

From Transport Phenomena to Systems Chemistry: Chemohydrodynamic Oscillations in $A + B \rightarrow C$ Systems

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Can simple chemistry drive the emergence of self-organised complex behaviours? Addressing this big-picture question crucially impacts the comprehension of fundamental mechanisms at the basis of stationary and dynamical spatio-temporal chemical patterns which represent an integral part of Origin of Life studies and morphogenesis. This is also of paramount importance in cutting-edge approaches for the design and control of bio-inspired self-organised functional materials as well as for understanding how complex biological networks work. So far, spontaneous chemical self-organisation has constituted the realm of Nonlinear Chemistry. Oscillations, waves, Turing structures have been typically obtained in systems characterised by a complex network of nonlinear reactions activated on appropriate relative timescales. Here we

revisit the emergence of oscillatory dynamics in systems characterised by a kinetics as simple and general as a bimolecular process, provided that it is actively coupled with transport phenomena, in the absence of any nonlinear or external kinetic feedback. We also present new numerical experiments to substantiate and clarify the minimal ingredients underlying these complex dynamics. The objective of this paper is to discuss chemo-hydrodynamics as a possible mechanism for activating self-organised structures and functional behaviours in contexts characterised by a minimal chemistry like prebiotic conditions. In this view, we also highlight the necessity to include convective phenomena in the paradigm of Systems Chemistry.

1. Introduction

Systems chemistry is rapidly learning from nature how complex mixtures of interacting molecules can bear collective emerging properties not deducible as a simple sum of the single components behaviours. Understanding and mastering such properties can deeply impact on several fields, ranging from practical applications (next-generation intelligent materials, smart medicine and drug delivery systems, etc.) to fundamental problems (order-out-of-disorder, origin of life, etc.), including grand challenges like the creation of synthetic life.

Systems chemists generally adopt a bottom-up approach to design chemical systems able to self-assembly in highly ordered supramolecular structures and/or to produce self-organised behaviours that accomplish complex functions inspired by biological processes (autopoietic behaviour, self-replication and biocatalysis, etc.). The strategies in pursuing these tasks rely on

few broadly accepted starting points:^[1–3] the systems have to be i) far-from-equilibrium and dissipative; ii) confined and compartmentalised, yet able to communicate and exchange matter and information with the environment (i.e. open); iii) governed by nonlinear mechanisms and kinetics (i.e. presence of feedbacks and loops). Within this essential list of prerequisites for emergent behaviours, the role of transport phenomena has been, in our opinion, somehow overlooked. If, since the seminal work of A. Turing, molecular diffusion in combination with nonlinear kinetics has become implicit in morphogenesis and spontaneous formation of patterns,^[4,5] convection and hydrodynamics flows are often regarded as an undesirable complication to be removed from the scene. Recently, the importance of complex transport such as chaotic advection has been reviewed.^[6]

Here, we discuss how convective flows, particularly when induced by chemical reactions, can create the conditions for self-organised compartmentalisation and functional behaviours, with possible application in origin of life studies and, more in general, in systems chemistry.

We first briefly review the potential of hydrodynamic instabilities in the formation of confined structures (convective cells) that can trap, accumulate and preserve chemical species in the absence of chemical or physical barriers. Secondly, we analyse in more details the input of convective flows to complex dynamics and spatio-temporal self-organisation in systems fueled by simple chemical processes, such as bimolecular kinetics. Any chemical reaction can, in fact, activate fluid motions by inducing *in-situ* local changes of the medium properties such as surface-tension and density, and, in turn, such chemically-driven hydrodynamic flows can feedback on the spatio-temporal evolution of the chemical species. This

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An invited contribution to a Special Collection on Chemobionics

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active interplay between chemistry and hydrodynamics, recently termed *chemo-hydrodynamics*^[7,8] and schematised in Figure 1a, has been already shown to induce spatio-temporal organisation^[9–11] and affect several applied problems as diverse as CO₂ geological sequestration, pollutants dispersion, crystal growth techniques and oil extraction.^[12–17]

We have recently exploited the chemo-hydrodynamic interplay to show that emergent behaviours like spatio-temporal oscillations, classically pertaining to nonlinear chemistry, arise spontaneously in the general class of simple $A+B\rightarrow C$ processes.^[18] Pulsations take place upon reactive mixing between two general fluids A and B, initially separated in space. The product actively fuels *in-situ* convective Marangoni flows by locally increasing the surface tension at the reactive area (see sketch in Figure 1b). These flows combine, in turn, with the reaction dynamics and diffusion, inducing damped spatio-temporal oscillations of the chemical concentrations and the velocity field. Antagonistic buoyancy forces arising from con-

current density changes can further sustain and modulate this oscillatory mechanism.

In this work, we revisit the main features of these chemo-hydrodynamic scenarios to substantiate the robustness and generality of this theoretical framework in terms of the essential building blocks: localisation of a reactive source, onset of chemically-driven transport phenomena, antagonistic orientation and optimal relative magnitude of the main contributions to the fluxes.

This delineates the ground for discussing the potential of chemo-hydrodynamic mechanisms as a pathway for the emergence of self-organised structures and functional behaviours in contexts characterised by elemental chemistry, including prebiotic conditions. We will finally suggest an experimental route to test this scenario in the presence of simple organic molecules, inorganic salts, or photosensitive surfactants.

We first start by reviewing some important features of complexity related to origin of Life.

