}\frac{\partial}{\partial \tau_2}.$$

The scalar density equation (17) therefore reads

$$\left(\frac{\partial}{\partial \tau_1} + \varepsilon^{-2}\frac{\partial}{\partial \tau_2}\right)\psi = \left(\varepsilon^{-2}\mathcal{L}_0 + \varepsilon^{-1}\mathcal{L}_1 + \mathcal{L}_2\right)\psi, \tag{19}$$

where

$$\begin{aligned}
\mathcal{L}_0\psi &= -\frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left[\Gamma U^i(\boldsymbol{Q},\tau_2)\psi\right] - \frac{1}{\Gamma}\frac{\partial \Gamma}{\partial \tau_2}\psi + \Delta_Q\psi,\\
\mathcal{L}_1\psi &= -\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left[\Gamma U^i(\boldsymbol{Q},\tau_2)\psi\right] + \Delta_{Qq}\psi,\\
&= -U^i(\boldsymbol{Q},\tau_2)\frac{\partial \psi}{\partial q^i} + \Delta_{Qq}\psi,\\
\mathcal{L}_2\psi &= (\alpha + \Delta_q)\psi.
\end{aligned}$$

We expand the function ψ in powers of ε, as

$$\psi(\boldsymbol{Q},\boldsymbol{q},\tau_1,\tau_2) = \psi_0(\boldsymbol{Q},\boldsymbol{q},\tau_1,\tau_2) + \varepsilon\psi_1(\boldsymbol{Q},\boldsymbol{q},\tau_1,\tau_2) + \varepsilon^2\psi_2(\boldsymbol{Q},\boldsymbol{q},\tau_1,\tau_2) + \cdots,$$

where $\psi_j(\boldsymbol{q},\boldsymbol{Q},\tau_1,\tau_2)$ are periodic in $\boldsymbol{Q}$ and τ_2 with periodicities 1 and T_{02} respectively, for $j = 0, 1, \cdots$. Equating powers of ε in the expansion of the equation (19), we obtain the following triad of problems:

$$\frac{\partial \psi_0}{\partial \tau_2} - \mathcal{L}_0\psi_0 = 0, \tag{20a}$$

$$\frac{\partial \psi_1}{\partial \tau_2} - \mathcal{L}_0\psi_1 = \mathcal{L}_1\psi_0, \tag{20b}$$

$$\frac{\partial \psi_2}{\partial \tau_2} + \frac{\partial \psi_0}{\partial \tau_1} - \mathcal{L}_0\psi_2 = \left(\mathcal{L}_1\psi_1 + \mathcal{L}_2\psi_0\right). \tag{20c}$$

We first compute the solution to Eq. (20a). Written out in full, this is

$$\frac{\partial \psi_0}{\partial \tau_2} = -\frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left[\Gamma U^i(\boldsymbol{Q},\tau_2)\psi_0\right] - \frac{1}{\Gamma}\frac{\partial \Gamma}{\partial \tau_2}\psi_0 + \Delta_Q\psi_0.$$

Here, we cannot simply set $\psi_0 = \psi_0(\boldsymbol{q},\tau_1)$ here, because the source-like term

$$\left[-\frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left(\Gamma U^i\right) - \frac{1}{\Gamma}\frac{\partial \Gamma}{\partial \tau_2}\right]\psi_0.$$

Instead, we take

$$\psi_0 = \widetilde{\psi}_0(\boldsymbol{q},\tau_1)m(\boldsymbol{Q},\tau_2), \tag{21a}$$

where

$$\frac{\partial m}{\partial \tau_2} = -\frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left[\Gamma U^i(\boldsymbol{Q},\tau_2)m\right] - \frac{1}{\Gamma}\frac{\partial \Gamma}{\partial \tau_2}m + \Delta_Q m. \tag{21b}$$

The maximum principle can be used to construct a solution $m \geq 0$ [Vergassola and Avellaneda, 1997]. Moreover, by linearity, we choose the normalisation of m such that $\int \Gamma \mathrm{d}^2 Q\, m = 1$, and this normalisation is preserved under the evolution of the PDE. Hence, m is a probability distribution function, and $\mathrm{d}\mu = \Gamma m \mathrm{d}^2 Q$ is a probability measure.

Using the solution (21), the second equation (20b) becomes

$$\begin{aligned} \frac{\partial \psi_1}{\partial \tau_2} - \mathcal{L}_0 \psi_1 &= \mathcal{L}_1 \psi_0, \\ &= \left[-U^i(\boldsymbol{Q}, \tau_2) \frac{\partial}{\partial q^i} + \Delta_{Qq} \right] m\widetilde{\psi_0}, \\ &= \left[-mU^i + \frac{1}{\Gamma} \frac{\partial}{\partial Q^i} \left(\Gamma g^{ij} m \right) + g^{ij} \frac{\partial m}{\partial Q^j} \right] \frac{\partial \widetilde{\psi_0}}{\partial q^i}, \end{aligned}$$

or

$$\begin{aligned} &\frac{\partial \psi_1}{\partial \tau_2} + \frac{1}{\Gamma} \left[\frac{\partial \Gamma}{\partial \tau_2} + \frac{\partial}{\partial Q^i} \left(\Gamma U^i \right) \right] \psi_1 + U^i \frac{\partial \psi_1}{\partial Q^i} - \Delta_Q \psi_1 \\ &\qquad = \left[-mU^i + \frac{1}{\Gamma} \frac{\partial}{\partial Q^j} \left(\Gamma g^{ij} m \right) + g^{ij} \frac{\partial m}{\partial Q^j} \right] \frac{\partial \widetilde{\psi_0}}{\partial q^i}. \end{aligned} \tag{22}$$

This equation has solution

$$\psi_1 = \theta^i(\boldsymbol{Q}, \tau_2) \frac{\partial \widetilde{\psi_0}}{\partial q^i},$$

where

$$\frac{\partial \theta^i}{\partial \tau_2} + \frac{1}{\Gamma} \left[\frac{\partial \Gamma}{\partial \tau_2} + \frac{\partial}{\partial Q^j} \left(\Gamma U^j \right) \right] \theta^i + U^j \frac{\partial \theta^i}{\partial Q^j} - \Delta_Q \theta^i = -mU^i + \frac{1}{\Gamma} \frac{\partial}{\partial Q^j} \left(\Gamma g^{ij} m \right) + g^{ij} \frac{\partial m}{\partial Q^j} \tag{23}$$

(Equation (23) is called the *cell problem*).

Note that the space-time average of the left-hand side of Eq. (23) is zero. Thus, the space-time average of the right-hand side is also zero:

$$\begin{aligned} 0 &= \int_0^{T_{02}} \iint_{\Omega_Q} \left[-mU^i + \frac{1}{\Gamma} \frac{\partial}{\partial Q^j} \left(\Gamma g^{ij} m \right) + g^{ij} \frac{\partial m}{\partial Q^j} \right] \Gamma \mathrm{d}^2 Q\, \mathrm{d}\tau_2, \\ &= \int_0^{T_{02}} \iint_{\Omega_Q} \left[-mU^i + g^{ij} \frac{\partial m}{\partial Q^j} \right] \Gamma \mathrm{d}^2 Q\, \mathrm{d}\tau_2. \end{aligned}$$

Thus, we have a centering condition:

$$\int_0^{T_{02}} \iint_{\Omega_Q} \left(\widehat{U}^i m \right) \Gamma \mathrm{d}^2 Q\, \mathrm{d}\tau_2 = 0, \qquad \widehat{U}^i = U^i - g^{ij} \frac{\partial}{\partial Q^j}.$$

The centering condition is equivalent to the requirement that the velocity should ‘average out’ of the problem. Note that

$$\widehat{U}^i = U^i - g^{ij} \frac{\partial}{\partial Q^j}$$

is an *effective velocity* and has been promoted to be an operator, rather than a vector field.

Finally, we introduce the *solvability condition*: Eq. (20c) has a solution provided

$$\int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(-\frac{\partial \psi_0}{\partial \tau_1} + \mathcal{L}_1 \psi_1 + \mathcal{L}_2 \psi_0 \right) \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2 = 0,$$

that is, if

$$\frac{\partial \widetilde{\psi}_0}{\partial \tau_1} \left(\tau_1, \boldsymbol{q} \right) = \left(\alpha + \langle g^{ij} \rangle \frac{\partial^2}{\partial q^i \partial q^j} \right) \widetilde{\psi}_0 \left(\tau_1, \boldsymbol{q} \right) + \varpi^{-1} \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(\mathcal{L}_1 \psi_1 \right) \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \quad (24)$$

where ϖ is a volume factor and

$$\langle g^{ij} \rangle = \varpi^{-1} \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(m g^{ij} \right) \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2.$$

The value of ϖ is computed as

$$\varpi = \int_0^{T_{02}} \iint\limits_{\Omega_Q} m \, \Gamma \mathrm{d}^2 Q \mathrm{d}\tau_2 = \int_0^{T_{02}} \mathrm{d}\tau_2 = T_{02},$$

while the second contribution to the right-hand side of Eq. (24) can be written as

$$\int_0^{T_{02}} \iint\limits_{\Omega_Q} \left[-U^i(\boldsymbol{Q}, \tau_2) \frac{\partial}{\partial q^i} + \frac{1}{\Gamma} \frac{\partial}{\partial Q^i} \left(\Gamma g^{ij} \frac{\partial}{\partial q^j} \right) + g^{ij} \frac{\partial}{\partial q^i} \frac{\partial}{\partial Q^j} \right] \theta^k \frac{\partial \widetilde{\psi}_0}{\partial q^k} \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2,$$

$$= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(-U^i \theta^j + g^{ik} \frac{\partial \theta^j}{\partial Q^k} \right) \frac{\partial^2 \widetilde{\psi}_0}{\partial q^i \partial q^j} \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2 = \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(-\widehat{U}^i \theta^j \right) \frac{\partial^2 \widetilde{\psi}_0}{\partial q^i \partial q^j} \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2.$$

We therefore introduce

$$M^{ij} := \varpi^{-1} \int_0^{T_{02}} \int_{\Omega_Q} \left(-\widehat{U}^i \theta^j \right) \Gamma \mathrm{d}^2 Q \, \mathrm{d}\tau_2,$$

such that the homogenised problem reads

$$\frac{\partial \widetilde{\psi}_0}{\partial \tau_1} \left(\tau_1, \boldsymbol{q} \right) = \left[\alpha + \left(\langle g^{ij} \rangle + M^{ij} \right) \frac{\partial^2}{\partial q^i \partial q^j} \right] \widetilde{\psi}_0 \left(\tau_1, \boldsymbol{q} \right). \quad (25)$$

The appropriate initial condition on Eq. (25) reads

$$\widetilde{\psi}_0(\boldsymbol{q}, \tau_1 = 0) = f(\boldsymbol{q});$$

see Goudon and Poupaud [2004], Papanicolaou [1995]. In Appendix A, we show that the quadratic form

$$Q(\boldsymbol{w}) := \varpi \left(\langle g^{ij} \rangle + M^{ij} \right) w_i w_j$$

is positive for non-zero constant covariant vectors w_i and hence, the homogenised diffusion operator in (25) is uniformly elliptic.

