Stochastic dynamical nonlinear behavior analysis of a class of single-state CSTRs

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Abstract: Motivated by the need of developing stochastic nonlinear model-based methods to characterize uncertainty for chemical process estimation, control, identification, and experiment design purposes, in this paper the problem of characterizing the global dynamics of single-state nonlinear stochastic system is addressed. An isothermal CSTR with Langmuir-Hinshelwood kinetics is considered as representative example with steady state multiplicity. The dynamics of the state probability distribution function (PDF) is modeled within a Fokker-Planck's (FP) global nonlinear framework, on the basis of FP's partial differential equation (PDE) driven by initial state and exogenous uncertainty. A correspondence between global nonlinear deterministic (stability, multiplicity and bifurcation) and stochastic (PDF stationary solution and mono/multimodality) characteristics is identified, enabling the interpretation of tunneling-like stationary-to-stationary PDF transitions, and the introduction of a bifurcation diagram with the consideration of stochastic features in the context of the CSTR case example.

Keywords: isothermal CSTR, multistability, nonlinear system, stochastic model, Fokker-Planck

1. INTRODUCTION

The study of stochastic nonlinear systems is motivated by the need of characterizing the effect of model uncertainty for model-based applications such as chemical process modeling, system identification, experiment design, estimation and control purposes, process safety assessment. While the deterministic approaches for nonlinear chemical processes are a rather mature field, the development of nonlinear stochastic approaches lags far behind. Deterministic descriptions suffice for chemical processes described by nonlinear models over the neighborhood of a steady-state (or nominal motion) for a continuous (or batch) process, but the same cannot be said for processes which evolve over ample (nonlocal) state-space domains, where nonlinearities become significant, and consequently, the inexorable presence of uncertainty due to measurement and modeling errors and its effect on the stability, observability and controllability features must be regarded within a stochastic global nonlinear framework. In chemical processes, the combination of measurement errors with high-frequency unmodeled dynamics manifests itself as random-like uncertainty, which imposes limits of estimation and control behavior.

In most of previous studies in chemical process engineering, the issue of uncertainty characterization has been performed with the so-called model sensitivity analysis with respect to initial values and/or parameters (Morbidelli and Varma, 1989, Dutta *et al*., 2001), on the basis of a linear model truncation. The drawback of this approach is that it does not allow the assessment of the combined effect of the uncertainties caused by the neglected nonlinear dynamics, which manifest itself when testing or implementing the model with the data generated by the actual nonlinear process (Horenko *et al.*, 2005).

In the nonlinear systems theory field, there are rather well established approaches to address the model uncertainty problem for multi-state nonlinear processes, with rigorous probability distribution function (PDF) evolution descriptions in terms of a set of Fokker-Planck (FP) partial differential equations (Risken, 1996). In fact, the nonlinear EKF estimator design can be seen as a second-order statistics approximation of the FP equation approach. However, in spite of being the EKF the most widely used estimation technique in chemical process systems engineering, its employment for uncertainty assessment purposes has been rather limited, and the consideration of the full nonlinear statistics FP equation approach has been circumscribed to a rather limited set of studies.

While the rigorous FP equation approach has been successfully applied in a diversity of problems in applied science, including physics, medical sciences (Mei *et al*., 2004; Lo, 2007), biology (Soboleva and Pleasants, 2003; Huang *et al*., 2008) and electronic circuits (Hanggi and Jung, 1988), in the chemical process systems engineering field only a few chemical reactor studies have been performed according to the FP equation approach. In a pioneering work, Pell and Aris (1969) studied the local-stochastic behavior of a

chemical reactor on the basis of a linear model truncation. In spite of the limited nature of the local results, recognized by the authors themselves, this work evidenced the benefit and possibilities of modeling the presence of random fluctuations within a stochastic framework. Later, Rao *et al.* (1974) addressed the same problem with a numerical algorithm to solve the associated nonlinear equation drawing nonlocal results and establishing that the linearization approach breaks down when the system is close to a saddle-node bifurcation. In a subsequent study, Ratto (1998) applied the FP equation approach to the linearization of a stable closed-loop reactor with PI temperature control subjected to measurement noise, sufficiently away from the possibility of Hopf bifurcations (whose consideration is a central point of the present study). This study evidenced the advantages of the FP equation-based theoretical approach (with quasi-analytical solutions), with respect to Monte Carlo methods (Ratto and Paladino 2000, Paladino and Ratto 2000, Sherer and Ramkrishna, 2008; Hauptmanns, 2008).