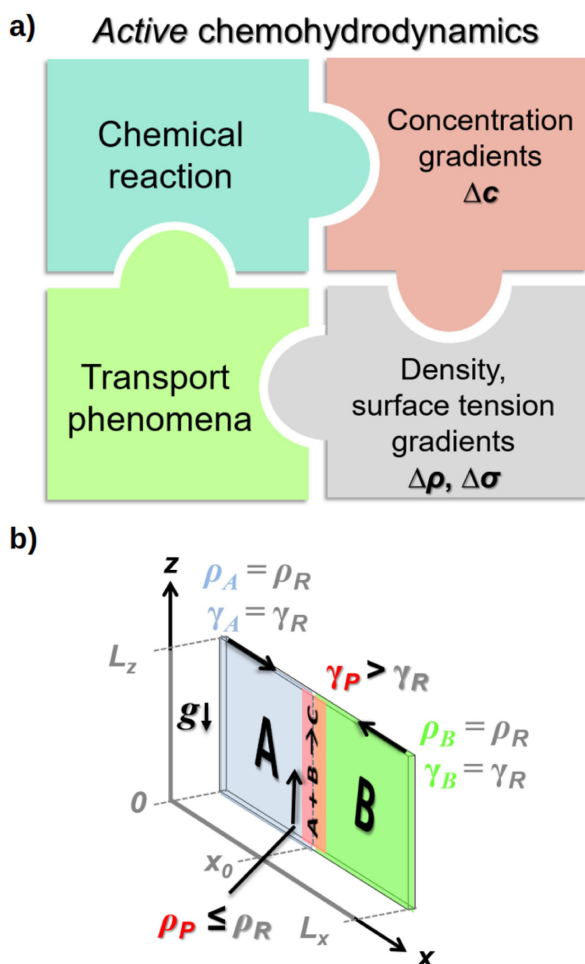


Figure 1. a) Scheme of an *active* chemohydrodynamic interplay.^[7,8] b) Initial configuration of the reactants and forces at play for the development of chemo-hydrodynamic oscillations. The two reactants solutions of A and B have the same surface tension $\gamma_A = \gamma_B = \gamma_R$ and density $\rho_A = \rho_B = \rho_R$, while in the reactive zone, where C forms, the surface tension locally increases $\gamma_P > \gamma_R$ and the density can decrease, $\rho_P \leq \rho_R$.

2. Origin of (Bio)chemical Complexity

Within abiogenesis theory, common opinion is that conditions for Life to emerge lie at the intersection between physics and chemistry.^[19] This is the reason why the scientific investigation on this fascinating topic involves the synergy of different expertise from several disciplines among which chemistry plays a prominent role.^[20] One of the focuses of abiogenetic theories is understanding, from a synthetic point of view, the transition from simple inorganic compounds of Earth's early atmosphere (methane, hydrogen, ammonia, etc.) to complex organic molecules relevant to life.^[21] In parallel, a more theoretical approach tries to understand how chemical processes can trigger self-organisation and emergent behaviours that can be involved in the minimal functionalities and traits of alive matter.^[22] In this respect, two concepts that we will review below seem to be essential prerequisites for the development of order from disorder:^[21] compartmentalisation and nonlinear kinetics (in far-from-equilibrium conditions). As I. Prigogine, used to say, *Matter out of equilibrium begins to see*, and nonlinear science provides fundamental keys for understanding how biological complexity may have developed from inorganic chemistry.^[5,23,24]

2.1. Compartments

Driven by the modern concept of cell, compartmentalisation is generally associated to the presence of semipermeable membranes made by amphiphilic molecules (fatty acids, phospholipids, surfactants, etc.). The confinement in membrane compartments is an evolutionary result, functional to keep important molecules readily available for metabolic reaction networks and increase the probability of many-body interactions; moreover molecules trapping boosts the metabolically inexpensive transport of chemical information by passive diffusion and allows to

control the in-out flow throughout the cell, preserving the cell core from unneeded or harmful species.

However, compartmentalisation can be intended in a broader sense the physico-chemical constriction of relevant molecules for life-type processes in sub-domains. Earlier forms of life probably developed in simpler confined environments such as surface of solid porous materials like clays, silicates or other ancient minerals that, beside their catalytic activity, allow for high concentration of chemical species in diluted conditions.^[25]

An extensive survey on the role played by interfaces and alkaline hydrothermal vents in the origin of life can be found in.^[26–28] In this context, convective structures may have also represented a plausible strategy for molecules accumulation and trapping. As the simple Bénard experiment taught us,^[5] convective motions driven by thermal gradients can break the symmetry of initially homogeneous systems to create ordered collective motions of one or more (reactive) chemical species in circumscribed spatial domains where they are locally more abundant. In a recent series of theoretical and experimental works (see [29–32] and references therein), Braun and co-workers proposed these thermally-driven convective scenarios, sustained by external temperature gradients and combined with thermophoresis, as first viable mechanisms for the accumulation and selection of biologically relevant molecules such as DNA and RNA. Thermophoresis is known to induce a flux of molecules (charged biomolecules^[32]) parallel to temperature gradients, leading to an accumulation in colder regions. In synergy with thermophoresis, thermally-driven convection favours the trapping of DNA molecules in local (stagnation) points, thus creating the necessary compartmentalisation. Apart from molecules accumulation, this mechanism was found to be particularly effective in terms of replication. Thermally-driven natural convection drives collective motion of molecules along cycles which sweep them from hotter to colder regions. This pathway favours a strong binding to template molecules during the residence in cold regions while double-stranded DNA easily detach into single-stranded DNA when transported in areas characterised by peaks of temperature (Figure 2). This cycle of replication repeats itself and it was verified that Rayleigh-Bénard-like laminar flows can sustain an exponential amplification of DNA replication by polymerase chain reaction (PCR). It proved to be even more efficient than PCR carried out in standard PCR cyler machines where the whole reaction vessel has to be periodically heated and cooled.^[31]

Braun et al. identified porous hydrothermal systems at the deep-sea floor, where water heated by magma meets cold ocean water, as the most suitable setting for this scenario. This agrees with other theories hypothesising hydrothermal porous rocks as the first hosts of the early forms of life.^[25]

When coupled with convective spatial self-organisation, even extremely simple chemical reactions can also generate complex and highly ordered structures. For example, Avnir and Kagan^[12,33] found that the evaporative cooling of a surface and density-driven instabilities, associated to the photolysis of simple organic molecules, bears evolving stripes and patterns in the spatial domain. They argued that such structures could have served as a prodrome for a hierarchical organisation, i.e.

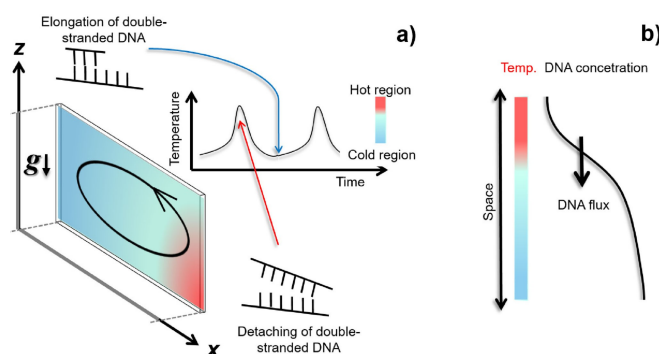


Figure 2. Sketch of the thermally-induced convective and thermophoretic scenario proposed by Braun et al.^[31] as a possible mechanism at the basis of DNA trapping and replication in early-life environments. Thermophoresis provides a means for DNA molecules accumulation sustained by externally sustained temperature gradients (the flux of the molecules is parallel to a spatial temperature gradient as illustrated in panel b)) while thermally-driven convective cycles (cartooned in panel a)) sustain the periodic binding and unbinding processes between single- and double-stranded DNA, in cold and hot regions, respectively. The profile characterising this periodic excursion from low to high temperature experienced by molecules along the circular flows is also shown.

