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REACTIVE PROCESSES IN A FLUCTUATING MEDIUM*

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Our general purpose is to study the influence of an external noise on a deterministic reactive process, and more especially to treat the memory effects due to a noise with a finite correlation time. In a first part, the microscopic theory of reaction rates is briefly reviewed, and a simple model, based on a random telegraph process, is discussed. The second part is devoted to macroscopic stochastic kinetics, excluding intrinsic fluctuations. The simulation of a changing environment by a white noise or a coloured noise with very small correlation time is studied; then we present new results on transitions induced by a noise with a finite correlation time applied in the neighborhood of a Hopf bifurcation.

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1. Introduction

During the last decades it has been recognized that chemical reactions play an important role not only in chemistry, but also in many fields of theoretical physics and applied mathematics, such as statistical mechanics or dynamics of unstable systems. For instance, they provide beautiful examples of transitions between several locally stable states, and chemical kinetics shows numerous cases of nonlinear systems where organized structures, as well as chaos, appear and can be studied theoretically or experimentally.

From this vast domain, we only address a small area in order to show how a stochastic environment can act upon the deterministic evolution of a chemical system, thus permitting behaviours that will otherwise be forbidden, such as bifurcations and transitions towards new stationary states. We first study the microscopic point of view of this problem with the theory of reaction rates; then we treat its macroscopic counterpart, which is the stochastic kinetics of chemical concentrations. In each case we focus on the effect of external noises, leaving aside all internal fluctuations, due to the limited scope of the present article.

The comparison of the microscopic and macroscopic problems is not only adequate because of the similarity of the mathematical formalism: it also yields a fruitful transposition of the microscopic definition of rate constants to the time constant of noise induced transitions.

2. Microscopic theory of reaction rates in a stochastic medium

2.1 Diffusion in a field and chemical reaction

In many cases the evolution of a reaction can be approximately described as the one-dimensional motion of a "particle" submitted to a bistable or multistable potential $U(x)$, and to a random force $f(x)$ due to the environment [1–3]. Here the position x of this particle is the *reaction coordinate*: it represents the configuration of the reacting complex measured along the most probable path from the initial stable species A (*(reactant)* to the final form B *(product)*; A and B correspond to minima of the potential $U(x)$ at a and b, separated by a maximum at c (Fig. 1).

The random force f can be decomposed into its average $\langle f(x) \rangle$, which is a viscous force $-\alpha dx/dt$, and the fluctuation δf, which is often approximated by a white noise. In the simplest case the system evolution is described by the Langevin equations [2, 3]

$$\frac{dx}{dt} = v\,, \tag{1a}$$

$$m\frac{dv}{dt} = \frac{\partial U}{\partial x} - \alpha v + \gamma \xi(t)\,, \tag{1b}$$

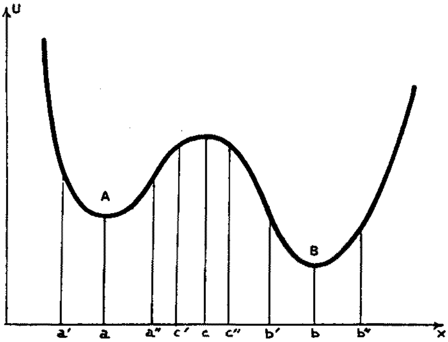

Fig. 1. The bistable potential $U(x)$.

where the reduced mass m, the viscous coefficient α and the coefficient γ are constants; the random variable $\xi(t)$ satisfies

$$\begin{aligned} \langle \xi(t) \rangle &= 0 \\ \langle \xi(t)\xi(t+\tau) \rangle &= C(\tau)\,, \end{aligned} \tag{2}$$

and in the white noise approximation the correlation function $C(\tau)$ is a Dirac distribution $\delta(\tau)$. Then system (1) corresponds to the Ito stochastic differential equations [1–3]

$$dx = v\,dt\,, \tag{3}$$

$$dv = -\frac{1}{m}\frac{\partial U}{\partial x} - \frac{\alpha}{m}v + \frac{\gamma}{m}dW\,, \tag{4}$$

where $(x,\ v)$ is the two-dimensional random process representing the phase space coordinates of the system, and W is the Wiener process.

Eq. (3) is equivalent [3] to the following Fokker–Planck equation for the conditional probability density $p(x, v, t | x_0, v_0, t_0)$ to find the particle at (x, v) at time t, knowing its coordinates (x_0, v_0) at time $t_0 < t$; this equation was first used by Kramers [4] in this context:

$$\frac{\partial}{\partial t}p = -\frac{\partial}{\partial x}(vp) + \frac{\partial}{\partial v}\left(\frac{1}{m}\left(\frac{\partial U}{\partial x} + \alpha v\right)p\right) + \frac{\gamma^2}{2m^2}\frac{\partial^2 p}{\partial v^2} \tag{5}$$

$$= -\nabla \cdot \boldsymbol{J}\,, \tag{5'}$$

J being the *probability current* with components

$$J_x = vP; \quad J_v = -\frac{1}{m}\left(\frac{\partial U}{\partial x} + \alpha v\right)p - \frac{\gamma^2}{2m}\frac{\partial p}{\partial v}\,. \tag{5''}$$

It is well known [3] that thermodynamic equilibrium corresponds to the stationary solution of (5):

$$p_0(x,v) \propto \exp\left[-\left(\tfrac{1}{2}mv^2 + U(x)\right)/kT\right] \tag{6}$$

provided the fluctuation-dissipation relation $\gamma^2 = 2\alpha kT$ holds. In general, however, the time-dependent solutions of (5) are unknown, and one often replaces (5) by the *high friction approximation.*

To obtain it, one replaces (1b) by the equivalent equation

$$v(t) = \mathrm{e}^{-\alpha t/m}v(0) + \frac{1}{\alpha}\int_0^t \left[-\frac{\partial U}{\partial x}(x(t') + \gamma\xi(t')\right]\frac{\alpha}{m}\mathrm{e}^{-\alpha(t-t')/m}dt' . \tag{7}$$

