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Dynamics of switching in nonlinear kinetics

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Abstract

Chemical systems giving rise to multiple steady states and subjected to fluctuations and a variation in time of the parameter controlling the instability are studied, with emphasis on the kinetics of the switching between two states. It is shown that the presence of a ramp in the control parameter in conjunction with the fluctuations considerably affects the switching process as compared to the predictions of the deterministic (mean field) analysis. Furthermore, both these factors have clear-cut signatures at the level of the system's thermodynamic properties, as described by the entropy production.

1. Introduction

Many chemical systems are described by evolution equations of the form

$$\frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t} = \boldsymbol{v}(\boldsymbol{x}, \boldsymbol{\mu}) + \boldsymbol{R}(t) \tag{1}$$

where $\boldsymbol{x} = (x_1, \ldots, x_n)$ denotes the set of concentrations of the species present; $\boldsymbol{v} = (v_1, \ldots, v_n)$ the evolution laws prescribing how these species are produced or consumed by the chemical reactions; $\boldsymbol{\mu}$ is a set of parameters describing how the system communicates with its environment; and $\boldsymbol{R}(t) = (R_1, \ldots, R_n)$ is a set of stochastic forcings accounting for the fluctuations generated spontaneously within the system or for the perturbations impinging randomly and in an essentially uncorrelated fashion from the external world.

It is by now well established that equation (1) generates a wide variety of complex behaviours, one of the ubiquitous manifestations of which is the occurrence of bifurcations leading to multiple, simultaneously stable states (Nicolis 1995). Basic ingredients needed for such transitions are, on the one side, the presence of suitable nonlinearities in the kinetics, particularly in the form of autocatalytic reactive steps; and, on the other side, the maintenance of nonequilibrium constraints keeping the system in a regime where the property of detailed balance familiar from standard chemistry in equilibrium is no longer satisfied.

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Ordinarily, when analysing the nature of a particular set of solutions of equation (1) the control parameters (which include, among others, the distance from thermodynamic equilibrium) are assumed to remain fixed. There are, however, situations in which this assumption proves to be inadequate. As an example, by suitably varying a parameter μ in time through, say, temperature or pH control, one may channel a reaction pathway in order to increase the selectivity of a desired product. Alternatively, a time-dependent μ may account for the effect of a constraint that is gradually switched on at some stage of the evolution as it happens, in particular, in mechanochemical processes at the mesoscopic level where adenosine triphosphate hydrolysis enables the system to produce mechanical work and to rectify the environmental fluctuations.

In the present paper, we report results on the response of nonlinear chemical systems subjected to fluctuations and to a slow variation of a control parameter during some time interval τ in the form of a *ramp* (Nicolis and Nicolis 2000),

$$\begin{aligned} \mu &= \mu_1 && t < t_1 \\ &= \mu_1 + \frac{\mu_2 - \mu_1}{\tau}(t - t_1) && t_1 \leqslant t \leqslant t_1 + \tau \\ &= \mu_2 && t > t_1 + \tau. \end{aligned} \tag{2}$$

We are especially interested in systems undergoing transitions associated with the emergence of two simultaneously stable steady states through a supercritical pitchfork bifurcation. As is well known, in the vicinity of such a bifurcation the dynamics reduces to a universal evolution law (normal form) displaying a single variable (the order parameter). Equation (1) can then be cast in the form (Nicolis 1995, Gardiner 1983)

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \mu(t)z - z^3 + F(t) \tag{3}$$

where $\mu(t)$ is given by (2) and z, F are linear combinations of the original variables $\{x_i\}$ and stochastic forcings $\{R_i(t)\}$. In what follows F will be assimilated to a Gaussian white noise,

$$\langle F(t)\rangle = 0, \qquad \langle F(t)F(t')\rangle = q^2\delta(t - t').$$

For later use it will be useful to notice here that since equation (3) involves a single dependent variable, it can be written in a variational form:

$$\frac{\mathrm{d}z}{\mathrm{d}t} = -\frac{\partial U}{\partial z} + F(t), \tag{4a}$$

where $U(z, t)$ is the kinetic potential,

$$U(z, t) = -\mu(t)\frac{z^2}{2} + \frac{z^4}{4}. \tag{4b}$$

It is instructive to keep track of the steps by which an equation like equation (3) may arise from a concrete chemical system. We choose for this purpose the following autocatalytic reaction scheme (Schlögl 1971):

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3X, \qquad X \underset{k_4}{\overset{k_3}{\rightleftarrows}} B \tag{5}$$

where A, B are initial and final products whose concentrations are supposed to be controlled externally, X denotes an intermediate, and k_i ($i = 1, \ldots, 4$) are the rate constants.

