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Stochastic Theory of Adiabatic Explosion

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A stochastic description of an exothermic reaction leading to adiabatic explosion is set up. The numerical solution of the master equation reveals the appearance of a long tail and of multiple humps of the probability distribution, which subsist for a certain period of time. During this interval the system displays a markedly chaotic behavior, reflecting the random character of the ignition process. An analytical description of this transient evolution is developed, using a piecewise linear approximation of the transition rates. A comparison with other transient phenomena observed in stochastic theory is carried out.

KEY WORDS: Fluctuations; master equation; combustion; ignition.

1. INTRODUCTION

The study of exothermic reactions provides us with some striking examples of nonlinear phenomena under nonequilibrium conditions: bistability, oscillations, and chaotic dynamics[1]; spatial structures associated to the formation of flames[2]; or finally violent transient behavior, like the ignition and thermal explosion accompanying typical combustion processes.[3]

In view of the presence of bifurcations or other kinds of abrupt transitions in all the above phenomena, one has the feeling that fluctuations should be an integral part of the analysis of exothermic reactions. So far, however, practically all the results obtained in the stochastic study of chemical reactions are limited to the behavior of the composition variables at constant temperature.[4] It is the purpose of the present paper to develop the theory of fluctuations in the particular—yet quite important—case of adiabatic explosion, that is to say, of combustion in a closed vessel.

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Let us briefly comment on the reasons for which the stochastic theory of nonisothermal chemical systems is conceptually more difficult than the theory of their isothermal counterparts. When a reactive collision takes place in an ideal mixture, certain molecular species disappear and other species are created, at a rate which is proportional to the frequency of encounters of the particles involved. This allows us to model chemical reactions as a *Markovian birth and death process* and to construct the explicit form of the matrix of transition probabilities per unit time. But when, in addition to composition, temperature is involved as a key variable, it becomes necessary to model the process of energy transfer taking place between the system and the external reservoirs, and possibly within the system itself as a result of the exothermic or endothermic character of the reaction.

Recently we studied this problem in the limiting case in which the reaction mixture is a dilute gas, derived the form of the transition rates appearing in the master equation, and discussed the range of validity of fluctuation–dissipation type of theorems in the presence of thermal constraints.[5] As expected, the temperature dependencies introduce exponential nonlinearities in the coefficients of the master equation, and this greatly complicates the analysis. For this reason we focus hereafter on a case in which the analysis of thermal fluctuations reduces to a pure death process, namely, the problem of adiabatic explosion. As we shall see, despite the uniqueness of the stationary state regime attained in this process, during the transient evolution of the system fluctuations present some quite unexpected properties.

In Section 2 we summarize the results of the phenomenological description. Section 3 is devoted to the construction of the master equation and the computation of mean first passages times. This analysis suggests that fluctuations tend to slow down the evolution prior to the explosion time and, on the contrary, to accelerate it afterwards. A confirmation of this result is obtained in Section 4, devoted to numerical simulations. We show that, in the course of time and for certain classes of initial conditions, the probability distribution flattens and subsequently develops two peaks corresponding, respectively, to molecules which have not yet reacted and to molecules for which combustion has already taken place. An analytical approach to this phenomenon of "bifurcation unfolding in time" is undertaken in Section 5. In the final Section 6 we comment on the implications of the results and make suggestions for further work.

2. PHENOMENOLOGICAL DESCRIPTION

When an exothermic reactive mixture (like for instance a fuel) is placed in a vessel heated at a sufficiently high temperature T_0, the heat

released by the reaction and the temperature will progressively increase and, if the rate of heat removal is insufficient, the reaction will end in an explosion. Such an explosion is referred to as *thermal*. We are interested in the limit in which the process is adiabatic, that is when all the reaction heat is disposed of in the heating of the mixture. Although this condition is not strictly verified in most experimental situations, the above idealization should still provide a satisfactory description of the ignition period in an open system, whereby an abrupt transient is observed during the evolution toward the final stable steady state.

The simplest nontrivial case is that of a single irreversible exothermic reaction:

$$\mathrm{X} \xrightarrow{k(\bar{T})} \mathrm{A} \tag{2.1}$$

Let $\bar{T}$ be the temperature, $k(\bar{T})$ the temperature-dependent rate constant, $\bar{x}$ a suitably scaled intensive variable describing chemical composition, r_v and c_v, respectively, the heat of reaction and the specific heat at constant volume. Assume furthermore that the system is well stirred, so that one can discard transport phenomena. The mass and energy balance equations then read:

$$\begin{aligned} \frac{d}{dt}\bar{x} &= -k(\bar{T})\bar{x} \\ c_v \frac{d}{dt}\bar{T} &= -r_v \frac{d}{dt}\bar{x} = r_v k(\bar{T})\bar{x} \end{aligned} \tag{2.2}$$

It is immediately seen that Eqs. (2.2) give rise to the conservation condition:

$$c_v T_0 + r_v x_0 = c_v \bar{T} + r_v \bar{x} = \text{const} \equiv c_v T_{\max} \tag{2.3}$$

where (T_0, x_0) are the initial values of $(\bar{T}, \bar{x})$ and $(T_{\max}, \bar{x} = 0)$ are the final ones, after the reaction has been completed. It should of course be realized that, in actual fact, combustion is never complete as the inverse reaction $\mathrm{A} \rightarrow \mathrm{X}$ is no longer negligible when the population of X becomes small. In the sequel however we shall adopt for simplicity the idealized picture, Eq. (2.3).

Substituting $\bar{x}$ and $\bar{T}$ from Eq. (2.3) to Eqs. (2.2) one obtains one of the alternative forms:

$$\frac{d}{dt}\bar{T} = k(\bar{T})\left(T_{\max} - \bar{T}\right) \tag{2.4a}$$

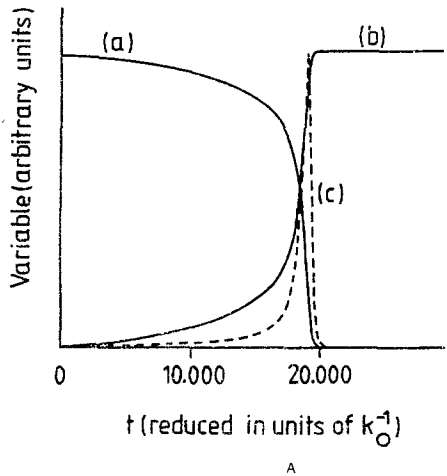
or

$$\frac{d}{dt}\bar{x} = -k\left(T_{\max} - \frac{r_v}{c_v}\bar{x}\right)\bar{x} \tag{2.4b}$$

