Chemical Dissipative Structures

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1. Historical perspective

One of the most outstanding achievements of I. Prigogine, for which he was awarded the Nobel prize for chemistry in 1977, deals with the way physico-chemical systems may spontaneously order in space or time when subjected to flows of matter or energy forcing them to function in a regime at a finite distance from equilibrium.

The first, and one of the most notorious example, first studied by H. Bénard in1900, is the extraordinary regular array of convection cells that spontaneously develop when a thin horizontal layer of fluid is heated uniformly from below as soon as the heat flux through the layer exceeds a well-defined threshold. Hexagonal patterns are the most familiar illustration, but simple rolls or squares are also possible. In each such cell the hot fluid rises and when cooled at the top sinks back again to reheat. Spurred on by this experiment some researchers immediately raised the possibility of generating stationary regular concentration patterns through the interplay of diffusion and chemistry. They failed because a key necessary property of the reactions was not apprehended at the time.

As explained in the paper of G. Nicolis, in the post World War 2, thanks to the work of I. Prigogine, L. Onsager, J. Meixner and S. De Groot and P. Mazur nonequilibrium thermodynamics became a well-organized discipline at least in the regime where there exists a linear relation between fluxes (heat in the Bénard experiment) and forces (temperature gradient). But Prigogine in collaboration with P. Glansdorff set out to reach further as they were interested in the behaviour of systems of coupled chemical reactions which are generally nonlinear and function rather far from equilibrium, outside the linear regime, if they are to be productive .

The British mathematician and computing pioneer A. Turing, in 1952, was the first to realize that the chemical interaction of two substances with different diffusion rates can cause pattern formation. This he showed on a complex kinetic model in the context of biological morphogenesis. Although Prigogine admits to have once discussed the matter with Turing, he was too involved with his research on generalizing thermodynamics to grasp, at that time, the full implications of Turing's work. Further discussion was prevented by Turing's untimely death. Thereafter in the framework of his more general research Prigogine showed with R. Balescu, in 1956, that the laws of nonequilibrium thermodynamics do not forbid the concentrations of chemically reactive systems functioning at a finite distance from equilibrium to oscillate periodically in time.

Such behavior emerged at the experimental level in the mid sixties with the self-oscillating Belousov-Zhabotinsky reaction that vindicated Prigogine's ideas. With his coworkers, in 1966, he then revived Turing's concept, showed that it was both thermodynamically and kinetically coherent but that it could only be sustained in continuously fed reactors at a finite distance from equilibrium using a class of *autocatalytic* reactions that could also give rise to temporal oscillations [1]. The necessity of such positive feedback was the element that was missing in the attempts made in the early 20th century. This step opened up a whole new field

of physical chemistry. Innumerable theoretical works followed and the *diffusion driven instability* that generates such *dissipative structures* has since popped up in many other domains relating to physics or chemistry.

2. Chemical dissipative structures

The Turing-Prigogine mechanism consists in the spontaneous instability of an homogeneous mixture of chemically reacting species, when some parameter crosses a *threshold* value (the feeding concentration of some chemical species for instance) as one moves away from the equilibrium conditions. It leads to stationary, space-periodic patterns for the concentrations of reactants (Fig.1) whose wavelength is a function of kinetic parameters and diffusion coefficients. In its minimal form the description of all the systems that exhibit such diffusive instability



Figure 1. Turing structures of different symmetries obtained with the chlorite-iodide-malonic acid reaction. Dark and light regions respectively correspond to high and low iodide concentration. The wavelength, a function of kinetic parameters and diffusion coefficients, is of the order of 0.2 mm. All patterns are at the same scale: view size 1.7 mm x1.7 mm (Courtesy P. De Kepper, CRPP).

can formally be cast in the common language of *reaction-diffusion* systems governed by the following set of equations:

$$\frac{\partial \boldsymbol{c}(\boldsymbol{r},t)}{\partial t} = \boldsymbol{f}(\boldsymbol{c},b) + \nabla \boldsymbol{.} \boldsymbol{D} \nabla \boldsymbol{c}(\boldsymbol{r},t)$$

where $c(r, t) = (..., c_i, ...)$ is the local concentration vector, f(c, b) is a vector function representing the reaction kinetics wherein lies the source of nonlinearity, b stands for the set of control parameters and D is the matrix of diffusive transport coefficients. Appropriate initial and boundary conditions, in relation with the experimental setup are added to complete the mathematical formulation.

