Journal of Statistical Physics, Vol. 46, Nos. 5/6, 1987

Intrinsic Fluctuations in Explosive Reactions

N. G. van Kampen[1]

Received July 15, 1986

A reaction is called "explosive" when the amount of a reactant becomes infinite in a finite time. When the intrinsic stochastic character of the reaction is taken into account, the explosion time is a random quantity. We compute its probability distribution, or at least its average and variance, for various kinds of reactions. If a reaction is unstable, so that a reactant can either explode or disappear, one first has to compute the probability for an explosion to occur at all, and then the average explosion time. Finally, the same ideas are applied to more general Markov processes.

KEY WORDS: Explosions; fluctuations; chemical reactions.

1. INTRODUCTION

Consider chemical reactions with a single reactant X whose concentration x varies with time according to some rate equation

$$dx/dt = f(x) \tag{1}$$

Until Section 5 we suppose

$$f(x) > 0 \qquad (\text{all } x \geqslant 0) \tag{2}$$

The solution of (1), with initial value y at $t=0$, is given in implicit form by

$$t = \int_y^x \frac{dx'}{f(x')} \tag{3}$$

If this integral converges as $x \to \infty$, the amount of X becomes infinite in a finite time and we call the reaction *explosive*.[1,2] This property does not

[1] Institute for Theoretical Physics of the University, Utrecht, Netherlands.

0022-4715/87/0300-0933$05.00/0

depend on the initial state y when (2) is satisfied. Of course, the actual explosion time

$$t_\infty(y) = \int_y^\infty \frac{dx'}{f(x')} \tag{4}$$

does depend on y.

This is the macroscopic picture, in which the evolution is given by a deterministic rate equation. We are interested in the effect of fluctuations caused by the fact that X consists of individual molecules. Accordingly, the reaction becomes a stochastic process and the explosion time is a random variable. We want to know its probability distribution.

These fluctuations are an *intrinsic* property of the reaction. They must be distinguished from *external* fluctuations, caused by external agencies, such as fluctuating supplies, a fluctuating temperature of the surroundings, or fluctuating irradiation. External fluctuations have the effect that the coefficients in the function $f(x)$ become random functions of time. They have been studied by Deutch *et al.*,[2] Dacol and Rabitz,[3] and Fernández,[4] but we are not concerned with them.

Intrinsic fluctuations in exploding reactions have been studied by Baras *et al.*[5] and Frankowicz and Nicolis.[6] What they call an explosion, however, is a steep increase in the rate at which a reactant is produced. In that case the explosion time is not a precisely defined physical quantity, unless one identifies it, somewhat arbitrarily, as the time at which the rate is maximal.

The shortcomings of our work should be clearly stated. First, intrinsic fluctuations are normally of negligible influence. Typically they are of the order of the square root of the number of molecules involved, and hence relatively very small in any macroscopic chemical reaction, except in the initial stage. Second, our rate coefficients are *constants*, which implies that the reaction is isothermal. Normal chemical explosions are caused by a rising temperature and the ensuing increase in the reaction rates. Our explosions are caused by an autocatalytic reaction. Moreover our reactions are rather unrealistic, since they involve three-body collisions. Finally, we ignore spatial variations and treat the system, including fluctuations, as homogeneous ("well-stirred"). The conclusion is that our explosions do not refer to bombs or fireworks, but rather to reactions in solution or perhaps to nuclear fission or populations.

2. THE PURE BIRTH PROCESS

As a first example, consider the reaction

$$\mathrm{A} + 2\mathrm{X} \rightarrow 3\mathrm{X} \tag{5}$$

Its rate equation is

$$\dot{x} = f(x) = \alpha x^2$$

According to (3), this process explodes. This is not true if initially $x = 0$, because $f(0)$ violates (2); we therefore restrict our considerations to $x > 0$.

The stochastic behavior is described, on the mesoscopic level, by a master equation for the probability $p_n(t)$ that there are n molecules X at time t in the volume Ω:

$$\dot{p}_n(t) = -\alpha\Omega^{-1} n(n-1)\, p_n + \alpha\Omega^{-1}(n-1)(n-2)\, p_{n-1} \tag{6}$$