primary templates where complex molecules aggregation and secondary (biochemical) reactions had the chance to develop in early evolutionary stages, ultimately bringing to life.^[34]

2.2. Nonlinearities

Autocatalytic and oscillatory reactions acquired great plaudits for their capability to describe symmetry breaking phenomena (e.g. the emergence of homochirality) and explain the origin of RNA world.^[35] As benchmark test-tube models, they also allow to get insights on metabolic oscillations as well as on the nonlinear behaviour characterising RNA replication and enzymatic reactions. Indeed, autocatalytic cycles have been considered an essential feature in the origin of life and are at the basis of chemically-driven biologic-like functionalities (catalysis, self-replication, chemotaxis, etc.), which appear to be a must-have requirement for the transition from nonliving to living environment.^[20]

Currently, these nonlinear mechanisms play a central role in promising bottom-up approaches for the design of synthetic life-like systems. Chemical oscillators and autocatalytic reactions combined with chemo-responsive gels can produce mechano-chemical contraction-relaxation cycles^[36] which can be exploited for artificial muscles, self-locomotion, smart strategies for drug delivery^[37] and to trigger cell division.^[38] Chemical oscillators encapsulated in compartmentalised structures are also used to imitate synthetic neurons as well as to get into chemical communication strategies and collective cellular synchronisation at the basis of organs activity and brain-like processes.^[39–41]

However, despite rather simple autocatalytic reactions being well documented,^[42] the establishment of complex chemical kinetics requires simultaneous and spatially localised multi-body interactions, occurring on suitable relative time-

scales. Since this appears quite difficult in highly diluted environments such as the primordial world, a fundamental question is, thus, whether it is possible to conceive alternative scenarios relying on a simpler chemistry for the emergence of such behaviours.

A + B → C systems,^[43] whereby two reactants A and B, initially separated in space, start reacting upon diffusive mixing yielding a localised reaction front, constitute a benchmark to address this question. These systems play a central role in the young discipline of *Chemobionics*.^[44] Here they are widely adopted for describing a wealth of self-organised structures including precipitation patterns like Liesegang bands and, in combination with more complex mechanical and transport mechanisms, to model the growth of chemical gardens.^[45,46] Firstly studied as conceptual systems for understanding biological morphogenesis,^[47] the new generation of chemical gardens is a subject of extensive and in-evolution interest in Chemobionics as environments for early forms of life^[44] as well as models to design and fabricate materials with unprecedented properties.^[48–51]

In A + B → C systems, a reaction front (i.e. a localised region with non-zero production rate) develops under control and influence of the transport processes feeding the reaction. The dynamical and structural properties of these fronts have been extensively studied in various conditions^[43,52–54] and contextualised to diverse scientific areas ranging from engineering to finance. Although periodic dynamics were induced by extending this problem to an A + B → *Oscillator* case, where A and B are pool solutions containing separated reactants of a chemical oscillator,^[55,56] the chance for oscillatory dynamics is intrinsic to the complex kinetics of the system and no evidence for truly emergent dynamics in A + B → C systems had never been reported.

We have recently shown^[18,57] that chemically-driven transport phenomena can introduce a nonlinear feedback, resulting in oscillatory dynamics of such systems that we will revisit below.

3. Chemo-hydrodynamic Oscillations in A + B → C Systems

Conditions for the birth of chemohydrodynamic oscillations in A + B → C are cartooned in Figure 1 and summarised in their minimal traits hereunder. Two pools of the general reactants A and B solutions (with same surface tension $\gamma_A = \gamma_B$, and density ρ_A and ρ_B) are put into contact in a two-dimensional isothermal reactor of length L_x and height L_z in a (x, z) reference frame, where the z axis is oriented vertically against the gravitational acceleration $\mathbf{g} = (0, g)$. A and B react upon diffusive mixing to yield species C and at the free top edge of the reactor, the reaction locally changes the surface tension, thus generating a convergent stress toward the reactor centre (initial reactant's contact line, x_0). A possible additional mechanism is that C can also decrease the local density, thus promoting an antagonistic upwardly oriented gravitational current at x_0 . The resulting nonlinear dynamics is governed by a set of partial differential

Reaction-Diffusion-Convection (RDC) equations discussed at length in refs. [18,57], where the bimolecular kinetics is coupled with Fickian diffusion and incompressible Navier-Stokes equations [Eqs. 1–4]:

$$\partial_t a + (\partial_z \psi \partial_x a - \partial_x \psi \partial_z a) = \nabla^2 a - ab, \quad (1)$$

$$\partial_t b + (\partial_z \psi \partial_x b - \partial_x \psi \partial_z b) = \nabla^2 b - ab, \quad (2)$$

$$\partial_t \omega + (\partial_z \psi \partial_x \omega - \partial_x \psi \partial_z \omega) = S_c (\nabla^2 \omega - \Delta R (\partial_x a + \partial_x b)) \quad (3)$$

$$\nabla^2 \psi = -\omega, \quad (4)$$

Here a, b are the dimensionless concentrations ($i_s = a_s, b_s$ are the surface dimensionless concentrations of the chemical species at $z = L_z$). For this system (reactants with same initial concentration $A_0 = B_0$ and all the species with same diffusivity, D), the concentration field c can be obtained as $c = (1 - a - b)/2$. The vorticity ω and the stream function ψ are related to the velocity field $\mathbf{v} = (u, v)$ as $\omega = \nabla \times \mathbf{v}$, $u = \partial_z \psi$ and $v = -\partial_x \psi$.^[10] The Schmidt number is defined as $S_c = \mu / D \rho_0$ where μ is the dynamic viscosity and ρ_0 is the solvent density. The dimensionless solution density $\tilde{\rho} = \sum_i R_i i$, where the solutal Rayleigh numbers R_i measures the contribution of each species i to the density. Since the reactants solutions have the same density, $R_a = R_b = R$ and $\tilde{\rho} = \Delta R (a + b) + R_c / 2$ where $\Delta R = R - R_c / 2$.

Shear flows, key for the instability scenarios discussed below, are induced by the Marangoni boundary condition [Eq. 5] at the free top surface $z = L_z$

$$\omega = -\Delta M (\partial_x a_s + \partial_x b_s). \quad (5)$$

The parameter $\Delta M = M - M_c / 2$ groups the solutal Marangoni numbers, M_i , each quantifying the weight of the i -th species to the dimensionless surface tension $\tilde{\gamma} = -\sum_i M_i i = -\Delta M (a_s + b_s) - M_c / 2$ ($M_a = M_b = M$ since the solutions of reactants are also assumed to have the same surface tension).

