

## Ruelle–Takens–Newhouse scenario in reaction-diffusion-convection system

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(Received 11 December 2007; accepted 15 February 2008; published online 17 March 2008)

Direct numerical simulations of the transition process from periodic to chaotic dynamics are presented for two variable Oregonator-diffusion model coupled with convection. Numerical solutions to the corresponding reaction-diffusion-convection system of equations show that natural convection can change in a qualitative way, the evolution of concentration distribution, as compared with convectionless conditions. The numerical experiments reveal distinct bifurcations as the Grashof number is increased. A transition to chaos similar to Ruelle–Takens–Newhouse scenario is observed. Numerical results are in agreement with the experiments. © 2008 American Institute of Physics. [DOI: 10.1063/1.2894480]

The process by which a laminar viscous flow undergoes transition to turbulence is a topic of notable fluid-dynamical interest. Experiments<sup>1</sup> and numerical simulations<sup>2</sup> of closed system flows like Rayleigh–Bernard convection<sup>3–5</sup> have pointed out how the evolution to turbulence follows a specific route and well-definite sequence of transition on the basis of flow features.<sup>6</sup> In particular it was observed<sup>7</sup> that transitions to chaos in self-sustained oscillatory flows are consistent with the well-known Ruelle–Takens–Newhouse (RTN) scenario.<sup>8</sup> The onset of convection in self-sustained oscillating chemical reactions such as the Belousov–Zhabotinsky (BZ) reaction<sup>9</sup> had been extensively studied<sup>10,11</sup> proving an effective coupling between kinetic and hydrodynamic of the system. On the other hand, it was shown<sup>12,13</sup> how autocatalytic systems exhibit aperiodic and chaotic dynamics by the coupling of reaction kinetics to transport phenomena. This coupling is expected in particular for the BZ reaction in closed unstirred reactors<sup>14,15</sup> by the strict experimental dependence in the onset of chaos on (i) the percent in volume of initial reactants concentrations,<sup>16</sup> (ii) the system viscosity,<sup>17</sup> (iii) the temperature,<sup>18</sup> and (iv) the reactor geometry.<sup>19</sup> A suitable choice of starting values for these parameters results in a RTN transition to chaos when the system is far from equilibrium and the inverse RTN scenario as the reaction drifts to the ultimate state.<sup>20</sup>

Taking into account the combination of the parameters controlling the fluid dynamics and the chemistry of the system would be useful to understand the instabilities occurring in the BZ reaction in a close unstirred reactor. The model used to simulate the system is a two-dimensional vertical slab which had been demonstrated to be a good approximation to the three-dimensional problem.<sup>10</sup> A set of reaction-

diffusion-convection partial derivative equations is solved by means of numerical integration over a suitable grid. This model allows one to focus on the contribution of convection and to neglect the consumption of reactants. Chemical kinetics is formulated using the well-known two-variables Oregonator model<sup>21–23</sup> proposed for the first time by Fields–Körös–Noyes. They defined two nonlinear coupled differential equations,

$$\frac{dc_1}{dt} = \frac{1}{\epsilon} \left[ c_1(1 - c_1) + fc_2 \frac{q - c_1}{q + c_2} \right] = k_1(c_1, c_2), \quad (1)$$

$$\frac{dc_2}{dt} = c_1 - c_2 = k_2(c_1, c_2), \quad (2)$$

where  $c_1$  and  $c_2$  are, respectively, the nondimensional concentrations of the intermediate species  $\text{HBrO}_2$  and  $\text{Ce}^{4+}$  derived by the dimensional ones  $C_1$  and  $C_2$  as follows:

$$c_1 = 2C_1 \frac{k_4}{k_5A},$$

$$c_2 = C_2 \frac{k_4 k_0 B}{(k_5 A)^2},$$

$A, B$  being the starting reactant dimensional concentrations, respectively, of  $\text{BrO}_3^-$  and Malonic acid; and  $k_0, k_4, k_5$  are dimensional rate constants involved in the related steps of the Oregonator model. The  $k_i(c_1, c_2)$  are the dimensionless kinetic functions scaled by  $t_0 = 1/k_0 B$ . The functions describing initial concentrations were set according to the model for a reaction-diffusion BZ system proposed by Jahnke *et al.*,<sup>24</sup>