The solution of Eqs. (2.4) is plotted in Fig. 1a, for a temperature dependence of $k(\bar{T})$ given by the Arrhenius law,

$$k(\bar{T}) = k_0 \exp(-U_0/R\bar{T}) \tag{2.5}$$

where U_0 is the activation energy. It is seen that the reaction rate reaches abruptly its maximum value at a time which will be referred to as the "explosion time."[6,7]



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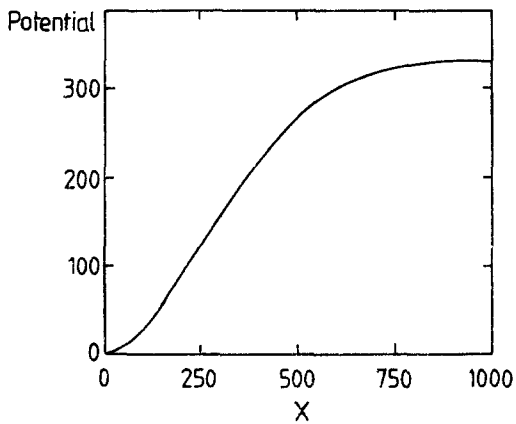

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Fig. 1. (a) Time evolution of composition variable (curve a), temperature (curve b) and reaction rate (curve c) in an adiabatic explosion. Parameter values: $U_0/R = 10000$, $T_{max} = 2000$, $r_v/c_v = 1200$. (b) Kinetic potential associated to Eq. (2.4b).

It is useful to visualize the evolution in terms of a *kinetic potential*, the integral of the right-hand side of Eq. (2.4b) over $\bar{x}$. As seen in Fig. 1b, this potential has a single minimum at $\bar{x} = 0$, an inflection point for values of $\bar{x}$ attained at the explosion time, and no further extremum in the region of high values of $\bar{x}$. In a typical situation the system is started in this latter region. A slow evolution, reflected by the flatness of the potential, first takes place; but when the vicinity of the inflection point is reached, $\bar{x}$ becomes quickly depleted and finally tends to extinction.

From the thermodynamic point of view the situation is particularly simple: the system eventually reaches equilibrium, but for certain classes of initial conditions, sufficiently far from the final state, it shows transiently a markedly nonequilibrium behavior. This is reminiscent of a variety of familiar phenomena observed in chemistry and hydrodynamics, like for instance, the chemical oscillations and wave trains appearing after an initial induction time, when the Belousov–Zhabotinski reaction takes place in a closed vessel (for a recent account, see Ref. 8).

3. STOCHASTIC FORMULATION

As has been pointed out in the Introduction, in view of the highly nonlinear and violent character of the phenomenon of explosion it would be desirable to incorporate the effect of fluctuations in the description. For the simple model considered in the previous section, the central quantity to be evaluated becomes thus the probability $P(X, E; t)$ of having, at time t, a number of particles equal to X and a translational energy content within the vessel equal to E.

Clearly, each time one molecule of X undergoes the reaction $X \rightarrow A$, the energy content of the system is increased by an amount equal to the heat of reaction per molecule, which we again denote by r_v (cf. Fig. 2). In

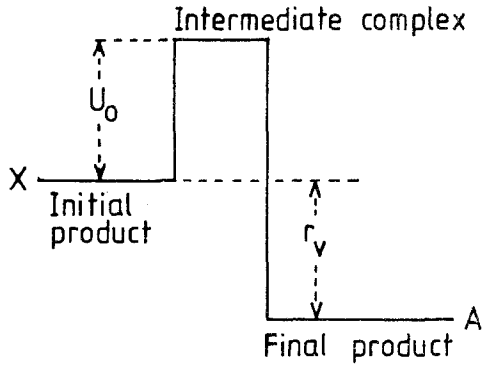

Fig. 2. Simple three-level model adopted for the mechanism of reaction $X \rightarrow A$.

other words, the conservation relation, Eq. (2.3), is exact even if fluctuations are included. In terms of the extensive quantities X, E it reads:

$$r_v X_0 + E_0 = r_v X + E = \text{const} = E_{\max} \tag{3.1}$$

It can also be expressed in terms of the intensive variables by introducing a suitable size scaling parameter N. Specifically,

$$N(r_v x + c_v T) = \text{const} = N c_v T_{\max} \tag{3.2}$$

which has the same structure as Eq. (2.3), except that x and T are now to be interpreted as random variables, distributed according to a probability ensemble P. The equation of evolution for this ensemble is readily found by realizing that Eqs. (3.1) or (3.2) allow us to reduce the number of independent variables to a single one. If we choose composition to be the pertinent variable, we are led, for our model defined by Eq. (2.1), to a *pure death process*

$$\frac{d}{dt} P(X;t) = \mu(X+1)P(X+1;t) - \mu(X)P(X;t) \tag{3.3a}$$

where the death rate is given by [cf. Eq. (3.2)]

$$\mu(X) = k_0 X \exp\left\{ \frac{-u_0}{k_B\left[T_{\max} - (r_v/c_v)(X/N) \right]} \right\} \tag{3.3b}$$

Notice the use of the Boltzmann constant instead of the gas constant. This is natural in the present context, since in the stochastic description we deal with changes of states associated with the disappearance of one molecule at a time. u_0 is defined such that

$$u_0/k_B = U_0/R$$

In the sequel we will be interested in the solution of the master equation (3.3) corresponding to the initial condition:

$$P(X;0) = \delta_{X,N}^{kr} \tag{3.4}$$

It is then clear that Eq. (3.3) needs only to be solved in the interval $0 \leqslant X \leqslant N$. Moreover,

$$\frac{d}{dt} P(N;t) = -\mu(N)P(N;t) \tag{3.5a}$$

whereas

$$\frac{d}{dt} P(j;t) = \mu(j+1)P(j+1;t) - \mu(j)P(j;t), \qquad 0 < j < N \tag{3.5b}$$

and

$$\frac{d}{dt} P(0;t) = \mu(1)P(1;t) \tag{3.5c}$$

By solving Eq. (3.5a) explicitly and by introducing the solution successively into the equations for $P(N-1;t)$, $P(N-2;t)$, etc., one obtains the following explicit representation of the probability function:

$$P(N-\nu;t) = \sum_{j=N-\nu+1}^{N} \frac{\prod_{m=N-\nu+1}^{N} \mu(m)}{\prod_{l\neq j, l=N-\nu}^{N} [\mu(l)-\mu(j)]} [e^{-\mu(j)t} - e^{-\mu(N-\nu)t}] \tag{3.6}$$

Unfortunately this form is not very helpful, as it constitutes an alternating sum whose coefficients increase factorially with increasing j. Numerical calculations show that beyond the rather low value of $N = 50$, the evaluation of (3.6) leads to convergence problems. For this reason we resort, for the remaining of this paper, to an alternative method.