In the context of a combustion engineering science problem, Oberlack *et al.* (2000) studied the stationary solution of the FP equation associated to a multistable homogeneous adiabatic flow reactor described by a one-dimensional deterministic system. In spite of having addressed only the steady-state aspect of the problem, this study further evidenced the capabilities and possibilities of the FP equation-based approach to tackle the chemical reactor stochastic modeling problem. These considerations on the employment of the FP equation-based approach for the treatment of dynamical nonlinear systems, in general, and of chemical reactor, in particular, motivate the present study on the global-stochastic dynamical behavior of chemical reactors with emphasis on: the presence of multistability, transient behavior and the connection between deterministic and stochastic modeling approaches.

As an inductive step towards the development of nonlocal, global, nonlinear stochastic uncertainty characterization methodology, in this work the problem of characterizing the concentration stochastic dynamical behavior of single-state nonlinear isothermal CSTR with Langmuir-Hinshelwood kinetics as representative case example with multistability phenomena has been addressed. The problem is treated within a global-nonlinear framework by combining deterministic multiplicity and bifurcation analysis tools with a FP equation-based stochastic behavior characterization, in the light of the particular system characteristics. The stochastic dynamical behavior is studied by looking at the response solution of the dynamic FP partial differential equation (PDE) to: (i) initial state uncertainty and (ii) modeling error described as a white noise exogenous input injection. As a result, a correspondence between stochastic features (mono or multimodality, potential, quasi-stability, and escape time) and deterministic features (stability, multiplicity and bifurcation) is established, enabling a better understanding of the nonlinear stochastic behavior and opening the possibility of extending the approach to multi-state chemical processes.

2. THE STOCHASTIC MODEL

Consider the single-state (x) nonlinear stochastic dynamical system:

$$\dot{x} = f[x, u(t)] + w(t),\ x(0) = x_o, \qquad w(t) \sim N[0, q(x)] \qquad (1)$$
$$x \in X = [0, \infty)$$

with exogenous deterministic input u, and driven by input uncertainty modeled as white noise with intensity $q(x)$. In the absence of noise, with $w(t) = 0$, the (single or multiple) steady-states satisfy, for the nominal input $\bar{u}$, the static-algebraic equation $f(\bar{x}, \bar{u}) = 0$. Due to the nonlinearity of $f(x)$, the deterministic system (i.e. when $w(t)=0$) can show structural instability, meaning the existence of steady-state bifurcation points as system parameters or inputs are varied. In the one-dimensional case, the more generic bifurcation is the saddle-node, which may imply the presence of multistability regions. This means that the deterministic system reaches one of the stable equilibrium points, depending on initial conditions and system input (Wiggins, 1990). Assuming the noise intensity $q(x)$ is constant for a fixed value of the input, $u(t) = \bar{u}$, the dynamics of the concentration (normalized) probability density function (PDF) $p(x,t)$ is governed by the Fokker-Planck partial differential equation (Risken, 1996):

$$p_t(x, t) = [d\, p_x(x, t)]_x - \{f(x, \bar{u})\, p(x, t)\}_x,\ 0 \le x < \infty,\ t > 0 \qquad (2a)$$

$$x = 0:\ d\, p_x(0, t) - f(0, \bar{u})\, p(0, t) = 0, \qquad x = \infty:\ p_x(\infty, t) = 0 \qquad (2b\text{-}c)$$

$$t = 0:\ p(x, 0) = p_0(x), \qquad d = q^2/2 \qquad (2d)$$

where d is the "diffusion constant" set by the noise intensity, (2b)-(2c) is the boundary condition pair and (2d) is the initial condition with initial PDF p_o. Condition (2b) establishes that x can have only positive values (Gardiner, 1997), in the understanding that this condition is easily met by writing the chemical process states in suitable scales.