Initially there is a given number m of molecules. We shall consider the more general equation

$$\dot{p}_n(t) = -g_n p_n + g_{n-1} p_{n-1}, \qquad p_n(0) = \delta_{n,m} \tag{7}$$

where g_n is some smooth function of n, usually a polynomial. The corresponding deterministic rate equation, obtained by taking the thermodynamic limit $\Omega \to \infty$, $n \sim \Omega$, is[7]

$$\dot{n} = g_n$$

The deterministic reaction is explosive if

$$\int_m^\infty \frac{dn}{g_n} < \infty \tag{8}$$

Now consider the mesoscopic description. The master equation (7) represents a pure birth process: from each site n only a step to $n+1$ is possible. This step occurs at a random time t after arrival at n. The probability density of this residing time is

$$w(t) = g_n e^{-g_n t} \tag{9}$$

Hence, the average time of residing at n is g_n^{-1}. The time to arrive from m at some $N > m$ is a stochastic quantity $t_N(m)$. Its average is the sum of the average durations of the individual steps:

$$\langle t_N(m) \rangle = \sum_{n=m}^{N-1} \frac{1}{g_n}$$

This is the mean first passage time at N. The reaction, in the mesoscopic description, is explosive if

$$\langle t_\infty(m) \rangle = \sum_{n=m}^{\infty} \frac{1}{g_n} < \infty \tag{10}$$

This criterion is the same as (8).

Having found the average explosion time, we now compute its entire probability distribution. The characteristic function of (9) is

$$\int_0^\infty e^{-\lambda t} w(t)\, dt = (1 + \lambda/g_n)^{-1}$$

Since the successive residing times are statistically independent, the characteristic function of the explosion time is the product:

$$G_m(\lambda) \equiv \langle e^{-\lambda t_\infty(m)} \rangle = \prod_{n=m}^{\infty} \left(1 + \frac{\lambda}{g_n}\right)^{-1} \tag{11}$$

The product converges if the explosion criterion (10) is satisfied.

This determines the probability distribution of the explosion time. On expanding the logarithm of (11) in powers of λ, one finds the successive cumulants of the distribution of $t_\infty(m)$:

$$\kappa_p = \sum_{n=m}^{\infty} \frac{1}{g_n^p}$$

This is the sum of the cumulants of the individual distributions (9), as it should be. The main contribution comes from the small g_n, that is, normally the g_n with small n, which correspond to the initial stage of the reaction.

For the example (6) the average explosion time (10) is given by

$$\langle t_\infty(m) \rangle = \frac{\Omega}{\alpha} \frac{1}{m-1} \tag{12}$$

It is infinite for $m = 1$, since the reaction cannot start with a single molecule. The characteristic function (11) is, for this example,

$$\langle e^{-\lambda t_\infty(m)} \rangle = \frac{\Gamma(m-\eta)\, \Gamma(m-1+\eta)}{\Gamma(m)\, \Gamma(m-1)} \tag{13}$$

where η is either root of $\eta - \eta^2 = \Omega\lambda/\alpha$. If $\Omega\lambda/\alpha > \frac{1}{4}$,

$$\langle e^{-\lambda t_\infty(m)} \rangle = \frac{1}{(m-1)!\,(m-2)!} \left|\Gamma(m - \tfrac{1}{2} \pm i(\Omega\lambda/\alpha - \tfrac{1}{4})^{1/2})\right|^2 \tag{14}$$

In particular, if $m = 2$, the expression (13) reduces to

$$\langle e^{-\lambda t_\infty(2)} \rangle = \frac{\pi\eta(1-\eta)}{\sin \pi\eta} = \frac{\pi\Omega\lambda/\alpha}{\cosh \pi(\Omega\lambda/\alpha - \frac{1}{4})^{1/2}} \tag{15}$$

Equation (13) is exact. We consider its asymptotic expansion for a large system, i.e., Ω large, m being of order Ω:

$$\langle e^{-\lambda t_\infty(m)}\rangle = \exp\left[-\frac{\Omega}{\alpha}\left(\frac{1}{m}+\frac{1}{m^2}\right)\lambda+\frac{1}{6}\frac{\Omega^2}{\alpha^2}\frac{\lambda^2}{m^3}+O(\Omega^{-3/2})\right]$$

The coefficient of λ gives $\langle t_\infty(m)\rangle$ in agreement with (12). The next term yields the variance

$$\langle t_\infty(m)^2\rangle - \langle t_\infty(m)\rangle^2 = \frac{1}{3}\frac{\Omega^2}{\alpha^2 m^3} = \frac{1}{3m}\langle t_\infty(m)\rangle^2$$

Thus, the width of the distribution is of order $\Omega^{-1/2}$, as might have been expected when a large number of molecules is involved.

On the other hand, large variations in the explosion time may be expected if one starts with a small m. For instance, for $m=2$ one finds, by expanding (15) in λ,

$$\langle t_\infty(2)^2\rangle - \langle t_\infty(2)\rangle^2 = (\pi^2/3-3)(\Omega/\alpha)^2 = 0.29\langle t_\infty(2)\rangle$$

These fluctuations arise in the initial stage of the reaction and therefore do not become small for large Ω.