Let us plot the transition rate $\mu(X)$ appearing in the master equation [cf. Eq. (3.3)] as a function of X. We obtain the bell-shaped curve shown in Fig. 3a. In order to get an insight about the effect of fluctuations on the time course of the process we evaluate the mean first passage time T_{X_0,X_f} for reaching some final state X_f starting from a state characterized by the presence of exactly X_0 molecules in the vessel. We use the well-known formula[9]

$$T_{X_0,X_f} = \sum_{j=X_f+1}^{X_0} \frac{1}{\mu(j)} \tag{3.7}$$

The Euler–Maclaurin asymptotic evaluation of the sum leads to the result

$$T_{X_0,X_f} = \int_{X_0}^{X_f} \frac{dz}{\mu(z)} - \frac{1}{2\mu(X_f)} + \frac{1}{2\mu(X_0)} + o\left(\frac{1}{N}\right) \tag{3.8}$$

The first term of the right-hand side is the deterministic value of the transition time, obtained by straightforward integration of the phenomenological equation (2.2). The remaining terms represent corrections due to the fluctuations. The point is that they lead to opposite effects, according as the $X_0 \to X_f$ transition occurs before or after the explosion time. Specifically, referring to Fig. 3a, we see that before explosion $\mu(X_0) < \mu(X_f)$, and as a result the correction to the deterministic result is positive. In other words, *fluctuations tend to slow down the evolution prior to explosion*. If on the other hand explosion has already occurred we see from Fig. 3a that $\mu(X_0) > \mu(X_f)$, which implies a negative correction to the deterministic result. Thus, *fluctuations tend to accelerate the evolution once explosion takes place*. Globally therefore, the phenomenon becomes more violent as compared to the time course predicted by the phenomenological description.

The mechanism at the origin of this enhanced violence becomes somewhat more transparent by invoking the moment equations. Let us first

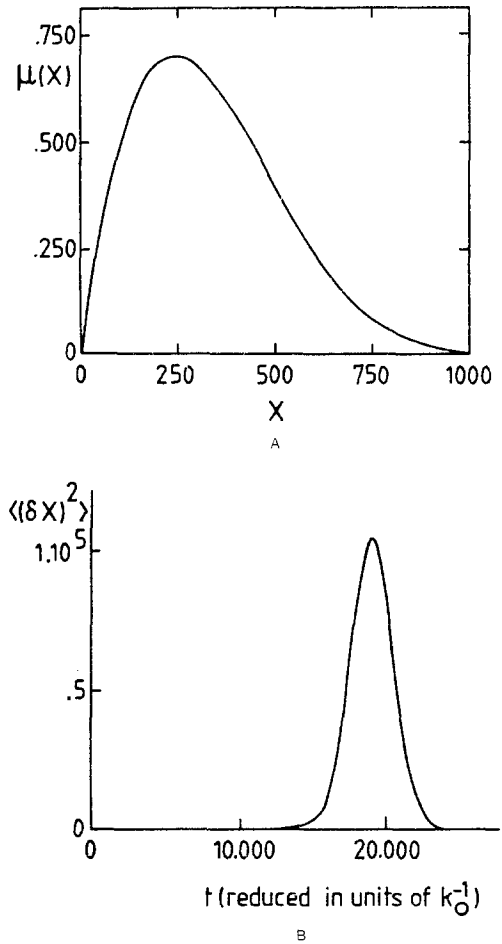

Fig. 3. (a) The death rate $\mu(X)$ plotted against the number of particles X. Parameter values: $U_0/R = 10000$, $T_{\max} = 2000$, $r_v/c_v = 1200$. Note the sharp decrease of μ for higher values of X, leading for $X = 10^3$ to a value as low as $\mu \simeq 10^{-3}$. (b) Time evolution of the variance $\langle(\delta X)^2\rangle_t$. Note the enhancement in the vicinity of the explosion time. Parameter values as in Fig. 3a.

perform a truncation at the level of the second order semi-invariants, which is expected to provide a satisfactory picture as long as fluctuations remain extensive. We obtain

$$\frac{d}{dt}\langle(\delta X)^2\rangle = \mu\left[\bar{X}(t)\right] - 2\left(\frac{\partial \mu}{\partial X}\right)_{\bar{X}(t)}\langle(\delta X)^2\rangle \tag{3.9}$$

Referring to Fig. 3a we expect that, before the maximum value of μ is reached ($\partial\mu/\partial X < 0$), fluctuations will be self-accelerated, whereas the

opposite will be true beyond the maximum value of $(\partial\mu/\partial X > 0)$. Now from the phenomenological equation it is obvious that

$$\frac{d^2}{dt^2}\bar{x} = -\frac{\partial\mu}{\partial\bar{x}}\frac{d\bar{x}}{dt}$$

hence the maximum of μ is visited when $\bar{x}(t)$ goes through an inflection point (cf. Fig. 1). This is the time referred to earlier as the explosion time. We expect therefore that an enhancement of fluctuations should take place in the vicinity of explosion time. Figure 3b, in which the solution of Eq. (3.9) is plotted against time, confirms this prediction. More importantly, it shows that the value of the variance at its maximum is extremely large. Specifically, choosing $\bar{X}_0 = 10^3$ and $\langle(\delta X)^2\rangle_0 = 0$ we see that $\langle(\delta X)^2\rangle_{\max} \simeq 10^5$. This is much larger than a Poissonian variance and suggests that there should be a time interval during which the system becomes unpredictable, developing some sort of "transient turbulence." Concomitantly, higher-order variances should become then as important as the second-order one, and the truncation leading to Eq. (3.9) should break down. These features are further confirmed by a series of numerical simulations, to which we now turn our attention.

4. NUMERICAL SIMULATIONS

The time evolution of the probability distribution $P(X;t)$ was determined by solving numerically the master equation (3.3). The results are shown in Fig. 4. At $t = 0$ we start with exactly $N = 1000$ particles [cf. Eq. (3.4)] in the region in which the kinetic potential, as function of x (Fig. 1b), is very flat. Because of the smallness of the deterministic rate in this region, we expect that stochastic effects would manifest themselves at a macroscopic level. Indeed, shortly after this initial condition the probability distribution develops a width, while its maximum moves only slightly to the region of low values of X. A pronounced flattening of the distribution then takes place, followed by the appearence of a second peak located at a value of X close to zero. Meanwhile the first peak is still centered at values of X well above the value characteristic of explosion. The long tail and the two peaks subsist for some time, but eventually the system collapses to zero, which is an absorbing state attained with probability one.[10]

An interesting way to summarize the above described stages of the evolution is to plot X_m, the most probable value of X, as a function of time. This is done in Fig. 5. We see that for short times we obtain a unique solution. But there exists a *critical time*, t_c, beyond which new branches of solution appear, reflecting the formation of a second peak of the probability distribution. Eventually two of these branches coalesce, and the system evolves to extinction as combustion is completed.

