6. SUSTAINED REACTION-DIFFUSION WAVES AND STATIONARY STRUCTURES IN AN OPEN REACTOR

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A severe hindrance to the development of studies of chemical spatial structures is the lack of reliable open reactors to provide a permanent feed of fresh reactants and simultaneously preserve the diffusion process. The Bordeaux group has developed an original reactor which satisfies these prerequisites, namely the "Continuous Couette Flow Reactor", made of a circular Couette flow fed at both ends by CSTRs. The tunable effective diffusion rate is much larger than common molecular diffusion rates allowing for large size reaction-diffusion structures. We report sequences of bifurcations between indefinitely sustained spatio-temporal structures exhibiting waves travelling back and forth as well as non-trivial stationary states obtained with a variant of the chlorite-iodide reaction. A simple dynamical model, analogous to those used in the description of excitable media, provides a good basis for a theoretical interpretation.

1. Introduction

The possible emergence of sustained spatio-temporal concentration patterns resulting from the sole coupling between reaction and diffusion processes in single phase isothermal chemical systems has been predicted as early as 1952 [1]. Ever since, these dissipative structures have been thoroughly studied both in their own right, in consideration of imaginable applications in the field of biology [2-5], and as a valuable prototype of non-equilibrium spatial structures in the field of non-linear science [6]. The evolution of the concentrations $c_i$ of the different species $i$ is ruled by a system of Reaction-Diffusion equations:

$$\frac{\partial c_i}{\partial t} = f_i(..., c_j, ... ) + D_i \Delta c_i$$

(1)

where the non-linear functions $f_i$ of the sole concentrations represent the contribution of reactive processes, the $D_i$ are the diffusion coefficients and $\Delta$ is the Laplacian operator. The relative simplicity of these systems comes
from the absence of advection terms associated with convective motions of the fluid. A number of chemical patterns, such as the so-called mosaic structures [7], have actually been shown to originate in parasitic convective motions [8] and will be discarded in the following. From a theoretical point of view, two classes of reaction-diffusion structures can be discriminated [9]:

- Structures resulting from destabilization of the homogeneous state by a non-homogeneous spatial mode [1,3,10-12]. They normally need differences between the diffusion coefficients of at least two different species, a generally unrealistic condition with small molecules for which the diffusion coefficient values are all about $10^{-5}$ cm$^2$/s.

- Structures associated with fronts, i.e. steep spatial changes of concentration which in turn correspond to a transition between two chemical states - in general an oxidized and a reduced state - with fast kinetics. Travelling waves in excitable media are the best known examples of such structures. This topic is extensively discussed in this book and in recent reviews [13-16]. Although they were generally observed as transient phenomena, indefinitely sustained wave patterns in chemical excitable media have recently been obtained experimentally [17-19]. A simple way to create a front structure is to impose a concentration gradient of initial reactants: if, for instance, the system is kept in the oxidized state at one position and in the reduced state at another position one expects a transition front to form between them. Such a gradient-imposed structure is somewhat trivial but we shall see that the front can be destabilized and start to move, and that additive stationary or moving fronts can form, leading to complex stationary or non-stationary patterns. The few theoretical studies of structures where the input species concentrations are fixed only on boundaries actually concern Turing type structures which are controlled by the gradient but there is almost no theoretical work on front structures intrinsically induced by this gradient [20-22].

Severe hindrances have delayed experimental research on sustained spatial chemical dissipative structures. Only recently the main practical problems have been solved and a few efficient reactors were designed to produce these structures [17,18,23,24]. We shall discuss results obtained with one of these pieces of apparatus, the Couette Flow Reactor. Another type of such reactor is presented in this conference by Dulos et al. [19]. The difficulties in devising a reactor to obtain a genuine reaction-diffusion process come both from the feeding procedure ensuring the non-equilibrium conditions and from the control of the transport processes (diffusion). We shall consider these questions successively.

- Difficulties raised by the feeding procedure: in most theoretical works on non-equilibrium chemical patterns the concentration of the input species is kept uniformly constant. This situation can only be approximated at the beginning of the reaction and cannot be sustained indefinitely without feeding the system with fresh reactants. Most practical feeding processes are associated with input streams and will most likely induce convective motions. An alternative, much more appropriate from an experimental point of view, is to feed the system only at boundaries where concentrations can easily be kept constant and let the reactants diffuse far into the core of the system where the influence of side effects induced by the feed is minimized. Since this easily achievable procedure implies the formation of concentration gradients, it is more likely suited to the study of the gradient-induced structures on which we shall focus in the following.

- Difficulties raised by the control of diffusion:
  - Any parasitic convection phenomena should be avoided. This can be