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Transient Evolution Towards a Unique Stable State: Stochastic Analysis of Explosive Behavior in a Chemical System

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A stochastic description of an isothermal chemical system showing explosive behavior is developed. Numerical analysis shows the appearance of multiple humps of the probability distribution. This implies the onset of chaotic behavior reflecting the random character of the ignition process. Various characteristics of the phenomenon, such as onset time and duration, are studied in terms of the size of the system, the intrinsic parameters, and initial conditions. The implications of the results in combustion are discussed.

KEY WORDS: Fluctuations; master equation; chemical explosions.

1. INTRODUCTION

The need for a stochastic analysis in problems involving bifurcations of new branches of stable states,[1] or an evolution from an initial unstable[2,3] or marginally stable[4] state is well recognized. In the absence of such conditions it is thus tacitly assumed that the system will essentially follow a deterministic course described by the phenomenological equations of evolution in which fluctuations will constitute only a minor perturbation, just like in the vicinity of an equilibrium state in the absence of phase transitions. In a recent paper one of us (G.N.) and coauthors[5] showed that

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there exists an important class of systems, those undergoing an adiabatic thermal explosion, that may escape from this rule. It is the purpose of the present work to extend the analysis to isothermal, chemical explosions, and also to point out some additional interesting features not considered explicitly in Ref. 5.

In Section 2 we summarize the phenomenological analysis of a nonlinear chemical system[6] which, depending on the parameters, can exhibit various types of behavior. One of these behaviors, the chemical explosion, is taken up in Section 3. It is shown that during the transient evolution to the unique stable steady state the probability distribution of the system can develop multiple humps and long tails, reflecting the onset of random behavior. Section 4 is devoted to the dependence of this behavior on the size of the system, the initial conditions, and the intrinsic parameters. Comments and suggestions are summarized in Section 5.

2. CHEMICAL EXPLOSION IN A SIMPLE MODEL

In what follows we consider a chemical system involving one variable intermediate and a cubic rate law. A typical example is provided by Schlögl's model[6]

$$\begin{aligned} A + 2X &\rightleftharpoons 3X \\ X &\rightleftharpoons B \end{aligned} \tag{2.1}$$

It will be convenient to write the rate equation in a canonical form which, on suitably redefining variables, parameters, and time scales reads[7]

$$\frac{d\bar{x}}{dt} = -\bar{x}^3 + 3\bar{x}^2 - (3 + \delta)\bar{x} + 1 + \delta' \tag{2.2}$$

where the bar over x is a reminder that one is dealing with a purely phenomenological description ignoring fluctuations. For $\delta = \delta' = 0$ one has a bifurcation point, corresponding to the triple root $\bar{x} = 1$ of Eq. (2.2) at the steady state. For $\delta, \delta' \neq 0$ the usual analysis leads to Fig. 1, in which the regime of three real solutions is contained between lines (a_1) and (a_2) of parameter space. On the lines (a_1) and (a_2) themselves the system exhibits one marginally stable state (arising from a limit point bifurcation) and one asymptotically stable state.

The point we want to make now is that even outside the bistable domain of Fig. 1 the situation is far from being uniformly simple. Undoubtedly, far away from (a_1) or (a_2) nothing special is to be expected: the system will follow its deterministic course and eventually it will evolve to the unique stable attractor. Close to these two curves, however, the situation is different: indeed, in these regions the system will be dominated during some time interval by a *slow mode*—the remnant of the limit point

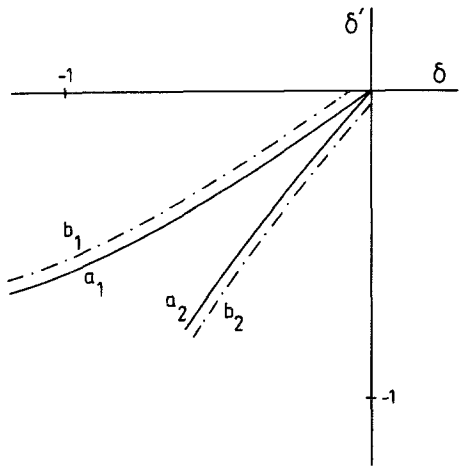

Fig. 1. Bifurcation diagram for the Schlögl model in (δ, δ') space. Lines (a_1) and (a_2) delimit the region of bistability; lines (b_1) and (b_2) delimit the regions of prominent explosive behavior.

bifurcation. As a result it will exhibit a long induction period followed by a quick evolution to the unique stable attractor. We call this the *chemical explosion* regime. It is this regime that constitutes the main point of focus of the present paper.