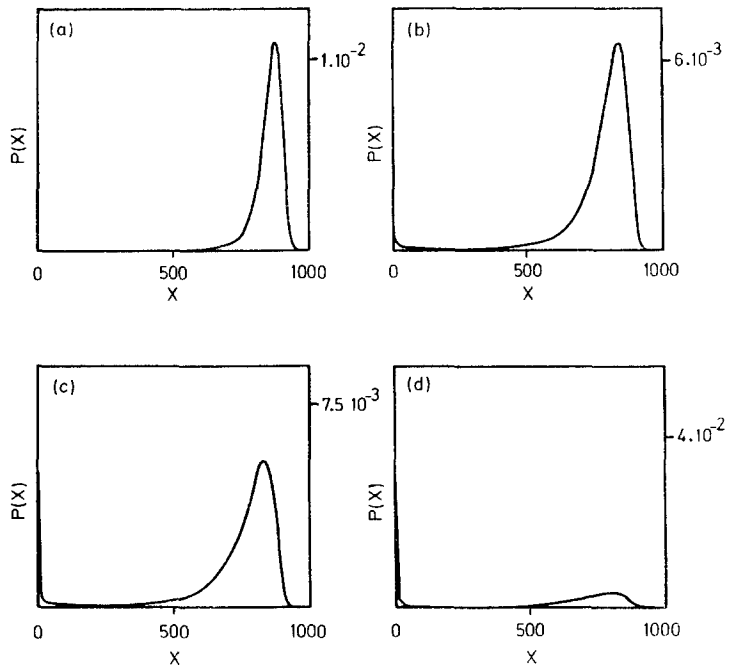

Fig. 4. Successive stages of evolution of the probability function $P(X; t)$. (a) The initial peak at $X = N$ flattens slightly and travels very slowly to the left. (b) A long tail of the probability function develops and a second hump appears. (c) The two humps are comparable. (d) The initial maximum has practically disappeared and the system is about to reach extinction. Parameter values: $U_0/R = 10000$, $T_{\max} = 2000$, $r_v/c_v = 1200$.

The situation described in Fig. 5 is strongly reminiscent of the phenomenon of bifurcation, whereby new branches of solutions come into play when some suitable control parameters are varied. The difference is of course that in the present case the appearence of new branches can only be a transient. We coin the term "bifurcation unfolding in time" for this phenomenon in order to capture both the similarities and the differences with its more familiar "static" counterpart.

Between the time of development of the long tail and the time of disappearance of one of the two peaks of the probability distribution, the system will display a markedly random behavior: there will be appreciable deviations between mean and most probable values, and the variance will attain macroscopic proportions. Numerical evaluation of the second, third, and fourth-order variances shows indeed that during the coexistence of the two maxima, these quantities are considerably enhanced. This corroborates the qualitative arguments developed in Section 3.

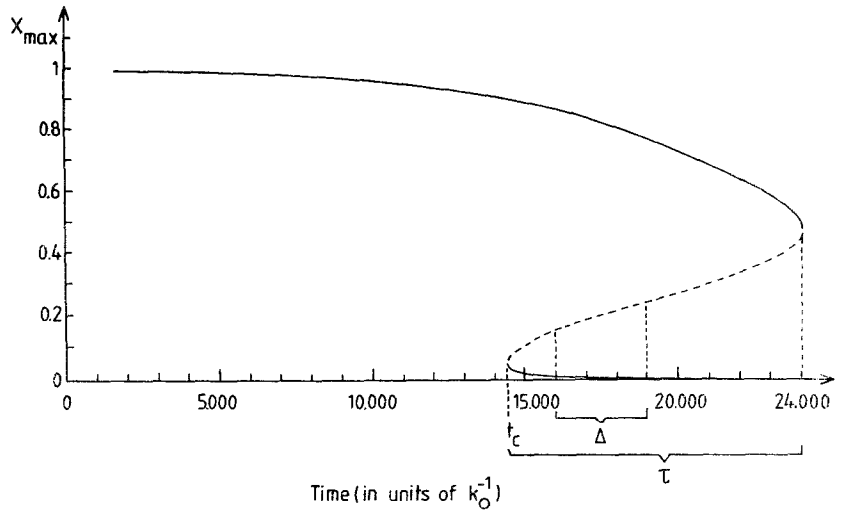

Fig. 5. The most probable value of the probability function, X_{max}, plotted against time for the evolution described by Fig. 4. At t_c two new extrema emerge through the mechanism of "bifurcation unfolding in time." After a time of coexistence only the new maximum subsists, as the system is reaching extinction. During the time interval Δ the two maxima are of the same order of magnitude.

From the standpoint of combustion our result means that temporarily the population of molecules will split into a part for which combustion has not yet taken place, and a part for which combustion is practically terminated. Within the framework of our assumption of a well-stirred mixture, this statement can only be understood in a statistical sense: namely, when a great number of independent combustion experiments is taking place, in some realizations ignition and explosion will tend to be delayed, whereas in others they will be accelerated. In other words, ignition time becomes a random variable whose variance is directly related to the coexistence time of the two probability peaks.

The significance of these results will become more transparent when spatially inhomogeneous fluctuations will be allowed. In this case, in a single experiment, the population of molecules involved in the process will tend to separate in *space*, thereby producing a "nucleus" of combustion which eventually will contaminate the entire system. Such a phenomenon will be the precursor of propagating wave fronts or flames that are known to occur in combustion.[2,11]

The computer simulations just reported involve, perforce, a finite number of particles. It is therefore natural to inquire about the effect of the size parameter N on our results. We have performed a series of Monte

Carlo simulation for values of N up to 10^5. We have found that the effects described earlier in this section subsist, provided that the initial condition is sufficiently far from the inflection point of the kinetic potential. An analytical study of this question is carried out in Section 5.

