Microscopic Chaos and Chemical Reactions

Pierre Gaspard

Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles,
Campus Plaine, Code Postal 231, B-1050 Brussels, Belgium

Microscopic chaos is the dynamical randomness in the collisional motion of atoms and molecules in fluids. This chaos animates different mesoscopic stochastic phenomena and, in particular, the reaction-diffusion processes. For different chemical reactions, we show how the reaction rate can be related to the characteristic quantities of chaos like the Lyapunov exponents and the Kolmogorov-Sinai entropy which are associated with a fractal repeller. In spatially extended deterministic chaotic systems, chemio-hydrodynamic modes with exponential decay are shown to exist as Schwartz-type distributions associated with Pollicott-Ruelle resonances. The problem of entropy production is also discussed.

I. INTRODUCTION

Today, macroscopic chaos has become a well-known phenomenon observed in many systems from fluid mechanics [1] and laser optics [2] to neurophysiology [3, 4], including the famous Belousov-Zhabotinskii autocatalytic chemical reaction [5], gas-phase reactions [6], and the indium/ thiocyanate electrochemical oscillator [7]. These chaotic systems are characterized by a sensitivity to initial conditions. This dynamical instability generates a dynamical randomness on long time scales in the evolution of the macroscopic variables which are the amplitudes of the collective modes of the chemio-hydrodynamics. This macroscopic dynamics is in general dissipative in contrast to the microscopic motion of the atoms and molecules composing the macrosystem. Indeed, this microscopic motion is described in terms of the Hamiltonian dynamics, which is unitary in the quantum Hilbert space or volume-preserving in the classical phase space of all the microscopic variables and which is moreover time-reversal symmetric.

Recent numerical simulations have shown that the motion of the atoms and molecules is itself classically chaotic, but on a much shorter time scale than in macroscopic chaos [8–10]. In the microdynamics, the sensitivity to initial conditions is due to the defocusing character of the collisions between the particles. This dynamical instability results into a dynamical randomness which is at the origin of the fluctuations observed in many noises and other stochastic processes like Brownian motion, in particular.

Experimental evidence for this microscopic chaos has very recently been provided in the observation of Brownian motion, which has shown that the system composed of the Brownian particle and of the surrounding fluid has a positive Kolmogorov-Sinai entropy per unit time [11]. This result gives a support to the chaotic hypothesis proposed by Gallavotti and Cohen [12] that the nonequilibrium systems can be modelled by Anosov-type dynamical systems with positive Lyapunov exponents.

The purpose of the present contribution is to study the application of the hypothesis of microscopic chaos to reactive systems. Indeed, the reactive processes are of great importance in the time evolution of many physico-chemical systems like in biochemistry, in chemical kinetics and, especially, in the catalytic steps of chemical synthesis, but also in the high-energy processes of nuclear physics and of astrophysics such as, for instance, in the nucleosynthesis of the elements in the stars.

In chemical reactive systems, the microscopic dynamics is in principle described by a Hamiltonian system of equations for the motion of the nuclei evolving in the force field created by the fast electrons, in the adiabatic approximation. Beyond the adiabatic approximation, the electronic degrees of freedom must also be included. On the other hand, the reactive systems are described at the macroscopic level by the phenomenological equations established, notably, by the mass action law [13]. Since Smoluchowski's pioneering work on diffusion-controlled reactions [14], mesoscopic descriptions have been introduced in terms of stochastic models like the master-equation approach developed by Nicolis and coworkers [15]. This approach is based on the recognition that the microscopic motion of the nuclei is irregular like in Brownian motion and generates stochasticity at the mesoscopic level, in particular, in the time evolution of the numbers of the particles of each chemical species in small subvolumes of the system. This stochastic assumption finds today a support in the discovery that the microdynamics of the molecular degrees of freedom composing the reactive systems is typically chaotic.