If $m/\alpha \ll \tau$, where τ is some characteristic variation time of $-\frac{\partial U}{\partial x} + \gamma\xi$, one has for $t \gg \tau$:

$$v(t) \cong \frac{1}{\alpha}\left[-\frac{\partial U}{\partial x} + \gamma\xi(t)\right] . \tag{8}$$

Eq. (8) corresponds to the *overdamped motion* of the particle, in which case the right-hand side of (1b) is equated to 0. Then $\bar{p}(x,t) = \int dv\, p(x,v,t)$ obeys the *Smoluchowski equation* [3]:

$$\frac{\partial}{\partial t}\bar{p} = \frac{1}{\alpha}\frac{\partial}{\partial x}\left[\left(\frac{\partial U}{\partial x}\right)\bar{p}\right] + kT\frac{\partial^2\bar{p}}{\partial x^2} \tag{9}$$

$$= -\frac{\partial J}{\partial x} \tag{9'}$$

with the current

$$J = \bar{p} = -\frac{1}{\alpha}\left[\frac{\partial U}{\partial x}\bar{p} + kT\frac{\partial\bar{p}}{\partial x}\right] . \tag{9''}$$

The 0-current stationary solution corresponds to thermostatic equilibrium:

$$\bar{p}^0(x) \propto \exp[-U(x)/kT] . \tag{10}$$

The time-dependent solution of (9) cannot be found easily in general, but it will be shown that the Smoluchowski equation is nevertheless well adapted for the calculation of the reaction rates in the high friction limit.

2.2. Definition of the reaction rate constant

Let us consider N particles evolving independently in the bistable potential $U(x)$ (see Fig. 1). Each of them will spend most of the time in the neighborhood of the minima a and b of U, corresponding to the chemical species A and B. In order to define the rate constants K_{AB} and K_{BA}, corresponding to the reactions $A \rightarrow B$ and $B \rightarrow A$ respectively, it is first necessary to decide in which conditions the species A and B can be identified. We just consider two possibilities:

(i) species A is detected as soon as $x < c$, and B is detected as soon as $x > c$, c being the intermediary maximum of U. This convention is applied because it gives a reasonable clear cut definition of A and B. However, it is not too realistic, unless $x = c$ corresponds to a physically identified complex, which is doubtful in many cases. Otherwise, there is practically no difference between the system for $x < c$ and $x > c$, and its evolution around c, where the external field vanishes, is a kind of a random walk implying many recrossings of c. In order for the species A and B to be defined with some stability, it is better to decide that

(ii) species A is recognized when $x \in (a', a'')$ where $a' < a < a'' < c$, (a', a'') being the "bottom" of the potential well around a; species B is recognized if $x \in (b', b'')$, which is the bottom of the potential well around b, with $c < b' < b < b''$; the region (a'', b') is the potential barrier. (a', a'') and (b', b'') can be defined more precisely as the regions where the harmonic approximations of U are valid:

$$U(x) \cong U(a) + \tfrac{1}{2} m\omega_a^2 (x-a)^2 \quad \text{if} \quad x \in (a', a''), \tag{11a}$$

$$U(x) \cong U(b) + \tfrac{1}{2} m\omega_b^2 (x-b)^2 \quad \text{if} \quad x \in (b', b'') \tag{11b}$$

whereas the top of the potential barrier $(c', c'') \subset (a'', b')$ is such that

$$U(x) \cong U(c) - \tfrac{1}{2} m\omega_c^2 (x-c)^2 \quad \text{if} \quad x \cong (c', c'') \tag{11c}$$

It should be understood that the definition of two stable species A and B only makes sense if the *mean residence time in regions A and B is much longer then the passage from A to B or from B to A*, that we always assume.

Now, to define the rate constant K_{AB} for $A \rightarrow B$ independently from the reverse one K_{BA}, it is convenient to imagine a process in which the reaction $B \rightarrow A$ is prevented by extracting B as soon as it formed. This amounts to make region (b', b'') *absorbing*: when a particle reaches it, it is trapped and never comes back. The kinetics of the passage $A \rightarrow B$ is not changed by the absorbing condition, because in the time scale of this passage, the residence time of the particle in B seems to be infinite. Then there are two main definitions of K_{AB}:

(i) K_{AB} can be defined from the *relative time variation* of the number N_A of particles A:

$$K_{AB}(t) = -\frac{1}{N_A}\frac{dN_A}{dt} = \frac{1}{N_A}\frac{dN_B}{dt} \tag{12}$$

$dN_B = -dN_A$ being the number of particles B created between t and $t+dt$.

This ratio generally depends on t but tends to an asymptotic value K_{AB} when $t \to \infty$: that is the rate constant, which is related to the *stationary probability flux* in an open system where A is continuously refilled in order to establish a steady state.

(ii) The rate constant can also be deduced from the *mean reaction time* τ_{AB}:

$$\tau_{AB} = \frac{1}{N_A(0)} \int_0^\infty t\, dN_B(t) \tag{13}$$

$dN_B(t)$ being the number of particles reaching region B between t and $t+dt$. Then one can define the reaction rate as

$$\overline{K}_{AB} = 1/\tau_{AB} ,$$

and relate it with the *mean first arrival time* at region B, starting from A initially. It is clear that $\overline{K}_{AB} = K_{AB}$ when $N_A(t)$ and $N_B(t)$ vary exponentially with t; otherwise these two rate constants can differ, but one expects that the difference, if any, is not significant in all cases where the rate constant can be given its usual meaning: this implies that $N_A^{-1}\, dN_A/dt$ relaxes to its asymptotic value on a time scale much shorter than the mean reaction time τ_{AB}.

With the aid of this discussion we now review some of the many estimations of the rate constant. A more complete review will be found, for instance, in Ref. [5].