2.1 Stationary probability density function

The stationary solution of (2) is given by:

$$p_s(x) = N_0 e^{-\frac{\phi(x)}{d}}, \qquad \phi(x) = -\int_x f(s)ds \qquad (3a\text{-}b)$$

where N_0 is the integration constant associated to the normalization of $p_s(x)$ and $\phi(x)$ is the potential function.

From the examination of the stationary solution (3) in the light of multiplicity features of the deterministic system, the next conclusions follow. When the deterministic system has a unique global attractor $\bar{x} \in X$, the potential function $\phi(x)$ has a single well shape with minimum at $\bar{x}$, and the stationary PDF $p_s(x)$ is monomodal with maximum at $\bar{x}$, meaning that the solution $\bar{x}$ is the more probable state over X. As noise intensity decreases (d tends to zero) the monomodal PDF tends to the Dirac Delta function $\delta(x - \bar{x})$ about $\bar{x}$. When the deterministic system has multiple steady state $\bar{x}_1, \ldots, \bar{x}_m \in X$,

with domains of attraction $X_1,\ldots, X_m$ such as $\bigcup_{i=1}^{m} X_i = X$: (i) the potential function $\phi(x)$ has a multi well shape potential with minima at $\bar{x}_1,\ldots, \bar{x}_m$, (ii) the multivalued stationary PDF $p_s(x)$ has maxima at $\bar{x}_1,\ldots, \bar{x}_m$, (iii) the most probable steady state solution is the one with the deepest potential well $\phi(\bar{x}_m)$ and therefore with the largest maximum, and (iv) the difference among PDF maxima grows exponentially with the decrease of d. As a consequence of (iv), at low d values the distribution appears monomodal and tends to a Dirac Delta when the noise intensity tends to zero. Multimodality is maintained, even at low d values, when the potential minima are equal and in this case the limit as d tends to zero is a multi Dirac Delta.

2.3 *Probability distribution function evolution*

The right hand side of (2a) can be written as follows:

$$p_t = d\, p_{xx} - f(x, \bar{u})\ p_x - f_x(x, \bar{u})\, p \tag{4}$$

evidencing that: (i) the shape of the PDF over time is due to a source/sink mechanism $-f_x\, p$ combined with two transport mechanisms, one diffusive $d\, p_{xx}$ and one convective $-f\, p_x$, and (ii) the PDF temporal evolution is obtained by giving an initial value $p(x,0) = p_0(x)$ and integrating numerically the FP equation. If the deterministic system has a unique global attractor, the potential function has a single minimum, and the PDF reaches asymptotically a monomodal distribution, regardless the initial PDF shape. Otherwise, when there is deterministic steady-state multiplicity with multiple potential minima, the PDF evolution may exhibit some behaviors, which seem atypical from a deterministic nonlinear system perspective. In fact, the PDF settles at some multimodal PDF with largest maximum at (probability around) the attractor $\bar{x}_1$, then after some time, the PDF eventually starts moving and reaches another multimodal shape with a different largest maximum at (probability around) the attractor $\bar{x}_2$. In fact, for the case of steady-state multiplicity with an asymptotic (stationary) bimodal PDF, the time necessary for a state x at the steady state $x = \bar{x}_1$, with domain of attraction X_1, to escape to the steady-state $x=\bar{x}_2$, with domain of attraction X_2, is approximated by the formula (Gardiner, 1997):

$$T \propto \exp[(\phi(\bar{x}_2)-\phi(\bar{x}_1))/d] \tag{5}$$

which resembles Arrhenius' equation in chemical kinetics.

