

Theory of chemical fluctuations in thermal explosions

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Autoignition phenomena in combustion problems exhibit a remarkable random behavior. We show on a simple model of an exothermic reaction that the phenomena has strong analogies with the transient behavior of a chemical explosion (Malthus model). These analogies lead to the construction of a simple theory of fluctuations. This theory is a natural extension of the theory already developed for the transient behavior associated with the Malthus-Verhulst problem and laser instability. Although we study only a very simple model, the approach that we propose is expected to be valid also in more complicated and realistic cases.

I. INTRODUCTION

Chemical kinetics relevant to combustion phenomena can be very complicated and only partially known. However, the presence of typical branching processes¹ and exothermic reactions are a common characteristic of all combustion processes. The formation of the first free radicals (or the dissociation of the first fuel molecules) is associated with a very high activation energy. As a consequence, the reaction rate is initially very small and ignition is characterized by a typical delay time. Ignition occurs abruptly after such a time delay which is affected by fluctuations of the active radicals in the initial regime. The knowledge of the ignition delay time and its fluctuations is important both from a fundamental point of view and for various engine design and operation problems.² From the first point of view the interest on the subject has grown only recently³ with the study of a simplified model of an exothermic reaction. This study evidences a new evolution pattern for the probability distribution function of the active species with a long tail and multiple humps during the transient. These results have been obtained by a numerical solution of the master equation associated with the probability time evolution and have been discussed in terms of analytical calculations based on a piecewise approximation for the probability rates.

The main difficulty in studying the explosion problem is how to match the initial linear regime dominated by fluctuation to the subsequent evolution in which nonlinear effects are essential but fluctuations are negligible.

The same difficulty is present in the well-known problem of fluctuations associated with the decay of an unstable state.⁴ In the transient anomalous enhancement of fluctuations has been detected by several experiments.⁵ A theory for the phenomenon has been developed in Ref. 6. An improved version of the theory has been developed in Ref. 7 and compared with available experiments in Ref. 8. On the other hand, the analogy between the laser instability problem and the autocatalytic chemical reaction known as the Schlögl model I, or Malthus-Verhulst (MV) problem in the population dynamics context, has been recognized since 1974 in Ref. 9 in the particular case in

which the multiplication probability rate is equal to the immigration rate. This relation between the two probability rates is a consequence of the Einstein relation between spontaneous and stimulated emission of photons in the laser instability problem, but appears quite peculiar in the chemical context. The results have been generalized in Ref. 10 for an arbitrary ratio of probability rates. The time evolution of the Schlögl model I is associated with a stochastic process which leaves an initial unstable state under the influence of an additive noise. The process is an n -dimensional vector whose modulus is related to the concentration of the reacting species. The number of components of the vector is associated with the ratio between the immigration and multiplication probability rates. The final results are shown to be valid, by means of an analytical continuation, also for noninteger values of n .

It is worth noting that the process for the concentration exhibits a multiplicative noise which vanishes at the initial unstable state. The presence of such a noise enhances the time spent by the system close to the unstable state. This feature and the strong nonlinearity is at the very origin of the bimodality phenomenon. It is worth recalling that strong multiplicative noise can produce a double-peaked probability distribution function also at the steady state (Refs. 11 and 12).

The master equation of the exothermic reaction can be linearized in the early stage of the evolution and in such a linear regime it coincides with the chemical explosions regime of the MV problem (i.e., in the regime in which the intraspecific competition is neglected).

In the chemical explosion problem, as we shall see in Sec. II, the exact solution of the stochastic evolution can be read as a mapping between the process x associated with the concentrations of the fluctuating species and an auxiliary Gaussian process h which in each realization approaches quickly a time-independent value.

The mapping is given by the solution of the deterministic evolution problem obtained by neglecting fluctuations. This peculiar structure of the solution of the linearized problem suggests to approximate the solution of the nonlinear problem using the same process h as in the linear case, but a nonlinear mapping.

As a consequence, each realization of the process approaches very quickly a deterministic trajectory which starts from an effective random initial state. The probability distribution function of these initial states is the asymptotic probability distribution of the process h .

This approximation scheme amounts to the QDT (quasideterministic theory) which has been fully discussed in Refs. 4, 7, 8, and 10. The QDT is expected to work in the present case because fluctuations are important only in the early stage of the evolution.