2.3. Estimations of K_{AB}

(i) **Transition State Theory** [5]. In the simplest version of this theory, it is supposed that

- species B is obtained as soon as $x > c$;
- thermodynamic equilibrium (6) is realized in region $A = (-\infty, c)$;
- the rate constant K_{AB}^{TST} is the probability flux c, that is to say, it is the equilibrium average of *positive* v at c (there is no return from B, according to 2.2). Then one has:

$$K_{AB}^{\mathrm{TST}} \cong \left(\frac{kT}{2\pi m}\right)^{1/2} \left[\int_{-\infty}^{c} \exp\left(-\frac{U(x)}{kT}\right) dx\right]^{-1} \exp -\left(\frac{U(c)}{kT}\right) \tag{14}$$

or with approximation (11):

$$K_{AB}^{\mathrm{TST}} \cong \left(\frac{\omega_a}{2\pi}\right) \exp -\left(\frac{U(c)-U(a)}{kT}\right) . \tag{14'}$$

However, it is clear from discussion in section 2.2. that a detailed description of the barrier crossing, involving possible returns to A, is necessary to obtain an accurate expression of the rate constant. Such a dynamics is not taken into account in the TST theory: it can be given by the Kramers or Smoluchowski equations.

(ii) **In the high friction limit** Kramers [4] used Eq. (9). When N_A is kept constant and N_B is kept 0, a steady state can be established, with a current of particles A continuously introduced at $x = -\infty$ in order to compensate exactly the reactive flux $N_A K_{AB}$ of particles transformed into B.

Then it corresponds to a probability current $J = K_{AB}$. This current should be such that the stationary solution $p_1(x)$ of (9) with current J practically vanishes for $x \cong b$, which gives

$$p_1(x) = J \frac{\alpha}{kT} \exp - \left(\frac{U(x)}{kT} \right) \int_x^b \exp \left(\frac{U(x')}{kT} \right) dx' .$$

The normalization of p_1 yields:

$$K_{AB} = J = \frac{kT}{\alpha} \left\{ \int_{-\infty}^{b} dx \exp \left(- \frac{U(x)}{kT} \right) \int_x^b dx' \exp \left(\frac{U(x')}{kT} \right) \right\}^{-1} \tag{15}$$

or with the harmonic approximations (11a)–(11c):

$$K_{AB} \cong \left(\frac{m\omega_a \omega_c}{2\pi\alpha} \right) \exp \left(- \frac{U(c) - U(a)}{kT} \right) . \tag{15'}$$

This method has been generalized to a n-dimensional space; in particular, Langer and other authors [6–8] used it to compute the lifetime of metastables states in the general case.

We just mention its application [5, 9] to the *complete Kramers equation* (7). In the phase space (x, v) the regions A and B are naturally separated by the plane $x = c$. The flux of the probability current J through this plane vanishes for the equilibrium solution $p_0(x, v)$. The steady state obtained when extracting molecules B and maintaining constant the number of molecules A corresponds to another stationary solution $p_1(x, 0)$, such that $p_1 \cong 0$ in region B; it can be formed by writing $p_1(x, v) = p_0(x, v)\, q(x, v)$ and calculating q approximately in the neighborhood of c in such a way that $q \cong 0$ if $x \cong b$. The flux of the corresponding current J_1 through the plane $x = c$ is

$$K_{AB} = \int_{-\infty}^{\infty} dv\, v p_1(c, v) \tag{16}$$

which gives, with the harmonic approximations (11) of U:

$$K_{AB} \cong \left(\frac{\omega_a}{2\pi\omega_c}\right)\left\{\left[\frac{\alpha^2}{4m^2}+\omega_c^2\right]^{1/2}-\frac{\alpha}{2m}\right\}\exp\left[-\frac{U(c)-U(a)}{kT}\right] \qquad (16')$$

If $\alpha \gg 2m\omega_c$ the high friction result (15) is recovered, whereas if $\alpha \ll 2m\omega_c$ one obtains the TST value (14′).

(iii) It has been seen that the rate constant can also be deduced from *first passage time* considerations. Let us assume that the particle obeys the high friction equation (8), and let $\theta(y|x)$ be the first arrival time at y, starting from x at time 0. The probability for θ to be $\leq t$ is also the probability $P(y,t|x)$ for the particle to be in y at t if y is an *absorbing point*:

$$\text{Proba}\ (\theta(y|x) \leq t) = P(y,t|x)\,. \qquad (17)$$

It is known [3] that $P(y,t|x)$ satisfies the backward Fokker–Planck equation corresponding to (8), so that $G(t,x) = \text{Proba}\ (\theta(y|x) > t)$ also satisfies this equation:

$$.\frac{\partial G}{\partial t} = -\frac{1}{\alpha}\frac{\partial U}{\partial x}\frac{\partial G}{\partial x}+\frac{1}{2}\frac{\gamma^2}{\alpha^2}\frac{\partial^2 G}{\partial x^2} \qquad (18)$$

with the boundary conditions

$$G(0,x) = 1 \qquad \text{if } x < y; \quad G(t,y) = 0 \text{ if } t \geq 0; \qquad (19a)$$

$$\frac{\partial}{\partial x}G(t,x) \to 0 \qquad \text{if } x \to \infty \qquad (19b)$$

the last condition ensuring that $x = -\infty$ is a reflecting boundary [3] (no particle can escape or stay at $x = -\infty$).

From (18) it results that the mean value of θ:

$$\langle\theta(y|x)\rangle = \int_0^\infty dt\, t\left(\frac{\partial}{\partial t}G(x,t)\right) = \int_0^\infty dt\, G(x,t) \qquad (20)$$

satisfies:

$$-1 = -\frac{1}{\alpha}\frac{\partial U}{\partial x}\frac{\partial\langle\theta\rangle}{\partial x}+\frac{1}{2}\frac{\gamma^2}{\alpha^2}\frac{\partial^2\langle\theta\rangle}{\partial x^2}\,. \qquad (21)$$

With the boundary condition corresponding to (19), it is found that

$$\langle\theta(y|x)\rangle = \frac{\alpha}{kT}\int_x^y dx'\exp\left(\frac{U(x')}{kT}\right)\int_{-\infty}^{x'} dx''\exp\left(-\frac{U(x'')}{kT}\right). \qquad (22)$$