We address whether the small-scale variations in the problem can stabilise the state $c = 0$. Our starting-point is the diffusion equation (25). The periodicity imposed on the solution (Eqs. (14) and (18)) amounts to an assumption that the manifold (13) is doubly periodic, with different periodicities for the small and the large spatial scales. Then, the solution of the diffusion equation (25) can be written in terms of a periodic Fourier sum,

$$\psi_0 = \sum_{n_i,n_j\in\mathbb{Z}} C_{n_i,n_j} \mathrm{e}^{\left(\alpha-4\pi^2\langle g\rangle^{ij}n_in_j-4\pi^2M^{ij}n_in_j\right)t}\mathrm{e}^{\mathrm{i}(2\pi n_i)q^1}\mathrm{e}^{\mathrm{i}(2\pi n_j)q^2}, \tag{26}$$

where C_{n_i,n_j} is a constant. The mode $(n_i, n_j) = 0$ is unstable, with growth rate $\mathrm{e}^{\alpha t}$. This is the usual reaction-driven instability, and is not influenced by the effective diffusion. Thus, the small-scale stirring and the surface oscillation do not stabilise the state $c = 0$. We therefore turn to flows whose metric tensor varies on the large scales and consider the same question.

3.2 The metric has large-scale variations (Case 2)

Here, the metric tensor g^{ij} is an explicit function of the large scales only, and the flow $\boldsymbol{U}$ is an explicit functions of the small scales; we take

$$g^{ij} = g^{ij}(\boldsymbol{q}, t), \qquad \boldsymbol{U} = \boldsymbol{U}(\boldsymbol{q}/\varepsilon, t/\varepsilon^2).$$

As before, we introduce auxiliary independent variables $\boldsymbol{Q} = \boldsymbol{q}/\varepsilon$ and $\tau_2 = t/\varepsilon^2$. We assume that the metric tensor and the flow are periodic in space and time, in the sense that

$$g^{ij}(q^1{+}1,\cdot,\cdot) = g^{ij}(q^1,\cdot,\cdot),\ g^{ij}(\cdot,q^2{+}1,\cdot) = g^{ij}(\cdot,q^2,\cdot),\ g^{ij}(\cdot,\cdot,\tau_1{+}T_{01}) = g^{ij}(\cdot,\cdot,\tau_1). \tag{27a}$$

The scale factor Γ inherits this structure from the metric tensor. Also,

$$\boldsymbol{U}(Q^1{+}1,\cdot,\cdot) = \boldsymbol{U}(Q^1,\cdot,\cdot),\ \boldsymbol{U}(\cdot,Q^2{+}1,\cdot) = \boldsymbol{U}(\cdot,Q^2,\cdot),\ \boldsymbol{U}(\cdot,\cdot,\tau_2{+}T_{02}) = \boldsymbol{U}(\cdot,\cdot,\tau_2). \tag{27b}$$

As before, we treat $\boldsymbol{q}$, $\boldsymbol{Q}$, τ_1, and τ_2 as though they were independent variables. In this way, we derive the Laplace operator, using the chain rule:

$$\begin{aligned}\Delta &= \frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma g^{ij}\frac{\partial}{\partial q^j}\right) + \frac{1}{\varepsilon}\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma g^{ij}\frac{\partial}{\partial Q^j}\right) + \frac{1}{\varepsilon}g^{ij}\frac{\partial}{\partial q^i}\frac{\partial}{\partial Q^j} + \frac{1}{\varepsilon^2}g^{ij}\frac{\partial^2}{\partial Q^i\partial Q^j},\\ &:= \Delta_q + \frac{1}{\varepsilon}\Delta_{Qq} + \frac{1}{\varepsilon^2}\Delta_Q.\end{aligned}$$

The partial differential equation to homogenise reads

$$\left(\frac{\partial}{\partial\tau_1} + \varepsilon^{-2}\frac{\partial}{\partial\tau_2}\right)\psi = \left(\varepsilon^{-2}\mathcal{L}_0 + \varepsilon^{-1}\mathcal{L}_1 + \mathcal{L}_2\right)\psi,$$

where

$$\begin{aligned}
\mathcal{L}_0\psi &= g^{ij}\frac{\partial^2\psi}{\partial Q^i\partial Q^j}-\frac{\partial}{\partial Q^i}\left(U^i\psi\right),\\
\mathcal{L}_1\psi &= -\frac{U^i}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma\psi\right)+\Delta_{Qq}\psi,\\
\mathcal{L}_2\psi &= \left(\alpha+\Delta_q-\frac{1}{\Gamma}\frac{\partial\Gamma}{\partial t}\right)\psi.
\end{aligned}$$

As in Case 1, there is a triad of sub-problems to solve:

$$\frac{\partial\psi_0}{\partial\tau_2}-\mathcal{L}_0\psi_0 = 0, \tag{28a}$$

$$\frac{\partial\psi_1}{\partial\tau_2}-\mathcal{L}_0\psi_1 = \mathcal{L}_1\psi_0, \tag{28b}$$

$$\frac{\partial\psi_2}{\partial\tau_2}+\frac{\partial\psi_0}{\partial\tau_1}-\mathcal{L}_0\psi_2 = \left(\mathcal{L}_1\psi_1+\mathcal{L}_2\psi_0\right). \tag{28c}$$

We first compute the solution to Eq. (28a). Written out in full, this is

$$\frac{\partial\psi_0}{\partial\tau_2}=-\frac{\partial}{\partial Q^i}\left[U^i(\boldsymbol{Q},\tau_2)\psi_0\right]+\Delta_Q\psi_0,$$

or

$$\frac{\partial\psi_0}{\partial\tau_2}+U^i\frac{\partial\psi_0}{\partial Q^i}+\psi_0\frac{\partial U^i}{\partial Q^i}=g^{ij}(\boldsymbol{q},\tau_1)\frac{\partial^2\psi_0}{\partial Q^i\partial Q^j}.$$

It is not possible to set $\psi_0=m(\boldsymbol{Q},\tau_2)\widetilde{\psi}_0(\boldsymbol{q},\tau_1)$ because the m-equation would have a parametric dependence on the large scales, through the metric tensor $g^{ij}(\boldsymbol{q},\tau_1)$. This hampers a separation-of-scales approach. A way to make progress and to clarify the homogenisation procedure is to stipulate that the flow be *incompressible on small scales*, since then the source-like term $-(\partial U^i/\partial Q^i)\psi_0$ vanishes and we can take $\psi_0=\psi_0(\boldsymbol{q},\tau_1)$ only.

Thus, we assume that the flow $\boldsymbol{U}$ is incompressible on the small scales, such that $\psi_0=\psi_0(\boldsymbol{q},\tau_1)$ only. Using this solution, the second equation (28b) becomes

$$\begin{aligned}
\frac{\partial\psi_1}{\partial\tau_2}-\mathcal{L}_0\psi_1 &= \mathcal{L}_1\psi_0,\\
&= \left[-\frac{U^i}{\Gamma}\frac{\partial}{\partial q^i}\left[\Gamma\left(\cdot\right)\right]+\Delta_{Qq}\right]\psi_0,\\
&= -\frac{U^i}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma\psi_0\right).
\end{aligned}$$

or

$$\frac{\partial\psi_1}{\partial\tau_2}+U^i\frac{\partial\psi_1}{\partial Q^i}=g^{ij}\frac{\partial^2\psi_1}{\partial Q^i\partial Q^j}-\frac{U^i}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma\psi_0\right).$$

This equation has solution

$$\psi_1=\theta^i(\boldsymbol{Q},\tau_2;\boldsymbol{q},\tau_1)\left[\frac{1}{\Gamma}\frac{\partial}{\partial q^i}\left(\Gamma\psi_0\right)\right],$$

where

$$\frac{\partial\theta^i}{\partial\tau_2} + U^k\frac{\partial\theta^i}{\partial Q^k} = g^{jk}\frac{\partial^2\theta^i}{\partial Q^j\partial Q^k} - U^i. \tag{29}$$

Eq. (29) is the cell problem. Note that θ^i depends only parametrically on the large scales. The scaling of the metric terms compared to the scaling of the flow field makes a separation-of-scales approach difficult, and Eq. (29) contains both large and small scales. Nevertheless, we continue with the method. Note also that the space-time average of the left-hand side of Eq. (29) is zero, with respect to the small scales. This follows from the space-time periodicity of the solution on the same small scales. Thus, the space-time average of the right-hand side of Eq. (29) is also zero:

$$0 = \int_0^{T_{02}}\iint\limits_{\Omega_Q} U^i\,\mathrm{d}^2Q\,\mathrm{d}\tau_2.$$

This is the centering condition.