To support such symmetry breaking instability, the chemical kinetics has to involve, as mentioned, some type of positive feedback loop controlled at least by an *activator* species that reinforces its own changes, the latter being counterbalanced by an *inhibitory* process. Spatial structures can form when the inhibitory effects are transported by diffusion over a larger space range than that of the activatory mechanism. An intuitive picture may be obtained when

a single activator (A) and inhibitor (H) are present. Species A autocatalytically promotes its own production and that of H, while the latter opposes the production of A. Consider such system in a nonequilibrium homogeneous steady state (hss) and quench it beyond the instability threshold. The hss then becomes very sensitive. A slight local fluctuation of the concentration of A will increase while it also spreads to the surroundings through diffusion. It will also start producing some H that however will diffuse away much faster from the point where the fluctuation occurred as $D_H > D_A$. H thereby hinders the propagation of A that would otherwise spread like a grass fire. A localized peak of activator surrounded by a barrier of H is thus created. In extended systems such peaks tend to emerge everywhere, randomly distributed. Their interaction will then lead to the periodic concentration patterns [2]. The beauty lies in the counterintuitive organization role of diffusive processes when they compete with the proper autocatalytic chemistry, although diffusion still locally strives to erase any concentration inhomogeneity.

3. Theoretical aspects

Nonlinear kinetic models for f(c, b) with a limited number of chemical species, typically two or three (e.g. the Brusselator) are the backbone of theoretical work. These models stand as a compromise between a minimum of chemical realism and mathematical tractability. For their part the experimentally determined kinetic schemes usually involve a large amount of species, often not yet unequivocally determined. For some reactions skeleton schemes that semi quantitatively represent their kinetics in a subset of conditions may nevertheless be obtained (the Oregonator model of the Belousov-Zhabotinsky reaction for instance) [3]. Because of the presence of the autocatalytic processes the reaction-diffusion equations constitute a set of non linear partial differential equations characterized by non unicity of solutions. Theoretical advances therefore rely heavily on *bifurcation theory*, a branch of the theory of non linear dynamics. It allows to determine, through the solution of equations for the amplitudes of the patterns, which structures of given symmetry are stable for specific conditions (pattern selection). The calculated bifurcation diagrams help to organize the results obtained by straightforward numerical integration of the reaction-diffusion equations. The information may finally be used to interpret the experimental results. Indeed as we see in Fig. 1 patterns of various symmetries show up depending on the experimental conditions.



Figure 2. Schematic representation of a disc shaped one side fed reactor (OSFR): CSTR (continuous stirred tank reactor), Membrane (mineral disc, pore size $0,02 \ \mu m$) often placed to protect the gel from mechanical stress produced by the stirrer of the CSTR, Gel, In and Out (input and output ports of chemicals), L (light source), CCD camera.

4. Experimental realization of chemical dissipative structures

Experiments in the chemical realm lagged behind theory for a long time and it was only near the end of 1989 that the first experimental evidence was obtained by P. De Kepper and his group [4] using the chlorite-iodide-malonic acid reactive system in so-called gel reactors. These open spatial reactors are specifically designed to control the reaction and the structures that eventually develop at a fixed distance from equilibrium. They allow to probe the true asymptotic states of the reaction-diffusion systems. Experiments are now usually performed in a one-side fed reactor (OSFR) sketched in Fig.2. The core consists of a piece of soft hydrogel fed by diffusion through one of its faces with chemicals contained in a continuous stirred tank reactor (CSTR) the contents of which are continuously renewed by pumps. The other faces of the gel are pressed against impermeable transparent walls (Plexiglas). Visualization can be achieved both along the feeding axis or orthogonal to it. The gel is used to avoid all perturbations induced by the hydrodynamic flows as those associated with the constant supply of fresh reactants, so that only reactive and diffusive processes compete. The necessary diffusion differential between activator and inhibitor species is obtained through the reversible binding of the activator molecules (iodide in the structures presented in Fig. 1, while the chlorite is the inhibitor) to the large molecular weight colour indicator species that is included for visualization purposes (starch in our example). An advantage of such reactors is that they allow for direct correlations to be made between the dynamics of the chemistry in the CSTR, the bifurcation behaviours of which have been extensively studied in the past, and that of the gel. The experimental discovery naturally refueled the research in the field. A recent detailed account of the status of Turing patterns and other symmetry breaking instabilities in solution chemistry is presented in [5].

The concept of chemical dissipative structures have been a source of inspiration for tackling problems involving pattern formation in an ever growing variety of fields, including areas of technological interest, from a new angle. A representative example is briefly presented in the next section. Curiously, in the field of biological morphogenesis from where it originated, Turing's idea has not yet received an unambiguously experimental support.