Thus stationary-to-stationary ($\bar{x}_1$-to-$\bar{x}_2$) state transition probability is favored by: i) a small well potential difference $[\phi(\bar{x}_1)-\phi\bar{x}_2)]$ and (ii) a well potential with large minima. When the minima have the same ordinate, there is not a dominant attractor and the probability of leaving one of the wells is the same.

3. STOCHASTIC MODEL OF AN ISOTHERMAL CSTR

3.1 CSTR with Langmuir-Hinshelwood kinetics

As a representative example in catalytic reactors, let us consider an isothermal CSTR with Langmuir – Hinshelwood kinetics, with the corresponding mass balance being described by the nonlinear differential deterministic system:

$$\dot{x} = f(\mathrm{x}, Da, \sigma),\ x(0) = x_o, \tag{6}$$
$$f(x, Da, \sigma) = (1 - x) - Da(1 + \sigma)^2\, x/(1 + \sigma x)^2$$
$$x = c/c_i,\quad \tau = t/(V_R/Q),\quad Da = (V_R/Q)k/(1 + \sigma)^2,\ \sigma = K\, c_i.$$

x is the dimensionless concentration (referred to the feed concentration c_i), t and τ are, respectively, the actual and dimensionless time, Q the volumetric feedrate, V_R the reactor volume, k the reaction-rate constant, K the equilibrium adsorption constant and Da the Damkohler number. In spite of its simplicity, the above single-state system exhibits a rather rich behavior over the parameter space pair (Da, σ), showing multiple steady-states for a specified range of parameter values. In the case of multiplicity, there are two (low and high concentration) stable steady-states and one (intermediate concentration) unstable steady-state. Moreover system (6) captures the important nonlinearities which underline the lack of global and local observability at the value $x = 1/\sigma$ (where the reaction rate is maximum), in the understanding that this feature makes difficult the design of nonlinear observers and controllers of an important class of chemical reactors with nonmonotonic kinetics (Schaum *et al*., 2008).

The stochastic system associated to the deterministic reactor (6) is given by (1) replaced by $f(x,Da,\sigma)$, and the corresponding stationary PDF is given by:

$$p_s(x) = N_0 \exp\left[-\frac{1}{d}\left(-x + \frac{x^2}{2} + \frac{Da(1+\sigma)^2}{\sigma^2(1+\sigma x)} + \frac{Da(1+\sigma)^2 \ln(1+\sigma x)}{\sigma^2}\right)\right]. \tag{7}$$

3.1 *Deterministic nonlinear dynamics*

The bifurcation analysis of system (6) evidences the occurrence of saddle-node bifurcation when $Da > 0$ (see Figure 1) and, on the parameter space (Da, σ), the deterministic reactor steady-state (SS) exhibits either: (i) a unique global attractor $\bar{x}$ with domain of attraction X[0, 1], or (ii) three-SS multiplicity, with two (low and high concentration) stable and one (intermediate concentration) unstable steady-state.

In the multiplicity case, there are two basins of attraction (X_1 and X_2), one per attractor. Thus, in the single SS case any state motion $x(t)$ beginning in $x_0 \in X$ remains in X, and asymptotically converges to the steady state $\bar{x}$ in X (see Figure 2a):

$$x_o \in X = [0, 1] \Rightarrow x(t) \in X,\ x(t) \to \bar{x}$$

In the three-SS case (with two stable attractors $\bar{x}_i$, i = 1, 2 with domain of attraction X_i) any state motion $x(t)$ beginning in $x_o \in X_i$ remains in X_i, and asymptotically converges to the steady-state $\bar{x}_i$ in X_i, this is (see Figure 2b):

$$x_o \in X_i = [0, 1] \;\Rightarrow\; x(t) \in X_i,\; x(t) \to \bar{x}_i,\; i = 1, 2$$

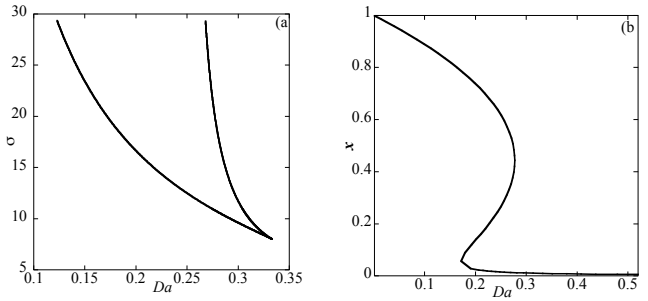

Figure 1: a) bifurcation diagram of system (6) and b) corresponding solution diagram at σ=20.