Finally, we introduce the solvability condition: Eq. (28c) has a solution provided

$$\int_0^{T_{02}}\iint\limits_{\Omega_Q}\left(-\frac{\partial\psi_0}{\partial\tau_1} + \mathcal{L}_1\psi_1 + \mathcal{L}_2\psi_0\right)\mathrm{d}^2Q\,\mathrm{d}\tau_2 = 0,$$

that is, if

$$\frac{\partial\psi_0}{\partial\tau_1}(\tau_1,\boldsymbol{q}) = (\alpha+\Delta_q)\psi_0 + \varpi^{-1}\int_0^{T_{02}}\iint\limits_{\Omega_Q}(\mathcal{L}_1\psi_1)\,\mathrm{d}^2Q\,\mathrm{d}\tau_2, \tag{30}$$

where ϖ is a volume factor,

$$\varpi = \int_0^{T_{02}}\iint\limits_{\Omega_Q}\mathrm{d}^2Q\,\mathrm{d}\tau_2 = T_{02}.$$

The second contribution to the right-hand side of Eq. (30) can be written as

$$
\begin{aligned}
&\int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(\mathcal{L}_1 \psi_1\right) \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left[-\frac{U^i}{\Gamma} \frac{\partial}{\partial q^i} \left[\Gamma\left(\cdot\right)\right] + \frac{1}{\Gamma} \frac{\partial}{\partial q^i} \left(\Gamma \frac{\partial}{\partial Q^i} \right) + g^{ij} \frac{\partial}{\partial q^i} \frac{\partial}{\partial Q^j} \right] \frac{\theta^k}{\Gamma} \frac{\partial}{\partial q^k} \left(\Gamma \psi_0\right) \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\
&\qquad = \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left[-\frac{U^i}{\Gamma} \frac{\partial}{\partial q^i} \left[\Gamma\left(\cdot\right)\right] \right] \frac{\theta^k}{\Gamma} \frac{\partial}{\partial q^k} \left(\Gamma \psi_0\right) \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\
&\qquad = \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left[-\frac{U^i}{\Gamma} \frac{\partial}{\partial q^i} \left(\theta^k \frac{\partial}{\partial q^k} \left(\Gamma \psi_0\right) \right) \right] \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\
&\qquad = \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left[-\frac{U^i}{\Gamma} \frac{\partial}{\partial q^i} \left(\theta^k \frac{\partial \Gamma}{\partial q^k} \right) \right] \psi_0 \, \mathrm{d}^2 Q \, \mathrm{d}\tau_2 \\
&\qquad + \int_0^{T_{02}} \iint\limits_{\Omega_Q} \mathrm{d}^2 Q \left[-\frac{U^i \theta^k}{\Gamma} \frac{\partial \Gamma}{\partial q^k} - \frac{U^k}{\Gamma} \frac{\partial}{\partial q^k} \left(\theta^i \Gamma\right) \right] \frac{\partial \psi_0}{\partial q^i} \mathrm{d}^2 Q \, \mathrm{d}\tau_2 \\
&\qquad + \int_0^{T_{02}} \iint\limits_{\Omega_Q} \mathrm{d}^2 Q \left(-U^i \theta^k\right) \frac{\partial^2 \psi_0}{\partial q^i \partial q^j} \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\
&\qquad := \varpi \left[A(\boldsymbol{q}, \tau_1) \psi_0 + B^i(\boldsymbol{q}, \tau_1) \frac{\partial \psi_0}{\partial q^i} + M^{ij}(\boldsymbol{q}, \tau_1) \frac{\partial^2 \psi_0}{\partial q^i \partial q^j} \right].
\end{aligned}
$$

We are therefore left with the equation

$$
\frac{\partial \psi_0}{\partial \tau_1}(\tau_1, \boldsymbol{q}) = \left(\alpha + \Delta_q\right) \psi_0 + M^{ij}(\boldsymbol{q}, \tau_1) \frac{\partial^2 \psi_0}{\partial q^i \partial q^j} + B^i(\boldsymbol{q}, \tau_1) \frac{\partial \psi_0}{\partial q^i} + A(\boldsymbol{q}, \tau_1) \psi_0. \tag{31}
$$

Again, the appropriate initial condition on Eq. (31) reads $\widetilde{\psi}_0(\boldsymbol{q}, \tau_1 = 0) = f(\boldsymbol{q})$. In Appendix A, we show that the quadratic form $M^{ij} w_i w_j$ is positive for non-zero constant covariant vectors w_i and hence, the homogenised second-order diffusion operator (31) is uniformly elliptic.

We address whether geometric variations in the problem can stabilise the state $c = 0$. Our starting-point is the diffusion-type equation (31). Two mechanisms for stabilisation suggest themselves. The first method concerns the term $A(\boldsymbol{q}, \tau_1)$. Clearly, if a flow $\boldsymbol{U}$ and a scale factor Γ can be chosen such that

$$
\alpha + A(\boldsymbol{q}, \tau_1) \leq 0,
$$

then the instability is quenched. This requires some coupling between the small and the large scales to render the integral $A(\boldsymbol{q}, \tau_1)$ negative, and this could be provided by the intermediate function $\theta^i(\boldsymbol{Q}, \tau_2; \boldsymbol{q}, \tau_2)$. Nevertheless, this criterion is difficult to interpret *a priori*.

The second mechanism by which surface oscillations might stabilise the homogeneous state is the same whether or not there is flow, and the flow is omitted herein without loss of generality to simplify the discussion. In the absence of flow, Eq. (31) reads

$$\frac{\partial \psi_0}{\partial \tau_1} = \left(\alpha + \Delta_q - \frac{1}{\Gamma}\frac{\partial \Gamma}{\partial t} \right) \psi_0. \tag{32}$$

We expand the solution in terms of the eigenfunctions of the Laplacian Δ_q,

$$\psi_0 = \sum_\ell A_\ell(t)\phi_\ell(\boldsymbol{q};t), \qquad \Delta_q \phi_\ell(\boldsymbol{q};t) = -\lambda_\ell^2(t)\phi_\ell(\boldsymbol{q};t), \qquad \iint\limits_{\Omega_q} \phi_\ell \phi_k \, \Gamma \mathrm{d}^2 q = \delta_{\ell k},$$

where we sum over the index ℓ labelling the eigenfunctions. Here, time appears as a parameter in the eigenfunctions because the substrate shape oscillates. Substitution of the trial solution into Eq. (32) yields

$$\frac{\mathrm{d}A_\ell}{\mathrm{d}t} = \left[\alpha - \lambda_\ell^2(t)\right] A_\ell + \sum_k C_{k\ell}(t) A_k, \tag{33a}$$

where

$$C_{k\ell}(t) = -\iint\limits_{\Omega_q} \frac{\partial}{\partial t}\left(\Gamma \phi_k\right)\phi_\ell \, \mathrm{d}^2 q. \tag{33b}$$

Thus, if the normal modes of Eq. (33a) decay, then the homogeneous state $c = 0$ is stable. A similar result holds for the full equation (Eq. (31)). Thus, the state $c = 0$ can in principle be stabilised. Indeed, an example that is closely related to the subject of this paper concerns chemical reactions on exponentially-growing spheres without flow [Gjorgjieva and Jacobsen, 2007], wherein the exponential growth in the manifold's scale factor (the sphere's radius) stabilises the homogeneous equilibrium states. Again, however, the general criterion (33) is rather involved. This means that a more practical approach – such as numerical simulations – is needed to address the problem of the extinction of the catalyst.

4 Numerical studies

The homogenisation theory of Sec. 3 leads to a characterisation of the reaction kinetics in the linear regime. However, this is a special case. To consider long-time, nonlinear evolution, we pass over to numerical simulations, and consider a chemical system residing on a thin film under flow. In studying this system, we are motivated by practical, fluid-mechanical applications. However, we have verified that the results are qualitatively very similar to the situation wherein the surface oscillation is explicitly prescribed as an oscillation that varies sinusoidally in space and time [Kamhawi, 2009]. Concerning the full fluid-mechanical system, in the limit where there is no backreaction between the concentration gradient of the chemicals and the film flow (e.g. no Marangoni forces [Oron et al., 1997]), the model derived in Sec. 2 applies, and the flow is given by the standard lubrication theory [Oron et al., 1997, Craster and Matar, 2009]. We first of all discuss this flow regime and then present our results.

We consider thin-film flow, wherein a layer of fluid rests on a flat plate with a free upper boundary (free surface), $h(x, y, t)$. In the limit where the vertical variations in the flow structure are large compared to the horizontal variations, the following equations for the free surface hold:

$$\begin{aligned}\frac{\partial h}{\partial t}+\nabla_1\cdot(\boldsymbol{U}h) &= 0, \qquad \nabla_1=(\partial_x,\partial_y), && (34a)\\ \boldsymbol{U} &= \frac{1}{3\mu}h^2\left(-\nabla_1\phi - S\nabla_1^2 h + \boldsymbol{f}_D\right), && (34b)\end{aligned}$$

where ϕ is the body-force potential evaluated at the surface, and $S\nabla_1^2 h$ represents surface tension, and $\boldsymbol{f}_D$ is an externally-prescribed driving force [Oron et al., 1997, Craster and Matar, 2009]. The constants μ and S represent dynamic viscosity and surface tension, respectively. In this section, we seek a minimal model in order to examine the effects of flow and surface variation on the chemical reaction. Therefore, we work in a limit where the variations in the free-surface height around an equilibrium value h_0 are small, and we write $h \sim h_0+\delta h_1(x,y,t)$. We also ignore body-force effects and focus on a situation wherein the driving force and the surface tension dominate (surface tension must be included if the nonlinear equation (34) is not to admit breaking waves). We restrict ourselves further by examining a limit where the surface tension and viscosity are large: $\mu=\widehat{\mu}/\delta$ and $S=\widehat{S}/\delta$. Then, the driving force appears only in the h_1-equation, and our approach is self-consistent. We therefore have the following model for the linearised free-surface height:

$$\frac{\partial h_1}{\partial t}=-\frac{\widehat{S}}{3\widehat{\mu}}h_0^3\nabla_1^4 h_1+\frac{h_0^3}{3\widehat{\mu}}\nabla_1\cdot\boldsymbol{f}_D, \tag{35a}$$

which is a linear hyperdiffusion equation with a source term. The associated flow is as follows:

$$\boldsymbol{U}=\delta\left(-\frac{\widehat{S}}{3\widehat{\mu}}\nabla_1\nabla_1^2 h_1+\frac{h_0^2}{3\widehat{\mu}}\boldsymbol{f}_D\right). \tag{35b}$$