It can be seen [3] that the variations of $\langle\theta(y|x)\rangle$ are very small when x is moved in region A and when y is moved in region B (Fig. 2); thus the mean time needed by a particle A to pass into region B is well defined and is given, after reversing the order of the integrations, by

$$\begin{aligned}\tau_{AB} &= \langle\theta(b|a)\rangle \cong \langle\theta(b|-\infty)\rangle \\ &= \frac{\alpha}{kT}\int_{-\infty}^{b} dx \exp\left(-\frac{U(x)}{kT}\right)\int_{x}^{b} dx' \exp\left(\frac{U(x')}{kT}\right). \end{aligned} \tag{23}$$

It is seen that $K_{AB} = (\tau_{AB})^{-1}$ agrees with the estimation (15), but in general such an exact agreement cannot be expected. In several dimensions, the present method cannot be easily handled, and the flux definition of K_{AB} is more practicable. We now give its most general and convenient formulation.

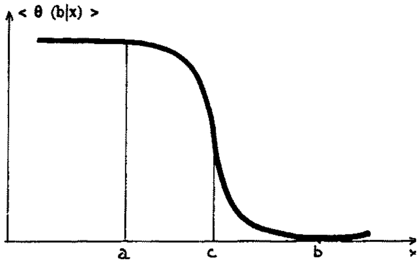

Fig. 2. Meand first arrival time $\langle\theta(b|x)\rangle$.

2.4. General definition of the rate constant K_{AB}

Modern theories define the rate constant in terms of *correlation functions*. Following Chandler [10], and Northrup and Hynes [11], we write

$$C(t) = \langle\delta N_A(0)\cdot\delta N_B(t)\rangle\,, \tag{24}$$

where $N_\alpha(t)$ is the number of particles α at time t, and δN_α is its fluctuation from the equilibrium value N_α^0, with $N_A+N_B = N$. $\langle\ \rangle$ denotes the average over equilibrium initial conditions in A and on stochastic evolution when the regions A and B are *absorbing*. Then K_{AB} is defined by

$$\frac{1}{N_A^0}\frac{dC}{dt} \to K_{AB} \qquad \text{when } t\to\infty\,. \tag{25}$$

This definition is similar to definition (8), but it only counts the molecules leaving A that finally reach B; it implies a careful description of the motion on the potential barrier. Using this method, Northrup, Hynes and coworkers [11, 12] computed the reaction constant in a number of cases, with the aid of projection techniques that will not be presented here. However, it is useful to give more explicit and general forms to rate constant defined by (25).

Using (24) and (25) one can present K_{AB} in the form [14]:

$$K_{AB} = \frac{1}{p_A^0} \int_{(S)} dS \int dv\, \boldsymbol{n} \cdot \boldsymbol{v} p^0(\boldsymbol{r}, \boldsymbol{v}) P(B|\boldsymbol{r}, \boldsymbol{v}) , \tag{26}$$

where $\boldsymbol{r}$ is the position of the particle in a n-dimensional space, $\boldsymbol{v}$ the velocity, (S) a surface separating the regions (A) and (B); $\boldsymbol{n}$ is the unit vector normal to (S) and pointing towards (B); $P(B|\boldsymbol{r}, \boldsymbol{v})$ is the probability to be absorbed in (B), starting from $(\boldsymbol{r}, \boldsymbol{v})$; $p_0(\boldsymbol{r}, \boldsymbol{v})$ is the equilibrium probability density at $(\boldsymbol{r}, \boldsymbol{v})$ and p_A^0 is the equilibrium probability of (A) ($p_0(\boldsymbol{r}, \boldsymbol{v})$ and p_A^0 being computed for the complete dynamics including (A) and (B)).

Finally, formula (26) can be extended to any Markov process in a m-dimensional space, the probability density of which obeys the generalized Fokker–Planck equation [3] in a n-dimensional phase-space:

$$\begin{aligned} \frac{\partial p}{\partial t}(\boldsymbol{x}, t) = &- \frac{\partial}{\partial x_1}(F_i p) + \frac{\partial^2}{\partial x_i \partial x_j}(D_{ij} p) + \int dy [W(\boldsymbol{x}|\boldsymbol{y}) p(\boldsymbol{y}, \boldsymbol{t}) \\ &- W(\boldsymbol{y}|\boldsymbol{x}) p(\boldsymbol{x}, \boldsymbol{t})] , \end{aligned} \tag{27}$$

where $\boldsymbol{x} = \{x_i\}_{i=1,\dots m}$ specifies the state of the system; $\{F_i(\boldsymbol{x})\}_{i=1,\dots m}$ is the drift force, $\{D_{ij}\}$ is the diffusion matrix, and $W(\boldsymbol{y}|\boldsymbol{x})$ is the transition rate from $\boldsymbol{x}$ to $\boldsymbol{y}$ if the particle can experience jumps; Einstein summation on repeated indices is implied in (27) and in the following formulae.

The probability $P(B|\boldsymbol{x}, t)$ to be absorbed in B, starting from $\boldsymbol{x}$ at time t, satisfies then the backward equation associated with (27) [3]. If we assume that *the possible jumps do not permit to cross the surface* (Σ) *that will be chosen to separate species A and B* (see Section 3 for application) the reaction rate K_{AB} can be defined as the surface integral

$$\begin{aligned} K_{AB} = \frac{1}{p_A^0} \int_{(\Sigma)} d\Sigma n^i \Big\{ & P^0(B|\boldsymbol{x}) \Big[F_i p^0 - \frac{\partial}{\partial x_j}(D_{ij} p^0) \Big] \\ & + p^0(\boldsymbol{x}) D_{ij} \frac{\partial}{\partial x_j} P^0(B|\boldsymbol{x}) \Big\} , \end{aligned} \tag{28}$$

where (Σ) is an hypersurface separating the regions R_A and R_B defining species A and B, n^i is the unit vector to (Σ) pointing toward B; $P^0(B|\boldsymbol{x})$ is the stationary value of $P(B|x,t)$ (or $P(B|x,t)$ itself for a time-homogeneous process); $p^0(x)$ is the stationary probability density for the complete dynamics (including R_A and R_B) (see Fig. 3). It can be shown that K_{AB}, as defined by (28), is *independent of the particular choice of the separatrix* (Σ). Formula (28) reduces to simpler form in important particular cases, for instance if $n^i D_{ij} = 0$. This occurs in formula (26), (Σ) being the cartesian product of (S) by the complete velocity space; however, if (Σ) was defined by conditions involving velocity or energy, we would have to apply (28).