5. AN ANALYTIC APPROACH

As has been pointed out, the explicit solution of the Master Equation for a pure death process as given by Eq. (3.6) is unfortunately of little use for the study of asymptotic properties. Instead one proceeds with the following Ansatz.[12] Set $P(X;t) = \exp N\Phi(x;t)$, where $x = X/N$ and Φ is assumed to be Taylor expandable in powers of N^{-1}. Then to lowest order the Master Equation (3.3a) is replaced by the nonlinear partial differential equation

$$\frac{\partial}{\partial t}\Phi_0 = \bar{\mu}(x)\left[\exp\left(\frac{\partial}{\partial x}\Phi_0\right) - 1\right] \tag{5.1}$$

where

$$\bar{\mu}(x) = \lim_{N\to\infty} \frac{1}{N}\,\mu(X)$$

Furthermore assume $\Phi_0(x;t)$ to be expandable in powers of $x - \bar{x}(t)$, where $\bar{x}(t)$ is the corresponding solution of the deterministic equation [cf. Eq. (4.5)]:

$$\begin{aligned} \frac{d}{dt}\bar{x} &= -\mu(\bar{x}) \\ \Phi_0(x;t) &= a_0 + a_1\left[x - \bar{x}(t)\right] + a_2\left[x - \bar{x}(t)\right]^2 + \cdots \end{aligned} \tag{5.2}$$

Identification of same powers of $x - \bar{x}(t)$ in (5.1) leads to the conclusion that $a_1 \equiv 0$ and that a_2, which is descriptive of the width of the distribution, satisfies the differential equation

$$\frac{d}{dt}a_2 = 2\bar{\mu}'(\bar{x})a_2 + 2\bar{\mu}(\bar{x})a_2^2 \tag{5.3}$$

For an infinitely sharp initial condition at $X = N$, i.e., $\bar{x} = 1$, the solution of (5.3) is simply

$$a_2^{-1}(\bar{x}) = -2\bar{\mu}^2(\bar{x})\int_{\bar{x}}^{1} ds\ \bar{\mu}^{-2}(s) \tag{5.4}$$

Thus for a linear pure death process where $\mu(X) = kX$, we find $a_2^{-1}(\bar{x}) = -2k^2\bar{x}^2\int_{\bar{x}}^{1} ds\,(ks)^{-2} = -2\bar{x}(1-\bar{x})$. As in this case $\bar{x} = e^{-kt}$, it follows that the probability distribution, initially centered with zero width at $\bar{x} = 1$, gradually spreads out as it follows the deterministic path until $\bar{x} = 1/2$,

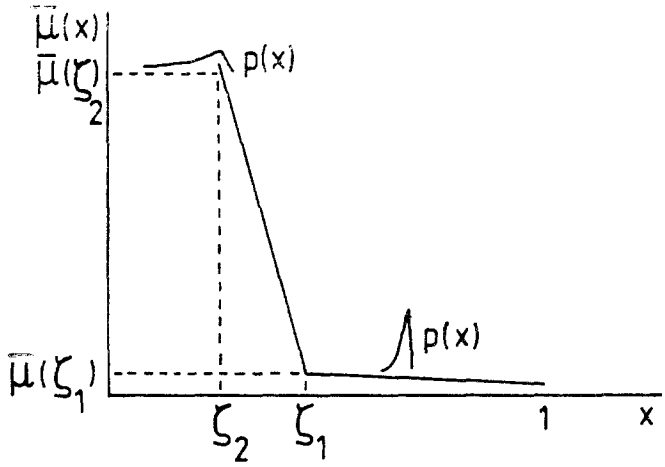

Fig. 6. Large amplification of the spread of probability packet occurs [cf Eq. (5.5)] when the death rate abruptly switches from a low value $\bar{\mu}(\xi)$ to the value associated to explosion, $\bar{\mu}(x)$.

whereupon it begins to narrow and become asymptotically infinitely sharp again at the absorbing boundary $\bar{x} = 0$.

Now in a pure death process the variation in time of each $P(X;t)$ depends solely on itself and or its *right*-hand neighbor(s). Consequently for a given initial condition the evolution of $P(X;t)$ is not changed if the death rate is modified for values *less* than X. Consider the case depicted in Fig. 6. We find

$$a_2^{-1}(\bar{x}) = -2\bar{\mu}^2(\bar{x})\int_{\bar{x}}^{1} ds\ \bar{\mu}^{-2}(s)$$

$$= -2\bar{\mu}^2(\bar{x})\int_{\bar{x}}^{\xi} ds\ \bar{\mu}^{-2}(s) + a_2^{-1}(\xi)\frac{\bar{\mu}^2(\bar{x})}{\bar{\mu}^2(\xi)} \tag{5.5}$$

Therefore if $\bar{\mu}(\bar{x})/\bar{\mu}(\zeta) \gg 1$, that is to say, if the system is started in a state sufficiently remote from explosion in which the kinetic potential (Fig. 1b) is very flat, there will be a large amplification of the spread of the probability packet. As we will see presently, this mechanism is at the basis of the appearance of the chaotic regime referred to in the previous section. To this end we examine the qualitative features of the behavior of the probability distribution as depicted in Fig. 4 when the death rate is of the form given by (3.3b).

As x decreases from 1 to some value ζ_1, the death rate $\bar{\mu}(x)$ scarcely varies and remains very small. As x further decreases from ζ_1 to some value

ζ_2, $\bar{\mu}(x)$ increases abruptly and reaches a value $\bar{\mu}(\zeta_2) \gg \bar{\mu}(\zeta_1)$. Finally as x diminishes to zero, $\bar{\mu}(x)$ subsides and eventually vanishes.

Now as time evolves, a probability packet, initially centered at $x = 1$, will move slowly to the left, its peak extremely close to the solution of the deterministic equation and with a slowly increasing spread. At some time the left edge of the packet will reach ζ_1. This part of the probability distribution will now travel at much greater speed to ζ_2 with a very large spread. As time proceeds a new packet will start to form to the left of ζ_2 as the packet to the right of ζ_1 gradually wanes. The time τ it takes for the transfer of probability from the neighborhood of ζ_1 to ζ_2 can be estimated by dividing the width of the probability packet at ζ_1 by the velocity of its peak as given by the deterministic equation. Thus

$$\tau \sim N^{-1/2} \frac{|a_2^{-1}(\zeta_1)|^{1/2}}{\bar{\mu}(\zeta_1)} \sim N^{-1/2} \left[\int_{\zeta_1}^{1} ds\ \bar{\mu}^{-2}(s) \right]^{1/2}$$

and if μ is assumed to be practically constant in the interval $[\zeta_1, 1]$, we have the following estimate:

$$\tau \sim O\left[\frac{N^{-1/2}}{\bar{\mu}(\zeta_1)} \right] \tag{5.6}$$

As one would expect, as N increases unboundedly, τ goes to zero for any given initial state ζ_1. Nevertheless this decrease, which is also observed in the numerical simulations, is relatively slow, all the more so that for the initial conditions of interest in the combustion problem $\bar{\mu}(\zeta_1)$ can be extremely small. For instance, for the numerical values of the parameters used in Figs. 4 and 5 $\bar{\mu}^{-1}(\zeta_1)$ is of the order of 10^3. It follows that the duration of the chaotic region remains macroscopic for N's as large as 10^{14}. This conclusion is significant in two respects. First, it shows that the thermodynamic limit acts in a less stringent way on the time-dependent properties of the system than on its static properties. More importantly, in any realistic situation fluctuations will originate as relatively short ranged, *local* events: a typical region encompassed by a coherent fluctuation will contain a restricted number of particles, probably even less than 10^{14}. The question of taking the thermodynamic limit will therefore simply not arise in this case. We conclude that the results described in this work reflect an intrinsic property of combustion, and should be observable with presently available experimental techniques.