3. BIRTH-AND-DEATH PROCESSES

Now consider a process in which also steps from n to $n-1$ are possible, as described by the master equation

$$\dot{p}_n = g_{n-1}p_{n-1} + r_{n+1}p_{n+1} - (g_n + r_n)p_n \tag{16}$$

To ensure that negative n will not occur, we suppose $r_0=0$; this is always true for chemical reactions and populations. The corresponding rate equation is

$$\dot{n} = g_n - r_n \tag{17}$$

As in (2), we suppose

$$g_n > r_n \qquad \text{for all} \quad n \tag{18}$$

The macroscopic criterion for the reaction to be explosive is

$$\int_m^\infty \frac{dn}{g_n - r_n} < \infty \tag{19}$$

The stochastic problem can no longer be treated so easily as for the pure birth process. Instead, we now have to use a general equation for the mean first passage time.[2] If we set $\langle t_\infty(m)\rangle = \tau_m$, this equation states

$$-1 = g_m(\tau_{m+1} - \tau_m) + r_m(\tau_{m-1} - \tau_m) \tag{20}$$

The index m is the starting point and the operator on the right is the adjoint of the one in (16). Of course $\tau_\infty = 0$. The other boundary condition is obtained by substituting $m = 0$:

$$\tau_0 - \tau_1 = g_0^{-1}$$

[We know from (18) that $g_0 > 0$.]

It is easy to solve (20) with these boundary conditions:

$$\tau_m = \sum_{\mu=m}^{\infty} \frac{1}{g_\mu}\left[1 + \sum_{\nu=0}^{\mu-1} \frac{r_\mu r_{\mu-1} \cdots r_{\mu-\nu}}{g_{\mu-1} g_{\mu-2} \cdots g_{\mu-\nu-1}}\right]$$

Thus, we have found the mean explosion time. The result can be written more conveniently with the aid of some abbreviations. Set

$$R_\nu^\mu = \frac{r_{\nu+1} r_{\nu+2} \cdots r_\mu}{g_{\nu+1} g_{\nu+2} \cdots g_\mu} \quad (\mu > \nu), \qquad R_\mu^\mu = 1$$

Then

$$\tau_m = \sum_{\mu=m}^{\infty} \sum_{\nu=0}^{\mu} \frac{1}{g_\nu} R_\nu^\mu \tag{21}$$

If one also agrees to set $R_\nu^\mu = 0$ for $\nu > \mu$ and

$$\sum_{\mu=m}^{\infty} R_\nu^\mu = S_\nu^m$$

one has

$$\tau_m = \sum_{\nu=0}^{\infty} \frac{1}{g_\nu} \sum_{\mu=m}^{\infty} R_\nu^\mu = \sum_{\nu=0}^{\infty} \frac{1}{g_\nu} S_\nu^m \tag{22}$$

It can be shown (for smooth functions g_n, r_n) that the convergence of this sum implies (19), but the converse is *not* true: one can construct g_n, r_n such that the macroscopic reaction explodes but the mean explosion time (22) is infinite (P. G. J. van Dongen, private communication).

As a generalization of (20), one can derive for the characteristic function $G_m(\lambda)$, defined as the average of $\exp[-\lambda t_\infty(m)]$ over all paths starting at m,

$$\lambda G_m(\lambda) = g_m[G_{m+1}(\lambda) - G_m(\lambda)] + r_m[G_{m-1}(\lambda) - G_m(\lambda)]$$

[2] Called the Dynkin equation in Ref. 8, but earlier references are given in Ref. 9.

This equation is as hard to solve as the master equation itself, but the successive powers of λ can be found. The terms of order λ give (22), and those of order λ^2 give, for $\langle t_\infty(m)^2\rangle \equiv \sigma_m$,

$$-2\tau_m = g_m(\sigma_{m+1} - \sigma_m) + r_m(\sigma_{m-1} - \sigma_m)$$

The solution is

$$\sigma_m = 2 \sum_{\mu=m}^{\infty} \left(\frac{\tau_\mu}{g_\mu} + \sum_{\nu=1}^{\mu} \frac{r_\mu r_{\mu-1} \cdots r_{\mu-\nu+1}}{g_\mu g_{\mu-1} \cdots g_{\mu-\nu+1}} \frac{\tau_{\mu-\nu}}{g_{\mu-\nu}}\right)$$

$$= 2 \sum_{\nu=0}^{\infty} \frac{\tau_\nu}{g_\nu} S_\nu^m$$

An example is the reaction scheme obtained by supplementing (5) with

$$\mathrm{B} \to \mathrm{X}, \qquad \mathrm{X} \to \mathrm{C}$$

The master equation is of the form (16) with

$$g_n = \alpha\Omega^{-1} n(n-1) + \beta\Omega, \qquad r_n = \gamma n$$

The condition (18) is obeyed provided that $\gamma^2 < 4\alpha\beta$. We compute τ_m for large Ω with fixed $y = m/\Omega$. First

$$R_\nu^\mu = \exp \Omega \int_{\nu/\Omega}^{\mu/\Omega} [\log \gamma u - \log(\alpha u^2 + \beta)]\, du$$