5. Dissipative microstructures in irradiated materials

Irradiation of materials with energetic particles may induce important variations in their physico-chemical properties. Irradiation effects are important in a wide range of technical applications, ranging from nuclear and fusion energy to micro-electronics and surface engineering. Such irradiated materials are subjected to the generation of non-equilibrium concentrations of atomic defects. Furthermore, strong deviations from thermodynamic equilibrium drive defects into the formation of defect clusters and regular spatial distributions with wavelength in the nano- and micrometer range. This phenomenon appears to be generic, and not confined to one type of defect. Furthermore, striking observations have shown that, complete spatial isomorphism may exist between the periodic structure of defect distributions and that of the fundamental atomic lattice, at least for the three main metal structures (FCC, BCC, and HCP). From a technological perspective a clear understanding of this phenomenon would allow better designs of radiation-resistant materials in nuclear technologies (e.g. fission and fusion energy). Also they arise in ion, plasma and electron beam processing that are becoming unavoidable tools in the manufacturing of electronic, photonic and micro

Since the first observation of lattices of voids in metal alloys subjected to irradiation, many models were used to explain their origin [6]. Here we focus on a description emphasizing the

basic interactions between defect populations, where the formation of irradiation-induced microstructures arises as a consequence of spatial instabilities as discussed above. In this approach, it is assumed that the evolution of defect populations, may be described with a dynamical model based on kinetic rate equations [7] analogous to chemical reaction-diffusion equations, and take into account defect production, motion and interactions.

Radiation-produced defects are represented by two equations for point defects (vacancies and interstitials), which are considered as mobile species, and a set of equations describing the evolution of dislocations loops and voids, which are considered as immobile species. Point defects may diffuse in the three-dimensional crystal lattice and account should therefore be taken of anisotropies since interstitial atoms move preferentially along close-packed crystallographic directions. Their mobility may be strongly different, according to temperature. The basic processes responsible for defect density evolution are the following. Point defect production corresponds to the irradiation-induced generation of Frenkel pairs. Vacancy and interstitial loops are produced by the collapse of point defects, which are also annihilated through pair recombination or absorption at line (dislocations and loops) or surface (voids) defects. Vacancies, interstitial loops and voids, are immobile, and their densities evolve by point defect absorption and thermal emission only.

Because of the non linear autocatalytic interactions and the highly different mobilities the conditions for the creation of periodic spatial modulation of defects densities are easily met on increasing the radiation dose. The multiplets of solutions of the resulting dynamic equations may again be apprehended by the combination of bifurcation theories and numerical analysis.

In the chemical problem conditions could be met such that the dissipative structures where quasi-bidimensional. Patterns in three dimensions can also readily be obtained by increasing the thickness of the gel. They are however deeply affected by the concentration gradients along the feeding direction and difficult to resolve optically. In the case of defects organization the structures are naturally three-dimensional. The generic patterns are then on increasing the constraint parameter: BCC lattices, hexagonal prisms or planar wall structures. Therefore BCC lattices, formed at low irradiation dose, should transform into planar arrays at high irradiation [7].



Figure 3. Snapshots of the evolution of the amplitude of the vacancy loop microstructure in space at different irradiation doses for annealed nickel under typical accelerator conditions and low temperatures (dislocation network density = 10^{13} m^{-2} , damage rate = $10^{6} \text{ dpa.s}^{-1}$, temperature = 773 K) in the case of isotropic point defect diffusion (top line: the dose is increasing to the right from 1 dpa to 20 dpa), and with a 1% anisotropy in the interstitials diffusion coefficient (lower line: the dose is increasing similarly). The typical length scale is of the order of 150 nm.

Because of the diffusion anisotropies the dislocation microstructure will be oriented parallel to the directions of high interstitial mobility. Hence, at low irradiation dose, the loop and void structures should exist in orientations parallel to the underlying crystal lattice with the same symmetry, while at high irradiation dose, they should consist of planar arrays parallel to close-packed crystalline axes. Some results of the numerical integration of the dynamic equations of defect densities are illustrated in Fig. 3. For isotropic point defect diffusion, the structure evolves towards mosaic-like patterns, while, for anisotropic interstitial diffusion, stripe patterns are obtained, in orientation parallel to the high interstitial mobility direction. This confirms that the anisotropies triggered by the crystalline structure of the material may be essential in determining the orientation of the defect microstructures, in general agreement with experimental observations [8].

6. Conclusion

The beauty of the self-organizations in Figs. 1 and 3 should not distract us from the fact that at the microscopic level the atomic or molecular processes that take place "chaotically" and are similar whatever the region of the system we focus on. It may be shown that the coherent behaviour at the macroscopic level results from the emergence of long-range correlations induced by the nonequilibrium constraints. To quote Prigogine *dissipative structures*, as those exhibited here, may be "visualized as a kind of 'factory' in which a better subdivision of the work leads to an increased efficiency" [9].

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Keywords

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