In the above discussion it was tacitly assumed that the time needed to attain state ζ_1 (Fig. 6) starting from the initial condition has a given, finite value of $O(1)$. It is, however, clear from the expression of $\mu(x)$, Eq. (3.3b), that the slope of μ can be made extremely small, provided that the initial temperature, T_0, is chosen to be sufficiently low. For instance for the

parameter values used in our paper, choosing $T_0 = 400°$ K instead of $T_0 = 800°$ K diminishes the initial reaction rate by a factor of the order of 10^{-6}. It follows that the time needed to attain the explosion region will become very long. This will allow the probability distribution of the system to develop a substantial width, leading to a much larger value of coexistence time of the two extrema. In short, we expect that the coexistence time could remain of $O(1)$ even in the thermodynamical limit $N \to \infty$, as long as the reaction rate remains small for sufficiently long time. The latter condition can in turn be ensured if the initial state is sufficiently far from the explosion region. This point is further elaborated in forthcoming work by Frankowicz and Malek Mansour[13] and Frankowicz and Nicolis.[14]

It would appear from the foregoing analysis that the time dependence of the probability distribution can be inferred, at least qualitatively, from one basic property of the death rate, namely, the abrupt variations of its slope. If this is the case, then a similar behavior for the probability distribution should be observed when the death rate μ is of the form given in Fig. 7.

It will now be shown that when the death rate has this piecewise linear form, the explicit solution of the Master Equation can be cast in a form that allows one to study directly its asymptotic behavior.

First consider the case where the death rate is as shown in Fig. 8. Beyond M the death rate is not given, but $P(M;t)$ is assumed to be a known function $f(t)$. It is required to find $P(J;t)$ for $L < J < M$. How μ is

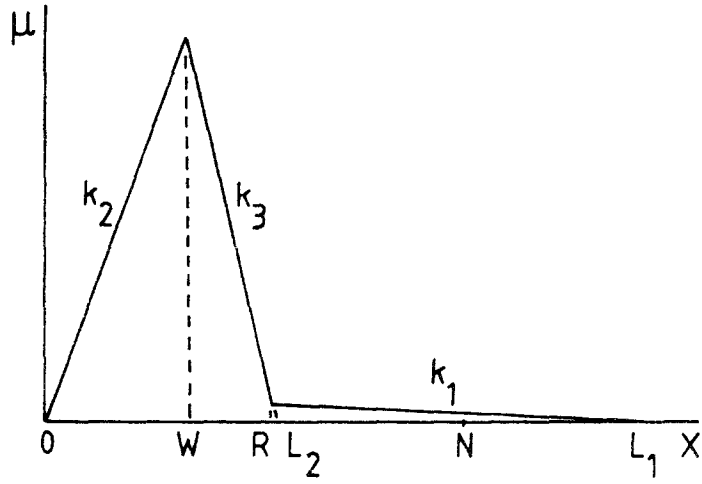

Fig. 7. Piecewise linear representation retaining the qualitative features of the death rate [cf Fig. 3a and Eq. (3.3b)].

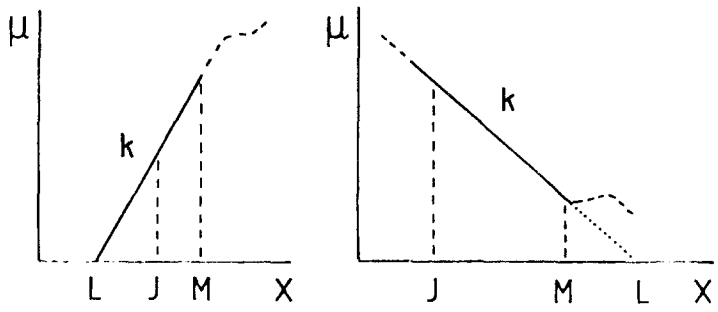

Fig. 8. Death rates used in the derivation of Eqs. (5.7a) and (5.7b).

defined to the left of L will not influence these values of $P(J;t)$, so let us simply make it vanish for $X \leqslant L$ (we shall assume throughout that the macroscopic quantity L is an integer). The generating function $G(s,t) = \sum_{x=L}^{M-1} s^{x-L} P(x;t)$ satisfies the inhomogeneous partial differential equation

$$\frac{\partial}{\partial t} G = k(1-s)\frac{\partial}{\partial s} G + \mu(M) s^{M-L-1} f(t), \qquad G(s,0) = 0$$

whence

$$G(s,t) = \mu(M) \int_0^t du\, f(u) \left[1 - e^{-k(t-u)} + s e^{-k(t-u)}\right]^{M-L-1}$$

and

$$P(J;t) = \mu(N) \binom{M-1-L}{J-L} \int_0^t du\, f(u) \left[1 - e^{-k(t-u)}\right]^{M-J-1} e^{-\mu(J)(t-u)} \tag{5.7a}$$

If L is negative the formula remains valid, as can be verified for instance by direct substitution into the Master Equation. However, should L lie to the right of M (i.e., when the slope k is negative) as in Fig. 8b, then the result needs to be amended to

$$P(J;t) = \mu(N) \binom{L-J-1}{L-M} \int_0^t du\, f(u) \left[e^{-k(t-u)} - 1\right]^{M-J-1} e^{-\mu(J)(t-u)} \tag{5.7b}$$

The main conclusion to be drawn from Eq. (5.7) is that if the death rate is linear in some interval $[A,B]$, and $P(B;t)$ is known, then $\forall X \in [A,B]$, $P(X;t)$ can be expressed as a known integral transform of $P(B;t)$. The piecewise case depicted in Fig. 7 can now be readily solved by repeating the previous result. Let $P(X;0) = \delta_{X,N}^{kr}$, so that $P(N;t) = e^{-\mu(N)t}$. Then $\forall X$

$\in [R, N]$, $P(X;t)$ [and in particular $P(R;t)$] is a known transform of $P(N;t)$. As μ is again linear in the interval $[W, R]$ and $P(R;t)$ is known, it follows that $\forall X \in [W, R]$, $P(X;t)$ is another known transform of $P(R;t)$, and consequently of $P(N;t)$. By repeating this process we see that when the death rate is piecewise linear, each $P(X;t)$ is expressible as some integral transform of $P(N;t)$. Furthermore these integral transforms are very convenient for asymptotic analysis.