In particular, for σ = 20, the deterministic reactor system (6) exhibits: (i) a low (or high) concentration unique global attractor for $0 < Da < Da^- \approx 0.172$ (or $Da > Da^+ \approx 0.277$), (ii) three steady-states for $Da^- < Da < Da^+$, and (iii) two saddle-node bifurcations at Da equal to Da^- and Da^+ (see Figure 1).

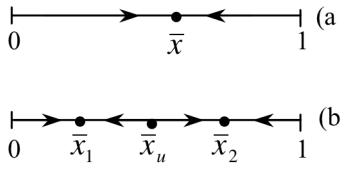

Figure 2: Phase diagram (a) in the single-SS case and (b) in the three-SS case.

3.2 *Stationary stochastic behavior*

The stationary (asymptotic) behavior of the PDF which satisfies the FP equation was investigated by setting σ equal to 20 (cf. Section 3.1), varying the value of Damkohler number $0 < Da < 1.0$ and the noise-related diffusion coefficient $10^{-5} < d < 10^{-3}$ (Ratto, 1998). The normalization constant in (3a) was calculated through the orthogonal collocation method on finite elements.

In Figure 3a (or 3b) the stationary PDF for $Da = 0.226$ (or $Da = 0.231$) with three SSs and two attractors, for two noise levels $d = 5.0\ 10^{-4}$ (continuous line) and $5.0\ 10^{-3}$ (dashed line) is shown. At the lowest d value only one peak is clearly detectable at $x \approx 0.683$ (or $x \approx 0.0178$), while the second peak corresponding to $x \approx 0.018$ (or $x \approx 0.671$) becomes evident only at the highest d value.

In Figure 4a (or 4b) is presented the potential function $\phi(x)$ (or stationary PDF for $d = 10^{-4}$) at three values of Da: 0.226 (dotted line), 0.229 (continuous line), and 0.231 (dashed line). In accordance with the deterministic bistability properties there are two attracting minima for the potential $\phi(x)$, meaning the possibility of well-to-well steady-state transition with longer residence in the deepest well. As expected, at low diffusion value only one peak is clearly visible for $Da = 0.226$ (extinction) and for $Da = 0.231$ (ignition). When the two minima have the same value, $Da \approx 0.229$, the stationary PDF exhibits bimodality made of nearly non overlapping monomodal PDFs or equivalently, a well-to-well potential without a dominant attractor.

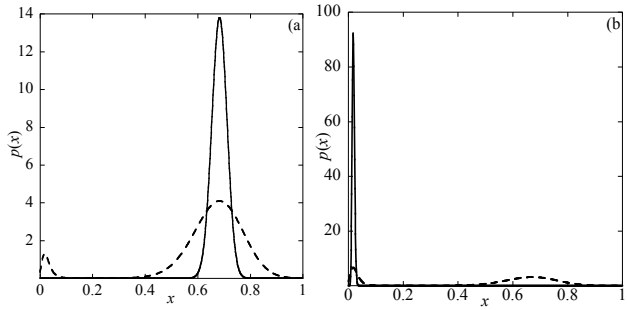

Figure 3: Stationary PDF when a) $Da = 0.226$ and b) $Da = 0.231$ for $d = 5.0\ 10^{-4}$ (solid line) and $d = 5.0\ 10^{-3}$ (dashed line).