The QDT accounts for the appearance of a doubly humped probability distribution function in reasonable agreement with the numerical integration of the master equation.

The paper is divided into four sections. In Sec. II, we summarize the stochastic representation of the exothermic solution in the linear regime where it reduces to a purely explosive chemical autocatalytic reaction (the Malthus model). We develop the QDT for the exothermic reaction.

Section III is devoted to the discussion of results and Sec. IV to conclusions.

II. THE LINEAR REGIME OF THE EXOTHERMIC REACTION

Following Ref. 3 we study the pure death process



We assume the Arrhenius formula for the kinetic constant

$$K(T) = K_0 \exp(-u_0/k_B T).$$

The reaction is exothermic and occurs adiabatically in a closed vessel.

In the previous hypothesis the temperature is determined by the instantaneous concentration of the X species. As a consequence we have

$$K \left[\frac{X}{N} \right] = K_0 \exp \left[- \frac{u_0}{k_B [T_{\max} - (r_v/c_v)(X/n)]} \right]. \quad (2.2)$$

Here r_v and c_v are, respectively, the heat of reaction and the specific heat at constant volume, u_0 is the activation energy associated with the disappearance of a single fuel molecule. k_B is the Boltzmann constant, N is the initial number of fuel molecules. T_{\max} is the asymptotic temperature which is reached when all the fuel molecules have disappeared. The master equation for the probability of having X fuel molecules at time t , $P(X,t)$, is

$$\begin{aligned} \frac{d}{dt} P(X,t) &= (X+1)K \left[\frac{X+1}{N} \right] P(X+1,t) \\ &\quad - XK \left[\frac{X}{N} \right] P(X,t), \end{aligned} \quad (2.3)$$

$$P(X,0) = \delta_{N,X}$$

for $0 \leq X \leq N$, where $K(X/N) = 0$ for $X > N$. We first introduce a complementary variable $Y = N - X$ which describes the already transformed fuel molecules. In terms of the new variable Y we have

$$\begin{aligned} \frac{d}{dt} P(Y,t) &= N \left[\mu \left[\frac{Y-1}{N} \right] P(Y-1,t) \right. \\ &\quad \left. - \mu \left[\frac{Y}{N} \right] P(Y,t) \right], \end{aligned} \quad (2.4)$$

$$P(Y,0) = \delta_{Y,0}, \quad (2.5)$$

where

$$\mu \left[\frac{Y}{N} \right] = \left[\frac{N-Y}{N} \right] K \left[\frac{N-Y}{N} \right]. \quad (2.6)$$

The linearized expression for μ is

$$\mu \left[\frac{Y}{N} \right] \sim \nu + \lambda Y/N, \quad (2.7)$$

where

$$\nu = K(1), \quad (2.8)$$

$$\lambda = K(1) \left[\frac{u_0}{k_B \left[T_{\max} - \left[\frac{r_v}{c_v} \right] \right]^2 \left[\frac{r_v}{c_v} \right] - 1} \right].$$

In this limit we recognize the MV model, where ν is the immigration probability rate and λ/N is the multiplication probability rate



With respect to the MV model of Ref. 10, we have neglected the intraspecific competition and the death of individuals, i.e., the reverse reaction rates of the kinetic scheme of Eq. (2.9).

We now introduce the standard Poisson representation technique of Ref. (13). The procedure can be easily summarized. First we introduce an integral transform of $P(Y,t)$ in terms of Poisson's distribution, i.e.,

$$P(Y,t) = \int_0^\infty f(\alpha,t) \frac{\alpha^Y}{Y!} e^{-\alpha} d\alpha \quad (2.10)$$

Then it can be shown that the distribution function $f(\alpha,t)$ satisfies the following Fokker-Planck equation:

$$\frac{\partial f(\alpha,t)}{\partial t} = - \frac{\partial}{\partial \alpha} [N(\nu + \lambda/N\alpha)f(\alpha,t)], \quad (2.11)$$

$$f(\alpha,0) = \delta(\alpha). \quad (2.12)$$

The distribution function $f(\alpha,t)$ acts as a probability distribution function in the sense that the binomial moments associated with the $P(Y,t)$ given by

$$C_n(t) = \sum_Y Y(Y-1) \cdots (Y-n+1) P(Y,t) \quad (2.13)$$

are equal to the moments of the distribution function $f(\alpha, t)$,

$$C_n(t) = \int_0^\infty d\alpha f(\alpha, t) \alpha^n. \quad (2.14)$$

The Fokker-Planck equation (2.11) is equivalent to the stochastic differential equation (SDE) in the Itô sense,¹⁴

$$d\alpha = N \left[\nu + \lambda \frac{\alpha}{N} \right] dt + \sqrt{2\lambda\alpha} dw(t). \quad (2.15)$$