More specifically, from Eq. (5.7b) and Fig. 7, we see that for $R \leqslant J < N$,

$$P(J;t) = \mu(N)\binom{L_1 - J - 1}{L_1 - N}\int_0^t ds\, e^{-\mu(N)s}\left[e^{-k_1(t-S)} - 1\right]^{N-J-1} e^{-\mu(J)(t-s)}$$

where k_1 is the slope of the linear death rate. In this case the integral transform is elementary and yields

$$P(J;t) = -\frac{1}{k_1}\frac{\mu(N)}{N-J}\binom{L_1 - J - 1}{L_1 - N} e^{-\mu(J)t}\left[e^{-k_1 t} - 1\right]^{N-J}, \qquad R \leqslant J < N \quad (5.8)$$

A direct asymptotic analysis of this form for large N leads to the result that $P(J;t) \sim e^{N\psi(j;t)}$ where the dominant term is

$$\psi_0(j;t) = (l_1 - j)\ln(l_1 - j) - (1-j)\ln(1-j) - (l_1 - 1)\ln(l_1 - 1) - k_1(j - l_1)t + (1-j)\ln(l^{-k_1 t} - 1) \qquad (l_1 \equiv L_1/N, j \equiv J/N)$$

Solving $\partial\psi_0/\partial j|_{j=j^*(t)} = 0$ to find the peak of the distribution yields

$$j^*(t) = 1 - (l_1 - 1)\left[e^{-k_1 t} - 1\right]$$

which is indeed the solution of the deterministic equation. Now in the interval $W \leqslant J < R$ we can write

$$P(J;t) = \int_0^t ds\, K_J(t - S)P(R;s) \qquad (5.9)$$

where

$$K_J(t-s) = \mu(R)\binom{L_2 - J - 1}{L_2 - R}\left[e^{-k_2(t-s)} - 1\right]^{R-J-1} e^{-\mu(J)(t-s)}$$

and $P(R;s)$ is given by an expression similar to Eq. (5.8). Asymptotic analysis shows that the dominant order for large N,

$$P(R;s) \sim \exp N\left[-\mu(r)s + (1-r)\ln(e^{-k_1 s} - 1)\right]$$

and

$$K_J(t-s) \sim \exp N\left[-\mu(j)(t-s) + (r-j)\ln(e^{-k_2(t-s)} - 1)\right] \quad (5.10)$$

where $j \equiv J/N$, $r \equiv R/N$. For typical values of the parameters as chosen in this paper, it turns out that $P(R;s)$ and $K_J(t-s)$ behave in the neighborhood of their maximum as Gaussians of very different width. For $P(R;s)$ a broad distribution is found, the width being inversely proportional to

$$\left\{ \left[\mu(r) + k_1(1-r) \right] \frac{\mu(r)}{1-r} \right\}^{1/2} \sim O(\mu(r))$$

thus confirming the result (5.6). On the other hand, $K_J(t-s)$ is a much sharper distribution, having its maximum at $s = t - \tau_J$, where

$$\tau_J \sim \frac{1}{k_2} \ln \left[\frac{\mu(j)}{\mu(r)} \right] \tag{5.11}$$

From Eq. (5.9) it follows that one can put approximately $P(J;t) \sim P(R;t-\tau_J)$, corresponding to an infinitely sharp distribution for K_J. Now one sees from Eq. (5.11) that even if J and J' are quite different, i.e., $J' - J \sim O(N)$,

$$\tau_{J'} - \tau_J \sim \frac{1}{k_2} \ln \frac{\mu(j')}{\mu(j)} \tag{5.12}$$

will be relatively small with respect to the width of $P(R,s)$ if $|k_2|$ is large.

Thus during some time interval of the order of Eq. (5.6), the values of $P(J;t)$ and $P(J';t)$ will be close for $J, J' \in [W, R]$, i.e., a flat distribution will appear in this interval.

Finally for $J \in [0, W]$ we have

$$\begin{aligned} P(J;t) &= \int_0^t K_J'(t-s) P(W;s)\, ds \\ &= \int_0^t K_J'(t-s) \int_0^s du\, K_s(s-u) P(R;u) \end{aligned} \tag{5.13}$$

and the asymptotic analysis can be pursued as before.

The main advantage of replacing the analytically awkward death rate (3.3b) by a piecewise linear form rests thus on the fact that in the latter case explicit forms can be given for the solution of the Master Equation which allow direct asymptotic analysis, while preserving at the same time the interesting qualitative features of the original problem.

It is perhaps worth pointing out that the idea of piecewise linearization can be extended to the general birth and death case. Although no simple solution can be given of course in this case, it nevertheless allows one to replace the original Master Equation by a finite subset of integrodifferential equations. The size of this subset is directly related to the combined number of segments that provide a sufficient qualitative representation of

the birth and death rates. We shall explore this point further in a subsequent publication.[15]

The behavior of general classes of birth and death processes in the limit of large size N of the system has also been investigated by Kurtz.[16] This author derived a number of powerful theorems connecting the original jump process, the diffusion process described by a Fokker–Planck equation whose drift and diffusion coefficients are, respectively, the first and second transition moments of the original process, and the Gaussian process described by a linearized Fokker–Planck equation. Specifically he showed that for $N \to \infty$ and for arbitrarily long but finite times, the three processes are related provided they are so initially and provided that the transition rates are sufficiently regular. For instance, the supremum of their difference is bounded (in probability) by terms of the order $\ln N/N$.

As in our problem we initially start with a deterministic condition ($T = T_0$, $x = 1$) and the process is terminated at a finite time when the system reaches the absorbing state, Kurtz' theorem should apply. There are, however, two new elements that come into play. First there are additional smallness parameters other than N^{-1} controlling the behavior of the system, like the slope of the death rate μ in the initial stage and the ratio of its values slightly below the inflection point and at the point of maximum reaction rate. As we saw previously this may well attenuate the effect of $(\ln N/N)$ term and produce momentarily appreciable deviations from the Gaussian regime. A second and related point is that in many realistic cases everything happens as if the reaction rate were not differentiable around the explosion regime. Such cases are well described by our piecewise linear idealization, but cannot be covered directly by Kurtz-type theorems. We believe therefore that our results suggest some new and hitherto unexplored aspects of certain classes of Markovian processes.