Next, we consider placing the chemical species on the surface $z=h(x,y,t)\sim h_0+\delta h_1(x,y,t)$. The position vector $\boldsymbol{x}$ of a point on the surface is given by

$$\boldsymbol{x}=\left(x,y,h\left(x,y,t\right)\right).$$

The metric tensor is thus

$$(g_{ij})=\left(\begin{array}{cc}1+h_x^2 & h_xh_y\\ h_xh_y & 1+h_y^2\end{array}\right),$$

with determinant

$$\Gamma^2=\det(g_{ij})=1+h_x^2+h_y^2:=1+\left(\nabla_1 h\right)^2,$$

while the inverse is

$$\left(g^{ij}\right)=\frac{1}{\Gamma}\left(\begin{array}{cc}1+h_y^2 & -h_xh_y\\ -h_xh_y & 1+h_x^2\end{array}\right).$$

Hence, the chemical equation reads

$$\frac{\partial c}{\partial t}=-\frac{1}{\Gamma}\frac{\partial}{\partial x^i}\left(\Gamma U^i c\right)+\frac{\kappa}{\Gamma}\frac{\partial}{\partial x^i}\left(\Gamma g^{ij}\frac{\partial c}{\partial x^j}\right)+\lambda c\left(1-c\right)-\frac{c}{\Gamma}\frac{\partial\Gamma}{\partial t}. \tag{36}$$

For the purpose of numerical calculations, we prescribe the driving force $\boldsymbol{f}_D = -\nabla_1 \mathcal{U}$, where $\mathcal{U}$ is given in what follows. We non-dimensionalise Eqs. (35)–(36) on the horizontal length scale L and the flow timescale

$$\tau = \frac{3\widehat{\mu}L^2}{h_0^2 U_0},$$

where U_0 is the typical magnitude of $\mathcal{U}$. This gives non-dimensional space and time variables $\tilde{\boldsymbol{x}} = \boldsymbol{x}/L$ and $\tilde{t} = t/\tau$, and $\tilde{h}_1 = h_1/h_0$. The result is the following non-dimensional system of equations:

$$\begin{aligned} \frac{\partial \tilde{h}_1}{\partial \tilde{t}} &= -\beta \tilde{\nabla}_1^4 \tilde{h}_1 - \tilde{\nabla}_1^2 \tilde{\mathcal{U}}, && \text{(37a)} \\ \tilde{\boldsymbol{U}} &= \delta \left(-\tilde{\nabla}_1 \tilde{\mathcal{U}} - \beta \tilde{\nabla}_1 \tilde{\nabla}_1^2 \tilde{h}_1 \right), && \text{(37b)} \\ \frac{\partial c}{\partial \tilde{t}} &= -\frac{1}{\Gamma} \frac{\partial}{\partial \tilde{x}^i} \left(\Gamma \tilde{U}^i c \right) + \frac{\gamma}{\Gamma} \frac{\partial}{\partial \tilde{x}^i} \left(\Gamma g^{ij} \frac{\partial c}{\partial \tilde{x}^j} \right) - \alpha c \left(1 - c\right) - \frac{c}{\Gamma}\frac{\partial \Gamma}{\partial t}, && \text{(37c)} \end{aligned}$$

where

$$\alpha = \lambda \tau, \qquad \beta = \frac{\widehat{S} h_0^3}{3\widehat{\mu}\lambda L^4}, \qquad \gamma = \frac{\kappa}{\lambda L^2} \tag{37d}$$

are non-dimensional groups (following standard practice, we henceforth omit the ornamentation over the non-dimensional variables). We prescribe the following driving force:

$$\mathcal{U} = \sin\left(k_1 x + A_1 \cos\left(\omega t\right)\right) \sin\left(k_2 y\right) \left[1 - A_2 \cos^2(\omega t)\right], \qquad \boldsymbol{f}_D = -\nabla_1 \mathcal{U}, \tag{38}$$

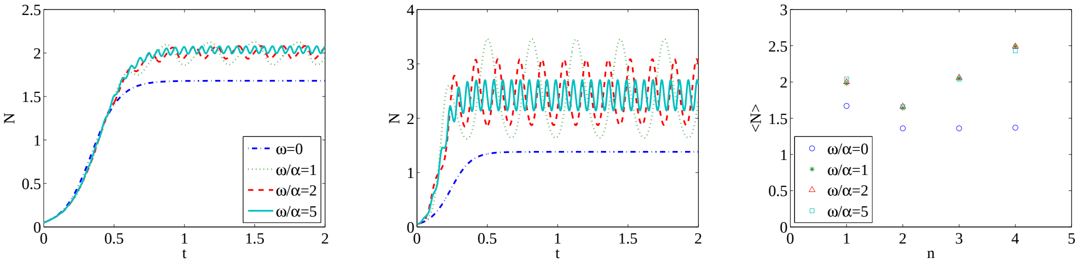
where k_1, k_2, A_1, A_2, and ω are constants (ω is the driving frequency). This particular choice of $\mathcal{U}$ is chosen to give the flow a cellular structure in space, with both an oscillating phase and an oscillating amplitude. Such a time-varying phase is helpful in enhancing transport [Solomon et al., 1998]. We set the following initial condition on the concentration:

$$c = 0.05 + 0.01 \sin\left(2\pi x/L\right) \sin\left(2\pi y/L\right). \tag{39}$$

The form of the global time-varying factor in Eq. (38) ensures that the area $\int \Gamma \, \mathrm{d}x\mathrm{d}y$ is increased relative to the steady state ($\omega = 0$).

We have solved the system of equations (37) on a doubly periodic domain with sides of length $L = 1$, where $\alpha = 10$, $\beta = 0.01$, $\gamma = 1$, $k_1 = k_2 = n(2\pi/L)$, $A_1 = 0.1$, $A_2 = 0.5$, and where n and ω are variable. We have used standard spectral methods [Boyd, 2001], and have obtained fully converged numerical results with a timestep 10^{-3} and a spatial resolution 256^2, up to the non-dimensional frequency $\omega = 50$. Our numerical results are focussed on the reaction yield. The yield is simply the quantity of product created in the reaction, and is defined by writing down a differential for the quantity of product present in a patch of area

$$\mathrm{d}N = c(\boldsymbol{q}, t)\, \mathrm{d}S\,(t) = c(\boldsymbol{q}, t)\Gamma \mathrm{d}q^1 \mathrm{d}q^2.$$



(a) $n = 1$ (b) $n = 4$ (c)

Figure 2: (a), (b) The instantaneous yield for $k_1 = k_2 = n(2\pi/L)$, and for various frequencies: $\omega = 0$ ($\cdot -$), $\omega = 10$ ($\cdots$), $\omega = 20$ ($--$), and $\omega = 50$ (—); (c) The time-averaged yield as a function of n and ω.

The integral of this quantity is the instantaneous yield:

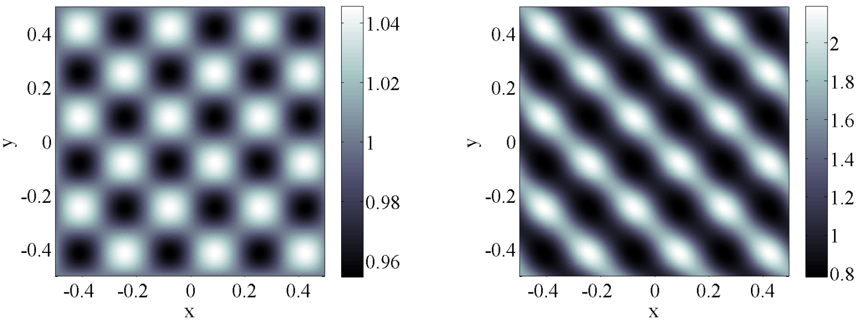
$$N(t) = \iint_{\Omega_1} c(\boldsymbol{q}, t)\Gamma \mathrm{d}q^1 \mathrm{d}q^2. \tag{40}$$

Sample graphs of the time-varying yield are shown in Fig. 2. For $\omega > 0$, the time-averaged yield is approximately independent of frequency. The yield corresponding to $\omega = 0$ differs discontinuously from the time average of the oscillating yield (for detailed explanation of this phenomenon, see Sec. 5). For $n > 2$, the time-averaged yield increases with increasing n – the driving force creates more surface area, which increases the reaction yield. Moreover, the amplitude of the yield-oscillations increases with increasing n. In each parametric study, the oscillating surface provides an enhanced yield relative to the $\omega = 0$ case. The period of oscillation is in fact *half* that associated with the frequency ω in Eq. (38). This is because it is the global, time-dependent factor in Eq. (38) that controls the free-surface variations (and hence the reaction), and this factor can be re-written as $1 - (A_2/2)[1 + \cos 2\omega t]$, such that the driving force is dominated by the frequency 2ω. The time-dependent phase $A_1 \cos \omega t$ has the sole effect of causing the locations of the free-surface maxima and minima to oscillate back and forth in the x-direction. A further description of the flow is obtained by taking a snapshot of the free-surface height and the chemical concentration (Fig. 3, $n = 3$, $\omega = 10$), in the quasi-steady regime, where the reaction yield oscillates. The instantaneous concentration is large in regions where the free surface is high, and lower in regions of lower free-surface height. The spatial structure of the concentration field mirrors closely that of the free-surface height; the latter can therefore be viewed as driving the chemical reaction.

It is tempting to conclude that any surface oscillation will enhance the reaction yield. However, the reaction yield depends delicately on the oscillation protocol. Thus, if instead of Eq. (38) we use the driving force

$$\mathcal{U} = \sin\left(k_1 x + A_1 \cos\left(\omega t\right)\right) \sin\left(k_2 y\right) \left[1 + A_2 \cos(\omega t)\right],$$

then the time average of the reaction yield is *reduced* relative to the case without oscillations. The reason for this difference lies in the fact that on average, the first choice of oscillation protocol increases the surface area available for the reaction, while the second choice of protocol decreases the surface area (Fig. 4).