Here dw is the Itô differential of the Wiener process

$$\begin{aligned} \langle dw \rangle &= 0, \\ \langle dw(t_1)dw(t_2) \rangle &= \begin{cases} 0, & t_1 \neq t_2 \\ dt, & t_1 = t_2. \end{cases} \end{aligned} \quad (2.16)$$

We find the formulation in terms of a stochastic differential equation of our problem very convenient in order to get an intuitive picture of the evolution in the linear regime. We first divide by the total number of fuel molecules, introducing instead of the extensive variable α the corresponding intensive variable $c = \alpha/N$. We have

$$dc = (\nu + \lambda c)dt + \left[\frac{2\lambda}{N} c \right]^{1/2} dw(t). \quad (2.17)$$

Fluctuations arise from the stochastic term of Eq. (2.17), which scales with the inverse of the square root of the system size parameter N . As expected, fluctuations disappear for very large N .

Typical values of parameters as those used in Ref. 3 are

$$\begin{aligned} \nu &= 3.7 \times 10^{-6} K_0, \\ \lambda &= 6.6 \times 10^{-5} K_0. \end{aligned} \quad (2.18)$$

Due to the smallness of the immigration rate ν fluctuations are expected to be relevant in early stage of the evolution.

The connection with the problem of the decay from an unstable state is easily established defining

$$c = \frac{1}{n} \sum_{i=1}^n c_i^2, \quad (2.19)$$

where

$$\begin{aligned} dc_i &= \frac{\lambda}{2} c_i dt + \sqrt{\nu} dw_i, \\ c_i(0) &= 0. \end{aligned} \quad (2.20)$$

The SDE equations (2.20) are equivalent to (2.17), as can be easily shown by means of the Itô differential calculus rules provided that

$$\nu = \frac{n}{N} \frac{\lambda}{2}. \quad (2.21)$$

Equation (2.21) is a constraint on the possible values of the probability rates which will be eventually removed by means of an analytical continuation of results to nonintegers n as in Ref. 10.

In the n -dimensional space the initial state is an unstable state. The model is that of a particle sitting on the top of a hyperparabola. It will leave the unstable position because of the stochastic perturbation. The process is Gaussian and the solution of Eqs. (2.20) can be expressed as

$$c_i(t) = e^{t\lambda/2} h_i(t), \quad (2.22)$$

where the process $h_i(t)$ is given by

$$h_i(t) = \sqrt{\nu} \int_0^t e^{-\lambda/2t'} dw_i(t'). \quad (2.23)$$

We see that Eq. (2.22) is a mapping between the process c_i and the process h_i . The mapping is that induced by the deterministic limit of SDE [Eq. (2.20)] between the position of the particle at time t and the initial position at time zero.

$$c_i(t) = e^{t\lambda/2} c_i(0). \quad (2.24)$$

Moreover, we see that the process h_i becomes time independent for $\lambda t \gg 1$. As a consequence, Eq. (2.23) in such a time range describes a deterministic trajectory starting from an "effective" initial position given by

$$\bar{c}_i(0) = \lim_{t \rightarrow \infty} \sqrt{\nu} \int_0^t e^{-t'\lambda/2} dw_i(t').$$

In the linear regime it is also easy to calculate the characteristic time spent by the system close to the unstable state and its fluctuations. The relevance of the first passage time concept for the study of the decay from an unstable state has been emphasized in Ref. 15. We shall use the results for a linear vectorial process of Ref. 16. The mean first passage time, i.e., the average time for the vectorial process c_i to attain a given value M^2 for the modulus squared and its variance are given in our notation by

$$[t]_{\text{av}}(M^2) = \frac{1}{\lambda} \left[\ln \left[\frac{M^2}{\nu} \right] - \psi \left[\frac{n}{2} \right] \right], \quad (2.25)$$

$$[\Delta t^2]_{\text{av}}(M^2) = [(t - [t]_{\text{av}})^2]_{\text{av}} = \frac{1}{\lambda^2} \psi' \left[\frac{n}{2} \right] \quad (2.26)$$

The ψ and ψ' are, respectively, the digamma and trigamma functions given in Ref. 17.