One convenient way to delimit the range of explosive behavior, at least at the level of the phenomenological description of this section, is through the properties of the deterministic potential from which Eq. (2.2) derives:

$$U(\bar{x}; \delta, \delta') = \frac{\bar{x}^4}{4} - \bar{x}^3 + (3 + \delta)\frac{\bar{x}^2}{2} - (1 + \delta')\bar{x} \tag{2.3}$$

The existence of an induction period for $\bar{x}$ implies necessarily that there must be a time, t_c, at which the graph of the solution $\bar{x}(t)$ to Eq. (2.2) has an inflection point. Differentiating Eq. (2.2) once again we obtain

$$\frac{d^2\bar{x}}{dt^2} = -\frac{\partial^2 U}{\partial \bar{x}^2}\frac{d\bar{x}}{dt} \tag{2.4}$$

from which it follows that for t_c to exist the deterministic potential must have an inflection point for values of $\bar{x}$ between the initial state $\bar{x}_0$ and the final stable state. We may further characterize explosion by introducing the criterion that the slope of the potential at the inflection point $\bar{x}_i$ be smaller than some value θ

$$|U'(\bar{x}_i)| < \theta \tag{2.5}$$

The two above conditions determine the curves (b_1) and (b_2) in (δ, δ') space (cf. Fig. 1)

$$\begin{aligned} \delta' &= 2(-\delta/3)^{3/2} - 3(-\delta/3) + \theta \\ \delta' &= -2(-\delta/3)^{3/2} - 3(-\delta/3) - \theta \\ \delta &\leqslant 0 \end{aligned} \tag{2.6}$$

delimiting the region of explosive behavior.

The violence of explosion will depend on the value of the slope of the potential at the inflection point. If the limit of marginal stability is approached, this value will go to zero and the induction period will tend to infinity. The explosion will then become more and more pronounced. This procedure may seem arbitrary at the level of the deterministic approach of the present section. It will, however, be given a sound motivation in the framework of the stochastic approach adopted in the subsequent sections. Moreover, in the region of violent explosion the stochastic approach will result in qualitative changes in the evolution which cannot be accounted for by the properties of the deterministic potential.

3. STOCHASTIC ANALYSIS OF THE EXPLOSIVE REGIME

The existence of various time scales in the explosive range implies that during some time interval fluctuations may compete with the deterministic evolution. This constitutes a strong motivation for undertaking a stochastic analysis of the evolution. To do this we regard, as usually,[1] chemical reactions as a birth and death process and write the master equation for the probability distribution $P(X,t)$. For Schlögl model, Eq. (2.1), we obtain

$$\begin{aligned} \frac{dP(X,t)}{dt} &= \lambda(X-1)P(X-1,t) + \mu(X+1)P(X+1,t) \\ &\quad - \left[\lambda(X) + \mu(X)\right]P(X,t) \end{aligned} \tag{3.1}$$

where

$$\lambda(X) = 3X(X-1)/V + V(1+\delta')$$

$$\mu(X) = X(X-1)(X-2)/V^2 + X(3+\delta)$$

and V denotes the size of the system. So far the time-dependent properties of the solution of this equation for general values of δ and δ' are poorly known. (See Ref. 2 for a survey.) In Ref. 5 it has been shown that for a pure death process (describing an adiabatic thermal explosion) detailed information could be obtained by representing the death rate by a piecewise linear function. It may be expected that a similar idealization could allow us to handle Eq. (3.1) as well. We do not attempt this however, but,

rather, resort to the numerical integration of Eq. (3.1) and to Monte Carlo simulations of the underlying stochastic process.