In fact, theoretical tools can be introduced in order to compare quantitatively the dynamical randomness in deterministic chaos and in stochastic processes [16, 17]. Moreover, in several deterministic systems, the reaction rate can be related to the characteristic quantities of chaos like the Lyapunov exponents, the Kolmogorov-Sinai (KS) entropy

as well as the fractal dimensions [17, 18]. Besides, simple chaotic models have been proposed in order to illustrate and test the theories [17, 19].

This paper is organized as follows. In Sec. II, we present the main theoretical tools which can be subdivided in three sets: (a) the dynamical entropies; (b) the escape-rate formula; (c) the Frobenius-Perron operator and its spectral properties like the Zeta function and the Pollicott-Ruelle resonances. In Sec. III, these theoretical tools are applied to several classes of reactive systems supposed to be described by simple classical dynamics: (a) unimolecular reactions in isolated molecules; (b) isomerisations in many-particle systems; (c) heterogeneous catalysis. Conclusions are drawn in Sec. IV.

II. THE CHARACTERIZATION OF MICROSCOPIC CHAOS

A. Dynamical Randomness and the Entropies per Unit Time

The dynamical instability in the motion of the atoms and molecules is characterized by the spectrum of Lyapunov exponents $\{\lambda_i\}$ which are the rates of exponential separation between a reference trajectory and infinitesimally perturbed trajectories in the phase space of the positions and momenta of all the nuclei of the reactive system [20].

On the other hand, dynamical randomness is characterized by the entropy per unit time which is the rate of decrease of n-time probabilities for the trajectory to visit different cells ω_n of phase space at successive times $t_n = n\Delta t$

$$p(\omega_0 \omega_1 \cdots \omega_{n-1}) \ \sim \ \exp[-n\Delta t \ h(\mathcal{P})] \ , \tag{1}$$

where $\mathcal{P}$ denotes the partition into the different cells and $h(\mathcal{P})$ is the entropy per unit time of the partition $\mathcal{P}$ [17]. The property (1) is known as the Shannon-McMillan-Breiman theorem which holds in ergodic systems.

In a deterministic dynamical system, the supremum over all the possible partitions exists and defines the KS entropy per unit time [20]

$$h_{\mathrm{KS}} \ = \ \mathrm{Sup}_{\mathcal{P}} \ h(\mathcal{P}) \ . \tag{2}$$

If the system is closed, the dynamical randomness is entirely generated by the dynamical instability of the classical motion and the KS entropy is equal to the sum of positive Lyapunov exponents which is the well-known Pesin formula [20]

$$h_{\mathrm{KS}} \ = \ \sum_{\lambda_i > 0} \lambda_i \ . \tag{3}$$

Different stochastic descriptions can be introduced for a given deterministic system. Some variables among the set of all the microscopic variables can be selected which are for instance the positions of a Brownian particle moving in a surrounding fluid or the coordinate allowing the distinction between two isomers. In some limits which have been discussed in the literature [21], these variables may obey a stochastic differential equation of Langevin type while the associated probability density evolves according to a Fokker-Planck equation. These processes are time and variable continuous.

Other stochastic descriptions can be set up by introducing variables like the number of particles of the chemical species in some subvolumes of the tridimensional physical space. Such variables can be defined in terms of functions over the phase space which are for instance the indicator functions of some regions of phase space. In some limits, these observables may follow a birth-and-death process which is time continuous and variable discrete [15]. The probability of such a process evolves according to a Pauli-type master equation.

We should here also mention the lattice gas automata which have been applied to the modelling of reactive systems, in which the positions and velocities of the particles are assumed to take discrete values [22]. These systems belong to the class of Markov chains which are time and variable discrete.