In the absence of both fluctuations and ramp the balance equation for the concentration x of X is (we limit ourselves to an ideal, well-stirred system)

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_2x^3 + k_1ax^2 - k_3x + k_4b. \tag{6}$$

As is well known, the behaviours produced by such a cubic equation can be fully accounted for with the help of just two control parameters, here denoted by μ and λ. This implies that upon a suitable scaling of a, b, x and t, it will be sufficient to set from now on

$$a = 3, \qquad k_1 = k_2 = k_4 = 1, \qquad b = 1 - \lambda, \qquad k_3 = k = 3 - \mu, \tag{7}$$

it being understood that $\lambda \leqslant 1, \mu \leqslant 3$. Under these conditions equation (6) becomes (for simplicity we use for the scaled variables the same notation as before)

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= -x^3 + 3x^2 - (3-\mu)x + 1 - \lambda \\ &= \mu x - (x-1)^3 - \lambda. \end{aligned} \tag{8a}$$

Introducing the variable

$$z = x - 1 \tag{8b}$$

one is led then to the equation

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \mu z - z^3 + \mu - \lambda \tag{9}$$

which is reduced to the normal form of a supercritical pitchfork bifurcation when the additional condition $\lambda = \mu$ is imposed. Notice that in this latter setting the system needs to be maintained beyond a finite distance from thermodynamic equilibrium. Indeed, in equilibrium, detailed balance implies for scheme (5) the condition $k_1 k_3 a = k_2 k_4 b$ or, with relations (7), $3(3-\mu) = 1 - \lambda$, yielding

$$\lambda_{\mathrm{eq}} = 3\mu - 8, \qquad x_{\mathrm{eq}} = 3 \tag{10}$$

with $z_{\mathrm{eq}} = 2$ by equation (8*b*). The aforementioned pitchfork bifurcation condition $\lambda = \mu$ would lead here to $\mu = 4$, an unacceptable value in view of relations (7).

In the following the effects arising from the noise and the ramp are combined to obtain the overall kinetics of the system during a transition between two steady states induced by the switching. In section 2, the deterministic dynamics of the noise-free system is first considered. The analytical formulation of the stochastic dynamics is given in section 3 and is compared to the results of numerical simulations. Section 4 is devoted to the thermodynamics of the transition process. The main conclusions are summarized in section 5.

2. The noise-free system: effect of switching on pitchfork bifurcation

In this section we are concerned with dynamical systems described by the evolution equation

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \mu(t) z - z^3 \tag{11}$$

where $\mu(t)$ is given by equation (2). We notice that in the absence of switching, $\mu = \mu_1 =$ const, equation (11) reduces to

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \mu_1 z - z^3. \tag{11a}$$

This equation admits for $\mu_1 < 0$ the unique, asymptotically stable steady-state solution

$$z_0 = 0 \qquad (\mu_1 < 0), \tag{11b}$$

and for $\mu_1 > 0$ the steady-state solutions

$$z_0 = 0, \qquad z_\pm = \pm\sqrt{\mu_1} \qquad (\mu_1 > 0), \tag{11c}$$

which are, respectively, unstable and asymptotically stable. When the time dependence of μ is taken into account equation (11) can still be integrated exactly by switching to the variable $u = z^{-1/2}$, as it is of the Bernoulli type. This solution is, however, rather formal, and it will be more instructive to resort to approximations. We hereafter seek for such perturbative solutions, for initial conditions near the state $z_0 = 0$ of the reference system (11*a*) and for two typical situations whereby the switching is started in the range of positive or of negative values of μ. In both cases we set, without loss of generality, $t_1 = 0$ in equation (2).

2.1. Switching from positive values of μ

We consider for concreteness, and without loss of generality, a positive initial condition. Owing to the instability of the ghost state $z_0 = 0$ in the limit where μ is kept constant, one expects a tendency to evolve immediately away from $z_0 = 0$. The first stage of this evolution can be determined from the linearized version of equation (11), whose solution reads

$$\begin{aligned} z(t) &= z(0)\exp\left(\mu_1 t + \varepsilon\frac{t^2}{2}\right) \qquad t \leqslant \tau \\ &= z(\tau)\exp(\mu_2(t-\tau)) \qquad t > \tau, \end{aligned} \tag{12a}$$

where we have set

$$\varepsilon = \frac{\mu_2 - \mu_1}{\tau}. \tag{12b}$$

This transient would saturate under the influence of nonlinearities to $\mu_1^{1/2}$ if μ were kept fixed. But in the presence of switching and as long as ε is small one expects that during the switching time τ one could seek for slowly varying solutions of equation (11) replacing $\mu_1^{1/2}$, of the form

$$z = z^{(0)} + \varepsilon z^{(1)} + \cdots, \tag{13a}$$

where $z^{(0)}$ is given by a form similar to $z_\pm$ in (11*c*) to which we may refer as the adiabatic approximation,

$$z^{(0)} = (\mu_1 + \varepsilon t)^{1/2} \qquad t \leqslant \tau. \tag{13b}$$

One expects that $z(t)$ as given by the first equation (12*a*) will merge with $z^{(0)}$ at a crossover time $t^* < \tau$ that can be estimated from the relation

$$(\mu_1 + \varepsilon t^*)^{1/2} \approx z(0)\exp\left(\mu_1 t^* + \varepsilon\frac{t^{*2}}{2}\right).$$

Finally, after following for a while the adiabatic approximation the solution will saturate to the final steady-state solution $\mu_2^{1/2}$ under the effect of the nonlinearities.

In figure 1 the different stages of the evolution as given by equations (12*a*) and (13*b*) are plotted against time, along with the numerical solution of the full nonlinear equation (11). We observe first a slow increase followed by an abrupt transition reflected by the presence of an inflexion point and, eventually, a saturation. These results corroborate the above qualitative picture, including the estimate of the crossover time.