Figure 2a gives a typical result for parameter values between curves (a) and (b) of Fig. 1. We start with exactly $X = X_0$ particles. As time goes by the probability function develops a width and the peak slowly travels towards the unique stable attractor. Well before the attractor is reached, however, the probability distribution flattens and develops a second peak situated on the other side of the inflection point of the potential. The two peaks coexist for a while but eventually the one centered near the initial state disappears as the system relaxes to its final, one-hump steady state distribution centered on the stable steady state.

A useful visualization of the evolution of $P(X, t)$ is provided in Fig. 2b, in which the surface $P(X, t)$ is plotted in the (X, t) space. A section by a line parallel to the X axis gives the probability profile for given t, while a section by a line parallel to the t axis gives the evolution of P for a given X. From this picture one can easily determine the way the most probable values of $P(X, t)$ evolve in time. The existence of a two-hump distribution will then be reflected by a curve exhibiting limit points and hysteresis. However, contrary to ordinary situations in which hysteretic behavior appears when a

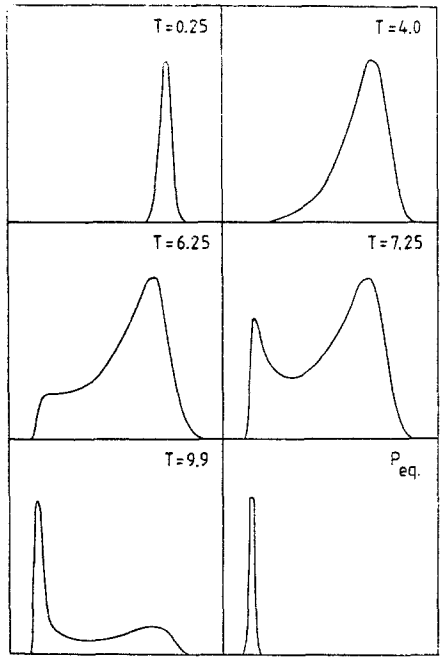

Fig. 2. (a) Time evolution of the probability distribution: $V = 1000$, $X_0 = 1500$, $\delta = -0.38$, $\delta' = -0.5$.