(a) Free-surface height (b) Concentration

Figure 3: Instantaneous snapshots of the free-surface height and the chemical concentration, for $\omega = 10$ and $k_1 = k_2 = 3(2\pi/L)$.

We comment on the likelihood that the flow and the surface oscillation will extinguish the reaction, and stabilise the state $c = 0$. In each numerical simulation reported on, we have initialised the concentration with a small-amplitude disturbance (Eq. (39)). However, no stabilisation is ever observed (we have varied the amplitudes of the normal modes in Eq. (39), and the results are the same in each case). It seems unlikely that the criterion (33) can be met for the kind of flow studied here, wherein the length- and timescales of the metric and the flow are intimately linked. Here, the metric must have the same scale of variation as the flow: we have demonstrated theoretically that small-scale variations are not stabilising (Sec. 3.1, Eq. (26)), and our numerical simulations in Figs. 2 and 4 suggest a similar outcome for large scales. Finally, the results in Fig. 3 indicate clearly the existence of a quasi-steady-state, wherein the system relaxes to a state determined entirely by the driving force. To further understand such states, we turn lastly to a simpler quasi-steady-state, wherein spatial structure is entirely absent.

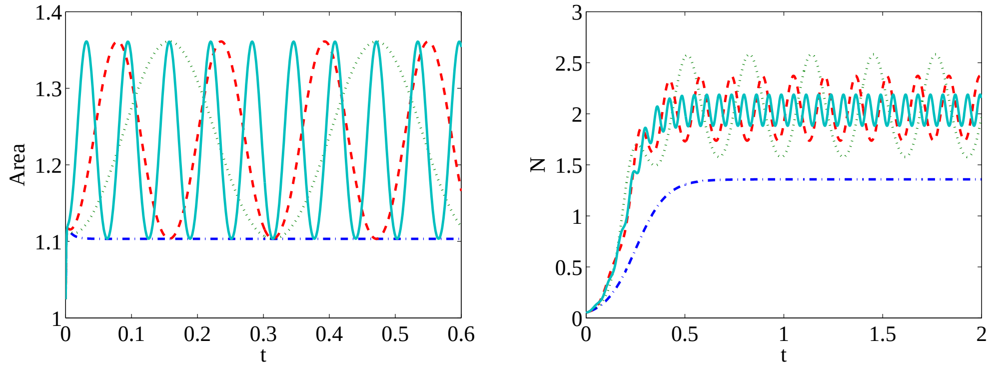
5 The homogeneous solution

If the metric tensor g_{ij} is separable, such that $g_{ij} = \rho^2(t)\, G_{ij}(\boldsymbol{q})$, then the geometric sink in Eq. (8) becomes uniform:

$$\frac{\partial \log \Gamma(\boldsymbol{q}, t)}{\partial t} = \frac{d \log \rho^2(t)}{dt}. \tag{41}$$

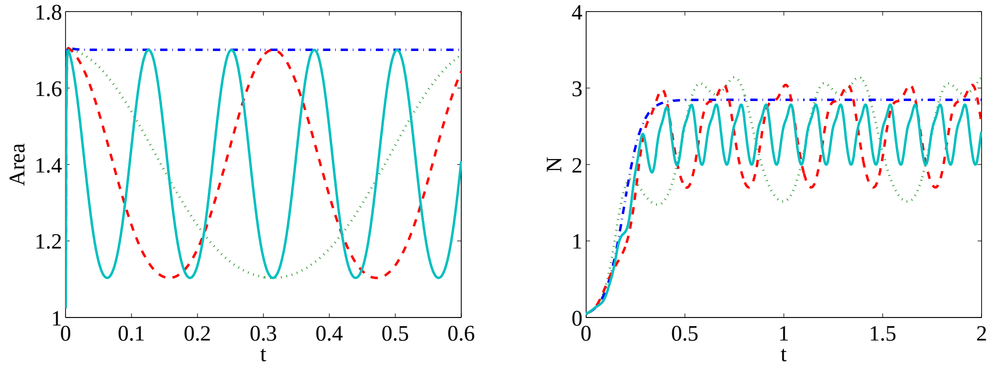
We call factor $\rho(t)$ is called the *scale factor*; the derivative $(1/\Gamma)\partial_t \Gamma$ is written throughout this section as $\partial_t \log \Gamma$ to emphasise the fact that it is a perfect derivative. This separability condition can be realised on a sphere of radius $R(t) = \rho(t)$, or on a torus, where the outer and inner radii are constrained as $R_1(t) = a\rho(t)$ and $R_2(t) = \rho(t)/a$ respectively, with $a > 1$. When we restrict ourselves to such metrics, a uniform solution is possible, which we now characterise.

When the geometric sink depends only on the scale factor, the presence of diffusion in the problem (8) makes the concentration relax to a uniform state. This is



(a) Area, first protocol

(b) Yield, first protocol



(c) Area, second protocol

(d) Yield, second protocol

Figure 4: The dependence of the reaction yield on the oscillation protocol. Here $n = 3$ and $\omega = 0$ ($\cdot-$), $\omega = 10$ ($\cdots$), $\omega = 20$ ($--$), and $\omega = 50$ (—).

given by the solution of the equation

$$\frac{\mathrm{d}c_0}{\mathrm{d}t} = \alpha c_0 \left(1 - c_0\right) - c_0 \frac{d \log \rho^2}{dt}, \tag{42}$$

with explicit solution [Polyanin, 2003]

$$c_0\left(t\right) = \frac{\mathrm{e}^{\int_0^t \left(\alpha - \frac{d \log \rho^2}{dt'}\right) \mathrm{d}t'}}{\frac{1}{c_0(0)} + \alpha \int_0^t \mathrm{e}^{\int_0^{t'} \left(\alpha - \frac{d \log \rho^2}{dt''}\right) \mathrm{d}t''} \mathrm{d}t'}. \tag{43}$$

We examine oscillating scale factors. In particular, we are interested in determining whether such oscillations enhance the yield of the autocatalytic reaction. We shall also extend our findings to bistable reaction kinetics. For definiteness, we consider the scale-factor variation

$$\rho(t) = \frac{r_0}{1 + \delta \sin\left(\omega t\right)}, \tag{44}$$

where r_0, $\delta < 1$ and ω are positive constants. The protocol (44) modifies the yield of the reaction, herein given by the formula

$$N\left(t\right) = g_0 \rho^2\left(t\right) c_0\left(t\right), \tag{45}$$

where g_0 is some geometric factor. We obtain the mean yield by taking the time-average of Eq. (45)

$$\langle N \rangle = \lim_{t\to\infty} \frac{1}{T} \int_0^T N\left(t\right) \mathrm{d}t.$$

To compute this, we use the oscillation protocol (44), together with the homogeneous solution (43), to obtain the asymptotic relation

$$\rho^2\left(t\right) c_0\left(t\right) \sim \frac{r_0^2}{1 + \frac{2\alpha\omega\delta}{\alpha^2+\omega^2}\left[\frac{\alpha}{\omega}\sin\left(\omega t\right) - \cos\left(\omega t\right)\right] + \frac{1}{2}\frac{\delta^2}{\alpha^2+4\omega^2}\left[\alpha^2 + 4\omega^2 - \alpha^2\cos\left(2\omega t\right) - 2\omega\alpha\sin\left(2\omega t\right)\right]}, \quad \text{as } t \to \infty. \tag{46}$$

(further details of this derivation are given in Appendix B. This gives the long-time average

$$\begin{aligned} \langle N \rangle &= g_0 \lim_{T\to\infty} \frac{1}{T} \int_0^T \rho^2(t) c_0(t)\,\mathrm{d}t, \\ &= g_0 r_0^2 \lim_{T\to\infty} \frac{1}{T} \int_0^T \frac{\mathrm{d}t}{1 + \frac{2\delta\alpha\omega}{\alpha^2+\omega^2}\left(\frac{\alpha}{\omega}\sin\left(\omega t\right) - \cos\left(\omega t\right)\right) + \frac{1}{2}\delta^2\left[1 - \frac{\alpha^2\cos(2\omega t) + 2\omega\alpha\sin(2\omega t)}{\alpha^2+4\omega^2}\right]}, && \text{(47a)} \\ &= g_0 r_0^2 \left[1 + \tfrac{1}{2}\delta^2 \frac{3\alpha^2 - \omega^2}{\alpha^2 + \omega^2}\right] + O\left(\delta^3\right), \qquad \omega > 0. && \text{(47b)} \end{aligned}$$

Thus, the amount of product created can either be raised or lowered, depending on the reaction rate and the oscillation frequency; for large frequencies, the yield is lowered.

The exact form of the yield $\langle N \rangle (\omega)$ is plotted in Fig. 5. Note that $\langle N \rangle (\omega)$ is not continuous at $\omega = 0$:

$$\langle N \rangle \left(\omega = 0\right) \neq \lim_{\omega\to 0} \langle N \rangle(\omega). \tag{48}$$

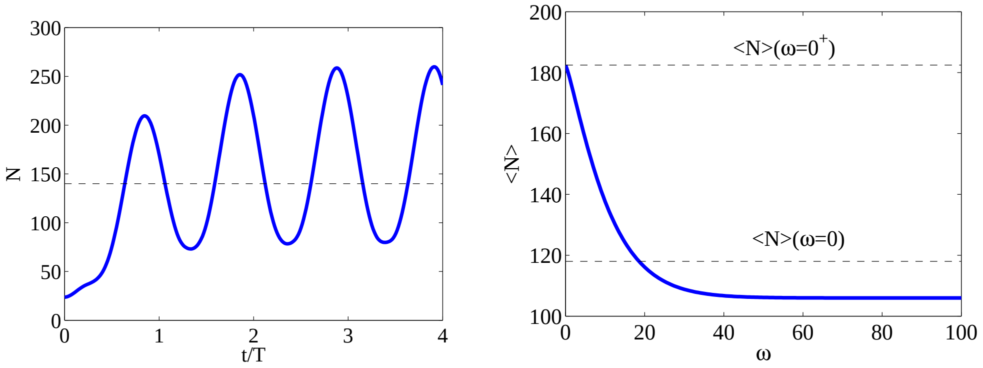
In more detail, if we set ω to zero in Eq. (45) and then average the result, we obtain $\langle N \rangle(\omega = 0) = g_0 r_0^2$. This corresponds to the case with no oscillations, and corresponds also to the left-hand side of relation (48). On the other hand, if instead we take ω to be a small but finite number in Eq. (45), compute the average, and then take $\omega \to 0$, we obtain the result

$$\langle N \rangle = g_0 r_0^2 \lim_{T\to\infty} \frac{1}{T} \int_0^T \frac{\mathrm{d}t}{1 + 2\delta\sin\left(\omega t\right) + \delta^2\sin^2\left(\omega t\right)} = g_0 r_0^2 \left[\frac{\sqrt{1-\delta^2} + 2\delta^2}{1-\delta^2}\right]. \tag{49}$$

This corresponds to the right-hand side of relation (48).