Then, according to (21), setting $\nu/\Omega = x$,

$$\tau_m = \Omega \int_y^\infty dy' \int_0^{y'} \frac{dx}{\alpha x^2 + \beta} \exp\left(-\Omega \int_x^{y'} \log \frac{\alpha u^2 + \beta}{\gamma u}\, du\right) \tag{23}$$

For large Ω the exponential increases sharply with x, so that the integral over x is dominated by the contribution from the vicinity of y':

$$\tau_m \simeq \Omega \int_y^\infty dy' \frac{1}{\alpha y'^2 + \beta} \left(\Omega \log \frac{\alpha y'^2 + \beta}{\gamma y'}\right)^{-1} \tag{24}$$

This reaction is explosive from both the macroscopic and mesoscopic points of view.

4. SYSTEMS OF DIFFUSION TYPE

We apply the same considerations to the Fokker–Planck equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} U'(x) P + D \frac{\partial^2 P}{\partial x^2} \tag{25}$$

$P(x, t)$ is a probability density, $U(x)$ is some function, and D is the diffusion constant. The mathematical properties of this equation are similar to those of the one-step master equation (16), but they are simpler.[10] That will give us the opportunity to introduce the case of unstable systems, which will be studied in Section 5 for birth-and-death processes. It is also true that the Fokker–Planck equation is a valid approximation for certain systems.[7,11,12] A drawback of using a Fokker–Planck equation to mimick the behavior of a one-step process for a chemical reaction is that the natural boundary at $n=0$ is not easy to take into account.[13] We therefore restrict (25) to $x>0$ by means of an artificial reflecting boundary on which the probability flow is required to vanish:

$$-U'P + D\,\partial P/\partial x = 0 \qquad \text{at} \quad x=0 \tag{26}$$

It is again possible to extract a deterministic equation from (25), in this case by setting $D=0$, which usually means zero temperature. Then (25) reduces to the Liouville equation belonging to

$$\dot{x} = -U'(x)$$

According to (4), this equation is explosive if $U'(x)<0$ and

$$\int_y^\infty \frac{dx}{|U'(x)|} < \infty \tag{27}$$

Now consider a diffusing particle described by (25) and (26) and starting out from a point y,

$$P(x, 0) = \delta(x-y) \tag{28}$$

At any $X>y$ the time of first arrival $t_X(y)$ is a random quantity. Its average $\tau_X(y)$ obeys

$$-U'(y)\frac{d\tau_X}{dy} + D\frac{d^2\tau_X}{dy^2} = -1, \qquad \tau_X(X)=0 \tag{29}$$

The left-hand side contains the adjoint of the operator in (25), provided that we also impose on $\tau_X(y)$ the boundary condition that is the adjoint of (26), namely

$$d\tau_X/dy = 0 \qquad \text{at} \quad y=0 \tag{30}$$

The physical reason for this condition is that a particle close to the boundary can reach X either directly or after being reflected; τ is the average of both contributions and when y increases, the former decreases and the latter increases.

The solution of (29) with (30) is the familiar expression

$$\tau_X(y) = \frac{1}{D} \int_y^X e^{U(y')/D}\, dy' \int_0^{y'} e^{-U(y'')/D}\, dy'' \tag{31}$$

If this integral converges as $X \to \infty$, there is a finite average explosion time

$$\tau_\infty(y) = \frac{1}{D} \int_y^\infty e^{U(y')/D}\, dy' \int_0^{y'} e^{-U(y'')/D}\, dy'' \tag{32}$$

To show the agreement with (27), we note that it is clearly necessary that $U(y)$ tends to $-\infty$. One may therefore use for the second integral the same asymptotic approximation as in (24):

$$\int_0^{y'} \exp\{-[U(y') + (y'' - y')\, U'(y') + \cdots]/D\}\, dy''$$

$$\simeq \{\exp[-U(y')/D]\}\, D/|U'(y')|$$

Thus, the convergence of (32) is equivalent to (27).