Two main parameters, ΔM and ΔR , by controlling the intensity of surface-tension- and buoyancy-driven convection, respectively, govern the global dynamics. Positive ΔR and ΔM mean that the density decreases while the surface tension increases during the reaction. L_z can also balance the relative importance of the two contributions to the flow.

The oscillatory behaviours sustained by the interplay of the reactive process and the chemically-driven flows can be classified into two main scenarios: *chemo-Marangoni* and *chemo-Marangoni-buoyancy* oscillations.

3.1. Chemo-Marangoni oscillations

Chemo-Marangoni oscillations are spatio-temporal damped oscillations of the concentration and the hydrodynamic fields

induced by the sole surface-tension-driven convection (Marangoni effect), for high surface forces ($\Delta M \gg 1$, $\Delta R = 0$).

The global dynamics and phenomenology of these waves are extensively described in Refs. [18,57] and illustrated in Figure 3. Briefly, the reactants A and B meet at the reactor centre, x_0 , where the product C forms in the reaction zone. The surface tension γ locally increases bearing convergent Marangoni flows at the air-liquid surface and, by continuity, a return-flow in the bulk of the reacting fluid. Two counter-rotating convective rolls grow laterally from x_0 . During this phase the product C is compressed towards the reactor bottom and the concentration field deforms into two symmetrical fronts

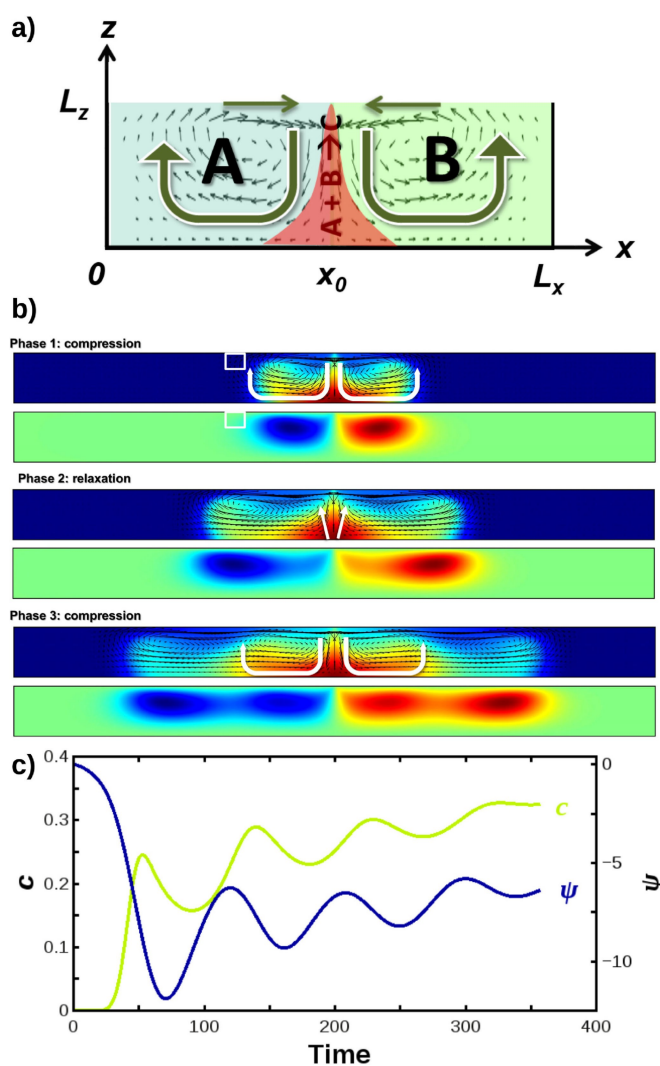


Figure 3. Phenomenology and mechanism of *chemo-Marangoni oscillations*. a) Sketch of the initial configuration of the reactants, the topology of the chemically-induced velocity field and related deformation of the product distribution due to convergent flow at the top free surface and bulk return flow. b) The snapshots illustrate the spatio-temporal evolution of the chemical (c , top) and hydrodynamic (ψ , bottom) fields, respectively, during an oscillatory cycle of the periodic dynamics obtained with $\Delta M = 200$ and $L_z = 20$. The mechanism consists of three main steps: flow-driven compression, vertical diffusive relaxation and further compression of c . c) Time series describing the local dynamics extracted at the representative point indicated by the white squares in b).

following the return flow, sweeping c towards the top of the reactor. The consequent formation of two new local regions out of x_0 where surface tension increases modifies the velocity field, causing the break of the two initial convective rolls and weakening the vertical down-flow forcing around x_0 . In this phase (relaxation phase), the front of c can thus relax from the reactor bottom to the surface by diffusion. After the lateral dissipation of the symmetric waves, the vertical down-flow at x_0 that opposes to the relaxation process reinforces again and restores initial conditions for a novel oscillatory cycle (compression phase).

3.2. Chemo-Marangoni-buoyancy oscillations

Chemo-Marangoni-buoyancy oscillations occur when an antagonistic interplay between chemically-driven gravitational currents and Marangoni flows is at play.

In particular, this scenario develops when the reaction locally decreases the density of the medium and induces a vertical current opposite to the Marangoni-induced convergent down-flow. The resulting topology of the velocity field becomes more complex, with the formation of two new upwardly oriented convective rolls at the bottom of the reactor that reduce the extent of the Marangoni-related rolls at the top. As a result, the forming product is compressed around the stagnation point S_p where the velocity vector changes sign (see sketch of Figure 4a).

An illustration of three typical oscillatory cycles in this system is given in Figure 4b with the evolution of the chemical field, c , paralleled to the corresponding hydrodynamic field, ψ . The oscillatory mechanism follows the same sequence of phases (compression-relaxation-compression) seen in the pure Marangoni scenario: surface-tension-triggered convergent down-flow starts upon formation of the product which is then pushed towards the bottom. However buoyancy forces reinforce here the upward vertical diffusion in the relaxation phase and bounce back the local accumulation of the less dense product towards the reactor surface. This natural convection can therefore enhance the oscillatory mechanism as confirmed by the local timeseries describing the system dynamics at a representative point. The ψ timeseries reported in Figure 4b (bottom) shows an initial growth of the oscillation, followed by a smooth decay of the oscillation amplitude as the system evolves towards equilibrium.

4. Minimal Ingredients for Chemohydrodynamic Oscillations

4.1. Role of the reactive process

The chemical reaction represents the fundamental and internal source for the onset of this emergent oscillatory behaviour by establishing *in-situ* an increase of the surface tension across the reactive zone proportional to the extent of the reaction (i.e.