In our case the number of components $n = (2\nu/\lambda)N$ is of the order of 10^2 ; as a consequence an asymptotic expansion of the polygamma function is justified:¹⁷

$$\begin{aligned} \psi \left[\frac{n}{2} \right] &= \ln \left[\frac{n}{2} \right] - \frac{1}{n} + O \left[\frac{1}{n^2} \right], \\ \psi' \left[\frac{n}{2} \right] &= \frac{2}{n} + O \left[\frac{1}{n^2} \right]. \end{aligned} \quad (2.27)$$

As a result we obtain

$$[t]_{\text{av}}(M^2) = \frac{1}{\lambda} \left[\ln \left[\frac{2M^2}{n\nu} \right] + \frac{1}{n} \right] O \left[\frac{1}{n^2} \right], \quad (2.28)$$

$$[\Delta t^2]_{\text{av}}(M^2) = \frac{1}{\lambda^2} \left[\frac{2}{n} \right] + O \left[\frac{1}{n^2} \right]. \quad (2.29)$$

If we now take into account that the concentration

$$c = \frac{1}{n} \sum_i c_i^2 = (M^2/n),$$

we obtain the first passage time for the concentration which does not depend to the leading order on the number of components n . This is equivalent to saying that the size of the system $N = (\lambda/2\nu)n$ does not play any role to the leading order in determining the time the system needs to leave the unstable state. This remarkable difference with respect to the usual phenomenology of the decay of an unstable state derives from the fact that in the present case we have a vectorial process with a large number of components and the ratio between the number of components and the number of particles is indeed constant. It is convenient to express the mean and the variance of the first passage time in terms of the reaction rates.

We have

$$[t]_{\text{av}}(c) = \frac{1}{\lambda} \ln \left[\frac{2c}{\nu} \right] + \frac{1}{2\nu N} + O \left[\frac{1}{N^2} \right], \quad (2.30)$$

$$[\Delta t^2]_{\text{av}}(c) = \frac{1}{\nu\lambda N} + O \left[\frac{1}{N^2} \right]. \quad (2.31)$$

The results for the contribution of fluctuation to the mean and the variance of the first passage time agree, as far as the dependence on the size of the system is concerned, with those of Ref. 3.

Finally, we want to emphasize that the above representation of the early stage of the exothermic explosion allows us to put the phenomenon in the general framework of the theory of the decay of an unstable initial state.

III. THE QDT AND THE NONLINEAR REGIME

The difficulty of the nonlinear regime is due to the lack of an exact stochastic representation of the master equation. We shall overcome this difficulty assuming, on physical basis, that fluctuations are negligible in the nonlinear regime. The point is therefore to match the deterministic evolution characteristic of this regime to the fluctuation-affected linear regime. This matching is naturally introduced assuming the solution of the deterministic nonlinear equation as a mapping between the process c and the process h defined in Eq. (2.22). This is the main idea of the QDT theory. The deterministic equation of motion in the vectorial representation is given by

$$\frac{dc_i}{dt} = f(c)c_i, \quad (3.1)$$

$$f(c) = \frac{\mu(c) - \mu(0)}{2c}, \quad (3.2)$$

where μ is given by Eq. (2.6).

Expansion to first order of Eq. (3.1) gives the linear regime. The nonlinear regime is defined for $\mu(c) \gg \mu(0)$. In this limit Eq. (3.1) is obviously equivalent to the deterministic evolution equation for the concentration

$$\frac{dc}{dt} = \mu(c). \quad (3.3)$$

The numerical integration of Eq. (3.3) is reported in Fig. 1. Equation (3.3) defines a mapping between the vector $c_i(t)$ and the vector $c_i(0)$ associated with the initial state.

We get the QDT substituting $c_i(0)$ with the process $h_i(t)$. Unlike the linear case the QDT is now an approximation which can be understood as the first step of a non-perturbative expansion. This expansion has been studied in some details at least in the case of bistable potentials in Ref. 4.