The dynamical randomness of these stochastic processes can be characterized by precisely the same concept of entropy per unit time as for the underlying deterministic system. If the stochastic model is faithful on the scale of the partition $\mathcal{P}$, we should expect that the n-time probabilities (1) predicted by the stochastic model be approximately equal to those calculated from the deterministic equations and, therefore, that the respective entropies $h_{\mathrm{stoch.}}(\mathcal{P})$ and $h_{\mathrm{exact}}(\mathcal{P})$ be approximately equal. Nevertheless, since the stochastic model does not provide a complete description some differences should appear between these entropies for certain partitions. Actually, important differences appear in the limit of fine partitions. Indeed, if the entropy of the deterministic dynamics saturates in general at the KS value (2), on the other hand, the entropy of the stochastic models continues to grow indefinitely in a way which characterizes the stochastic process [16]. When the partition $\mathcal{P}$ is performed into cells of size ϵ, the entropy $h(\mathcal{P})$

defines a so-called ϵ-entropy, as discussed in the literature [16, 17]. We also notice that the n-time probabilities (1) are related to the other n-time probabilities introduced in the work by Onsager and Machlup [23]. In this regard, the entropy $h(\mathcal{P})$ and the related ϵ-entropies could be calculated using the methods developed by Onsager and Machlup for Gaussian stochastic processes.

If a reactive system like the chaotic Belousov-Zhabotinskii reaction [5] is observed with finer and finer partitions, different scaling behaviours would be measured for the entropy $h(\mathcal{P})$. For coarse macroscopic partitions, a plateau at the value of the KS entropy of macroscopic chaos would appear. For finer mesoscopic partitions resolving the thermodynamic fluctuations, an intermediate scaling would be observed in which the entropy would in general grow in a way characterizing the stochastic process of the fluctuations. For microscopic partitions, the deterministic microdynamics of the nuclei would be revealed and the entropy would saturate at the KS value of the microscopic chaos. However, the stochastic models would predict an indefinite growth which is incompatible with the underlying deterministic microdynamics [17, 24].

After this general discussion about dynamical randomness in nonequilibrium statistical mechanics, we turn to the presentation of the escape-rate formalism and the theory of the Frobenius-Perron operator, in both of which reaction rates can be defined rigorously.

B. Escape-Rate Formalism

Open systems have very often been considered in reactive systems, for instance, in the Kramers problem of the escape above a potential barrier [25]. A first-passage problem can be set up by introducing an absorbing boundary in phase space and by counting the number of trajectories still meandering in the region surrounded by the absorbing boundary as a function of time [18, 26–28]. In many systems such as the hyperbolic deterministic systems, the Langevin stochastic systems, the birth-and-death processes and the Markov chains, this number of trajectories decays exponentially and an escape rate can be defined [17]. In the phase space, the never-escaping trajectories form a fractal object which is called the *repeller* [29]. The escape rate γ of the repeller can be related to its Lyapunov exponents and its KS entropy by the formula [20, 30]

$$\gamma = \sum_{\lambda_i > 0} \lambda_i - h_{\text{KS}} . \tag{4}$$

For closed systems with no escape, the escape rate vanishes and Eq. (4) reduces to Pesin's formula (3). Moreover, the repeller is also characterized by its fractal dimensions which can also be expressed, in particular, for two-degree-of-freedom systems in terms of the KS entropy and the positive Lyapunov exponent [26].

The variety of different first-passage problems leads to a variety of possible repellers in different systems. In particular, first-passage problems can be defined for each irreversible process in terms of its associated Helfand moment [27]. In this way, connections can be established between the irreversible coefficients and the characteristic quantities of chaos. In Sec. III, we shall explicitly carry out such a connection for the reaction rate of isomerization.

C. Frobenius-Perron Operator and its Spectral Properties

Out of equilibrium, we have to consider ensembles of trajectories described by probability measures which differ from the equilibrium probability measure. The nonequilibrium measures are not always stationary and their density $p(\mathbf{X}, t)$ evolves in time according to the Frobenius-Perron operator which is the time integral of the well-known Liouville operator [31, 32]

$$p(\mathbf{X}, t) = \hat{P}^t p(\mathbf{X}, 0) = \int d\mathbf{X}_0 \, p(\mathbf{X}_0, 0) \, \delta(\Phi^t \mathbf{X}_0 - \mathbf{X}) , \tag{5}$$

where Φ^t denotes the flow generated by the deterministic mechanical system in phase space.