We also extend our investigation of the homogeneous state to more complicated mass-action laws, focussing on the bistable reaction. Here, in the absence of surface oscillation, there are two stable states: $c = 0$, and $c = 1$; there is also an intermediate, unstable state, $c = c_{\mathrm{mid}}$, where $0 < c_{\mathrm{mid}} < 1$. We study this reaction for the scale factor (44); the relevant homogeneous equation is

$$\frac{dc}{dt} = \alpha(c-1)(c_{\mathrm{mid}} - c)c + c\left(\frac{2\delta\omega\cos\omega t}{1 + \delta\sin\omega t}\right). \tag{50}$$



(a)

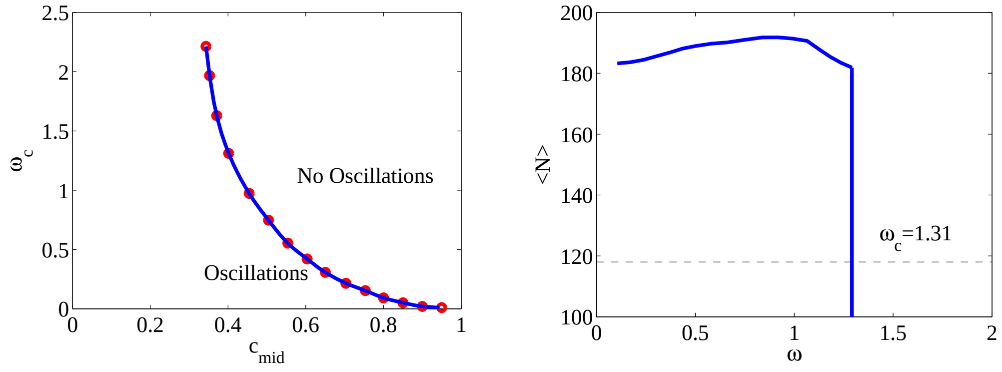
(b)

Figure 5: Homogeneous solution, separable metric. (a) The instantaneous yield $\langle N\rangle(t)$ for $\omega = 10 = \alpha$, and $\delta = 0.5$. The system settles down to a periodic state wherein the concentration oscillates with the driving-force frequency. The dashed line indicates the yield in the absence of oscillation; (b) The time-averaged yield as a function of the oscillation frequency. The units on the vertical axis in (a) and (b) are arbitrary, since only the difference between the stationary and driven yield curves matters.

The preferred state depends on the oscillation parameters and the unstable level c_{mid}. To see the relation between these parameters, we fixed $\delta = 0.5$ and $\alpha = 10$, and investigated the state selection as a function of ω and c_{mid}. For each value of c_{mid} there is a critical frequency such that above that frequency, the zero state is preferred, while below that frequency, an oscillatory state is selected. This relationship is shown in Fig. 6 (a). For large values of c_{mid}, close to $c_{\mathrm{mid}} = 1$, the critical frequency is shifted downward, indicating that the zero state is preferred for all but the slowest of oscillation frequencies. We have investigated the time-averaged mean yield as a function of ω and fixed c_{mid}. Fig. 6 (b) shows this relationship for $c_{\mathrm{mid}} = 0.4$. For $\omega < \omega_{\mathrm{c}}\,(c_{\mathrm{mid}} = 0.4)$, the time-averaged mean yield exceeds the stationary value (where $\omega = 0$), while for $\omega > \omega_{\mathrm{c}}$ the mean yield is zero.

The physical explanation of this state selection is as follows. Consider again (50). When $\delta = 0$, the states $c = 0$ and $c = 1$ are stable equilibria. Now, when δ is nonzero, the equilibrium state $c = 1$ ceases to exist. However, for small values of ω, the driving term can be treated as though it were a constant (since it varies slowly in this case), and the solution consists of slowly-varying oscillations around the original equilibrium points. Thus, the solution $c = 1 +$ oscillations is possible for small ω-values. On the other hand, when ω is large, the geometric sink can no longer be treated adiabatically, and this term drives the system. In this case, the evolution is always towards the only equilibrium state that persists, $c = 0$. In spite of this apparently simple explanation, care must be taken in describing the system fully: Eq. (50) is a nonlinear parametric oscillator equation, and a full quantitative description requires the kind of detailed numerical simulations performed herein.

In conclusion, the results in Fig. 6 demonstrate that for the correct parameter-tuning, it is still possible to obtain a yield above the stationary yield simply by an appropriate oscillation of the surface on which the chemical system resides. Further numerical results, along the same lines, can be found in the work of Kamhawi [2009].



(a) (b)

Figure 6: Characterisation of the bistable reaction. Subfigure (a) gives the parameter regimes in which either the zero state $c = 0$, or the oscillatory state, is selected as the asymptotic state. The oscillatory state is preferred at small frequencies, and the critical frequency is reduced at large c_{mid}-values. Subfigure (b) gives the time-averaged yield as a function of ω for $c_{\mathrm{mid}} = 0.4$. The time-averaged yield exceeds the stationary ($\omega = 0$; dotted line) yield for $\omega < \omega_{\mathrm{c}}$, while for $\omega > \omega_{\mathrm{c}}$, the yield is zero. The units on the vertical axis in (b) are arbitrary.

6 Conclusions

We have reviewed the theory of mass balance for flow-driven chemical reactions on arbitrary, time-varying surfaces. The associated partial-differential equation involves a geometric source / sink, which affects the reaction kinetics. In particular, we have reduced the problem to a diffusion-type problem, in the limit when the flow varies only on small scales, and when the manifold varies either on the small scales, or on the large scales. We focus on the state $c = 0$ of the autocatalytic reaction, and determine whether surface oscillations can stabilise this state. We have demonstrated that stirring and surface oscillation fail to stabilise this state when the scales of variation are small; however, if the manifold has large-scale variations, then stabilisation is possible. This condition for stabilisation is difficult to interpret, and we therefore turn in the latter part of the paper to numerical simulations.

Using numerical simulations, we have examined chemical reactions on the surface of a thin film under flow. We have investigated the behaviour of the reaction kinetics wherein the thin-film flow is forced using different oscillation protocols. Typically, those protocols that increase the surface area of the thin film are those that enhance the reaction yield. For the choices of oscillation protocol considered, it is the spatial scale of the flow, rather than its frequency, that controls the reaction. Finally, we have investigated separable metric tensors, wherein the geometric sink reduces to a function of time alone, and a homogeneous solution emerges. We have carried out numerical studies, for two kinds of reaction kinetics. For the logistic case, the reaction yield associated with the homogeneous solution can be enhanced by including an oscillating scale factor. The same is true for the bistable reaction, albeit with a twist: below a critical oscillation frequency the chemical concentration oscillates, giving an enhanced time-averaged yield; above this threshold however, the state $c = 0$ is selected, and the yield is zero. Both sets of numerical simulations exhibit some of the same generic features: that the geometric sink dramatically alters the outcome of the reaction (in particular the reaction yield), and that careful parameter tuning is required to generate an enhanced reaction yield.

Acknowledgements

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A The homogenised diffusion operator is uniformly elliptic

A.1 The metric has small-scale variations (Case 1)

We consider the homogenised problem (25)

$$\frac{\partial\widetilde{\psi}_0}{\partial\tau_1}\left(\tau_1,\boldsymbol{q}\right)=\left[\alpha+\left(\langle g^{ij}\rangle+M^{ij}\right)\frac{\partial^2}{\partial q^i\partial q^j}\right]\widetilde{\psi}_0\left(\tau_1,\boldsymbol{q}\right), \tag{51}$$

where the coefficients are defined in Sec. 3.1. In this appendix, we show that the quadratic form

$$Q(\boldsymbol{w}):=\varpi\left(\langle g^{ij}\rangle+M^{ij}\right)w_iw_j$$

is positive for non-zero constant covariant vectors w_i.