The QDT allows to calculate the moments of C

$$\begin{aligned} \langle c^k(t) \rangle &= \left\langle \left[\frac{1}{n} \sum_{i=1}^n c_i^2 \right]^k \right\rangle \\ &= \int_{-\infty}^{+\infty} dh_1 \cdots dh_n \left[\frac{1}{n} \sum_{i=1}^n C_i^2(t, h_i) \right]^k \\ &\quad \times P(h_1 \cdots h_n, t), \end{aligned} \quad (3.4a)$$

where $P(h_1 \cdots h_n, t)$ is the multivariate Gaussian probability distribution function given by

$$P(h_1 \cdots h_n, t) = \prod_{i=1}^n P(h_i, t), \quad (3.4b)$$

$$P(h_i, t) = \frac{1}{[2\pi\sigma^2(t)]^{1/2}} \exp \left[-\frac{1}{2} \frac{h_i^2}{\sigma^2(t)} \right], \quad (3.4c)$$

$$\sigma^2(t) = \frac{\nu}{\lambda} (1 - e^{-\lambda t}). \quad (3.4d)$$

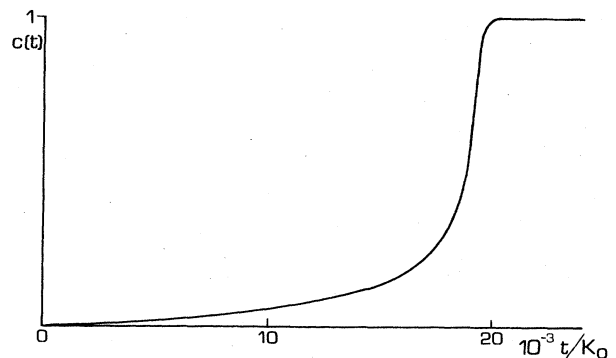


FIG. 1. The deterministic evolution of the exothermic explosion. The curve is derived by numerical integration of Eq. (3.3).

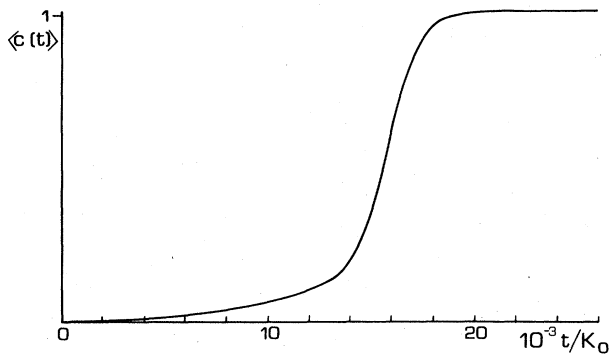


FIG. 2. The average concentration C of already transformed fuel particles as a function of time in the QDT approximation.

The multidimensional integral of Eq. (3.4) is easily done in generalized spherical coordinates. In fact, it can be easily seen from Eqs. (3.1) and (3.2) that

$$c = \frac{1}{n} \sum_i c_i^2(t, h)$$

is the solution of the differential equation (3.2) and therefore it depends only on t and on its initial condition

$$h = \frac{1}{n} \sum_i h_i^2.$$

The result is

$$\langle c^K \rangle = \int_0^\infty P(h, t) c(t, h)^K dh, \quad (3.5a)$$

$$P(h, t) = \left[2^{n/2} \Gamma \left[\frac{n}{2} \right] \left[\frac{\sigma^2(t)}{n} \right]^{n/2} \right]^{-1} \times h^{n/2-1} \exp \left[-\frac{h}{2\sigma^2(t)/n} \right]. \quad (3.5b)$$

At this point we note that the analytical continuation of Eq. (3.5) to noninteger values of n is straightforward. This allows to release the constraint for the ratio between the probability rates given in (2.19).