Recent works have shown how relaxation processes can be characterized in terms of the Pollicott-Ruelle resonances of the Frobenius-Perron operator [33]. These resonances are generalizations to the deterministic systems of the eigenvalues of a Fokker-Planck operator or of the transition matrix of a Markov chain and, therefore, they provide the rates of relaxation of the system. We remark that the Pollicott-Ruelle resonances can also be calculated as the zeros of a so-called Zeta function which is defined as a product over all the unstable periodic orbits [34, 35]. The Frobenius-Perron method has been applied to diffusion in spatially extended systems like the multibaker map and the periodic Lorentz gas where the dispersion relation of the diffusive hydrodynamic eigenmode can be obtained as a Pollicott-Ruelle resonance [19, 36].

In reactive systems, a proper physical interpretation of the Pollicott-Ruelle resonances and of the associated eigenmodes allows us to identify the chemical reaction rate, as shown in Sec. III.

III. CHAOS IN REACTIVE SYSTEMS

A. Unimolecular Reactions

Unimolecular reactions can occur in isolated molecules which have been energetically excited, for instance, by light absorption. This excitation of the molecule may result into a dissociation in several molecular fragments. Such a photodissociation is characterized by the evolution of the population of excited molecules as a function of time. This population typically presents a complicated decay which may be multiexponential [37, 38]. As far as the decay can be described by classical mechanics, the motion of the nuclei of the dissociating molecule is typically chaotic and can be characterized by the theoretical tools presented in Sec. II. The Frobenius-Perron operator here depends on the total energy of the excited molecule so that each characteristic quantity also depends on energy. The different exponential decay rates can in principle be associated with the Pollicott-Ruelle resonances. The slowest decay rate defines the escape rate which can be related to the Lyapunov exponent and the KS entropy of the fractal repeller (when it exists) according to Eq. (4). Therefore, the escape rate can here be identified with the smallest unimolecular reaction rate [39].

We notice that the dependence on energy of the reaction rates can be estimated in many-degree-of-freedom systems thanks to the RRKM theory [40]. In systems with few degrees of freedom, a more precise determination of the classical reaction rates have been obtained thanks to the Frobenius-Perron and periodic-orbit methods in the disk scatterers [35, 39] as well as in models of HgI_2 and CO_2 [41].

B. Isomerizations in Many-Particle Systems

Let us consider a many-particle system where takes place the isomerization between the two states or colors,

$$A \rightleftharpoons B \,, \tag{6}$$

of some molecules in solution in an inert fluid. The total number of molecules in both states is conserved $N_A + N_B = N$. Under the condition that the isomerization can be described by a birth-and-death process, the probability $P(N_A)$ that the system contains N_A molecules in the state A obeys the following master equation [15]

$$
\begin{aligned}
\frac{d}{dt}P(N_A) \;=\; & \kappa_+(N_A+1)\,P(N_A+1) \;+\; \kappa_-(N-N_A+1)\,P(N_A-1) \\
& -\; \kappa_+ N_A\,P(N_A) \;-\; \kappa_-(N-N_A)\,P(N_A) \,,
\end{aligned}
\tag{7}
$$

where $\kappa_\pm$ are the forward and backward reaction rates. If $a = N_A/N$ is the fraction of molecules in the state A, the master equation reduces to a Fokker-Planck equation in the large-system limit $N \to \infty$

$$\frac{\partial p}{\partial t} \;+\; \frac{\partial}{\partial a}\left\{ \left[\kappa_- - (\kappa_+ + \kappa_-)a\right]p \right\} \;=\; \frac{\kappa_+\kappa_-}{N(\kappa_+ + \kappa_-)}\,\frac{\partial^2 p}{\partial a^2}\,, \tag{8}$$

for the probability density $p(a) = P(N_A)$ [42]. As a consequence, we may infer that the fraction a is a fluctuating variable which follows an Ornstein-Uhlenbeck process around its average equilibrium value $a_{eq} = 1/2$.