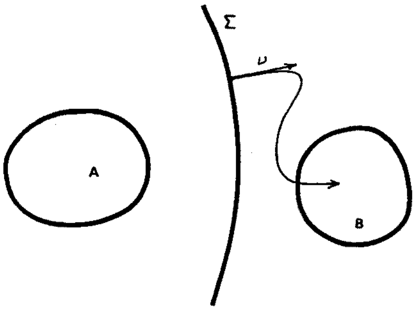

Fig. 3. Regions A and B, and separatrix Σ.

2.5. A simple solvable model

Let us assume that the motion of the particle in a bistable potential (see Fig. 1) is mimicked in the following way [13,14]:

— when the particle is in the potential well $(-\infty, c')$ it can be either in a bound state A corresponding to the stable species A, either in an excited state A^*; similarly if x is in $(c'', +\infty)$ the particle can be either in a bound state B, or in an excited state B^*;

— when the particle is on the top of the barrier (c', c''), it moves with two possible velocities $\pm v$, the sign being reversed when a collision with a solvent molecule occurs;

— when the particle reaches c'', it enters B^*; it can only pass to the bound state B if it is deexcited from B^* to B by a collision. If no collision occurs while in B^*, the particle returns to c'' after a finite time τ_B, and reenters the barrier (c', c''). The behaviour is similar in A^*, which also have a finite deterministic lifetime τ_A;

— while in A the collisions can excite the particle and inject it in the barrier through c'; the rate of excitation, normalized by the equilibrium number of particles A, is just the Transition State Theory constant K_{AB}^{TST};

— once the particle is introduced in (c', c''), the bound state A and B are considered to be absorbing, in conformity with the discussion in 2.2.

Despite its simplicity, this model includes some features that are not present in the purely classical descriptions by Smoluchowski or Kramers equations, such as a crude notion of a quantum state in the well. It assumes that classical mechanics applies on the barrier, which is certainly not true in general, but is an acceptable approximation for some reactions, such as, for example, butane isomerization. In any case, a realistic quantum treatment is out of the scope of the present paper.

Then, the rate constant is, by (26):

$$K_{AB} = \frac{1}{p_A^0} P(B|c', v) v p^0(c', v) = K_{AB}^{\mathrm{TST}} P(B|c', v) .$$

The probability to reach the bound state B starting from c' with positive velocity, can be found after some calculations [13,14], and one gets the exact formula:

$$\frac{K_{AB}^{\mathrm{TST}}}{K_{AB}} = \frac{1}{\exp(\lambda\tau)A - 1} + \frac{1}{\exp(\lambda\tau)B - 1} + \lambda\tau + 1 , \tag{29}$$

where λ is the collision frequency (supposed to be constant) and $\tau = (c'' - c)/v'$ is the time needed to cross the barrier in absence of collisions.

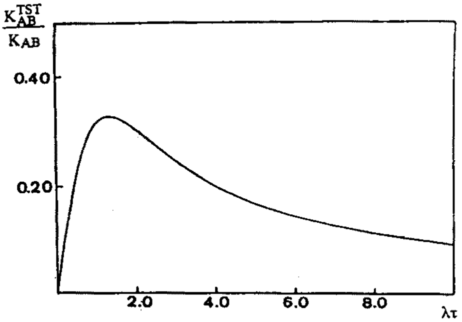

Fig. 4. Rate constant in function of noise frequency.

This result is a qualitatively correct (Fig. 4) for all values of the collision frequency λ, and it agrees with numerical simulations by Chandler [10] and Berne and coworkers [15]. The corresponding time-dependent problem can also be solved [13]. The model can be improved in number of ways, although an exact solution is generally not possible in more complicated cases: for instance, the constant velocity v can be replaced by a position dependent velocity; one can introduce continuous velocities, with randomization at each collision; one can also replace the motion on the barrier by an overdamped motion in a harmonic potential (Orstein–Uhlenbeck process). Complex reaction schemes can be studied [14], and random potentials can be considered [16]. This last point is one of the more interesting generalizations; in the next section it will be studied in details in the scope of the macroscopic theory.

3. Chemical kinetics in a fluctuating medium

We now consider chemical reaction on a *macroscopic level*: the system contains a large number of molecules of different species, and we want to study the evolution of the concentrations in time. Their deterministic behaviour is given by the laws of classical chemical kinetics; however, many internal or external factors can cause these concentrations to fluctuate around their deterministic value, and a stochastic description is needed.

This subject has been extensively studied and reviewed in papers and books during the last three decades [3,4,18,19]. Here we only address the problem of external noise in simple cases, before presenting new results on the stationary states that can appear due to fluctuating environment; then we show that the theory developed in the previous section applies and can provide the time scale of the noise induced transitions.

3.1. External noise with vanishing correlation time

Let us consider the chemical system

$$X + A \underset{\bar{k}}{\overset{k}{\rightleftarrows}} 2X\,, \tag{30a}$$

$$X \xrightarrow{k'} B\,, \tag{30b}$$

where the reaction constants are k, $\bar{k}$ and k' as indicated. We suppose that the concentrations a and b of A and B are kept constant by convenient flows of A and B, and that the medium remains homogeneous and in thermal equilibrium. Then, if the ordinary kinetic laws apply, the concentration x of X obeys the equation

$$\frac{dx}{dt} = (ka - k')x - \bar{k}x^2\,, \tag{31}$$

which can be solved easily.

However, concentration x experiences fluctuations around its macroscopic value due to internal factors such as the stochastic nature of the elementary reactive events, or due to external causes. We focus our attention on these external noises, which can be, for instance, small variations of the flow of molecules feeding the reactor, or fluctuations of the temperature due to imperfect monitoring.