2.2. Switching from negative values of μ

We consider again positive initial conditions and take the final value μ_2 to be positive. Since the ghost state $z_0 = 0$ is initially stable, the system first tends to stay in its vicinity and is thus reducible to the linearized solution, equation (12*a*). One would think that this will last until $\mu(t)$ as given by (2) crosses zero, which happens at $t_0 = \tau|\mu_1|/(\mu_2 + |\mu_1|)$. The unexpected feature (Mandel and Erneux 1984) is that there exists an extra delay during

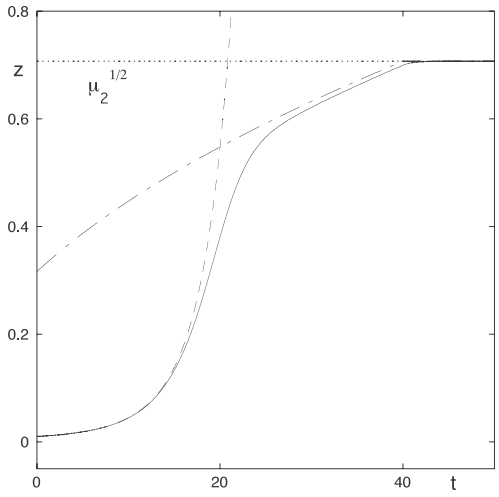

Figure 1. Time evolution of z, equation (11) as obtained numerically (full line) with $\mu_1 = 0.1, \mu_2 = 0.5, \varepsilon = 10^{-2}$ and $z(0) = 0.01$. The dashed–dotted line stands for the adiabatic approximation equation (13*b*) and the dashed line for the analytic result in the linearized approximation, equation (12*a*).

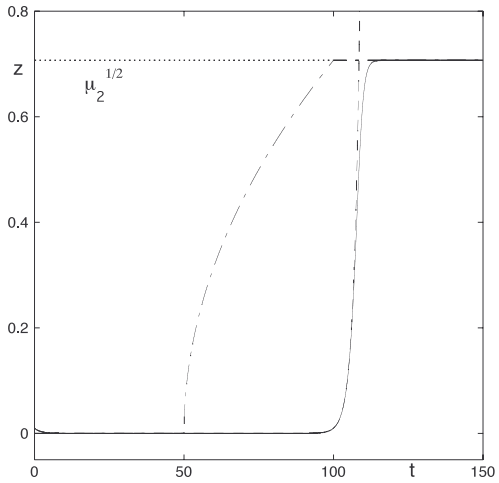

Figure 2. As in figure 1 but for $\mu_1 = -0.5$.

which the system stays in the vicinity of $z_0 = 0$. The delay time corresponds to the time necessary to build a positive exponent in the first equation (12*a*) and is thus given by $t_d = 2\tau|\mu_1|/(\mu_2 + |\mu_1|) = 2t_0$. Once this delay has elapsed the solution (12*a*) will in principle cross over as in the previous subsection with the adiabatic approximation (equation (13*b*)) and follow it for some (possibly short) time until nonlinear effects leading to saturation to the final state $\mu_2^{1/2}$ are again taking over. Figure 2 depicts the results of the numerical integration of the full nonlinear equation (11) under the conditions of this subsection. Again, the qualitative picture drawn above is reproduced quite satisfactorily. Notice that there is here no time for the regime of the adiabatic approximation to manifest itself prior to the rapid jump of the solution to the saturation value.

3. Stochastic dynamics of switching

We now augment the description of section 2 to account for the effect of the fluctuations. We use for this purpose the full Langevin equation (3) and the associated Fokker–Planck equation (Gardiner 1983),

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial z}(\mu(t)z - z^3)P + \frac{q^2}{2}\frac{\partial^2 P}{\partial z^2}. \tag{14}$$

We first address the role of the fluctuations in the early stages of the switching starting, as in section 2, with an initial condition close to $z = 0$. Within the range of validity of equation (12*a*) one may then limit the drift term in equation (14) to its linear part. Multiplying both sides by z^2 and integrating over z, this yields the following equation of evolution for the second moment $\overline{z^2}$,

$$\frac{\mathrm{d}\overline{z^2}}{\mathrm{d}t} = 2\mu(t)\overline{z^2} + q^2 \tag{15}$$

whose formal solution is (cf equation (2))

$$\overline{z_t^2} = \exp\left(2\left(\mu_1 t + \varepsilon\frac{t^2}{2}\right)\right)\overline{z_0^2} + q^2\int_0^t \mathrm{d}t' \exp\left(-2\left[\mu_1(t'-t) + \frac{\varepsilon}{2}(t'^2 - t^2)\right]\right)$$
$$(t \leqslant \tau) \tag{16a}$$

$$\overline{z_t^2} = \exp(2\mu_2(t-\tau))\overline{z_\tau^2} + \frac{q^2}{2\mu_2}(\exp(2\mu_2(t-\tau)) - 1) \qquad (t > \tau). \tag{16b}$$

We notice that the first term of these expressions is identical to the (squared) deterministic response (equation (12*a*)), whereas the second one accounts for the effect of the fluctuations.