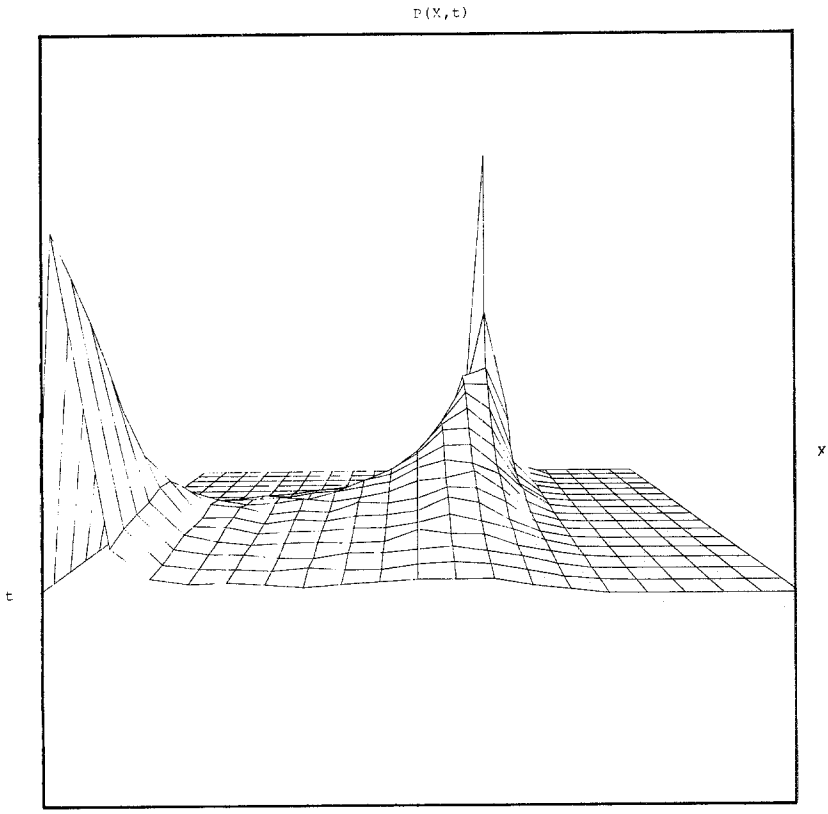

Fig. 2. (b) The surface $P(X, t)$ in the (X, t) space. Parameter values as in Fig. 2(a).

parameter is varied, in the present case both the new branches of most probable values and the hysteresis region will be observed as time follows its course. We have here an additional example of the phenomenon of "bifurcations unfolding in time" studied in Ref. 5 in the context of adiabatic thermal explosion.

An appealing way to visualize the evolution of the system under different conditions is suggested in Fig. 3, in which the variable X_m, corresponding to the extremum of $P(X, t)$ is plotted in terms of one of the parameters (say δ) and time. We see that the explosion regime, sandwiched between bistability and deterministic behavior, shows clearly a "flat" part corresponding to the induction period, followed by a faster evolution ignited near the inflection point. If δ approaches the marginal stability point, a fold with the limit point appears; the time coordinate of the limit point eventually tends to infinity, and beyond the value of $\delta = \delta_{\text{marg}}$ we have bistable behavior.

During the time interval of coexistence of two humps of comparable

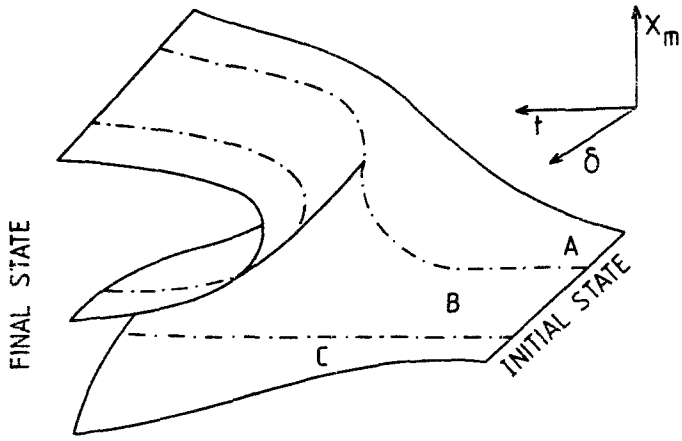

Fig. 3. Time dependence of the extrema of the probability distribution as a function of the parameter: visualization of various regimes. From the right-hand side: region of monotonous relaxation (A), region with limit points corresponding to the violent explosion (B), and true bistability corresponding to bimodal stationary probability distribution (C).

amplitude the system will exhibit a markedly chaotic behavior, which will be reflected by an enhanced value of the various moments of the probability distribution. In more physical terms, what is happening is that the "ignition time"—the time at which the system reaches the inflection point of the potential—is no longer fixed but becomes, instead, a random process. As the system evolves according to widely separated time scales on the two sides of the inflection point, small differences in the time of reaching this point will be amplified considerably. The probability mass will therefore split into two parts, one of which will be enriched at the expense of the other through a rapid flow across a potential barrier.[8] The important difference with respect to the usual Kramers type of problems is that in the present case we do not have an analog of "activation energy," since there is only one stable steady state available to the system.

4. INFLUENCE OF SIZE, PARAMETERS, AND INITIAL CONDITIONS

4.1. Dependence on Size

We carried out a series of Monte Carlo simulations for sizes varying from $V = 1000$ to $V = 40000$. Figure 4 summarizes the results on the graph of the most probable values plotted against time. We see that as V increases the extent of the hysteresis loop diminishes and the time course of the most probable value tends to the curve corresponding to the deterministic evolution.