The latter case could be considered as an important bifurcation characteristic related to the stochastic behavior, and not to the deterministic one. This Damkohler critical number Da_C is determined by the enforcement of the next equipotential conditions:

$$\left.\frac{d\phi}{dx}\right|_{(\bar{x}_1;Da_C)} = \left.\frac{d\phi}{dx}\right|_{(\bar{x}_2;Da_C)} = 0 \qquad \left(\bar{x}_1 \neq \bar{x}_2\right)$$
$$\phi\left(\bar{x}_1;Da_C\right) = \phi\left(\bar{x}_2;Da_C\right) \qquad (8)$$

In conclusion, the Da_C value corresponds to a transition between two qualitatively different behaviors of the stochastic reactor system. This transition appears smooth for high d values, meaning that a bimodal distribution is apparent in a wider neighborhood of Da_C, and becomes sharper as the diffusion coefficient tends to zero.

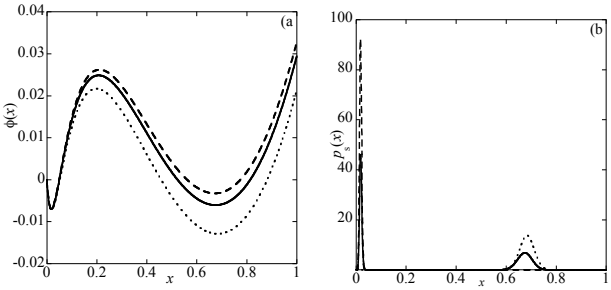

Figure 4: a) Potential function and b) stationary PDF (d=10^{-4}) for different Da values: Da=0.226 (dotted line), Da=0.229 (solid line), Da=0.231 (dashed line).

The one-dimensional manifold satisfying (8) can be derived by resorting to standard continuation algorithms (Doedel *et*

al., 1997), and the stochastic bifurcation diagram, over the (*Da*-σ) plane, was constructed and reported in Figure (5) together with the bifurcation diagram of (6).

Observe that the passage from the deterministic (Figure 1a) to the stochastic (Figure 5) bifurcation diagram evidences: (i) the correspondence between the deterministic steady-state and stochastic stationary nonlinear features, and (ii) the kind of information contained in the stochastic diagram and not in the deterministic one.

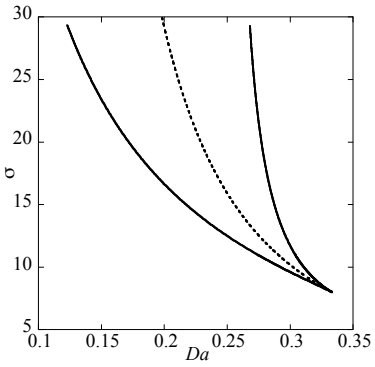

Figure 5: Diagram of the saddle-node bifurcation of the deterministic system (solid line) and the (Da_C, σ) curve (dashed line).

3.3 *Dynamic behavior*

According to the preceding developments, in a deterministic framework, the domain of attraction determines the steady-state which will be reached asymptotically by the system. However, from a stochastic point of view it may happen that one of the deterministic steady states has a low or negligible asymptotic probability of being reached, regardless the initial condition.

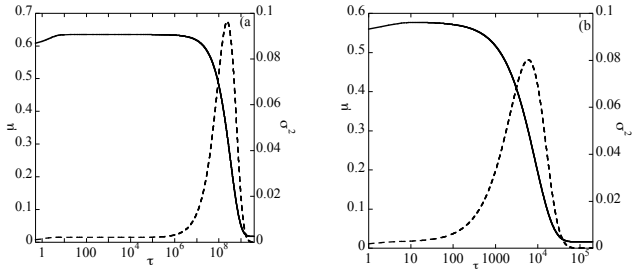

Figure 6: Dynamic behavior of mean (solid line) and variance (dashed line) of the PDF when $d = 10^{-3}$ at a) Da = 0.244 and b) Da = 0.260. The time scale is logarithmic.

Figure 6 represents the transient of mean and variance of the probability distribution function when $d = 10^{-3}$, and the initial condition is a Gaussian distribution with mean equal to 0.6 and variance equal to 0.02, at Da = 0.244 (Figure 6a) and Da = 0.260 (Figure 6b). In both cases, the absolute minimum of the potential function is positioned on the lower branch of the solution diagram, but the initial distribution is inside of the basin of attraction of the other solution, meaning that the probability that the initial condition is outside the weaker attractor is almost negligible.