Expression (16*a*) reduces straightforwardly, through an appropriate change of variables, to

$$\overline{z_1^2} = \exp\left(2\left(\mu_1 t + \varepsilon\frac{t^2}{2}\right)\right)\overline{z_0^2} + \frac{q^2}{2}\sqrt{\frac{\pi}{\varepsilon}}\exp\left(\frac{(\mu_1+\varepsilon t)^2}{\varepsilon}\right)$$
$$\times\left[\mathrm{erf}\left(-\frac{\mu_1}{\sqrt{\varepsilon}}\right) - \mathrm{erf}\left(-\frac{\mu_1+\varepsilon t}{\sqrt{\varepsilon}}\right)\right]. \tag{17}$$

For $\mu_1 > 0$ and much larger than $\sqrt{\varepsilon}$, asymptotic expansion of the error functions of the opposite arguments to those appearing in equation (17) yields

$$\overline{z_t^2} \approx \exp\left(2\left(\mu_1 t + \varepsilon\frac{t^2}{2}\right)\right)\overline{z_0^2} + \frac{q^2}{2}\left(\frac{\exp\left(2\left(\mu_1 t + \varepsilon\frac{t^2}{2}\right)\right)}{\mu_1} - \frac{1}{\mu_1+\varepsilon t}\right)$$
$$(\mu_1 > 0). \tag{18a}$$

For $\mu_1 < 0$ the argument of the first error function in (17) is positive, whereas for the second one it switches from positive to negative values at the time t_0 defined in section 2.2. Accordingly, the associated asymptotic expansions differ from equation (17) in that the second term is to be replaced by

$$\begin{array}{ll} \dfrac{q^2}{2}\left(\dfrac{1}{\mu_1+\varepsilon t} - \dfrac{\exp\left(2\left(\mu_1 t + \varepsilon\frac{t^2}{2}\right)\right)}{\mu_1}\right) & t < t_0 \\ q^2\sqrt{\dfrac{\pi}{\varepsilon}}\dfrac{\exp(\mu_1+\varepsilon t)^2}{\varepsilon} & t > t_0. \end{array} \tag{18b}$$

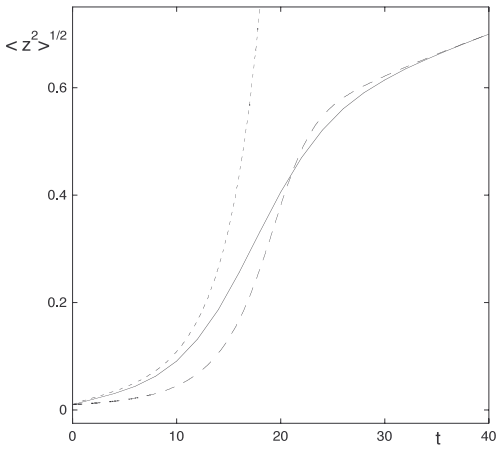

Figure 3. Time evolution of the square root of the second moment of variable z (full line) in the presence of an additive stochastic forcing as obtained from the Fokker–Planck equation with an initial condition delta picked at $z = 0.01$. The dashed line stands for the deterministic behaviour and the dotted line for the approximate analytic solution, equation (18). Parameter values as in figure 1 with $q^2 = 10^{-4}$.

The results in equations (17) and (18) will now be complemented and extended to the nonlinear range by numerical solution of the Fokker–Planck equation (14). We adapt for this purpose to the time-dependent case a method originally developed by Chang and Cooper (1970) for the computation of steady-state solutions. Figure 3 (full line) depicts the time dependence of the square root of $\overline{z_t^2}$ (for the purposes of comparison with the deterministic response, dotted line) for initial conditions and ε values as in figure 1 and for a variance $q^2 = 10^{-4}$. For comparison we also plot (dashes) the analytic result, equations (17) and (18). As can be seen, the switching keeps the general features of figure 1, but under the effect of fluctuations the time of switching tends to be advanced. This tendency is overestimated by the analytic result, which follows the numerical result of the full Fokker–Planck calculation for a while, but subsequently gives rise to a runaway behaviour.

A more detailed view of the role of fluctuations on switching is afforded by the computation of the probability distribution of the switching times associated with the different realizations of the underlying stochastic process. For this purpose the full Langevin equation (3) is simulated numerically, using the same initial condition as in section 2. For clarity, only those realizations that switch towards the attractor in the region of positive z are retained in the statistics. Figure 4(a) depicts one such realization of the stochastic process, and in figure 4(b) the probability distribution of switching times, defined as the times of crossing by the trajectory of a value corresponding to the inflexion point of the kinetic potential (equation (4)) at $\mu = \mu_2$, is drawn. While the general features of switching identified in the deterministic analysis (section 2) are preserved, there is now a considerable dispersion of switching times. Indeed, the mean and the standard deviation in figure 4(b) amount to about 20 and 3.2 time units respectively, their ratio being more than one order of magnitude larger than the noise strength. As for the switching times observed in the simulations, they span a range with a minimum at 12.4 and a maximum at 45.5.