6. DISCUSSION

In this paper we have studied the time-dependent aspects of a simple model of combustion. We have shown that, if the system is started in a range of values corresponding to a very slow deterministic rate, certain stages of the subsequent evolution are characterized by markedly random behavior, reflected by the appearance of long tails and multiple humps in the probability distribution. We have proposed a plausible interpretation of this onset of *internal differentiation* in time and carried out an analytical study for an idealized piecewise linear death rate.

We believe that the behavior outlined here should be detectable by presently available experimental techniques and that it is shared by a host

of other problems of interest in physics and chemistry including the problem of nonthermal, purely chemical explosion.[4,6] Actually, the principal requirement appears to be the existence of a rate function displaying the characteristics of Fig. 1a: A long slow induction period, followed by a sharp increase up to a maximum, and terminating to zero after another period of reduced activity. Such rate functions describe systems possessing a final state which is reached in time without having to overcome a threshold, or "activation energy" related to the coexistence of multiple attractors. This is clearly seen from the structure of the kinetic potential associated to Eqs. (2.4), which was already given in Fig. 1b.[3]

Some remarks concerning the difference between this type of evolution and other cases envisaged in the literature are now in order. An interesting class of problems, studied in depth by Suzuki,[17] refers to the passage from an initial unstable state to a final stable one. As it turns out, in a bistable system in which the stable states are completely symmetrical around the unstable state, the evolution acquires an essentially statistical character, since the system can depart from the initial state only by fluctuations. In this case one also observes the phenomenon of "bifurcation unfolding in time," as illustrated in Fig. 9a. The difference from the results of Figs. 4 and 5 is twofold. First, the bifurcation shown in Fig. 9a is completely symmetrical. And second the critical time t_c in Suzuki's theory increases with the size of the system, varying roughly as $\ln N$, whereas in our case it has a finite value since the time evolution leading to explosion occurs within a finite time interval whose length depends on the system's intrinsic parameters. Alternatively, while in Suzuki's theory the new peaks of the probability distribution subsist forever once they appear, in our case they have a finite life span which depends on N.

A different class of problems arises when, in a bistable system, the initial condition is asymmetrically disposed with respect to the attractors. As illustrated in Fig. 9b, what happens then is that the system evolves to the closest attractor via a one-humped distribution, but eventually it develops a second hump as a result of the diffusion over the potential barrier that inevitably takes place as long as N^{-1} is not strictly zero.[18,19] The "bifurcation in time" is now asymmetrical in much the same way as in Fig. 5. One difference subsists however, which is again related to the time

[3] Note that the existence of a kinetic potential does not guarantee automatically that one can write a Fokker–Planck equation for the probability distribution, and even less that one can argue in terms of a state and/or time-independent diffusion coefficient. As a matter of fact, as we see from the analysis of the preceding sections, the coupling between systematic and stochastic factors is quite intricate in the present problem, and it is not clear whether it can be expressed adequately in terms of a "drift" and a "random force" as in simple diffusionlike processes.

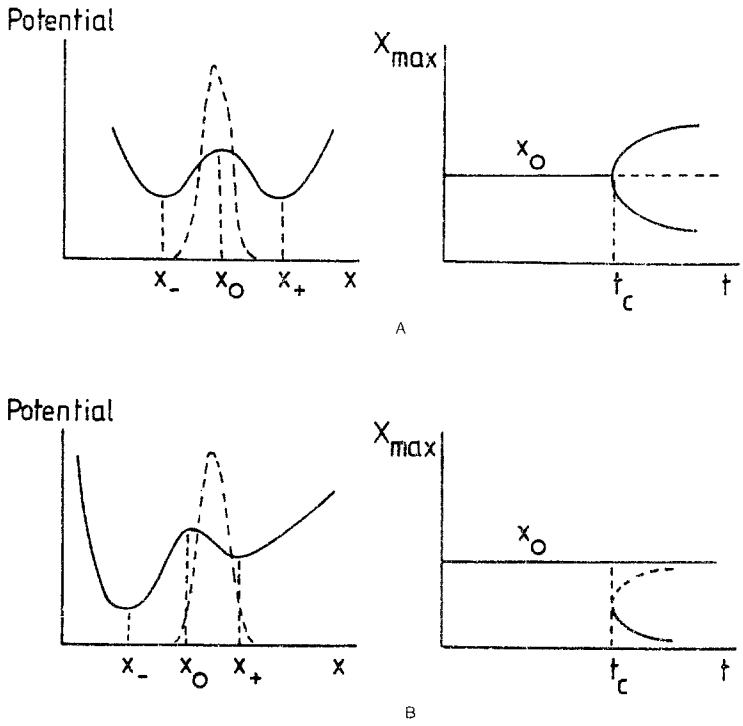

Fig. 9. (a) Kinetic potential and time evolution of the most probable value X_{max} in Suzuki's problem. (b) Kinetic potential and time evolution of the most probable value X_{max} in Kramers' problem.

scales involved. Specifically, as diffusion over the barrier is an extremely slow process, the critical time t_c in Fig. 9b is the Kramers' time, $t_c \sim \exp(N\Delta U/\sigma^2)$, ΔU being the magnitude of the barrier and σ an effective diffusion coefficient. This is exceedingly long whenever $\Delta U/\sigma^2$ has a finite value.

External noise constitutes still another class of problems leading to internal differentiation in time.[20] Specifically, starting from a one hump distribution centered on a unique solution of the deterministic equations, external multiplicative noise having a sufficiently large value of the variance may transform this initial condition into a multihumped distribution. This evolution looks qualitatively like Fig. 9a, except that t_c is now size independent since the variance of intensive quantities in the case of external noise is of $O(1)$.

In conclusion, this short comparison shows that the "bifurcations in time" analyzed in the present paper provide a new, hitherto unexplored

model of differentiation in nonequilibrium system, having a purely internal origin: Unlike problems involving external noise[20] or structural stability[21,22] the system need not be continuously perturbed by the external world. Rather, the deviations of the dynamics from equilibrium that are created temporarily are sufficient to induce, during some time interval, an internal differentiation within the system.

Several extensions of the work reported in this paper can be envisaged. The analysis of open systems and of inhomogeneous fluctuations are two obvious possibilities. Moreover, it would undoubtedly be of interest to investigate the implications of this behavior in a field like biology in which, more than anywhere else, the potentialities of living matter are unfolding as time flows. A beautiful example has recently been pointed out by Goldbeter and Segel[23] in connection with the successive developmental events occurring during the life cycle of the amoebae *Dictyostelium discoidum*. Further examples should be found in problems related to evolution, in which the historical element is ubiquitously present.

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