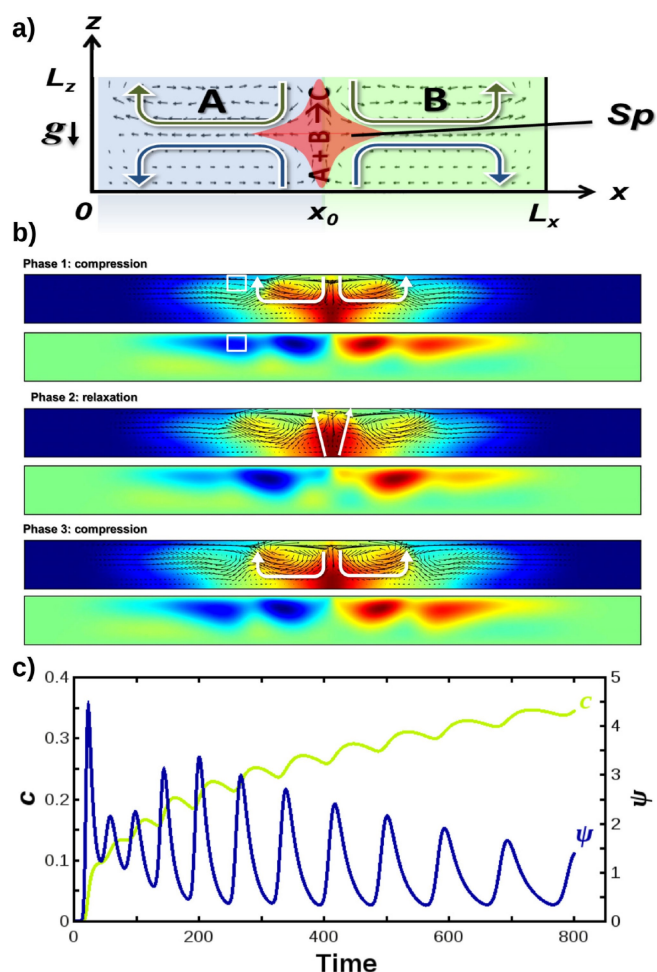


Figure 4. Phenomenology and mechanism of chemo-hydrodynamic oscillations when both buoyancy and surface tension forces are at play in an $A + B \rightarrow C$ system. a) Sketch of the initial reactants configuration, topology of the chemically-induced velocity field and related deformation of the product distribution. The antagonistic buoyancy and surface flows generate a stagnation area, indicated with Sp . b) The snapshots illustrate the spatio-temporal evolution of the chemical (c , top) and hydrodynamic (ψ , bottom) fields, respectively, during an oscillatory cycle of the periodic dynamics obtained with $\Delta R = 0.75$, $\Delta M = 200$ and $L_z = 20$. The mechanism follows three main steps: flow-driven compression, buoyancy-driven relaxation and further compression of c . c) Time series describing the local dynamics extracted at the representative point indicated by the white squares in b).

relative amount of the species) and to the contribution of each species to the fluid dimensionless surface tension, according to the relation $\tilde{\gamma} = -\sum_i M_i i = -\Delta M(a_s + b_s) - M_c/2$. When chemically-induced surface tension gradients are beyond a critical threshold, the resulting flows undergo an oscillatory instability which entrains the dynamics of the chemical fields. As a whole, the phenomenon presents then an intrinsic hydrodynamic nature,^[57] similar to the well-known cases where Marangoni flows and related oscillations are promoted through an external fixed spatial gradient of temperature.^[16]

Here the chemical process self-sustains surface tension gradients thanks to a twofold action: it consumes the initial reactants responsible for low surface-tension and replaces them

with a species able to increase the global surface tension. It could be virtually the same mechanism in a non-reactive system where a species with high-surface-tension is fed externally into a pool of a low-surface-tension species, while exhausting the latter one at the same time and point (i.e. imposing at x_0 a fixed non-null value for the former and zero for the latter species).

We can express this double-function of the reaction in parametric terms. The critical threshold $\Delta M > \Delta M_{crit} = M - M_c$ beyond which chemo-hydrodynamic oscillations start can be achieved if the Marangoni number of the product, M_c , is much smaller than M characterising initial reactants. However, if we write M_c in terms of M , $M_c = \zeta M$, we can see that condition $\Delta M > \Delta M_{crit}$ can be also met for values of M_c comparable or even larger than M , provided that [Eq. (6)]

$$M > \frac{2}{2 - \zeta} \Delta M_{crit}, \quad (6)$$

with $\zeta \in [0, 2)$. This confirms that, if M is large enough such that [Eq. (6)] holds (corresponding to reactants with very low surface tension), the occurrence of oscillations is essentially independent on the specific contribution of the product and a local increment of the surface tension emerges from the consumption of the reactants. This condition suggests that a large number of chemo-physical systems can undergo this instability.

Figure 5 displays another crucial feature of the reaction in this scenario, namely the localisation of the reactive source. Both in chemo-Marangoni and chemo-Marangoni-buoyancy scenarios the reaction zone (i.e. where $a \times b \neq 0$) remains essentially sandwiched between the two reactants pools, across x_0 , during the whole dynamics. $a \times b \neq 0$ slowly decreases in time with the reactants depletion. Indeed the characteristic configuration of the $A + B \rightarrow C$ systems allows to localise the reactive source in the course of the chemical process which translates into the possibility to build and maintain a spatially defined gradient of the medium properties that feed convective flows (i.e. surface tension and density). Interestingly, the convective contribution does not induce any delocalisation in the reaction development but simply advects and reshapes the spatial distribution of the product with a topology that reflects the coupled flow.

Nevertheless it is important to detail in which sense localisation plays a favourable role for the emergence of

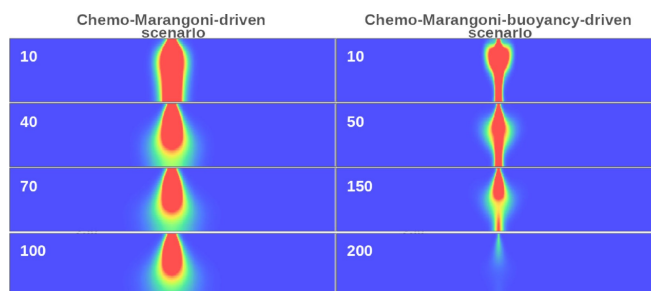


Figure 5. Spatio-temporal evolution of the reactive source $a \times b$ in the chemo-Marangoni and chemo-Marangoni-buoyancy scenarios.

oscillations in such simple bimolecular processes. Imagine, for instance, that the chemical transformation can be forced within a limited and tunable region (this can be obtained experimentally *via* photochemical irradiation transforming a focused area of a pool of a certain reactant A into B). Would this trigger and sustain chemo-hydrodynamic oscillations? To answer this question we run *ad hoc* numerical simulations where the Heaviside function $H(x, z)$ multiplies the kinetic term of Eqs. [(1–2)] to activate the reaction within a limited region of width w_r around x_0 :

$$H(x, z) = \begin{cases} 1 & \text{if } |(x - x_0)| \leq w_r \\ 0 & \text{elsewhere.} \end{cases}$$

The results, shown in Figure 6, indicate that by decreasing the spatial width where the reaction can occur (i.e. strictly localising the chemical process at x_0) drastically shortens the duration of the oscillatory transient. This is because constrained reactive domains reduce the reaction extent (see panel b) and, in turn, the related surface tension and density gradients needed for the instability cannot be maintained or even be achieved. In this context, this numerical experiment shows that the spatio-temporal development of the reactive front represents the mechanism through which fresh fuel is provided to the instability.