An alternative view of the variability of the switching process is provided by the evolution of the probability distribution of the variable z itself at different times, as seen in figure 5. As the switching region is swept the probability, first centred at a value close to zero, develops a

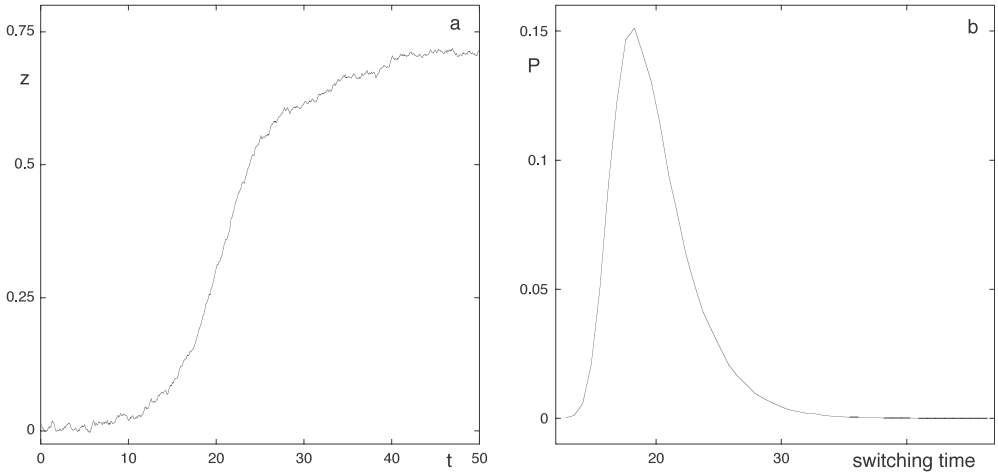

Figure 4. Stochastic evolution toward state $\mu_2^{1/2}$ (a) and probability density of the transition times to that state (b) as obtained numerically from the Langevin equation (3). Parameter values as in figure 1 with $q^2 = 10^{-4}$. The number of realizations for figure 4(b) is 2×10^6.

long tail. This tail initiates a 'seeding' process whereby there is a buildup of probability mass for increasingly large z values until a very narrow distribution centred on the final attractor $z_+ = \mu_2^{1/2}$ is reached at a time t larger than τ. This is reminiscent of the behaviour found in explosive systems operating in the vicinity of a limit point bifurcation (Nicolis and Baras 1987). In addition to the transient long-tailed probability distributions found here such systems are also known to give rise to transient bimodality. This latter behaviour has not been observed here, at least not under the switching scenarios explored.

We close this section by analysing the transition dynamics between the local minima of the kinetic potential, equation (4). The evolution is now started at a z value far from zero, close to one of these minima—say the positive one—corresponding to the starting value of μ in the switching process (equation (2)). Under standard conditions, in the presence of fluctuations transitions between this and the second minimum will take place on a characteristic timescale given by Kramers' formula, (Gardiner 1983)

$$\theta_\pm = \pi[-U''(z_0)U''(z_\pm)]^{-1/2}\exp\left(\frac{2}{q^2}\Delta U_\pm\right), \tag{19a}$$

where ΔU is the potential barrier

$$\Delta U_\pm = U(z_0) - U(z_\pm) = -\frac{1}{4}\mu^2. \tag{19b}$$

Eventually, as $U(z_+) = U(z_-)$ an equipartition regime will be established in which the probability masses N_+ and N_- in each of the two wells will be equal. The question raised here is, to what extent under the prescribed initial condition and the action of the ramp the state at the end of the switching process $t = \tau$ will instead be sufficiently biased for the system to remain preferentially in the vicinity of one of the states $z_\pm = \pm\mu_2^{1/2}$.

In order to disentangle the transient behaviour starting with an initial state favouring z_+ or z_-, from the equipartition case we set