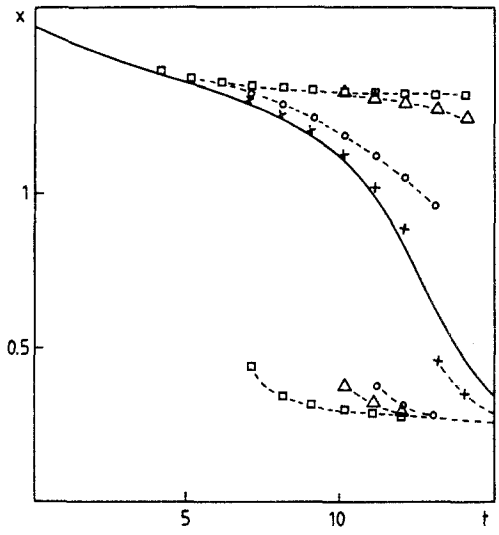

Fig. 4. Maxima of the probability distribution as a function of time for different sizes of the system. Squares denote $V = 2000$, triangles $V = 5000$, circles $V = 10000$, crosses $V = 40000$. Solid line corresponds to the deterministic trajectory. $X_0 = 1.5V$, $\delta = -0.38$, $\delta' = -0.5$.

In order to sort out the rules governing the onset of new branches of most probable values and the extent of the hysteresis loop we also represent, in Figs. 5 and 6, the time variation of the reduced second and third order variances $V2 = \langle(\delta X)^2\rangle^{1/2}/\langle X\rangle$ and $V3 = \langle(\delta X)^3\rangle^{1/3}/\langle X\rangle$, respectively. The first of these quantities provides an adequate measure of the importance of fluctuations relative to the deterministic evolution, whereas the second one measures the skewness of the probability distribution. We notice in Fig. 5 an enhancement of fluctuations which, even for large systems, may attain values comparable to the mean. On the other hand the skewness exhibits a transition from negative to positive values which becomes very sharp as V increases. This reflects the gradual shift of the probability mass from the right to the left of the instantaneous mean value, accompanying the appearance and subsequent dominance of a second peak in the region of low values of X.

Using this information we may now characterize better stochastic behavior during explosion. Let us define the onset time to be the time of appearance of the second peak of the probability distribution. The end of stochastic behavior may then be tentatively defined as the time at which the variance or skewness fall to half of their maximum value. Denoting the resulting interval by Δt we verify that

$$\Delta t = \varphi V^{-\alpha} \tag{4.1}$$

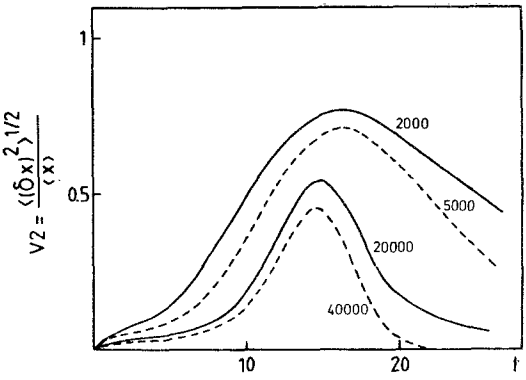

Fig. 5. Reduced second variance as a function of time and size of the system. $X_0 = 1.5V$, $\delta = -0.38$, $\delta' = -0.5$.

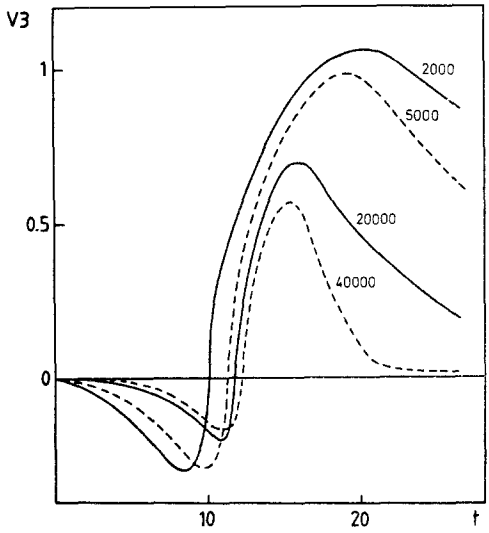

Fig. 6. Reduced third variance as a function of time for different sizes of the system. $X_0 = 1.5V$, $\delta = -0.38$, $\delta' = -0.5$.