4.2. Role of chemically-coupled flows and their antagonism

The birth and maintenance of chemo-hydrodynamic scenarios relies on a delicate balance between orthogonal fluxes that

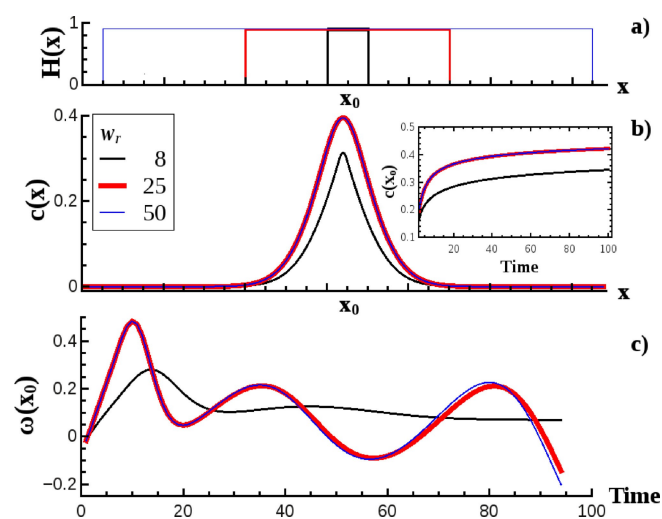


Figure 6. Dynamics of the chemo-Marangoni-buoyancy instability when the reaction is forced within a limited region of width w_r , defined by the Heaviside functions $H(x, z)$ shown in panel a). In panel b) we report the reaction-diffusion surface profile of c concentration for different values of w_r . c) The local timeseries describing the system dynamics show how, reducing the area where the reaction is activated, oscillations progressively die. Beyond the threshold $w_r = 50$, the system dynamics converge to the same profile that can be obtained in the absence of $H(x, z)$.

alternately dominate the dynamics and need to be oppositely oriented, settling an antagonistic interplay. This represents, indeed, a prerequisite for the occurrence of chemohydrodynamic pulsatory dynamics and the relative magnitude of the competitive contributions determines conditions for the effective onset of the instability as well as for controlling its properties.

Hierarchically, the Marangoni contribution is the most prominent contribution after the reactive primer. Horizontal Marangoni return flow undergoes a dynamical competition with the upwardly-oriented relaxation driven by diffusion in the chemo-Marangoni case and by buoyancy forces in the case of chemo-Marangoni-buoyancy oscillations.

As it can be appreciated in Figure 7a, in the chemo-Marangoni scenario, the fluid thickness L_z modulates the fluxes antagonism: the characteristic length, λ of chemohydrodynamic oscillations and the period at which waves are emitted from the centre, T , increase with the fluid height, scaling as $\lambda \sim L_z$ and $T \sim L_z^2$, respectively.^[18,57] Below an inferior height threshold, L_c , the diffusion process overcomes Marangoni-driven dynamics and oscillations cannot develop.

The antagonism due to buoyancy forces is also controlled by the reactor height, L_z , and by the density difference established by the reaction, ΔR . These tune the relative importance of gravitational and surface-driven currents in a similar way: increasing ΔR or L_z increases buoyancy forcing and, as a result, the vertical extent of the Marangoni-dominated convection is reduced by larger buoyancy competitive convective rolls at the reactor bottom. Since the size of Marangoni convective rolls determines the wavelength of chemohydrodynamic oscillations, increasing ΔR or L_z corresponds to decreas-

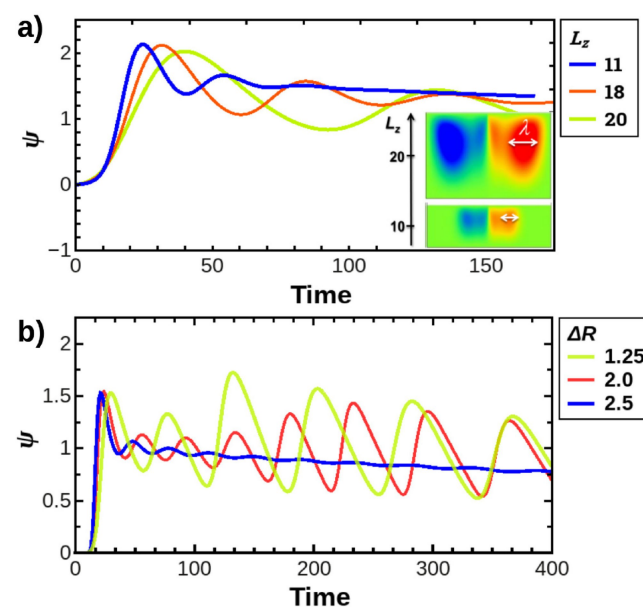


Figure 7. Typical timeseries of *chemo-Marangoni* (a) and *chemo-Marangoni-buoyancy* (b) scenarios, reporting ψ at a representative point of the reactor ($x_0 = 20$, $L_{z/2}$) for 3 different values of L_z (with $\Delta M = 200$) and ΔR (with $\Delta M = 200$, $L_z = 20$), respectively. The inset of panel a) also illustrates the shrinking of Marangoni convective rolls when decreasing L_z .

ing characteristic length and period of the oscillations. The enhancing effect of the buoyancy contribution on the oscillatory mechanism works in a circumscribed range of ΔR and oscillations progressively dampen out when buoyancy forces prevail over surface-tension-driven flows, which typically happens when the extent of the Marangoni domain falls below L_c (see Figure 7b and refs. [18,57]).

The fact that the antagonism between different contributions to the fluxes is a general potential for oscillatory behaviours finds further confirmation in other chemo-hydrodynamic systems.