$$N_\pm(t) = \tfrac{1}{2} \pm \delta N(t). \tag{20}$$

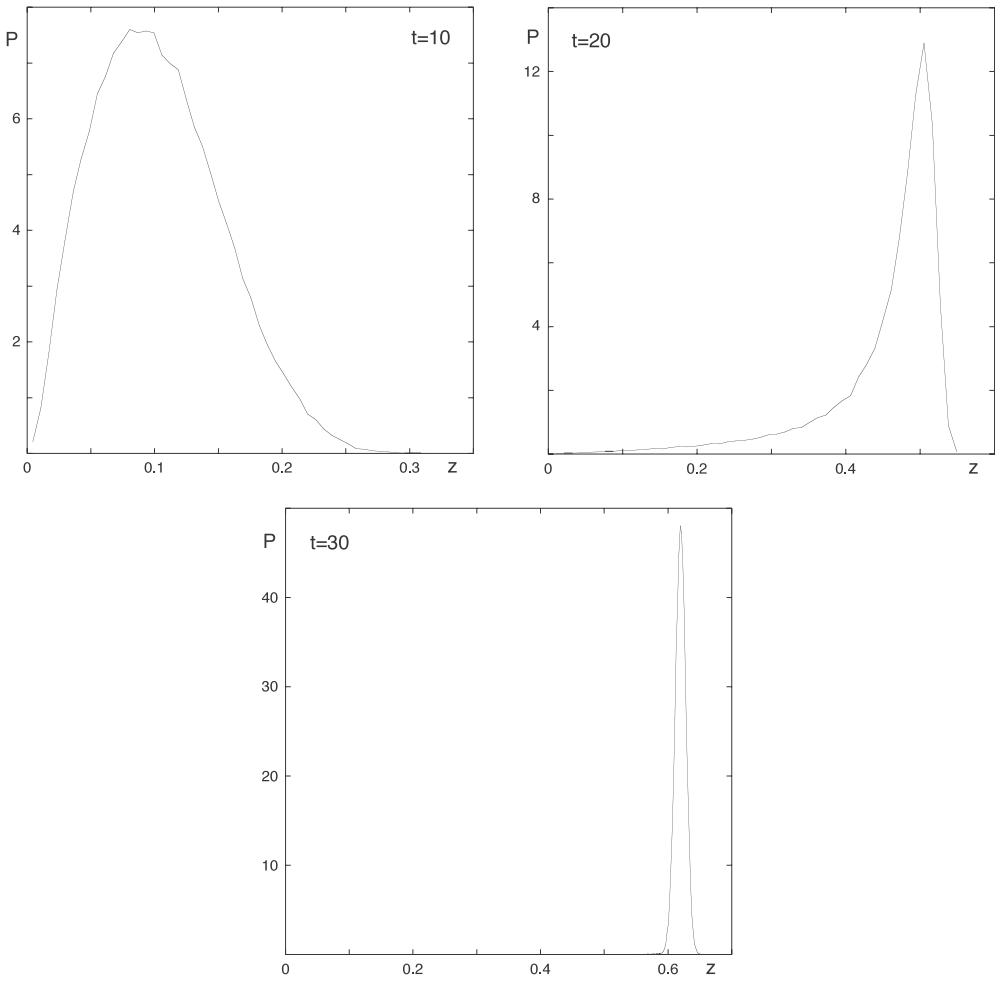

Figure 5. Probability density of z at different stages of the switching process. The parameter values as in figure 4(b) and the number of stochastic realizations is 10^6.

Within the framework of a stochastic extension of the adiabatic approximation (equation (13)), the excess probability mass obeys the rate equation (Nicolis and Nicolis 2000)

$$\frac{\mathrm{d}\delta N}{\mathrm{d}t} = -\frac{1}{\theta(t)}\delta N, \tag{21}$$

where $\theta(t)$ is formally given by equation (19*a*), in which U and ΔU now account for the presence of the ramp:

$$\theta^{-1}(t) = \frac{\sqrt{2}}{\pi}(\mu_1 + \varepsilon t)\exp(-(\mu_1 + \varepsilon t)^2/2q^2) \qquad t \leqslant \tau. \tag{22}$$

Equation (21), subject to (22), can be integrated exactly, yielding

$$\delta N(t) = \delta N(0)\exp\left\{-\frac{\sqrt{2}}{\pi}\frac{q^2\tau}{\mu_2 - \mu_1}\left[\exp\left(-\frac{\mu_1^2}{2q^2}\right) - \exp\left(-\frac{\left(\mu_1 + \frac{\mu_2-\mu_1}{\tau}t\right)^2}{2q^2}\right)\right]\right\}$$
$$(t \leqslant \tau). \tag{23}$$

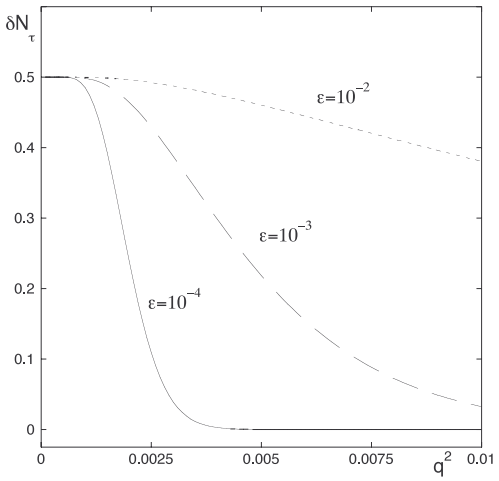

Figure 6. Sensitivity of the excess probability mass δN_τ on the strength q^2 of the fluctuations and on the ramp as obtained from equation (23). Parameter values $\mu_1 = 0.1$ and $\mu_2 = 0.5$.

Figure 6 depicts the deviation from equipartition predicted by this relation at $t = \tau$ (i.e. $\delta N(\tau)$ substantially different from 0, or equivalently $N_\pm(\tau)$ substantially different from $1/2$) as a function of q^2, for various values of the ramp $\varepsilon = (\mu_2 - \mu_1)/\tau$, for an initial $\delta N(0) = 0.5$ (i.e. $N_+(0) = 1$). As can be seen, values as far as desired from equipartition can be achieved through appropriate control of q^2 and ε. This provides a bias to the evolution for the post-switching regime where $\mu = \mu_2$ entailing that if the barrier $\Delta U(\mu_2)$ is sufficiently large, the system will remain frozen around the attractor at $\mu_2^{1/2}$ for any length of time of physical relevance. Notice that freezing can never be complete, as $\delta N(t)$ is bound to be zero for all t if initially $\delta N(0)$ is zero.