A second question may be asked. If a particle diffuses according to (25) and (26), what is the probability $\pi_X(y)$ that it reaches X before it ever touches the boundary 0? One may derive for $\pi_X(y)$

$$-U'(y) \frac{d\pi_X}{dy} + D \frac{d^2\pi_X}{\partial y^2} = 0, \qquad \pi_X(x) = 1, \qquad \pi_X(0) = 0 \tag{33}$$

The solution is

$$\pi_X(y) = \int_0^y e^{U(y')/D}\, dy' \Big/ \int_0^X e^{U(y')/D}\, dy'$$

If the integral in the denominator converges for $X \to \infty$, there is a nonzero probability for the particle to reach infinity without touching $n = 0$. This is certainly the case when (31) is finite.

For this second question the boundary condition (26) was not relevant. The result is equally valid if this boundary is absorbing. In that case no explosion occurs once the particle has reached this boundary. Thus, in this case

$$\pi_\infty(y) = \int_0^y e^{U(y')/D}\, dy' \Big/ \int_0^\infty e^{U(y')/D}\, dy'$$

is the probability that, starting at y, an explosion will occur.[1]

Suppose one has a diffusion process that can either explode or end up in an absorbing boundary, with probabilities $\pi_\infty(y)$ and $\pi_0(y) = 1 - \pi_\infty(y)$, respectively. If it explodes, what is the average time at which the explosion occurs? We call this conditional mean first passage time again $\tau_\infty(y)$ and set $\pi_\infty(y)\,\tau_\infty(y) = \theta(y)$. This quantity obeys the equation[12]

$$-U'(y)\frac{d\theta}{dy} + D\frac{d^2\theta}{dy^2} = -\pi_\infty(y), \qquad \theta(0) = \theta(\infty) = 0 \tag{34}$$

The solution is

$$\theta(y) = \int_0^y dy_1 \int_y^\infty dy_2\, e^{[U(y_1) + U(y_2)]/D} \times \int_{y_1}^{y_2} e^{-U(y_3)/D}\pi_\infty(y_3)\, dy_3 \Big/ D \int_0^\infty e^{U(y')/D}\, dy'$$

5. UNSTABLE REACTIONS

As an example in which the condition (18) is violated, consider the reaction scheme

$$A + 2X \to 3X, \qquad X \to C$$

(This is the same reaction as studied in Refs. 1–3 from a different point of view.) The master equation has the form (16) with

$$g_n = \alpha\Omega^{-1}n(n-1), \qquad r_n = \gamma n \tag{35}$$

Thus, $g_n > r_n$ for $n > \Omega\gamma/\alpha$, but $g_n < r_n$ for $n < \Omega\gamma/\alpha$. Moreover, the pair of states $n = 0$, 1 constitutes an absorbing set. The rate equation

$$\dot{x} = \alpha x^2 - \gamma x$$

has a stable equilibrium solution $x = 0$ and an unstable one $x = \gamma/\alpha$. A solution with initial value $m < \Omega\gamma/\alpha$ ends up in $n = 0$ and a solution with $m > \Omega\gamma/\alpha$ explodes. (This statement makes sense only if $\Omega\gamma/\alpha \gg 1$, since the macroscopic approximation holds only for large n.)

In the mesoscopic treatment, however, every initial m may lead to explosion with a probability $\pi_\infty(m)$ and to disappearance of the reactant with probability $\pi_0(m) = 1 - \pi_\infty(m)$. The explosion probability obeys the equation, similar to (33),

$$0 = g_m[\pi_\infty(m+1) - \pi_\infty(m)] + r_m[\pi_\infty(m-1) - \pi_\infty(m)] \tag{36}$$

Of course, $\pi_\infty(\infty)=1$, and $\pi_\infty(0)=\pi_\infty(1)=0$, since the reaction cannot get started with less than two molecules. On solving this equation, one obtains first

$$\pi_\infty(m)=\pi_\infty(2)\sum_{v=1}^{m-1}\frac{r_2r_3\cdots r_v}{g_2g_3\cdots g_v}=\pi_\infty(2)\sum_{v=1}^{m-1}R_1^v$$

Subsequently, $\pi_\infty(2)$ is found by requiring that for $m=\infty$ this expression equals unity, so that

$$\pi_\infty(m)=\sum_{v=1}^{m-1}R_1^v\Big/\sum_{v=1}^{\infty}R_1^v=1-S_1^m/S_1^1$$

In the example (35) this works out to

$$\pi_\infty(m)=e^{-\Omega\gamma/\alpha}\sum_{v=0}^{m-2}\frac{1}{v!}\left(\frac{\Omega\gamma}{\alpha}\right)^v=1-e^{-\Omega\gamma/\alpha}\sum_{v=m-1}^{\infty}\frac{1}{v!}\left(\frac{\Omega\gamma}{\alpha}\right)^v \tag{37}$$

To see how this corresponds to the macroscopic result, take Ω large. Then the summand has a peak at $v_1\simeq\Omega\gamma/\alpha$ with width $\Delta v\sim(\Omega\gamma/\alpha)^{1/2}$. If $m<v_1-\Delta v$, the explosion probability is small, while if $m>v_1+\Delta v$, it is close to 1. In the intermediate range of width $2\Delta v$ it rises from 0 to 1. Thus, *the abrupt transition of the deterministic picture is smoothed out by the fluctuations.* Discontinuous transitions occur only in the thermodynamic limit $\Omega\to\infty$.