Periodic deformation of self-propagating exothermic autocatalytic fronts can develop due to the competition between the solutal and the thermal contribution to surface-driven flows, in the presence of differential diffusion.^[58,59] Here, the autocatalytic species increases the surface tension at the reactive interface while the heat released at the same time diffuses faster, inducing a local cooling across the reacted area. This drags some of the autocatalytic product along the top surface into the reactant area, initiating thereby the chemical clock further ahead. The reaction rapidly converts the reactant into product, thus restoring an almost flat front ready to undergo periodically the same deformation process. Similar mechanisms, triggered by the competition of solutal and thermal density-driven convection, sustain spatio-temporal oscillations in exothermic autocatalytic fronts.^[60,61]

Another possible antagonistic scenario can be activated by the competition between buoyancy and Marangoni forces in isothermic autocatalytic fronts, in which the autocatalytic species decreases the surface tension and increases the density with respect to fresh reactants through which the front develops.^[10,62]

New oscillatory structures reminiscent of these latter dynamics can be obtained in the model presented in section 3 by reverting the orientation of the fluxes at play while maintaining their mutual antagonism. In Figure 8a we illustrate a representative example of such $A+B\rightarrow C$ system where the production of C decreases the surface tension and, concurrently, increases the density, thus inducing a diverging flux at the top liquid-gas interface combined to downward gravitational currents. The system shows an oscillatory dynamics with chemohydrodynamic structures moving laterally towards the reactor center (Figure 8b). The mechanism appears as an inversion of the scenarios described above, with a Marangoni-driven forcing of the reaction product towards the reactor top, which spreads laterally along the top liquid-air interface. Being denser than the initial reactants, the product stratification deforms progressively into fingers that sink under the action of the gravitational field while experiencing a drifting towards the reactor centre due to the residual converging return flow induced by the Marangoni convection in the bulk.

5. Summary and Outlook

We have presented and reviewed the crucial contribution that convective motions coupled to chemical processes may bring

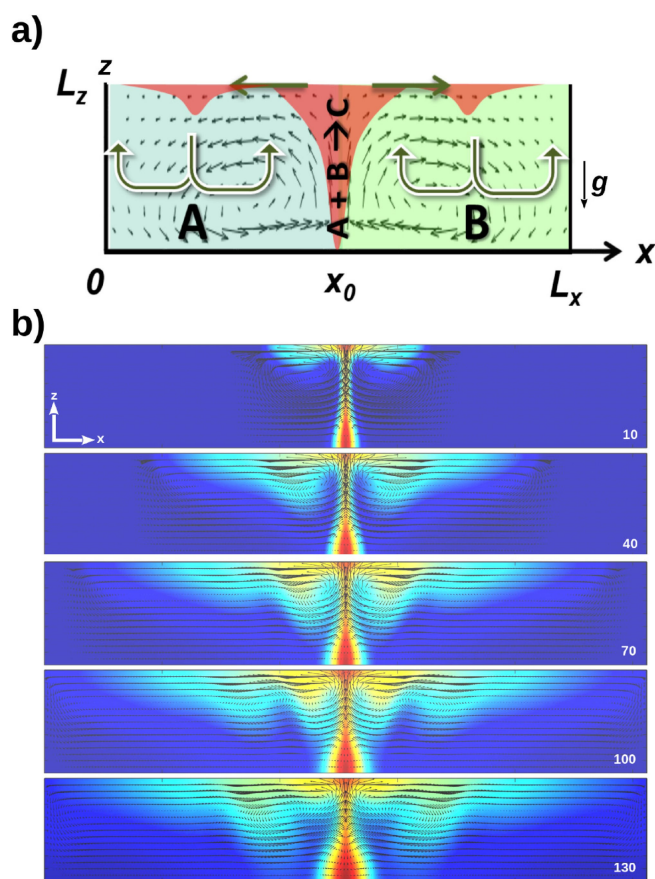


Figure 8. a) Sketch of the initial reactants configuration and topology of the chemically-induced velocity field in the antagonistic case where the product decreases the surface tension and, concurrently, increases the density. b) The snapshots illustrate the spatio-temporal waves of the product concentration c .

to disciplines like origin of life studies, chemobionics and systems chemistry. In particular, we emphasised how physical hydrodynamic and chemohydrodynamic mechanisms can provide two fundamental prerequisites for the emergence of self-organisation, namely a way to compartmentalise and concentrate chemicals without the presence of semi-permeable membranes, and a way to introduce nonlinearities in simple bimolecular reactions.

For the first time, we showed that complex dynamics may occur in a medium at rest thanks to a reactive trigger as general as an $A+B\rightarrow C$ process. The minimal ingredient is spatial localisation of the reaction to build large surface tension gradients that fuel Marangoni flows, key for this self-organised scenario. Pulsations finally emerge from the transversal competition of these surface-driven flow with diffusion and/or buoyancy-driven convection that further enhances and modulates the oscillatory dynamics.

Conceptually, chemo-hydrodynamic scenarios adhere to the evidence that patterns and functional behaviours in biology generally involves a tight and cooperative combination of both chemical signals and transport phenomena.^[63] This aspect, currently attracting the attention of several groups in nonlinear

chemistry, is typically explored by using as model systems nonlinear chemical oscillators encapsulated in heterogeneous compartments such as micelles, vesicles and microemulsions and communicating *via* active diffusion (i.e. involving a cooperative feedback with reaction) and passive diffusion (simply driven by concentration gradients).^[39–41] In these approaches the two elements at the basis of the development of life-like structures described above, i.e. compartmentalisation and nonlinear chemical kinetics able to sustain self-organised behaviours, are integral part of the system.

Chemo-hydrodynamic mechanisms may offer an alternative view on how such complex machinery could have taken shape autonomously driven by a minimal chemistry.

The dynamics activated and sustained by chemo-hydrodynamic mechanisms show consistent analogies with the scenarios proposed by Braun et al. and discussed above, including laminar convective flows that create stagnation spots for species accumulation as well as an effective and organised spreading of the reactive species. Here these spatio-temporal functional flows arise *in-situ* spontaneously thanks to internal and localised sources as simple and general as bimolecular transformations, able to maintain the system transiently out of equilibrium. Bimolecular processes are ubiquitous and can be tailored to specific reactions yielding molecules relevant for life. This avoids the need for external energy fluxes and gradients to sustain natural convection and related constraining boundary conditions for self-organisation, conferring to chemohydrodynamic mechanisms high generality and the possibility to take shape in any active films, typically at surfaces where molecular evolution is traditionally pursued.^[25]

Laminar flows in our picture firstly rely on large chemically-driven surface tension gradients. A change (either increment or drop) of surface tension that can trigger Marangoni-driven flows may come from a localised formation or degradation of simple amphiphilic molecules like short-chain fatty acids. Once the flow is activated *via* Marangoni effect, molecules can find suitable flow topology for trapping in stagnation points where reactive autopoietic processes (chain elongation, catalysis, replication etc.) can be enhanced. Differently from previous thermally-driven mechanisms, the isothermal chemo-hydrodynamic process cannot benefit from the thermal switch that guides the binding-detaching cycles, useful, for example, for DNA reproduction. Nevertheless, the energy for this action could be provided by mechanical shear stresses taking place at the contact line between reacted and unreacted fluid as well as at the air-liquid interface. Also, exothermic reactions start chemohydrodynamic mechanisms to favour collective cyclic excursions of the molecules from low to high temperature regions and fulfill this task.