The simplest way of implementing such external noises is to replace the deterministic kinetics equations like (31) by Langevin equations, which in one-dimension can be written

$$\frac{dx}{dt} = F(x) + G(x)\xi(t), \tag{32}$$

where x is the concentration of the variable reacting species (all other concentration being kept constant); $F(x)$ is a deterministic "reaction velocity" (for reactions (30) it is represented by the r.h.s. of (31)), and $G(x)\xi(t)$ stays for the external perturbation. $\xi(t)$ in general, is not precisely known, but it should be rapidly fluctuating, and by construction we have

$$\langle \xi(t) \rangle = 0\,, \tag{33a}$$

$$C(t) = \langle \xi(t_0)\xi(t_0 + t) \rangle = \langle \xi(0)\xi(t) \rangle\,. \tag{33b}$$

(ξ is homogeneous in time if external conditions do not change). Finally a proper choice of G permits to suppose that:

$$\tau = \int_{-\infty}^{+\infty} |t|C(t)dt\,. \tag{33c}$$

Furthermore we assume that when $t \to 0$, the correlation function $C(t)$ of the noise tends so rapidly to 0 that the correlation time $\tau = \int_{-\infty}^{+\infty} |t|C(t)dt$ is much smaller than the typical variation time of any quantity of interest. In these conditions two models of $\xi(t)$ have been widely used:

(i) either $\xi(t)$ is a *white noise* (so that $\tau = 0$) and the following forward Fokker–Planck equation holds for the probability $p(x,t)$ to measure concentration x at time t:

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}[F(x)p] + \frac{1}{2}\,\frac{\partial^2}{\partial x^2}[G^2(x)p]\,; \tag{34}$$

(ii) or $\xi(t)$ is a *coloured* noise, which means that $C(t)$ is not a Dirac function as supposed in *(i)*, but the correlation time τ is so small that $p(x,t)$ can be replaced by its limit when $\tau \to 0$. Then $p(x,t)$ approximately obeys the following Fokker–Planck equation [2,3]

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial t}\left[\left(F(x) + \tfrac{1}{2}G(x)G'(x)\right)p\right] + \frac{1}{2}\,\frac{\partial^2}{\partial x^2}[G^2(x)p]\,. \tag{35}$$

The first model correspond to an Ito stochastic differential equation, whereas the second one corresponds to a Stratonowich differential equation, and the difference between (34) and (35) can be important if the amplitude $G(x)$ of the noise term depends significantly on x. It is not always easy to choose the proper model for an actual phenomena; the question is discussed in details in Refs [1–3].

3.3. External noise on a system undergoing a Hopf bifurcation

Many examples of transitions induced by noises with vanishing correlation time can be found in Ref. [2]. As a non conventional case, we now study the influence of an external noise on a Hopf bifurcation [25]. Third order *chemical* systems have been extensively used in chemical kinetics to simulate autocatalytic reactions which can lead to spatio-temporal self-organization as well as to chemical chaos [18]. The following system, with the constant concentrations of A, D, E are constant:

$$A \rightarrow X\,, \tag{36}$$

$$B + X \rightleftarrows Y + D\,, \tag{37}$$

$$2X + Y \rightleftarrows 3X\,, \tag{38}$$

$$X \rightarrow E \tag{39}$$

can exhibit an oscillatory behaviour provided $B = B_c = 1+A^2$. By changing from the variables (x, y) (concentrations of X, Y), to a new set $(x', y') = (X - A, Y - B/A)$ and assuming $B = B_c + \epsilon$, the deterministic kinetic equations describing the reaction scheme (36)–(39) can be transformed into the simplest possible form for observing this behaviour, *i.e.*to their normal form. In polar coordinates (r, θ), the normal form for this system reads:

$$\frac{dr}{dt} = -\mu r - ar^3 \equiv F(r) \quad (a > 0)\,, \tag{40}$$

$$\frac{d\theta}{dt} = \Omega(r)\,, \tag{41}$$

where μ and a are constant parameters; and $\Omega(r)$ is given function of r. General considerations of (40)–(41) leads to the following conclusions:

(i) $r = 0$ is a stable stationary solution of (40) if $\mu > 0$, whereas it becomes unstable if $\mu < 0$; it corresponds to a *fixed point* x'_0, y'_0 of the system (x', y');

(ii) if $\mu < 0$, the stable stationary solution of (40) is

$$r = \rho = (-\mu/a)^{1/2}\,, \tag{42}$$

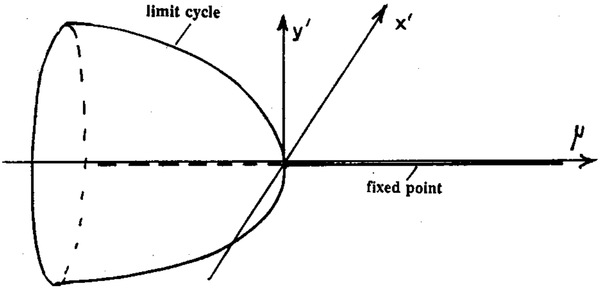

Fig. 5. Hopf bifurcation.

which corresponds to a *limit cycle* of the system (x', y') (see Fig. 5).

Let us now suppose that the parameter μ is subject to an external noise modelled as:

$$\mu = \bar{\mu} + \gamma\xi(t)\,, \tag{43}$$

$\xi(t)$ being a white noise. Equation (34) for the probability density is then

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial r}\Big[(\bar{\mu} r + a r^3)p\Big] + D\frac{\partial^2}{\partial r^2}(r^2 p)\,, \tag{44}$$

where the diffusion coefficient D is

$$D = \frac{\gamma^2}{2}\,. \tag{45}$$

The 0-current stationary solution is

$$p_0(r) \propto \frac{1}{r^2} r^{-\bar{\mu}/D} \exp\Big(-\frac{ar^2}{2D}\Big)\,, \tag{46}$$

which is normalizable in the (x', y') plane if

$$\int_0^\infty p_0(r) 2\pi r dr < \infty\,.$$

This is only true if $\bar{\mu} < 0$. In this case the radial density $q(r) = 2\pi r p_0(r)$ is infinite for $r = 0$ if $-D < \bar{\mu} < 0$, whereas it vanishes for $r = 0$ and is maximum for $r = \left|\frac{D+\bar{\mu}}{a}\right|^{1/2}$ when $\bar{\mu} < -D$.