To find out how in the transition region $\pi_\infty(m)$ rises from 0 to 1 one might of course analyze the behavior of (37). It is of more interest, however, to give a direct calculation, which is not based on this exact solution and can therefore also be used in more general situations. To study the behavior in the region around $v_1=\Omega\gamma/\alpha$ of width $\Delta v\sim\Omega^{1/2}$, we set

$$m=\Omega\gamma/\alpha+\Omega^{1/2}\xi,\qquad \pi_\infty(m)=\varphi(\xi)$$

It follows that

$$\pi_\infty(m\pm 1)=\varphi(\xi)\pm\Omega^{-1/2}\varphi'(\xi)+\tfrac{1}{2}\Omega^{-1}\varphi''(\xi)+O(\Omega^{-3/2})$$

One also has

$$g_m=\Omega\gamma^2/\alpha+2\gamma\Omega^{1/2}\xi+O(\Omega^0),\qquad r_m=\Omega\gamma^2/\alpha+\gamma\Omega^{1/2}\xi$$

On substituting all this in (36), one finds that the terms of order $\Omega^{1/2}$ cancel, while the terms of order Ω^0 yield

$$(\gamma^2/\alpha)\,\varphi''(\xi)+\gamma\xi\varphi'(\xi)=0$$

The general solution is

$$\varphi(\xi)=A\int_{-\infty}^{\xi}\exp[-(\alpha/2\gamma)\,\xi'^2]\,d\xi'+B$$

We know that $\varphi(\xi)\to 0$ for $\xi \ll -1$; hence, $B=0$. Also, $\varphi(\xi)\to 1$ for $\xi \gg 1$; hence, $A=(\alpha/2\pi\gamma)^{1/2}$. Thus, we find

$$\pi_\infty(m)=\left(\frac{\alpha}{2\pi\gamma}\right)^{1/2}\int_{-\infty}^{(m-\Omega\gamma/\alpha)\Omega^{-1/2}} e^{-(\alpha/2\gamma)\xi^2}\,d\xi$$

This gives for sufficiently large Ω the behavior of $\pi_\infty(m)$ in the transition region, but evidently the same expression is a good approximation for all m. This treatment is similar to the way in which Schuss and Matkowski computed the escape time from a potential well.[14]

The next question is: Suppose an explosion does occur, what is the average time at which it occurs? We call this conditional mean first passage time again τ_m and put $\pi_\infty(m)\,\tau_m=\theta_m$. Then one can derive the equation analogous to (34):

$$-\pi_\infty(m)=g_m(\theta_{m+1}-\theta_m)+r_m(\theta_{m-1}-\theta_m), \qquad \theta_\infty=0$$

The other boundary condition is $\theta_1=0$, since in our example the absorbing boundary is at $n=1$. The solution gives first

$$\theta_m=\sum_{\nu=2}^{\infty}\frac{\pi_\infty(\nu)}{g_\nu}S_\nu^m-\theta_2 S_1^m$$

from which θ_2 is found by inserting $m=2$, and finally

$$\theta_m=\frac{1}{1+S_1^2}\sum_{\nu=2}^{\infty}\frac{\pi_\infty(\nu)}{g_\nu}\left(S_\nu^m+S_\nu^m S_1^2-S_1^m S_\nu^2\right)$$

6. MORE GENERAL MARKOV PROCESSES

Finally we consider a more general Markov process, having a probability density $P(x,t)$ in the range $-\infty<x<\infty$ governed by the master equation

$$\frac{\partial P(x,t)}{\partial t}=\int_{-\infty}^{\infty}\{W(x\,|\,x')\,P(x',t)-W(x'\,|\,x)\,P(x,t)\}\,dx' \qquad (38)$$

$W(x\,|\,x')$ is the transition probability per unit time from x' to x, and is non-negative. (It may consist of a sum of delta functions, so that this case includes the previous master equations.) We erect a reflecting boundary at $x=0$ by putting

$$W(x \mid x') + W(-x \mid x') = \bar{W}(x \mid x')$$

and restricting the process to positive x:

$$\frac{\partial P(x, t)}{\partial t} = \int_0^\infty \{\bar{W}(x \mid x')\, P(x', t) - \bar{W}(x' \mid x)\, P(x, t)\}\, dx' \quad (0 < x < \infty) \tag{39}$$