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$$c_1^0 = 0.8 \text{ if } 0 < \theta < 0.5, \quad (3)$$

$$= c_{1(ss)} \text{ elsewhere,} \quad (4)$$

$$c_2^0 = \left\{ c_{2(ss)} + \frac{\theta}{8\pi f} \right\} \times 1.3, \quad (5)$$

where  $c_{2(ss)} = c_{1(ss)} = q(f+1)/(f-1)$ ,  $\theta$  is the polar coordinate angle and, as suggested by the experimental results about the influence of the initial concentrations on the onset of chaos,<sup>16</sup> the original function for  $c_2^0$  was multiplied by a factor of 1.3. The kinetic parameters related to initial concentrations  $\epsilon = k_0 B / [H^+] k_5 A$  and  $t_0$  are, respectively, set equal to 0.005 and 21 s. This configuration describes a general inhomogeneous starting point for the unstirred system. The parameters which rule the oscillating behavior were set  $f = 1.6$  and  $q = 2k_3 k_4 / k_2 k_5$  arbitrarily to 0.01 instead that 0.0002 found by Tyson,<sup>21</sup> since for values  $\leq 0.01$  it has little effect on rotating-wave solutions. In the rest of the paper, when we refer to species concentration  $c_i$ , we mean the average value of the nondimensional concentrations calculated over the grid at each time step.

The Navier–Stokes equations governing the velocity field in the slab were coupled to the reaction-diffusion equation, to model natural convection. They are written in a dimensionless form using the time scale defined above  $t_0 = 21$  s and the space scale  $x_0 = 0.06$  cm, arbitrarily imposed to be equal to the entire space domain explored, just greater than the value 0.05 cm (the minimal dimension for which in the real experiment chaos is observed<sup>19</sup>). The set of dimensionless equations was formulated in the  $\omega$ - $\psi$  form and in the Boussinesq approximation<sup>25</sup>

$$\frac{\partial c_i}{\partial t} + D_\nu \left( u \frac{\partial c_i}{\partial x} + v \frac{\partial c_i}{\partial y} \right) - D_i \nabla^2 c_i = k_i(c_1, c_2) \quad i = 1, 2, \quad (6)$$

$$\frac{\partial \omega}{\partial t} + D_\nu \left( u \frac{\partial \omega}{\partial x} + v \frac{\partial \omega}{\partial y} \right) - D_\nu \nabla^2 \omega = - D_\nu \sum_i Gr_i \frac{\partial c_i}{\partial x}, \quad (7)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\omega, \quad (8)$$

$$u = \frac{\partial \psi}{\partial y}, \quad (9)$$

$$v = -\frac{\partial \psi}{\partial x}, \quad (10)$$

where  $D_\nu = \nu t_0 / x_0^2 = 58.50$  is the dimensionless viscosity ( $\nu$  being the kinematic viscosity set equal to the water viscosity  $0.01 \text{ cm}^2/\text{s}$ ),  $D_i = D t_0 / x_0^2 = 0.00350$  is the dimensionless diffusivity ( $D$  being the dimensional diffusivities of the two species assumed be equal to  $0.6 \times 10^{-7} \text{ cm}^2/\text{s}$ );  $u = U/v_0$  and  $v = V/v_0$  are dimensionless horizontal and vertical components of the velocity field; and  $v_0$  is the velocity scale (namely the ratio of the kinematic viscosity with our length scale times the dimensionless viscosity).  $Gr_i = g x_0^3 \delta \rho_i / \rho_i \nu^2$  is

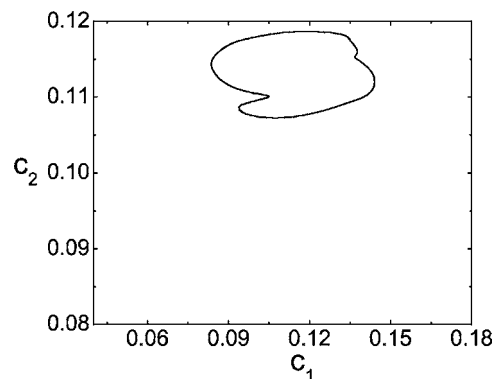


FIG. 1. Phase space trajectories of  $Ce^{4+}$  vs  $HBrO_2$  for the Grashof number = 0.00.