When $\bar{\mu} = 0$ the only acceptable 0-current stationary solution of (45) is the Dirac distribution, which corresponds to the accumulation of "particles" at the fixed point.

Finally, when $\bar{\mu} > 0$, there is no normalizable 0-current stationary solution; however, one can find a normalizable stationary solution

$$p_1(r) = -\frac{J}{D} p_0(r) \int_0^r \frac{1}{r'^2 p_0(r')} dr' \tag{47}$$

corresponding to the stationary probability current J. This means that for the system to have a steady state, an external stationary flow of particles X crossing the reactor region is required. Naturally the continuous representation of the chemical content of the reactor is then inadaptable.

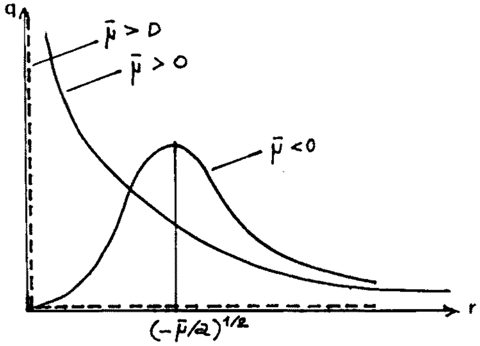

Fig. 6. Radial density for coloured noise with vanishing memory.

It is seen that there are now two-phase transitions (whereas these is only one deterministic), and that the radius of the stochastic limit cycle is $\left(\frac{-\bar{\mu}-D}{a}\right)^{1/2}$ instead of $\left(\frac{-\bar{\mu}}{a}\right)^{1/2}$ for the deterministic case. If, however, we model the fluctuations of μ as a *coloured noise* with vanishing correlation time (model *(ii)* of section 5.2) these conclusions still hold if $\bar{\mu}$ is replaced by $\bar{\mu} - D$ and the radius of the stochastic limit circle now coincides with the deterministic one (see Fig. 6).

It will be seen in the next section that noise with a finite correlation time can have much more serious effects.

3.5. Noises with a finite correlation time: random telegraph model

The time correlation of an external noise is caused by the memory of the environment, which does not change instantaneously. Thus the noise correlation time is often finite in a dense medium, because physical quantities do not diffuse very rapidly. A detailed analysis of the problem, which could permit to choose a relevant model, is generally difficult and phenomenological treatments are necessary: small noise expressions [3], small correlation times expressions [2], or generalized Langevin equations [21] can be used to address the problem.

Another possibility is to represent the noise as a *random telegraph* process [2,3]: it can take only two different values, the waiting time in each of them following an exponential law. This leads to models with a finite correlation time that can be exactly solved in some cases [22–24]. We now use this procedure for perturbing the chemical system (36)–(39) in the neighborhood of the Hopf bifurcation from a fixed point to a limit cycle described by equation (41).

We suppose that the parameter μ can take two values: $\mu_1 > 0$ and $\mu_2 < 0$; the waiting time T_α in μ_α $(\alpha = 1, 2)$ is independent of past events and is such that:

$$P(T_\alpha > \tau) = \mathrm{e}^{-\lambda_\alpha t}. \tag{48}$$

The coordinates of the system are then (r, θ, α) and the process is defined by the drift vector in space (r, θ) with components $(F(r, \mu_\alpha) - \Omega(r))$ corresponding to the deterministic equations (41), and by the transition rates λ_α corresponding to the jumps from μ_α to $\mu_{\bar{\alpha}}$ (where $\bar{\alpha}$ denotes the state which differs from α).

The probability density $p(r, \theta, \alpha, t)$ obeys the forward equation (34):

$$\begin{aligned}\frac{\partial}{\partial t} p(r, \theta, \alpha) = &- \frac{\partial}{\partial r}[F(r, \mu_\alpha) p(r, \theta, \alpha)] - \frac{\partial}{\partial \theta}[\Omega(r) p(r, \theta, \alpha)] \\ &+ \lambda_{\bar{\alpha}} p(r, \theta, \bar{\alpha}) - \lambda_\alpha p(r, \theta, \alpha),\end{aligned} \tag{49}$$

and the stationary solution reads:

$$p_0(r, \theta, \alpha) \equiv p_0(r, \alpha) \quad \frac{1}{|F(r, \mu_\alpha)|} \exp\left[- \sum_\alpha t_\alpha(r | r_0)\right], \tag{50}$$

with

$$F(r, \mu_\alpha) = -\mu_\alpha r - a r^3, \tag{51}$$

$$t_\alpha(r | r_0) = \int_{r_0}^{r} \frac{\lambda \alpha}{F(r, \mu_\alpha)} dr. \tag{52}$$

The stationary radial density is

$$q(r) = \sum_\alpha 2\pi r \, p_0(r, \alpha) \tag{53}$$

and it is normalizable if and only if

$$\sum_\alpha \lambda_\alpha / \mu_\alpha > -1. \tag{54}$$

A lot of phase transitions can occur. Taking $\lambda_1 = \lambda_2 = \lambda$ and writing

$$\bar{\mu} = \frac{\mu_1 + \mu_2}{2}$$

it can be shown that

(i) if $\bar{\mu} < 0$, $q(r)$ is always normalizable; for $\lambda > -2\mu_2$, $q = 0$ for $r = 0$, and $q \to \infty$ if $r \to (-\mu_2/\alpha)^{1/2} = \rho_2$; for $\lambda > -2\mu_2$, $q = 0$ for $r = 0$ and $r = \rho_2$, and q is maximum for $r = (-\bar{\mu}/a)^{1/2} \equiv \bar{\rho}$ (see Fig. 7); then both deterministic attractors are destroyed, and a new limit cycle with mean radius $\bar{\rho}$ is built up due to the noise.