where $a \simeq 0.48$, $\varphi \simeq 40/\theta$ or $a \simeq 0.495$, $\varphi \simeq 45/\theta$ for the second- and third-order variance, respectively. Let us recall that θ gives the order of magnitude of the derivative of the deterministic potential U at the inflection point [cf. (2.5)].

From the above it is tempting to infer an asymptotic law of the form

$$\Delta t = A|U'(x_i)|^{-1}V^{-1/2} \tag{4.2}$$

in which A is a numerical factor and $U'(x_i)$ reflects the violence of the explosion. In our case, for values of δ ranging from -0.34 to -0.38, $A|U'(x_i)|^{-1}$ yields values between 400 and 1300. Both the presence of such a larger factor multiplying the volume dependence of Δt and of the exponent $-1/2$ in the volume dependence itself are in agreement with the analytical results developed in Ref. 5. As regards the onset time, it appears that it becomes longer as V increases. This is natural, since for large V diffusion is smaller and thus the probability mass needs a longer time to cross the inflection point of the potential.

An alternative criterion, leading to a similar result, is to compute the probability mass concentrated in some interval (of order $V^{1/2}$) around the final steady state as a function of V and to see how this varies during explosive behavior.

In summary it appears that although stochastic behavior is bound to disappear in infinite systems, its decay law is a weak one. It is therefore expected that a local description, in which one is interested in the behavior of fluctuations in small volumes, will be considerably influenced by stochastic effects.

4.2. Dependence on Intrinsic Parameters

It has been mentioned in Section 3 that within the region in (δ, δ') space, in which we may expect explosive behavior [i.e., the region beyond curves (a_1) and (a_2)] there exist two subregions: one characterized by the appearance of transient bimodality and another in which $P(X,t)$ remains unimodal during the process of relaxation towards the steady state. The position of the boundary between these subregions (curve b_1–b_2 in Fig. 1) depends on the size of the system: when the size increases, the extension of the chaotic region tends to zero (we discussed this fact in Section 4.1) and curves (b) tend to (a).

In order to show the influence of parameters on the dynamics of relaxation for a system with finite size we performed a series of Monte Carlo simulations for $V = 1000$, $\delta' = -0.5$, and the following values of δ: $-0.28, -0.34, -0.35, -0.38$. For $\delta' = -0.5$ the marginal point predicted by deterministic analysis is at $\delta = -0.4$, so all the values of δ given above correspond to a unimodal stationary distribution. The transient evolution resulting from stochastic analysis is summarized in Figs. 7–9. Figure 7 shows how the change in δ gives rise to a fold catastrophe and influences the extension of the hysteretic region during the evolution of the most probable value of $P(X,t)$. Figures 8 and 9 show the gradual increase of the amplitude and range in time of the second variance and skewness.

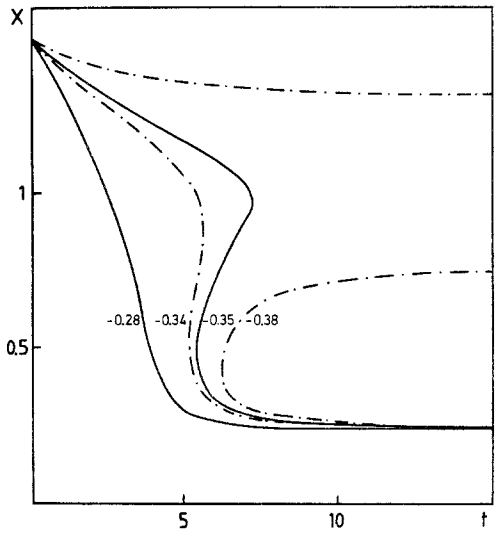

Fig. 7. Extrema of the probability distribution as a function of time for different values of parameter δ. $V = 1000$, $X_0 = 1500$, $\delta' = -0.5$.