The responses of the PDF show that during the transient, the mean of the distribution does not directly move towards its steady state value in the ignited zone, but first approaches the higher solution. It should be noted that, at Da = 0.244 (Figure 6a), mean and variance are almost constant for a wide interval of time (the time scale in Figure 6 is logarithmic), looking as if a stable stationary solution was definitely reached. Thus, the high concentration solution appears as a *quasi-stationary* solution. In other words, only after a long transient the system departs from the extinction steady-state and eventually reaches the ignited region. The variance reaches a maximum during the transition from the quasi-stationary to the stationary solution, implying that the PDF becomes bimodal with its two peaks corresponding to the two deterministic attractors. As time elapses, one of the peaks becomes negligible and the other one finally prevails. When Da = 0.260 (Figure 6b), the system again moves first towards the solution contained in the attraction basin where the initial distribution is centered (low conversion solution), but after a while the mean starts decreasing towards its stationary value. Some snapshots of the evolving probability distribution are shown in Figure 7 for Da = 0.244. It must be pointed out that the *quasi-stationary* condition duration can range from several to orders of magnitude the reactor natural deterministic dynamics (set by the residence time), depending on the noise intensity, and this is a fact that must be carefully accounted for in long-term prediction assessments, with applicability in safe process design.

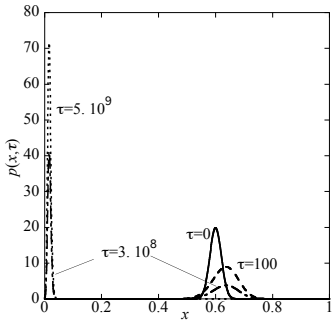

Figure 7: Snapshots of the PDF at τ=0 (solid line), τ =100 (dashed line), τ =3.0 10^8 (dashed-dotted line) and τ =5.0 10^9 (dotted line).

The duration of the *quasi-stationary* state can be related to the escape time, evaluated by means of (5). Calculating the escape time for Da = 0.244 and Da = 0.260 we found, respectively, T_1=4.3 10^8 and T_2=8.4 10^3. These results establish that stationary conditions are reached for a time greater than the calculated escape time, as confirmed by the simulation. The decreasing of the escape time as Da approaches the bifurcation value reflects the fact that the relative minimum is less and less deep until it disappears at the bifurcation point.

6. CONCLUSIONS

The global-nonlinear stochastic behavior of the concentration in an isothermal CSTR reactor with multistability has been characterized on the basis of standard deterministic tools in conjunction with FP equation theory. In addition to issues considered in previous studies in chemical reactor (Pell and Aris, 1969; Ratto 1998) and combustion engineering (Oberlack, 2000), in this study the presence of multistability, transient behavior, and the connection between deterministic and stochastic modeling approaches were considered. In particular, the interplay between the stochastic (mono or multimodality, potential, quasi-stability, and escape time) and deterministic (stability, multiplicity and bifurcation) features was identified. The stationary analysis revealed that, even when multistability was expected for the deterministic model, the probability distribution function usually appeared as monomodal, indicating that there is one dominant attractor, with higher probability of being reached asymptotically. However, the occurrence of multi-stabilities in the deterministic model did affect the behavior of the transient dynamics and the system could stay in a neighborhood of the weaker attractor for a long time interval, thus appearing as a *quasi-stationary* state.

The results of this paper constitute a point of departure: (i) to study the multi-state nonlinear stochastic system case, and (ii) to explore the implications and applications for global nonlinear estimation, control, and safe process designs.

*A*cknowledgement.

J. Alvarez kindly acknowledges Regione Sardegna for the support, through the program "Visiting Professor 2008", for the realization of this work at the Dipartimento di Ingegneria Chimica e Materiali of the University of Cagliari.

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