A first-passage problem can be defined by requiring that this fluctuating variable remains in the interval

$$\mathcal{R}_{N,\xi} \;:\; \qquad -\frac{\xi}{2} \;\leq\; a - \frac{1}{2} \;\leq\; +\frac{\xi}{2}\,. \tag{9}$$

In the phase space of the microdynamics, the trajectories for which the fraction a never escapes out of the interval (9) form a fractal repeller composed of highly unstable trajectories if the motion is chaotic. This repeller is characterized by its escape rate, its positive Lyapunov exponents, and its KS entropy, which satisfy Eq. (4).

On the other hand, the Fokker-Planck equation (8) allows us to obtain an estimation of this escape rate in terms of the reaction rates in the limit where ξ is small with respect to the amplitude of the equilibrium fluctuations. In this limit, the diffusive term dominates in the equation and the escape rate is approximately given by

$$\gamma \;\simeq\; \frac{\kappa_+\kappa_-}{N(\kappa_+ + \kappa_-)}\left(\frac{\pi}{\xi}\right)^2\,. \tag{10}$$

Assuming that both reaction rates are equal $\kappa = \kappa_+ = \kappa_-$ and replacing Eq. (10) into Eq. (4), we obtain the reaction rate in terms of the chaotic properties of the repeller as

$$\kappa = \lim_{N,\xi \to \infty} 2N \left(\frac{\xi}{\pi}\right)^2 \left(\sum_{\lambda_i > 0} \lambda_i - h_{\mathrm{KS}}\right)_{\mathcal{R}_{N,\xi}} . \tag{11}$$

The conditions of validity of such a relationship are that the microdynamics is chaotic and that the chemical reaction is well described by the master equation (7).

C. Heterogeneous Catalysis

Further connections between reaction rates and chaotic properties can be obtained by studying the spectral properties of the Frobenius-Perron operator, which gives all the relaxation rates of the reactive system.

1. Reactive Lorentz Gas

Here, we consider Lorentz-type models of reaction in which a point particle carrying a color A or B undergoes elastic collisions on fixed disks, some of which are catalysts and induce an instantaneous change of color at the collision [17, 43]. The catalytic disks may form a superlattice over the disk lattice. By its periodicity, the dynamics of this spatially extended system can be reduced to the dynamics inside a single cell of the superlattice. Moreover, the flow can be reduced to a Poincaré-Birkhoff map ruling the dynamics from collision to collision. Let us denote by $\mathbf{x} = (r, v)$ the Birkhoff coordinates which are the perimeter coordinate r and the velocity v parallel to the disk at each impact point. The sign $c = \pm 1$ gives the color A or B of the particle. t_n is the time of the nth collision and $\mathbf{l}_n$ gives the cell of the superlattice $\mathcal{L}$, which the particle visits at the time t_n. The mapping of the reactive Lorentz gas is thus

$$\begin{cases} \mathbf{x}_{n+1} = \varphi(\mathbf{x}_n) , \\ t_{n+1} = t_n + T(\mathbf{x}_n) , \\ \mathbf{l}_{n+1} = \mathbf{l}_n + \mathbf{a}(\mathbf{x}_n) , \\ c_{n+1} = \varepsilon(\mathbf{x}_n) \, c_n , \end{cases} \tag{12}$$

where $\varphi(\mathbf{x})$ is the Poincaré-Birkhoff map itself; $T(\mathbf{x})$ is the ceiling or first-return time function; $\mathbf{a}(\mathbf{x})$ is a vector giving the jump carried out on the superlattice during the free flight from $\mathbf{x}_n$ to $\mathbf{x}_{n+1}$; and

$$\varepsilon(\mathbf{x}) = \begin{cases} -1 \text{ if } \mathbf{x} \in \varphi^{-1}(\mathcal{D}_{\mathrm{r}}) , \\ \\ +1 \text{ otherwise} , \end{cases} \tag{13}$$