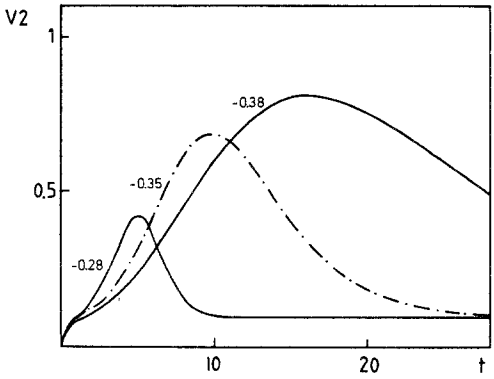

Fig. 8. Reduced second variance as a function of time and parameter δ. $V = 1000$, $X_0 = 1500$, $\delta' = -0.5$.

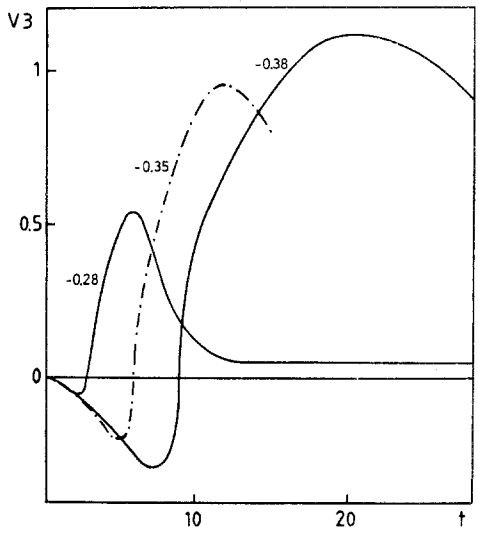

Fig. 9. Reduced third variance as a function of time and parameter δ. $V = 1000$, $X_0 = 1500$, $\delta' = -0.5$.

4.3. Dependence on Initial Conditions

As remarked in Section 2, a necessary condition for the chemical explosion to appear is the existence of an inflection point of the deterministic potential between the initial state and the final steady state. For the initial conditions close to the final steady state the stochastic model undergoes rapid relaxation following essentially the deterministic path. On the other hand, for various initial conditions sufficiently prior to the inflection point the pattern of evolution may change radically: because of the smallness of the deterministic rate, fluctuations can build up and compete with the deterministic evolution. Specifically, after rapid relaxation to the "flat" region of potential the probability distribution develops a second hump. Moreover the evolution in this region independently of the initial state appears to be "universal."

We performed a series of simulations for the following parameter values: $\delta = -0.38$, $\delta' = -0.50$, $V = 1000$, $X_0 = 1100, 1200, 1500, 1700$. For these values the deterministic potential has the shape presented in Fig. 10 with inflection points located at $x_{i1} = 0.664$ and $x_{i2} = 1.356$ ($x = X/V$). If the initial conditions are located beyond x_{2i}, the system shows a bifurcation in time. For the initial conditions closer to $x_{\text{station}}, x_0 < x_{2i}$, the system relaxes to the steady state without showing the above phenomenon. This is well visualized in Fig. 11, where the graphs of the skewness for various initial conditions are superposed, taking the positions of their maxima as