If the system starts at y as in (28), the mean first passage time $\tau_X(y)$ at some $X > y$ obeys

$$-1 = \int_0^X \tau_X(y')\, \bar{W}(y' \mid y)\, dy' - \tau_X(y) \int_0^\infty \bar{W}(y' \mid y)\, dy' \qquad (0 \leqslant y \leqslant X) \tag{40}$$

I prove that the solution is unique. The difference $v(y)$ between any two solutions obeys the homogeneous equation

$$0 = \int_0^X [v(y') - v(y)]\, \bar{W}(y' \mid y)\, dy' - v(y) \int_X^\infty \bar{W}(y' \mid y)\, dy' \tag{41}$$

Let $v(y)$ take its maximum value at y_1; clearly, one may assume $v(y_1) > 0$. On taking $y = y_1$ in (41) one obtains two negative terms, and hence a contradiction. It follows that one cannot impose as an additional boundary condition the requirement $\tau_X(X) = 0$; in fact, we shall see that this boundary condition is not obeyed.

If the unique solution $\tau_X(y)$ of (40) remains finite as $X \to \infty$, the system is explosive and its mean explosion time $\tau_\infty(y)$ is the solution of

$$-1 = \int_0^\infty [\tau_\infty(y') - \tau_\infty(y)]\, \bar{W}(y' \mid y)\, dy' \tag{42}$$

Note that if the master equation (39) has a deterministic limit, it must be of the form (1), in which $f(x)$ is the first jump moment

$$f(x) = \int_0^\infty (x' - x)\, \bar{W}(x' \mid x)\, dx' \tag{43}$$

One then expects that in this limit the solution of (42) is given by (4).

The following explicit example may serve to illustrate the mathematics. Take

$$W(x \mid x') = w(x)\, e^{-|x - x'|} \qquad (-\infty < x < \infty) \tag{44}$$

where $w(x)$ is some positive, even function. Then

$$\bar{W}(x \mid x') = w(x)(e^{-|x-x'|} + e^{-x-x'})$$

Equation (40) becomes

$$-1 = \int_0^X \tau_X(y')\, w(y')(e^{-|y'-y|} + e^{-y'-y})\, dy' - I(y)\, \tau_x(y) \tag{45}$$

where

$$I(y) = \int_0^\infty w(y')(e^{-|y'-y|} + e^{-y'-y})\, dy'$$

The integral equation (45) can be solved by applying the operator $d^2/dy^2 - 1$, noting that

$$(d^2/dy^2 - 1)\, e^{-|y'-y|} = -2\delta(y'-y)$$

$$(d^2/dy^2 - 1)\, I(y) = -2w(y)$$

That gives

$$1 = -I(y) \frac{d^2\tau_X}{dy^2} - 2I'(y) \frac{d\tau_X}{dy}$$

This differential equation has the general solution

$$\tau_X(y) = \int_y^X \frac{dy'}{[I(y')]^2} \int_0^{y'} I(y'')\, dy'' + A + B \int_y^X \frac{dy'}{[I(y')]^2} \tag{46}$$

We were free to choose the limits of integration X and 0, but in return we have two unknown integration constants A and B. They must be determined by the requirement that (46) satisfies the integral equation (45) itself. Note $A = \tau_X(X)$ and $B = \tau'_X(0)$.

To find B, first differentiate (45) with respect to y,

$$0 = \int_0^X \tau_X(y')\, w(y')[e^{-|y'-y|} \operatorname{sgn}(y'-y) - e^{-y'-y}]\, dy'$$
$$- I'(y)\, \tau_X(y) - I(y)\, \tau'_X(y) \tag{47}$$

In this identity substitute $y = 0$. The integral vanishes and in the same way one sees that also $I'(0) = 0$. Hence $\tau'_X(0) = 0$, as could be expected for a reflecting boundary.