The above conclusions are confirmed by the results of the numerical integration of the Fokker–Planck equation (14). Figure 7 depicts the probability distributions at $t = \tau$ deduced from this integration for a deterministic initial condition at $z = 0.01$. We observe situations where there is a marked imbalance between the probability masses in the region of the two instantaneous minima of U or even an almost 100% selection of one particular state.

4. Thermodynamics of switching

In this section we study how dissipation—a ubiquitous feature of nonequilibrium—is generated within the system and exchanged between system and surroundings during the switching process.

As is well known from irreversible thermodynamics, key information about these questions is provided by the *entropy production*. In a chemical system, and within the framework of the *local equilibrium assumption*, this quantity is the sum of products of the rates times the affinities of the individual reactions (De Groot and Mazur 1961). As these cannot be evaluated uniquely on the sole basis of the normal form equation (3), one needs to provide more specific information on the reaction mechanism. We use for this purpose the Schlögl model, equation (5). Utilizing the expression of the affinities in terms of chemical potentials as well as relation (7), one is led to

$$\sigma = (3x^2 - x^3)\ell n\frac{3}{x} + (kx - b)\ell n\frac{kx}{b}, \tag{24}$$

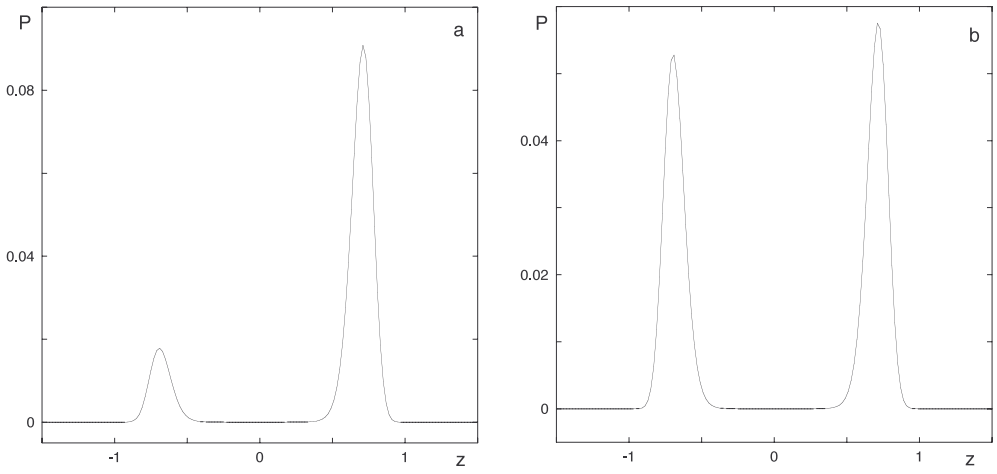

Figure 7. Probability distributions at $t = \tau$ obtained numerically from equation (14) with an initial condition delta picked at $z = \mu_2^{1/2}$. Parameter values $\mu_1 = 0.1$, $\mu_2 = 0.5$, $q^2 = 10^{-2}$, $\varepsilon = 10^{-2}$ (a) and $\varepsilon = 10^{-3}$ (b).

it being understood that x is here a fluctuating quantity to be evaluated from the Langevin equation (3), with $x = 1 + z$. Actually, in addition to this part one should in principle include a contribution involving explicitly the random forces $F_1(t)$, $F_2(t)$ associated to each of the two fluxes, the random force appearing in equation (3) being $F(t) = F_1(t) - F_2(t)$. This contribution is not considered here, as it is beyond the range of the local equilibrium assumption.

In what follows we will be interested in the behaviour of σ at different stages of the switching process and, in particular, in its dependence on the strength of the fluctuations q^2 and on the duration τ of switching. We will also evaluate the total dissipation, $\sum_t$ released up to time t, $0 \leqslant t \leqslant \tau$, defined as

$$\sum_t = \int_0^t \mathrm{d}t' \sigma_{t'}. \tag{25}$$

Figures 8(a) and (b) summarize the results concerning entropy production averaged over many realizations of the stochastic process, $\langle \sigma \rangle_t$, starting with a deterministic initial condition at $x = 1.01$. As can be seen from (a), mean dissipation increases substantially with the strength of the fluctuations for intermediate times. Furthermore, while its time dependence follows the pattern of figure 1 for small and moderate q^2, for larger q^2 the sigmoidal structure tends to be blurred and replaced by an almost immediate substantial increase in time. It should also be noticed that while the switching time τ under the conditions of figure 8(a) is $\tau = 40$, $\langle \sigma \rangle_t$ becomes practically q^2 independent at $t = 25$ and onwards, as the system reaches a state close to the final deterministic attractor $x_+ = 1 + z_+ = 1 + \mu_2^{1/2}$. As regards the dependence on switching time for a given value of q^2, figure 8(b) shows that dissipation is transiently enhanced as the switching gets slower: owing to the fact that the transition is more steep in the second case, the system spends a relatively longer period of time in the range of large values of x where it dissipates more. Again, the values of $\langle \sigma \rangle_t$ for different τ become indistinguishable well prior to t equal to the corresponding switching times.