Importantly, in chemo-hydrodynamic scenarios the product locally formed, compressed and accumulated in the stagnation points is periodically pulsed away, suspended in hydrodynamic structures, featuring possibility for primordial chemo-convective cell rich in some relevant chemical species. This describes a self-organised functional behaviour that provides a viable means for nucleation, growth, transport and proliferation of organised packets of chemical information.

The involvement of macromolecules (like RNA and DNA) in chemo-hydrodynamic mechanisms introduces the possibility that, beside diffusion and thermophoresis (taken into account by Braun et al.), also another powerful and “flexible” transport phenomenon like cross-diffusion may come into play, and feedback with convective contributions to enhance functional molecular trapping and behaviours. In this context, in fact, the cross-terms of the diffusion coefficient matrix, generally neglected, become important as it typically occurs with charged species because of electrostatic forces as well as with large molecules like polymers and self-assembled structures such as micelles due to excluded volume reasons.^[64] When cross-diffusion is active, gradients in one species generates a co- or counter-flux of other components of the system, sustaining a wealth of patterns in both non-reactive and reaction-diffusion systems. Among others, cross-diffusion has been already shown to trigger hydrodynamic patterns and instabilities in initially stable stratifications of fluids separating species able to entrain a cross-diffusive interplay. Examples are the stratifications of microemulsions with different composition^[65–67] and other ternary systems containing macromolecules like polyvinylpyrrolidone(PVP)-dextran-H₂O.^[68] Future studies more oriented to the possible impact of multicomponent diffusion as a source of emergence in the context of origin of life are needed.

Compartmentalization and nonlinearity are necessary but not sufficient prerequisites to consider a system or a process as alive. Nevertheless any plausible hypothesis on the abiogenetic origin of life must contemplate those characteristics. The convective scenarios proposed in this paper cannot provide a direct connection with biological self-organisation. For example, with respect to the most popular hypothesis that protocells evolved from a semi-permeable membrane compartment, the convection-induced confinement lacks many traits typical of the modern biological cells. In a recent review, Monnard and Walde^[69] draw up a list of four distinctive abilities of contemporary membranes, somehow fulfilled by the commonly accepted prebiotic compartments (coacervates, amphiphilic aggregates, hydrogels, etc.). Essentially, the list consists in *i*) to ensure cell integrity, *ii*) to offer catalytic surfaces, *iii*) to regulate the trafficking of molecules, *iv*) to support energy uptake to accomplish complex functions. Convection-induced “compartments” certainly provide a physical confinement that favor the concentration of molecules and probably also guarantee a functional energy flux, but lack evolutive properties like replication, division and transmission of heritable traits. A high level of organisation of the molecular trafficking, based on the surface tension and density-driven flows, can also be attained in convective cells, but it is by far less selective as compared to the control of in-out fluxes provided by semi-permeable membranes. However, the mechanism we proposed can represent a realistic step in the pathway of increasing complexity that led to protocells and ultimately to modern cells. In an early ages Earth, where a great diversity of simple precursors was available at infinite dilution, nonlinear processes and confinement provided by this kind of simple chemico-physical mechanisms, could have favored the synthesis of more complex molecules, yet without any biological activity.

This idea of chemo-hydrodynamic scenarios as a further example of rudimentary mechanisms for the emergence of functional and evolutionary behaviours has to be substantiated through experiments, starting from proof-of-concept systems where these dynamics can be isolated by taking into account the minimal ingredients described in previous sections, i.e., the localisation of the reactive source, that has to sustain a large surface-tension gradient. In a recent paper,^[57] we have suggested that lab-scale model systems may rely on hydrolysis, dissolution or photochemical processes that might also include thermal contributions. In particular, chemo-Marangoni-driven oscillations could be obtained in very shallow quasi-2D reactors (or in microgravity flights) through endothermic processes such as the endothermic alkyl-formate hydrolysis^[70] or dissolution of salts like NH_4NO_3 , since decreasing temperature is normally associated with an increase in the surface tension.

Photochemical isomerisation of thermoreversible photochromic spiro-oxazine or azobenzene surfactant molecules, which are associated with a considerable change of surface-tension, are also good candidates that can allow to maintain the system in far-from-equilibrium conditions under constant irradiation.^[71,72] With this kind of systems, the heat provided by a localised irradiation to promote the photochemical transformation can also induce a density decrease, thus matching minimal conditions for chemo-Marangoni-buoyancy oscillations.

A crucial step will be devising ad-hoc experiments for understanding how chemohydrodynamic mechanisms can be compatible with the chemical processes and chemical precursors of biologically relevant species that characterised the prebiotic world.

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Conflict of Interest

The authors declare no conflict of interest.

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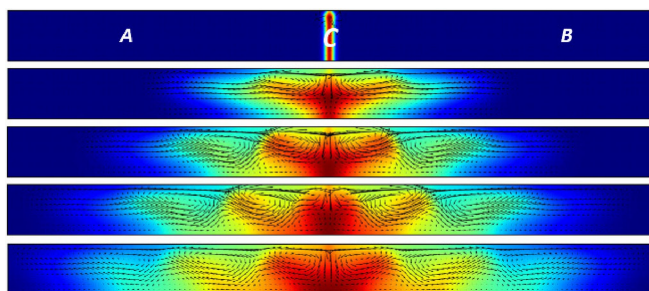
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REVIEWS



Catch the wave: We review the relevance of chemically-induced convection as a source of self-organisation in environments characterized by minimal chemistry like prebiotic conditions. Chemo-hydrodynamics can provide a pathway for metabolically

inexpensive compartmentalisation of biologically relevant molecules and collective behaviours, functional to the formation, preservation and proliferation of chemical information in the form of waves.

Dr. M. A. Budroni, Prof. F. Rossi,
Prof. L. Rongy*

1 – 12

**From Transport Phenomena to
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