To prove this, we proceed in a manner similar to the calculation for compressible flow on flat surfaces Goudon and Poupaud [2004] (note, however, that the adjoint problem defined below differs substantially from the flat case). We introduce the notation

$$\frac{\partial\theta^i}{\partial\tau_2}+\frac{1}{\Gamma}\left[\frac{\partial\Gamma}{\partial\tau_2}+\frac{\partial}{\partial Q^j}\left(\Gamma U^j\right)\right]\theta^i+U^j\frac{\partial\theta^i}{\partial Q^j}-\Delta_Q\theta^i=-mU^i+\frac{1}{\Gamma}\frac{\partial}{\partial Q^j}\left(\Gamma g^{ij}m\right)+g^{ij}\frac{\partial m}{\partial Q^j},$$

or

$$\frac{\partial\theta^i}{\partial\tau_2}-\mathcal{L}_0\theta^i=-mU^i+\frac{1}{\Gamma}\frac{\partial}{\partial Q^j}\left(\Gamma g^{ij}m\right)+g^{ij}\frac{\partial m}{\partial Q^j},$$

or

$$\mathcal{T}_0\theta^i=-mU^i+\frac{1}{\Gamma}\frac{\partial}{\partial Q^j}\left(\Gamma g^{ij}m\right)+g^{ij}\frac{\partial m}{\partial Q^j}.$$

We also introduce the adjoint problem

$$\mathcal{T}_0^*\theta^{i*}=-\widehat{U}^{i*}:=-U^i-\frac{1}{\Gamma}\frac{\partial}{\partial Q^j}\left(\Gamma g^{ij}\right).$$

Here,

$$\begin{aligned}
\mathcal{T}_0 &= \frac{\partial}{\partial\tau_2} + \frac{1}{\Gamma}\left[\frac{\partial\Gamma}{\partial\tau_2} + \frac{\partial}{\partial Q^i}\left(\Gamma U^i\right)\right](\cdot) + U^i\frac{\partial}{\partial Q^i} - \Delta_Q\psi_1, \\
&= \frac{\partial}{\partial\tau_2} + \frac{1}{\Gamma}\frac{\partial\Gamma}{\partial\tau_2}(\cdot) + \frac{1}{\Gamma}\frac{\partial}{\partial Q^i}\left[\Gamma U^i(\cdot)\right] - \Delta_Q, \\
\mathcal{T}_0^* &= -\frac{\partial}{\partial\tau_2} - U^i\frac{\partial}{\partial Q^i} - \Delta_Q.
\end{aligned}$$

Consider now the diffusion matrix

$$\begin{aligned}
M^{ij} &= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\left(-\widehat{U}^i\theta^j\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\left(-U^i\theta^j + g^{ik}\frac{\partial\theta^j}{\partial Q^k}\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\left[-U^i\theta^j - \frac{\theta^j}{\Gamma}\frac{\partial}{\partial Q^k}\left(\Gamma g^{ik}\right)\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\left(-\widehat{U}^{i*}\theta^j\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\left(\mathcal{T}_0^*\theta^{i*}\right)\theta^j\,\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\theta^j\left(-\frac{\partial}{\partial\tau_2} - U^k\frac{\partial}{\partial Q^k} - \Delta_Q^2\right)\theta^{i*}\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2.
\end{aligned}$$

The part involving the time derivative can be re-written as

$$\begin{aligned}
\text{Time part} &= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\theta^j\left[-\frac{\partial}{\partial\tau_2}\left(\theta^{i*}\right)\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\theta^{i*}\left(\frac{\partial\theta^j}{\partial\tau_2} + \frac{\theta^j}{\Gamma}\frac{\partial\Gamma}{\partial\tau_2}\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2.
\end{aligned}$$

Similarly,

$$\begin{aligned}
\text{Space part} &= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\theta^j\left(-U^k\frac{\partial}{\partial Q^k} - \Delta_Q^2\right)\theta^{i*}\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}}\iint\limits_{\Omega_Q}\theta^{i*}\left[\frac{1}{\Gamma}\frac{\partial}{\partial Q^k}\left(U^k\Gamma\theta^j\right) - \Delta_Q\theta^j\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2.
\end{aligned}$$

Hence,

$$\begin{aligned}
M^{ij} &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta^{i*}\left[\frac{\partial\theta^j}{\partial\tau_2} + \frac{\theta^j}{\Gamma}\frac{\partial\Gamma}{\partial\tau_2} + \frac{1}{\Gamma}\frac{\partial}{\partial Q^k}\left(U^k\Gamma\theta^j\right) - \Delta_Q\theta^j\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta^{i*}\left[-mU^j + \frac{1}{\Gamma}\frac{\partial}{\partial Q^k}\left(\Gamma g^{jk}m\right) + g^{jk}\frac{\partial m}{\partial Q^k}\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta^{i*}\left[-\left(U^j + \frac{1}{\Gamma}\frac{\partial}{\partial Q^k}(\Gamma g^{jk})\right)m + \frac{1}{\Gamma}\frac{\partial}{\partial Q^k}(\Gamma g^{jk})m\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(m\theta^{i*}\mathcal{T}_0^*\theta^j\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2 + 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta^{i*}\left[\frac{1}{\Gamma}\frac{\partial}{\partial Q^k}\left(\Gamma g^{jk}m\right)\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2.
\end{aligned}$$

Consider therefore the quadratic form

$$\begin{aligned}
Q(\boldsymbol{w}) &= \varpi\left(\langle g^{ij}\rangle + M^{ij}\right)w_iw_j,\\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\langle\boldsymbol{w},\boldsymbol{w}\rangle\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2 + \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(m\theta_w\mathcal{T}_0^*\theta_w\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2\\
&\qquad + 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta_w^*\left[\frac{1}{\Gamma}\frac{\partial}{\partial Q^k}\left(\Gamma w_j g^{jk}m\right)\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&:= Q_1 + Q_2 + Q_3,
\end{aligned}$$

where

$$\theta_w^* = w_i\theta^{i*}, \qquad \theta_w = w_i\theta^i,$$

and $\langle\boldsymbol{w},\boldsymbol{w}\rangle = w_iw_ig^{ij}$. We now do the integral Q_2, herein performed on a generic test function ϕ:

$$\begin{aligned}
Q_2 &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(m\phi\mathcal{T}_0^*\phi\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\phi\left[-\frac{\partial}{\partial\tau_2} - U^k\frac{\partial}{\partial Q^k} - \Delta_Q\right]\phi\,\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\phi\left(\frac{\partial\phi}{\partial\tau_2} + U^k\frac{\partial\phi}{\partial Q^k} - \Delta_Q\phi\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2 - 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} \phi g^{ij}\frac{\partial\phi}{\partial Q^i}\frac{\partial m}{\partial Q^j}\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2.
\end{aligned}$$

Hence,

$$\begin{aligned}
&\int_0^{T_{02}} \iint\limits_{\Omega_Q} m\phi\left[-2\frac{\partial\phi}{\partial\tau_2} - 2U^k\frac{\partial\phi}{\partial Q^k} - \Delta_Q\phi\right]\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,\\
&\qquad = \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\phi\left(-\Delta_Q\phi\right)\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2 - 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} \phi g^{ij}\frac{\partial\phi}{\partial Q^i}\frac{\partial m}{\partial Q^j}\Gamma\mathrm{d}^2Q\,\mathrm{d}\tau_2,
\end{aligned}$$

or

$$2Q_2 = 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} m\phi\left(-\Delta_Q\phi\right)\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2 - 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} \phi g^{ij}\frac{\partial\phi}{\partial Q^i}\frac{\partial m}{\partial Q^j}\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2.$$

An application of integration by parts once on the first term yields

$$Q_2 = \int_0^{T_{02}} \iint\limits_{\Omega_Q} m g^{ij}\frac{\partial\phi}{\partial Q^i}\frac{\partial\phi}{\partial Q^j}\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2 \geq 0,$$

since g^{ij} is the metric tensor and is therefore positive definite.

We assemble these results now:

$$\begin{aligned}
Q &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\left(g^{ij}w_iw_j + g^{ij}\frac{\partial\theta_w^*}{\partial Q^i}\frac{\partial\theta_w^*}{\partial Q^j}\right)\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2 \\
&\qquad + 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta_w^*\left[\frac{1}{\Gamma}\frac{\partial}{\partial Q^k}\left(\Gamma w_j g^{jk} m\right)\right]\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\left(g^{ij}w_iw_j + m g^{ij}\frac{\partial\theta_w^*}{\partial Q^i}\frac{\partial\theta_w^*}{\partial Q^j}\right)\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2 \\
&\qquad - 2\int_0^{T_{02}} \iint\limits_{\Omega_Q} m w_j g^{jk}\frac{\partial\theta_w^*}{\partial Q^k}\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\left(\langle \boldsymbol{w},\boldsymbol{w}\rangle + \Big\langle \frac{\partial\theta_w^*}{\partial \boldsymbol{Q}},\frac{\partial\theta_w^*}{\partial \boldsymbol{Q}}\Big\rangle - 2\Big\langle \boldsymbol{w},\frac{\partial\theta_w^*}{\partial \boldsymbol{Q}}\Big\rangle\right)\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2, \\
&= \int_0^{T_{02}} \iint\limits_{\Omega_Q} m\Big\langle \boldsymbol{w}-\frac{\partial\theta_w^*}{\partial \boldsymbol{Q}},\boldsymbol{w}-\frac{\partial\theta_w^*}{\partial \boldsymbol{Q}}\Big\rangle\Gamma \mathrm{d}^2Q\,\mathrm{d}\tau_2 \geq 0.
\end{aligned}$$

Here, the penultimate line follows because g^{ij} is the metric tensor and is therefore positive symmetric; the last line follows because the metric tensor is positive definite.

A.2 The metric has large-scale variations (Case 2)

We consider Eq. (31), viz.

$$\frac{\partial\psi_0}{\partial\tau_1}\left(\tau_1,\boldsymbol{q}\right) = \left(\alpha+\Delta_q\right)\psi_0 + M^{ij}(\boldsymbol{q},\tau_1)\frac{\partial^2\psi_0}{\partial q^i\partial q^j} + B^i(\boldsymbol{q},\tau_1)\frac{\partial\psi_0}{\partial q^i} + A(\boldsymbol{q},\tau_1)\psi_0, \quad (52)$$

where the coefficients are defined in Sec. 3.2. We are going to show that M^{ij} is a positive-definite matrix and hence, the homogenised problem (31) is parabolic.