As expected the above differences become accentuated when looking at the mean total dissipation $\langle \sum \rangle_t$, equation (25). One obtains $\langle \sum \rangle_t$ equal to 295, 305 and 320 for q^2 equal to

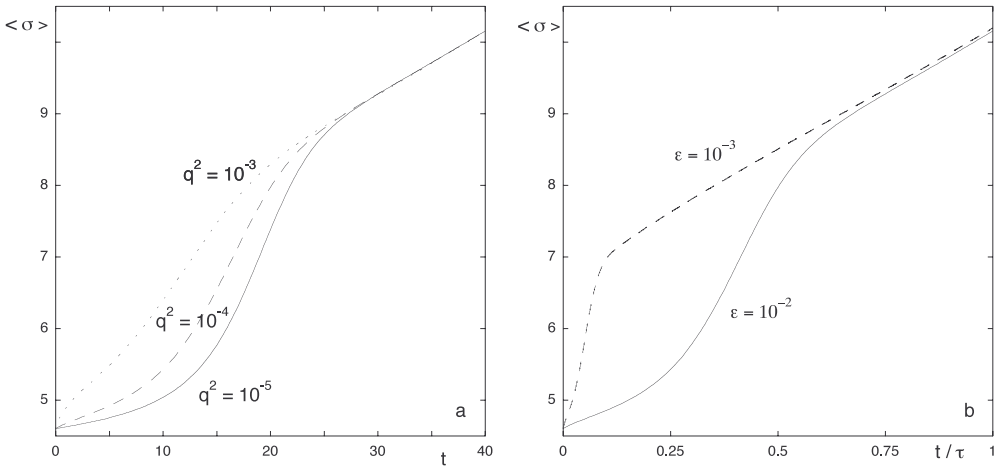

Figure 8. Time evolution of the instantaneous entropy production during the switching process for different values of the fluctuation strength with $\varepsilon = 10^{-2}$ (a), and of the ramp with $q^2 = 10^{-4}$ (b).

10^{-5}, 10^{-4} and 10^{-3} respectively, under the conditions of figure 8(a); and $\langle\sum\rangle_t$ equal to 305, and 3354 for ε equal to 10^{-2} and 10^{-3} respectively, under the conditions of figure 8(b).

These results can be understood qualitatively by expanding equation (24) around the instantaneous deterministic value $\overline{x}(t)$. Keeping the first nontrivial term yields

$$\langle\sigma\rangle_t = \sigma(\overline{x}(t)) + \sigma'(\overline{x}(t))(\langle x\rangle_t - \overline{x}(t)) + \cdots \tag{26}$$

where σ' denotes the derivative of σ and the difference between $\langle x\rangle_t$ and $\overline{x}(t)$ arises from the tendency of the fluctuations to advance the switching process (cf figure 3). Numerical evaluation of the second term in (26) shows that both σ' and $\langle x\rangle_t - \overline{x}(t)$ remain positive for times up to those where the three curves in figure 8(a) begin to merge. The enhancement of dissipation induced by the fluctuations is thus a first-order, rather than a second-order (related to the variance $\langle\delta x^2\rangle_t$) effect.

5. Discussion

In this paper the kinetics of the switching between two steady states in chemical systems undergoing a pitchfork bifurcation has been analysed, in the presence of fluctuations and of a ramp in the parameter controlling the bifurcation. Two types of switching were considered: the system is started initially close to the state that loses its stability across the bifurcation and ends up in one of the new attractors arising beyond bifurcation; or it is started near one of the stable states corresponding to the initial value of the control parameter and is subsequently performing during the switching process transitions across the barrier separating it from the other stable state. It was shown that the presence of the ramp in conjunction with the fluctuations considerably affects the kinetics of the switching process as compared to the prediction of the deterministic (mean field) analysis and has, furthermore, a clear-cut signature on the system's thermodynamic properties as described by the entropy production.

More specifically, in the first scenario fluctuations tend to advance, in the mean, the switching process and to introduce a wide dispersion of switching times. And in the second scenario, they may be at the origin of a drastic redistribution of probability masses across the barrier at the end of the switching process as compared to the predictions of classical Kramers

theory. The extent of this redistribution depends in a very sensitive way on the strength of the fluctuations and on the length of the switching time (equation (23) and figure 6), and may eventually lead to the practical freezing of the system on a preferred state. Both the advancement of the switching (first scenario) and the freezing (second scenario) provide an interesting method of control of the time evolution of multistable chemical systems. Of special relevance in this respect are mesoscopic level systems such as those involved in biological metabolic processes or in reactions taking place on supports of restricted geometry, where the strength of the fluctuations is drastically enhanced as compared to bulk phase systems encountered in standard physical chemistry.

A natural extension of this work is to consider bistable systems in the range of hysteretic behaviour, which would amount to keeping the two control parameters μ and λ independent in equation (9). This would allow one to follow in detail the crossover between switching joining two equilibrium states (equation (10)) and the switching under nonequilibrium conditions considered in the present paper. It has been suggested (Jarzynski 1997) that dissipation along irreversible paths joining two equilibrium states possesses some universal features. It would undoubtedly be of interest to investigate the influence of nonequilibrium constraints on these properties and to assess their status on a concrete system amenable to a full thermodynamic description like the Schlögl model considered in our work.

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