where $\mathcal{D}_{\mathrm{r}}$ is the reactive domain inside the domain $\mathcal{D}$ of definition of the Poincaré-Birkhoff map. Thanks to this map, a suspended flow can be defined which gives the current position and state of the particle in terms of the coordinates $(\mathbf{x}, \tau, \mathbf{l}, c)$ where $\mathbf{x} \in \mathcal{D}$, $0 \le \tau < T(\mathbf{x})$, $\mathbf{l} \in \mathcal{L}$, and $c = \pm 1$ [17, 36].

The particle density in phase space, $p(\mathbf{x}, \tau, \mathbf{l}, c)$, evolves in time under a Frobenius-Perron operator $\hat{P}^t$. A Fourier transform in space allows us to define the components of this density corresponding to a given wavenumber $\mathbf{k}$. Because of the periodicity of the system, the time evolution acts separately on each of the components [36]. Furthermore, a Laplace transform in time reduces the Frobenius-Perron operator of the flow to an operator associated with the map (12) and which incorporates the decay rate s introduced by the Laplace transform [17, 33]. If we define the total particle density and the difference of particle densities as

$$f(\mathbf{x}) = \tilde{p}(\mathbf{x}, +) + \tilde{p}(\mathbf{x}, -) , \tag{14}$$
$$g(\mathbf{x}) = \tilde{p}(\mathbf{x}, +) - \tilde{p}(\mathbf{x}, -) , \tag{15}$$

in terms of the probability densities $\tilde{p}(\mathbf{x}, \pm)$ of the map (12), we observe the decoupling between the time evolutions of the functions f and g which are governed by the respective operators:

diffusion :
$$(\hat{V}_{\mathbf{k},s} f)(\mathbf{x}) = \exp\left[-sT(\varphi^{-1}\mathbf{x}) - i\mathbf{k} \cdot \mathbf{a}(\varphi^{-1}\mathbf{x})\right] f(\varphi^{-1}\mathbf{x}) , \tag{16}$$

reaction :
$$(\hat{W}_{\mathbf{k},s} g)(\mathbf{x}) = \varepsilon(\varphi^{-1}\mathbf{x}) \, \exp\left[-sT(\varphi^{-1}\mathbf{x}) - i\mathbf{k} \cdot \mathbf{a}(\varphi^{-1}\mathbf{x})\right] g(\varphi^{-1}\mathbf{x}) . \tag{17}$$

The operator (16) controlling the diffusive motion of the total particle density has already been studied elsewhere [36]. Its Pollicott-Ruelle resonances are functions of the wavenumber $\mathbf{k}$ and the leading resonance provides the dispersion relation of the diffusive eigenmodes of relaxation [17, 36].

The new operator (17) is associated with the reactive dynamics. Its Pollicott-Ruelle resonances provides the relaxation rates of the reactive eigenmodes. The Fredholm determinant of this operator defines a Selberg-Smale Zeta function which is given for symplectic-type systems by

$$
\begin{aligned}
Z(s;\mathbf{k}) &\equiv \mathrm{Det}\big(\hat{I} - \hat{W}_{\mathbf{k},s}\big) \\
&= \prod_p \prod_{m_1 \cdots m_u=0}^{\infty} \left[1 - \frac{\varepsilon_p \exp\big(-sT_p - i\mathbf{k}\cdot\mathbf{a}_p\big)}{|\Lambda_p^{(1)}\cdots\Lambda_p^{(u)}||\Lambda_p^{(1)m_1}\cdots\Lambda_p^{(u)m_u}|} \right]^{(m_1+1)\cdots(m_u+1)} .
\end{aligned}
\tag{18}
$$

We have here assumed for definiteness that all the periodic orbits are unstable of hyperbolic type with real stability eigenvalues $|\Lambda_p^{(i)}| > 1$ for the n_p^{th} iteration of the Poincaré-Birkhoff map linearized at the periodic orbit p. n_p is the bounce period of the periodic orbit while T_p is its continuous-time period. $\mathbf{a}_p$ is the displacement of the particle on the superlattice and $\varepsilon_p = \prod_{j=0}^{n_p-1} \varepsilon(\varphi^j \mathbf{x}_p) = \pm 1$ is the net change of color during a period, where $\mathbf{x}_p$ is a point of the periodic orbit.