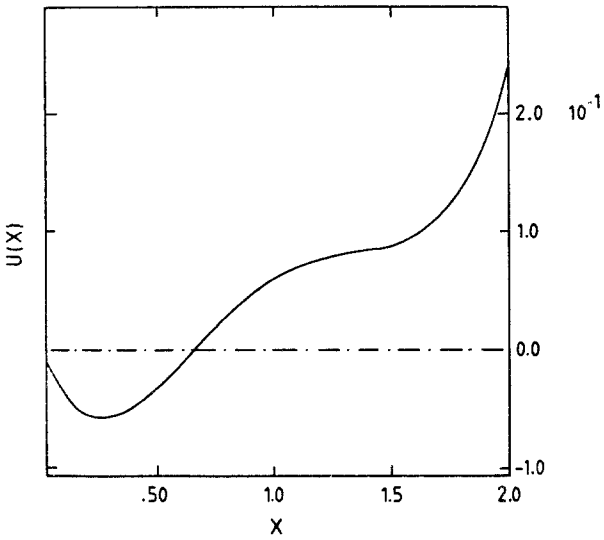

Fig. 10. The deterministic potential for the parameter values: $\delta = -0.38$, $\delta' = -0.5$.

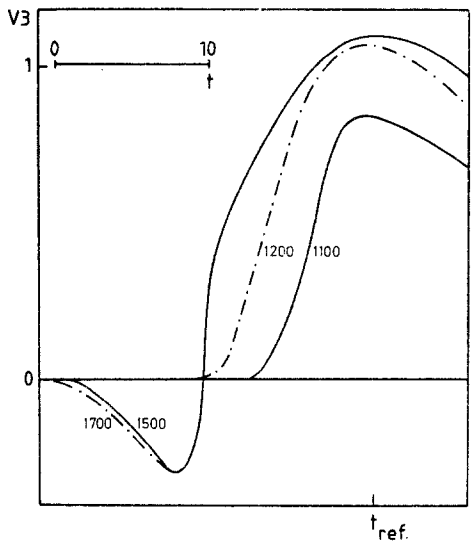

Fig. 11. Reduced third variance as a function of time and initial conditions. $V = 1000$, $\delta = -0.38$, $\delta' = -0.5$. t_{ref} corresponds to the position of maxima of $V3$.

the reference points in the time scale. The curves corresponding to $X_0 = 1500$ and $X_0 = 1700$ (i.e., $x_0 = 1.5$ and $x_0 = 1.7$) eventually coalesce: this means that after rapid relaxation to the "flat" region of potential the probability distribution is stabilized for some period of time (cf. minima of $V3$) and then "chemical explosion" with "transient bimodality" occurs. As for the initial conditions $X_0 = 1100$ and $X_0 = 1200$ we observe the usual relaxation to the X_{station} accompanied by the enhancement of fluctuations around the deterministic path.

5. DISCUSSION

We have seen that the evolution of the probability distribution of a chemical system showing explosive behavior can be decomposed into three stages: an initial one, characterized by a Gaussian-like distribution whose maximum travels with a speed close to the one predicted by the deterministic equations; the explosion proper, characterized by a flattening of the distribution, a rapid change in the skewness, and eventually the appearance of a second hump for some period of time; and finally, a regime of relaxation towards the unique stable attractor, characterized by the gradual disappearance of the peak generated by the initial condition.

Our results suggest that the above dynamics cannot be viewed as an evolution in a constant potential. Rather, it is more appropriate to think in terms of an evolution in a stochastic potential whose qualitative aspect depends on time: at the beginning it is similar to the deterministic potential, but subsequently it deforms (the deformation depending on the volume and initial conditions) and develops a second minimum corresponding to the "flat" region of its deterministic counterpart. This minimum is responsible for the transient "stabilization" of the maximum of $P(X,t)$ before the inflection point. As the tunneling towards the other minimum on the stable attractor goes on, the first minimum disappears and the asymptotic form of the stochastic potential, determining the stationary properties of $P(X)$, reduces again to the deterministic one.

Needless to say, real world chemical explosions are multistep phenomena involving the competition between various pathways, many of which contain autocatalytic or inhibitory effects associated with the appearance of free radicals and chain reactions.[9] We expect that in such a complex dynamics the role of fluctuations will be even more important than in the simple model studied in the present paper. More generally, it seems to us that chain reactions and explosive behavior should be characteristic examples of a *fluctuation chemistry*,[1] in which probabilistic elements are built into the system and confer on the process of ignition an essentially statistical character.

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