The explicit calculation is more easily done recalling the known result valid for large n

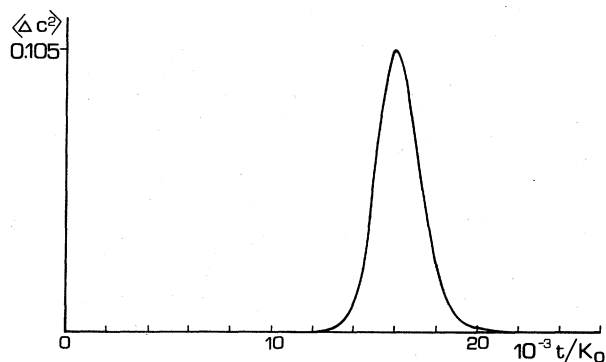


FIG. 3. The variance of the concentration c as a function of time in the QDT approximation.

$$P(h, t) \sim [2\pi v(t)]^{1/2} \exp \left[-\frac{(h^2 - m(t))^2}{2v(t)} \right] \quad (3.6)$$

with

$$m(t) = \sigma^2(t),$$

$$v(t) = 2 \frac{\sigma^4(t)}{n}.$$

The numerical integration has been performed for the first two moments. The results are reported in Figs. 2 and 3. It is remarkable how the enhancement of fluctuations in the early stages of the explosion is able to give rise to a

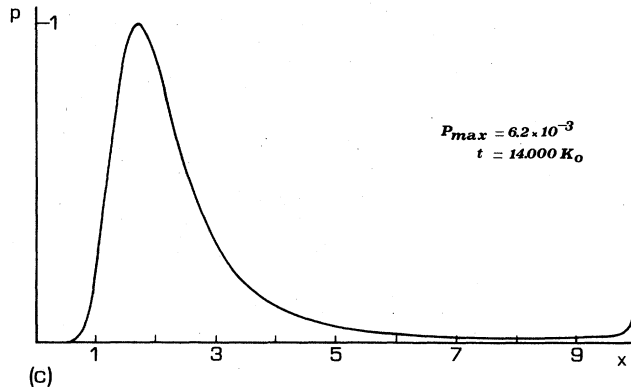
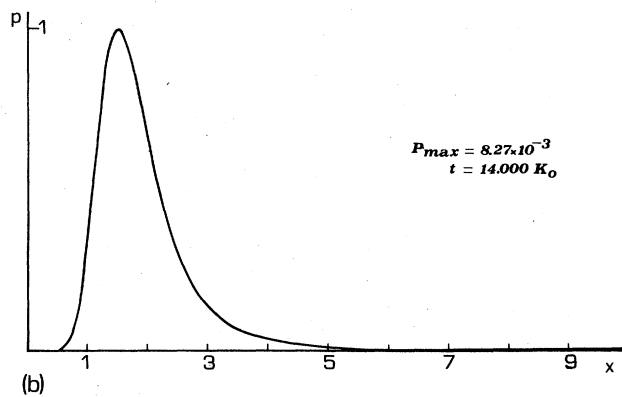
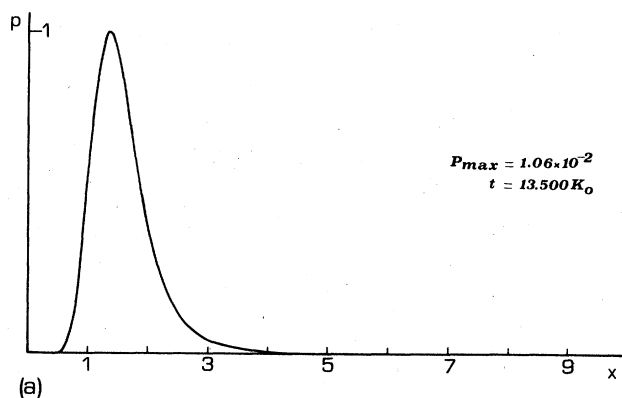


FIG. 4. The ratio between the probability distribution and its maximum value at various times as a function of the concentration of already transformed fuel particles. Note the appearance of a double peaked structure at intermediate times.

quite large variance in the neighborhood of the explosion time. It must be noted, however, that the maximum value of the variance decreases as the number n of components increases. The present phenomenon is different from the previously studied case of "microscopic activation process" of Ref. 10 because the number of components n is proportional to the total number of fuel particles N . As a consequence anomalous fluctuations will eventually disappear for N very large.

The main advantage of the QDT is not in the possibility of calculating moments, which in this case can be more accurately derived by a perturbation expansion around the deterministic trajectory, but in the capability of describing very easily the transient bimodality phenomenon which is the main characteristic of the evolution pattern of the probability distribution function.