the Grashof number for the  $i$ th species [ $g$  is the gravitational acceleration ( $980 \text{ cm/s}^2$ ) and  $\delta \rho_i / \rho_i$  is the density variation due to the change of the concentration of the  $i$ th species with respect to a reference value  $c_{0i}$ ]. This number is the control parameter chosen to follow the transition to chaos. It represents the entity of convection only ascribed to isothermal density changes and is related to the hydrodynamic instability, giving the balance between momentum and viscosity forces acting in the system. The temperature terms are neglected since it has been demonstrated that diffusion of chemicals is two orders of magnitude smaller than thermal diffusivity and has a stronger influence for the onset of convection.<sup>11,26,27</sup> Equations (6)–(10) were solved numerically using the alternating direction finite difference method: this method allows the reduction of the problem to a set of linear algebraic equations where the matrix of coefficients is cast in a tridiagonal form. Numerical integration was performed using the time step of  $1.0 \times 10^{-5}$  on a square grid of 100 points in each direction. Other computations were carried out changing either the time step or the number of grid points, in order to check the stability and numerical accuracy. The boundary conditions are no-slip boundary conditions for the fluid velocity and no-flow boundary conditions for chemical concentrations at the wall of the slab.

In our calculations we varied  $Gr_i$  between 0.00 and 12.50. Following the route to chaos various dynamical regimes can be discerned but in this paper are evidenced three fundamental moments.

*Periodic regime.* In Fig. 1 a limit cycle characterized by fundamental frequency  $\omega_1 = 0.747$  Oregonator frequency units is shown. It was obtained by hindering convective flow, i.e., with  $Gr_i = 0.00$ .

The result of the numerical solution of the problem for both Grashof numbers = 9.40 is shown in Fig. 2. After a transient regime (about  $70t_0$ ) the dynamics of  $HBrO_2$  and  $Ce^{4+}$  was periodic with one fundamental frequency  $\omega_1 = 0.397$ , different from that observed in Fig. 1. The frequency observed shows that the convection is coupled with the kinetic-diffusion system. The periodicity of the new solution presents a retard with respect to the convectionless stationary state probably because of the hydrodynamic inertia.

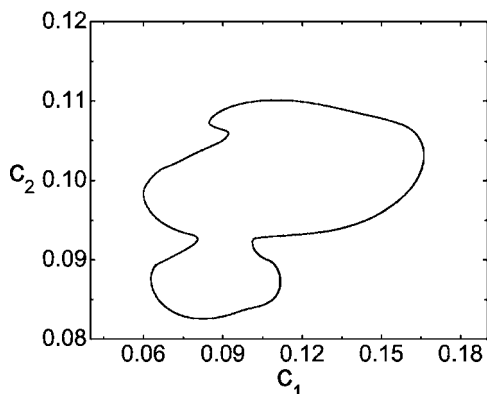
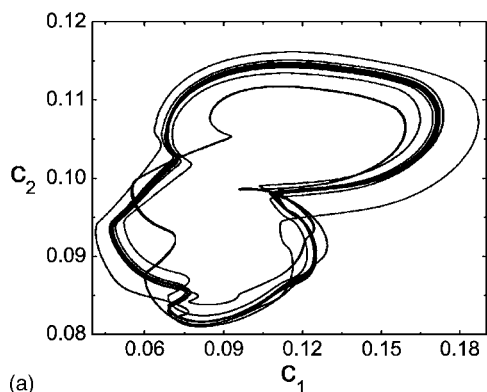


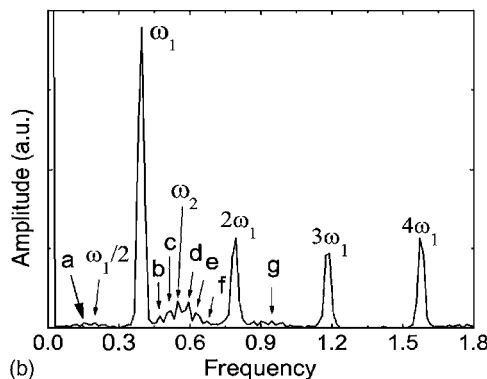
FIG. 2. Phase space trajectories of  $Ce^{4+}$  vs  $HBrO_2$  for the Grashof number = 9.40.