To find A, substitute $y = X$ in (45):

$$-1 = e^{-X} \int_0^X \tau_X(y')\, w(y')(e^{y'} + e^{-y'})\, dy' - I(X)\, \tau_X(X)$$

Also substitute $y = X$ in the differentiated equation (47):

$$0 = -e^{-X} \int_0^X \tau_X(y')\, w(y')(e^{y'} + e^{-y'})\, dy' - I'(X)\, \tau_X(X) - I(X)\, \tau'_X(X)$$

Combining both equations, one gets

$$\begin{aligned} [I(X) + I'(X)]\, \tau_X(X) &= 1 - I(X)\, \tau'_X(X) \\ &= 1 + \frac{1}{I(X)} \int_0^X I(y')\, dy' \end{aligned}$$

This determines $\tau_X(X)$ and hence A. The final result is

$$\begin{aligned} \tau_X(y) = {} & \int_y^X \frac{dy'}{[I(y')]^2} \int_0^{y'} I(y'')\, dy'' \\ & + [I(X) + I'(X)]^{-1} \left[1 + \frac{1}{I(X)} \int_0^X I(y')\, dy' \right] \end{aligned} \tag{48}$$

The system is explosive when this expression has a finite limit as $X \to \infty$. It is clearly necessary that $I(y)$ grows sufficiently rapidly with y. Then the second term is

$$\sim \frac{1}{[I(X)]^2} \int_0^X I(y')\, dy'$$

which is the same as the integrand of the first term. Hence it must vanish: $\lim \tau_X(X) = 0$ and the explosion time is

$$\tau_\infty(y) = \int_y^\infty \frac{dy'}{[I(y')]^2} \int_0^{y'} I(y'')\, dy'' \tag{49}$$

provided the integral converges.

To estimate how fast $I(y)$ must grow, set $I(y) = e^{u(y)}$ so that approximately

$$\begin{aligned} \int_0^{y'} e^{u(y'')}\, dy'' &= e^{u(y')} \int_0^\infty e^{-u'(y')y''}\, dy'' \\ &= e^{u(y')}/u'(y') \end{aligned}$$

The convergence of (49) is equivalent to that of

$$\int^{\infty} dy'\, e^{-u(y')}/u'(y') = \int^{\infty} dy'/I'(y') \tag{50}$$

Finally, here one may replace $I(y)$ with $w(y)$, since it is clear that $I(y) \sim 2w(y)$ for large y.

In order to compare this result with a deterministic criterion, we should have a parameter that makes it possible to scale down the fluctuations. Such a parameter could have been introduced in (44) if we had written $\gamma w(x)\, e^{-\gamma|x-x'|}$, which for $\gamma \to \infty$ reduces to a delta function. However, even without this formal procedure it is easy to see what the result is. The deterministic limit is (1) with f given by (43):

$$f(x) = \int_0^{\infty} (x'-x)\, w(x')(e^{-|x'-x|} + e^{-x'-x})\, dx'$$

For large x the second term, due to the reflecting boundary, is immaterial and

$$f(x) = \int_{-\infty}^{\infty} (x'-x)[w(x) + (x'-x)\, w'(x) + \cdots]\, e^{-|x'-x|}\, dx' = 2w'(x)$$

Thus, the criterion for deterministic convergence (4) coincides with the stochastic criterion (50).

REFERENCES

1. D. R. Cox and H. D. Miller, *The Theory of Stochastic Processes* (Methuen, London, 1965); D. Kannan, *An Introduction to Stochastic Processes* (North-Holland, New York, 1979).
2. A. A. Rigos and J. M. Deutch, *J. Chem. Phys.* **76**:5180 (1982); E. Chandler and J. M. Deutch, *J. Chem. Phys.* **78**:4186 (1983).
3. D. K. Dacol and H. Rabitz, *J. Chem. Phys.* **81**:4396 (1984).
4. A. Fernández, *J. Chem. Phys.* **83**:4488 (1985).
5. F. Baras, G. Nicolis, M. Malek-Mansour, and J. W. Turner, *J. Stat. Phys.* **32**:1 (1983).
6. M. Frankowicz and G. Nicolis, *J. Stat. Phys.* **33**:595 (1983).
7. N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
8. Z. Schuss, *Theory and Applications of Stochastic Differential Equations* (Wiley, New York, 1980).
9. G. H. Weiss, *J. Stat. Phys.* **42**:3 (1986).
10. N. G. van Kampen, *Prog. Theor. Phys. Suppl.* **64**:389 (1978).
11. T. G. Kurtz, *J. Appl. Prob.* **7**:49 (1970); **8**:344 (1971); *J. Chem. Phys.* **57**:2976 (1972).
12. C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1983).
13. N. G. van Kampen and I. Oppenheim, *J. Math. Phys.* **13**:842 (1972); C. Knessl, B. J. Matkowsky, Z. Schuss, and C. Tier, *J. Stat. Phys.* **42**:169 (1986).
14. R. B. Griffiths, C. Y. Wang, and J. S. Langer, *Phys. Rev.* **149**:301 (1966); Z. Schuss and B. J. Matkowski, *SIAM J. Appl. Math.* **36**:604 (1979); B. J. Matkowski, Z. Schuss, and C. Tier, *J. Stat. Phys.* **35**:443 (1984).