We take

$$\begin{aligned} Q(\boldsymbol{w}) &= \varpi M^{ij} w_i w_j, \\ &= -\int_0^{T_{02}} \iint\limits_{\Omega_Q} \left(U^i \theta^j\right) w_i w_j \, \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\ &= -\int_0^{T_{02}} \iint\limits_{\Omega_Q} \boldsymbol{U} \cdot \boldsymbol{w} \, \boldsymbol{\theta} \cdot \boldsymbol{w} \, \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\ &= -\int_0^{T_{02}} \iint\limits_{\Omega_Q} \boldsymbol{U} \cdot \boldsymbol{w} \, \theta_w \, \mathrm{d}^2 Q \, \mathrm{d}\tau_2. \end{aligned}$$

But recall Eq. (29):

$$\frac{\partial \theta_w}{\partial \tau_2} + U^k \frac{\partial \theta_w}{\partial Q^k} - g^{jk} \frac{\partial^2 \theta_w}{\partial Q^j \partial Q^k} = -\boldsymbol{U} \cdot \boldsymbol{w}, \tag{53}$$

or

$$\mathcal{T}_0 \theta_w = -\boldsymbol{U} \cdot \boldsymbol{w}.$$

Hence,

$$\begin{aligned} Q(\boldsymbol{w}) &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta_w \mathcal{T}_0 \theta_w \, \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\ &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \theta_w \left[\frac{\partial \theta_w}{\partial \tau_2} - g^{jk} \frac{\partial^2 \theta_w}{\partial Q^j \partial Q^k} + U^k \frac{\partial \theta_w}{\partial Q^k} \right] \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\ &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} \left[\frac{\partial}{\partial \tau_2} \left(\tfrac{1}{2}\theta_w^2\right) - \theta_w g^{jk} \frac{\partial^2 \theta_w}{\partial Q^j \partial Q^k} \right] \mathrm{d}^2 Q \, \mathrm{d}\tau_2, \\ &= \int_0^{T_{02}} \iint\limits_{\Omega_Q} g^{ij} \frac{\partial \theta_w}{\partial Q^i} \frac{\partial \theta_w}{\partial Q^j} \, \mathrm{d}^2 Q \, \mathrm{d}\tau_2 \geq 0, \end{aligned}$$

since g^{ij} is the metric tensor. Here, the integral involving the time derivative vanishes because of the temporal periodicity. Thus, the ordinary diffusion Δ_q is enhanced by the transport. This is not surprising, as the results of this section are clearly inherited from the flat-space calculation; the difference being the presence of lower-order terms A and B^i due to the spatial variations in the metric tensor.

B Asymptotic solutions of the uniform reaction-diffusion equation

In this appendix, we study in detail the asymptotic ($t \to \infty$) solutions of the equation

$$\frac{\mathrm{d}c_0}{\mathrm{d}t} = \alpha c_0 \left(1 - c_0\right) - c_0 \frac{d \log \rho^2}{dt}, \tag{54}$$

subject to

$$\rho(t) = \frac{r_0}{1 + \delta \sin\left(\omega t\right)}, \tag{55}$$

To do this, we use the following explicit solution for Eq. (54):

$$c_0\left(t\right) = \frac{\mathrm{e}^{\int_0^t \left(\alpha - \frac{d\log\rho^2}{dt'}\right)\mathrm{d}t'}}{\frac{1}{c_0(0)} + \alpha\int_0^t \mathrm{e}^{\int_0^{t'}\left(\alpha - \frac{d\log\rho^2}{dt''}\right)\mathrm{d}t''}\mathrm{d}t'}.$$

Hence,

$$c_0(t) = \frac{1/\rho(t)^2}{\frac{\mathrm{e}^{-\alpha t}}{c_0(0)\rho(0)^2} + \alpha\mathrm{e}^{-\alpha t}\int_0^t\left[\mathrm{e}^{\alpha t'}/\rho^2(t')\right]\mathrm{d}t'}.$$

In what follows, we take $t \to \infty$ and therefore omit terms that are proportional to $\mathrm{e}^{-\alpha t}$. Thus,

$$c_0(t) \sim \frac{[1+\delta\sin(\omega t)]^2}{\alpha\mathrm{e}^{-\alpha t}\int_0^t\mathrm{e}^{\alpha t}\left[1+2\delta\sin(\omega t')+\delta^2\sin^2(\omega t')\right]\mathrm{d}t'}, \qquad \text{as } t \to \infty.$$

We perform the integral and again omit terms that are proportional to $\mathrm{e}^{-\alpha t}$:

$$c_0(t) \sim \frac{[1+\delta\sin(\omega t)]^2}{1+\frac{2\delta\alpha\omega}{\omega^2+\delta^2}\left[\frac{\alpha}{\omega}\sin(\omega t)-\cos(\omega t)\right]+\frac{1}{2}\frac{\delta^2}{\alpha^2+4\omega^2}\left[\alpha^2+4\omega^2-\alpha^2\cos\left(2\omega t\right)-2\omega\alpha\sin(2\omega t)\right]}, \quad \text{as } t \to \infty.$$

Hence,

$$\rho^2\left(t\right)c_0\left(t\right) \sim \frac{r_0^2}{1+\frac{2\alpha\omega\delta}{\alpha^2+\omega^2}\left[\frac{\alpha}{\omega}\sin\left(\omega t\right)-\cos\left(\omega t\right)\right]+\frac{1}{2}\frac{\delta^2}{\alpha^2+4\omega^2}\left[\alpha^2+4\omega^2-\alpha^2\cos\left(2\omega t\right)-2\omega\alpha\sin\left(2\omega t\right)\right]}, \quad \text{as } t \to \infty.$$

References

G. Allaire and A. Piatnitski. Homogenization of nonlinear reaction-diffusion equation with a large reaction term. *Ann. Univ. ferrara*, 56:141, 2010.

G. Allaire and A.-L. Raphael. Homogenization of a convection-diffusion model with reaction in a porous medium. *C. R. Acad. Sci. Paris, Ser. I*, 344:523, 2007.

R. Aris. *Vectors, Tensors, and the Basic Equations of Fluid Mechanics*. Prentice-Hall, New Jersey, 1962.

J. Bicak and B. G. Schmidt. Self-gravitating fluid shells and their nonspherical oscillations in Newtonian theory. *The Astrophysical Journal*, 521:708, 1999.

D. A. Birch, Y.-K. Tsang, and W. R. Young. Bounding biomass in the Fisher equation. *Phys. Rev. E*, 75:066304, 2007.

J. P. Boyd. *Chebyshev and Fourier Spectram Methods*. Dover, second edition, 2001.

M. A. J. Chaplain, M. Ganesh, and I. G. Graham. Spatio-temporal pattern formation on spherical surfaces: Numerical simulation and application to tumour growth. *J. Math. Biol.*, 42:387, 2001.

S. Cox and G. Gottwald. A bistable reaction-diffusion system in a stretching flow. *Physica D*, 216:307, 2006.

E. J. Crampin, E. A. Gaffney, and P. K. Maini. Reaction and diffusion on growing domains: Scenarios for robust pattern formation. *Bull. of Math. Biol*, 61:1093, 1999.

R. V. Craster and O. K. Matar. Dynamics and stability of thin liquid films. *Rev. Mod. Phys.*, 81:1131, 2009.

A. Fannjiang and G. Papanicolaou. Convection enahnced diffusion for periodic flows. *SIAM Journal on Applied Mathematics*, 54:333, 1994.

J. Gjorgjieva and J. Jacobsen. Turing patterns on growing spheres: The exponential case. *Journal of Discrete and Continuous Dynamical Systems*, Supplement:436, 2007.

J. Gomatam and F. Amdjadi. Reaction-diffusion equations on a sphere: Meandering of spiral waves. *Phys. Rev. E*, 56:3913, 1997.

T. Goudon and F. Poupaud. Homogenization of transport equations: Weak mean field approximation. *SIAM J. MATH. ANAL.*, 36:856, 2004.

D. Hu and P. Zhang. Continuum theory of a moving membrane. *Phys. Rev. E*, 75: 041605, 2007.

K. Kamhawi. *Transport in Thin Films*. PhD thesis, Imperial College London, 2009.

S. Kondon and R. Asal. A reaction-diffusion wave on the skin of the marine angelfish *Pomacanthus*. *Nature*, 376:765, 1995.

R. Mauri. Dispersion, convection, and reaction in porous media. *Phys. Fluids A*, 3: 743, 1990.

P. McCarty and W. Horsthemke. Effective diffusion coefficient for steady two-dimensional convective flow. *Phys. Rev. A*, 37:2112, 1988.

D. W. McLaughlin, G. C. Papanicolaou, and O. R. Pironneau. Convection of microstructure and related problems. *SIAM J. Appl. Math.*, 45:780, 1985.

J. D. Murray. *Mathematical Biology*. Springer, Berlin, second edition, 1993.

Z. Neufeld. Excitable media in a chaotic flow. *Phys. Rev. Lett.*, 87:108301, 2001.

Z. Neufeld, C. López, and P. H. Haynes. Smooth-filamental transition of active tracer fields stirred by chaotic advection. *Phys. Rev. Lett.*, 82:2606, 1999.

S. A. Newman and H. L. Frisch. Dynamics of skeletal pattern formation in developing chick limb. *Science*, 205:4407, 1979.

A. Oron, S. H. Davis, and S. G. Bankoff. Long-scale evolution of thin liquid films. *Rev. Mod. Phys.*, 69:931, 1997.

G. C. Papanicolaou. *Diffusion in random media, in* Surveys in Applied Mathematics*, page 205.* Plenum Press, 1995.

G. Pavliotis and A. M. Stuart. *Multiscale Methods.* Springer, Berlin, 2008.

A. Pereira and S. Kalliadasis. On the transport equation for an interfacial quantity. *Eur. Phys. J. Appl. Phys.*, 44:211, 2008.

R. G. Plaza, P. Padilla F. Sánchez-Garduno, R. A. Barrio, and P. K. Maini. The effect of growth and curvature on pattern formation. *Journal of dynamics and differential equations*, 16:1093, 2004.

A. D. Polyanin. *Handbook of exact solutions for ordinary differential equations.* CRC Press, Boca Raton, FL, second edition, 2003.

S. Rosencrans. Taylor dispersion in curved channels. *SIAM J. Appl. Math.*, 57:1216, 1997.

J. G. Skellam. Random dispersal in theoretical populations. *Biometrika*, 38:196, 1951.

T. H. Solomon, S. Tomas, and J. L. Warner. Chaotic mixing of immiscible impurities in a two-dimensional flow. *Phys. Fluids*, 10:342, 1998.

H. Stone. A simple derivation of the time-dependent convective-diffusion equation for surfactant transport along a deforming interface. *Phys. Fluids A*, 2:111, 1990.

S. Strogatz. *Nonlinear dynamics and chaos.* Perseus, Massachussetts, 1994.

C. Varea, J. L. Aragón, and R. A. Barrio. Turing patterns on a sphere. *Phys. Rev. E*, 60:4588, 1999.

M. Vergassola and M. Avellaneda. Scalar transport in compressible flow. *Physica D*, 106:148, 1997.