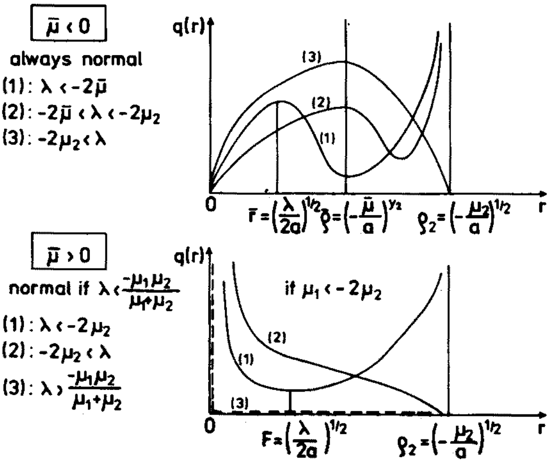

Fig. 7. Stationary radial density q for random telegraph noise.

(ii) if $\bar{\mu} > 0$, for $\lambda < -2\mu_2$, q is infinite at $r = 0$ and $r = \rho_2$, which means that both deterministic attractors exist; for $-2\mu_2 < \lambda < -\mu_1\mu_2/(\mu_1 + \mu_2)$, q is infinite at $r = 0$ and $q = 0$ at $r = 0$: only the fixed point subsists; finally, for $\lambda > -\mu_1\mu_2/(\mu_1 + \mu_2)$, q is not normalizable, which indicates that the system coalesces at the fixed point. The phase diagram, shown in Fig. 8 is complex.

It is seen that the behaviour of the system is quite different from its behaviour in the case of a noise with vanishing correlation time, studied in section 3.4. However, as expected, some similarity appears when comparing with the limit of a coloured noise (model *(ii)* of section 3.2): the deterministic fixed point is preserved when $\bar{\mu} > 0$, but disappears when $\bar{\mu} < 0$, $\bar{\mu}$ being the average value of the parameter μ. Furthermore, in the random telegraph model, the particles coalesce at the fixed point (unnormalizable

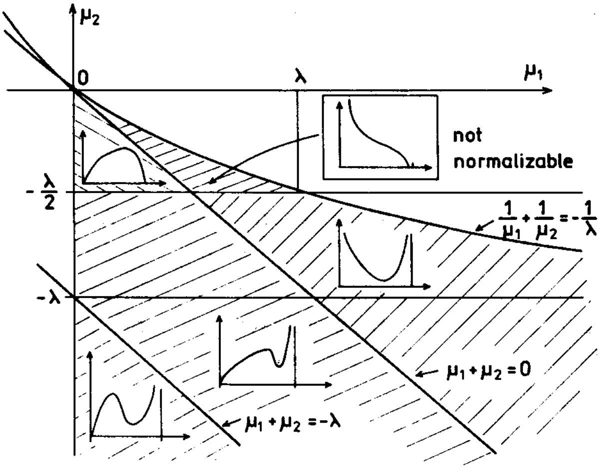

Fig. 8. Phase diagram of bifurcations for random telegraph noise.

$q(r)$) when

$$\lambda > -\frac{\mu_1\mu_2}{\mu_1+\mu_2} = \frac{\chi^2-\bar{\mu}^2}{2\mu}, \tag{55}$$

with $\chi = \mu_1\mu_2/2$, or

$$\bar{\mu}^2 > \frac{\chi^2}{2\lambda} - \frac{\bar{\mu}^2}{2\lambda}, \tag{55'}$$

If $\lambda \to \infty$ and $\chi \to \infty$, with $\chi^2/2\lambda = D$, diffusion coefficient, (55′) agrees with the corresponding condition in section 3.3.

The last point is to characterize the time scale of possible transitions. The formalism developed for defining the rate constant in section (2.4) can be applied for this purpose. Let us suppose, for instance, that the system is in the neighborhood of the fixed point at time 0. Then a random telegraph noise is switched on between the values $\mu_1 > 0$ and $\mu_2 < 0$ of the parameter, in such a way that $\bar{\mu} < 0$, with $-2\mu_2 < \lambda$ (see Fig. 7). The fixed point disappears and the new attractor is the limit cycle radius with $\rho_2 = (-\mu_2/a)^{1/2}$, the stationary probability density $q(r)$ being infinite there. Let us imagine a small circle with radius r_1, and a large circle with radius $r_2 < \rho_2$, both centered on 0: the interior of the first one will be the "reactant" region A, the exterior of the second one will be the "product" region B. Applied to this case, the general definition (28) gives for the rate constant K_{AB}:

$$K_{AB} = \frac{2\pi r_1 p(r_1,2)\cdot F(r_1,2)}{\int_0^{r_1} dr \sum_\alpha 2\pi r p(r,\alpha)} \cdot P(B|r_1,2), \tag{56}$$

where $P(B|r_1, 2)$ is the probability to reach region B before returning to A, starting from r_1 with value μ_2 of the parameter.

Naturally, k_{AB} in principle depends on r_1 and r_2. However, in the given conditions it can be shown [26] that expression (54) tends to a finite limit, independent of r_2, when $r_1 \to 0$:

$$K_{AB} \to \frac{1 + \lambda(1/\mu_1 + 1/\mu_2)}{1/\mu_1 + 1/|\mu_2|}(1 + \mu_1/\mu_2)\,, \tag{57}$$

which, if $\lambda \to \infty$, $\chi \to \infty$ and $\chi^2/2\lambda = D$, gives

$$K_{AB} = -\bar{\mu}(1 - \bar{\mu}/D) > 0\,. \tag{58}$$

The limit (57) does not exist always. Sometimes a saddle point approximation may be used [26] to show that the result given by (56) does not depend strongly on r_1 and r_2. In any case, it is interesting and useful to notice that the microscopic theory of rate constants can be profitably applied for these macroscopic rate processes.

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