*Quasiperiodic regime.* As the Grashof number reaches the value 9.80, a quasiperiodic behavior is found [see Fig. 3(a)]. The toroidal nature of the flow is confirmed by the Fourier power spectrum [Fig. 3(b)]. Two characteristic fundamental frequencies ( $\omega_1, \omega_2$ ) and their linear combinations are shown. The ratio  $\omega_1/\omega_2$  is an irrational number.

*Chaotic regime.* If the Grashof number is further increased (12.50), an aperiodic behavior, associated with a strange attractor [Fig. 4(a)], is observed. The time series manifest sensitivity to initial conditions consistent with one of the most distinctive features for chaotic dynamics. To test for chaos, we have also calculated the largest Lyapunov exponents,  $\lambda$ , using the Rosestein algorithm from TISEAN

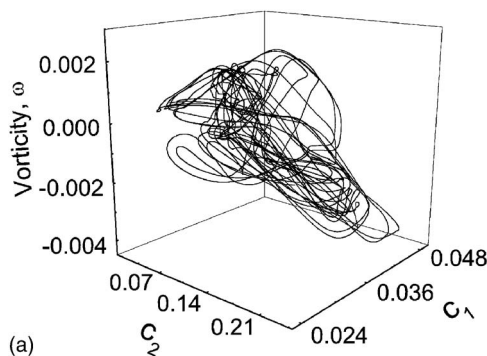


(a)

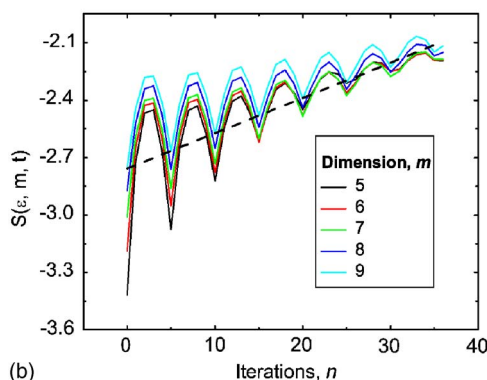


(b)

FIG. 3. (a) Phase space trajectories of  $Ce^{4+}$  vs  $HBrO_2$  for the Grashof number = 9.80. (b) Fourier amplitude spectrum of the  $Ce^{4+}$  concentration (a =  $\omega_2 - \omega_1$ , b =  $3\omega_2 - 3\omega_1$ , c =  $6\omega_2 - 7\omega_1$ , d =  $\omega_1 + 1/2\omega_1$ , e =  $4\omega_2 - 4\omega_1$ , f =  $7\omega_2 - 8\omega_1$ , and g =  $\omega_1 + \omega_2$ ).



(a)



(b)

FIG. 4. (Color online) (a) Chaotic attractor for the Grashof number = 12.50. (b) Computation of the maximum Lyapunov exponent by the Rosestein algorithm. The value of  $\lambda=0.018$  is obtained by the linear regression of the curves  $S(\epsilon, m, t)$  for  $m=5-9$ , in the zone between 0 and 40 iterations.

package<sup>28</sup> [Fig. 4(b)]. A value of  $\lambda=0.018$  was found.

To summarize, self-sustained oscillations are investigated by direct numerical simulations of a reaction-diffusion-convection model. The numerical results reveal a transition process from periodic to chaotic behavior due to instabilities induced by convection. Chaos occurs by a Ruelle–Takens–Newhouse scenario characterized by a finite number of successive supercritical Hopf bifurcations as the Grashof number is increased. A direct connection to experiment, though, is not feasible because the Grashof number is not measured in batch experiments. Nevertheless, this number is known to be correlated with experimental parameters such as the medium viscosity or the reactor geometry. According to such relation, our simulation results agree with previous experiments<sup>19,20</sup> and explain the observed behavior, i.e., that the transition to chaos is related with the onset of convection.

We gratefully acknowledge the Cybersar project managed by the Consorzio COSMOLAB.

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- <sup>28</sup> The TISEAN software package is publicly available at <http://www.mpiik-sdresden.mpg.de/~tisean>.