Performing an obvious change of integration variables in Eq. (3.5) we have

$$\int c^n P(c, t) dc = \int c^n(h, t) P(h, t) dh, \quad (3.7a)$$

$$P(c, t) = P(h(c, t), t) \frac{dh}{dc}. \quad (3.7b)$$

The mapping is defined through the integration of Eq. (3.3), i.e.,

$$\int_h^c \frac{dc}{\mu(c) - \mu(0)} = t. \quad (3.8)$$

Differentiating Eq. (3.8) with respect to the concentration c , we have

$$\frac{dh}{dc} = \frac{\mu(h) - \mu(0)}{\mu(c) - \mu(0)}. \quad (3.9)$$

It is just the above factor which depresses the probability distribution in the concentration range which corresponds to high-velocity rates values.

As shown in Fig. 4 a typical double peaked probability distribution function appears in the transient. Some realizations still leave close the unstable state while some oth-

ers have already reached the stable state. Due to the abrupt variation of the kinetic potential very few realizations are found in the intermediate states.

IV. CONCLUSIONS

This work is intended to contribute to a deeper understanding of the fluctuations enhancement in thermal explosions. It has been shown that early stages of the evolution of such systems can be usefully represented as the decay from an unstable state in a multidimensional space. From this point of view there is a complete analogy with the well-known enhancement of fluctuations during the transient behavior associated with the laser transition problem. The essential difference is that the dimensionality of the order parameter instead to be two as in the laser case is now of the order of magnitude of the number of fuel particles. The transient bimodality is a consequence of the abrupt switch from a very low reaction velocity regime to a very high one.

A simple theory which predicts bimodality has been developed along the lines which were successful in the laser problem. The quantitative predictions of the theory could be improved by successive expansion of the process around the QDT process. The same approach should be successful in more realistic ignition chemical models. The idea is that also in more involved kinetic schemes the early stage behavior should be easily understandable and the QDT actually needs only the knowledge of the early stage fluctuations and of the deterministic evolution laws.

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¹N. N. Semenov, *Chemical Kinetics and Chain Reactions* (Oxford University, London, 1935).

²M. P. Halstead, L. J. Kirsch, A. Prothers, and C. P. Quinn, *Proc. R. Soc. London, Ser. A* **346**, 515 (1975).

³F. Baras, G. Nicolis, M. Malek-Mansour, and J. W. Turner, *J. Stat. Phys.* **32**, 1 (1983).

⁴F. de Pasquale, P. Tartaglia, and P. Tombesi, *Z. Phys. B* **43**, 353 (1981).

⁵T. Arecchi, V. Degiorgio, and B. Querzola, *Phys. Rev. Lett.* **19**, 1168 (1967); *Phys. Rev. A* **3**, 1108 (1971); D. Meltzer and L. Mandel, *Phys. Rev. Lett.* **25**, 1151 (1970).

⁶M. Suzuki, *Phys. Lett.* **67A**, 339 (1978); *Prog. Theor. Phys.* **64**, 402 (1978).

⁷F. de Pasquale and P. Tombesi, *Phys. Lett.* **72A**, 7 (1979).

⁸F. de Pasquale, P. Tartaglia, and P. Tombesi, *Phys. Rev. A* **25**,

466 (1982).

⁹K. J. McNeil and D. F. Walls, *J. Stat. Phys.* **10**, 439 (1974).

¹⁰F. de Pasquale, P. Tartaglia, and P. Tombesi, *Nuovo Cimento* **69B**, 228 (1982).

¹¹W. Horsthemke and R. Lefever, *Phys. Lett.* **64A**, 19 (1977).

¹²A. Schenzle and H. Brand, *Phys. Rev. A* **20**, 1628 (1979).

¹³J. W. Gardiner and S. Chaturvedi, *J. Stat. Phys.* **17**, 429 (1977).

¹⁴I. I. Gihman and A. V. Skorohod, *Stochastic Differential Equations* (Springer, Berlin, 1972).

¹⁵F. T. Areccai and A. Politi, *Phys. Rev. Lett.* **45**, 1219 (1980).

¹⁶F. Haake, J. W. Haus, and R. Glauber, *Phys. Rev. A* **23**, 3255 (1981).

¹⁷M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970).