The zeros of the Zeta function (18) in the half complex plane Re $s < 0$ gives the relaxation rates $s(\mathbf{k})$ as functions of the wavenumber $\mathbf{k}$. The spectral gap between $s = 0$ and the leading zero gives an estimation of the relaxation rate of the reactive system and, thus, a lower bound on the reaction rate.

2. Reactive Multibaker Map

The complicated Poincaré-Birkhoff map of the Lorentz gas can be caricatured by a baker-type map, leading to the one-dimensional discrete-time model

$$
\Phi(x,y,l,c) = \begin{cases} \left(2x, \frac{y}{2}, l-1, c'\right), & 0 \leq x \leq \frac{1}{2}, \\[2mm] \left(2x-1, \frac{y+1}{2}, l+1, c'\right), & \frac{1}{2} < x \leq 1, \end{cases}
\tag{19}
$$

where $c' = -c$ if $l = 0, \pm L, \pm 2L, \ldots$ and $c' = c$ otherwise, recently proposed by Gaspard and Klages [43] who derived its reactive evolution operator

$$
(g_{t+1})(x,y,l) = (\hat{R}_k\, g_t)(x,y,l) .
\tag{20}
$$

The Pollicott-Ruelle resonances and the associated eigenmodes of relaxation can be obtained by the eigenvalue problem

$$
(\hat{R}_k\psi)(x,y,l) = \chi(k)\, \psi(x,y,l), \qquad \text{with} \quad \chi(k) = \exp\, s(k) .
\tag{21}
$$

Since the eigenstates are expected to be uniform along the unstable direction but Schwartz distributions along the stable direction [17], their cumulative functions are assumed to be linear in the unstable x direction

$$
\Psi(x,y,l) \equiv \int_0^x dx' \int_0^y dy'\, \psi(x',y',l) = x\, C(y,l) .
\tag{22}
$$

The coefficients $C(y = 1, l)$ have been shown to be solutions of the eigenvalue problem of an $L \times L$ matrix [43]. Supposing that the eigenvectors of this matrix are of the form $\exp(\pm i\theta l)$, the equation for the eigenvalues can be expressed in terms of the parameter θ as

$$
\sin\theta\,(\cos kL - \cos\theta L) + 2\cos\theta\,\sin\theta L = 0, \quad \text{with} \quad \chi = \cos\theta .
\tag{23}
$$

Two cases arise whenever L is even or odd. We shall here summarize the situation for the case where L is odd. Moreover, the systems with $L \leq 4$ present peculiarities so that we suppose that $L \geq 5$.

When L is odd, there are two leading eigenvalues, one positive χ_+ and one negative χ_-, which are related by the symmetry: $\chi_+(k) = -\chi_-(-k + \pi/L)$. The absolute values of these eigenvalues vary between the extreme values reached, for instance, at

$$
k = 0 : \begin{cases} \chi_+ = \cos\left[\frac{\pi}{L-1} + \frac{\pi^3}{4(L-1)^4} + \frac{\pi^5}{16(L-1)^6} + \frac{3\pi^5}{16(L-1)^7} + \cdots\right], \\[3mm] \chi_- = -\cos\frac{\pi}{L} . \end{cases}
\tag{24}
$$

It turns out that only the eigenvector associated with the positive eigenvalue χ_+ contributes to the color autocorrelation function which decays at long times like

$$\langle c(0)c(t)\rangle \sim (\chi_+)^t \,, \tag{25}$$

even in the case where $|\chi_-| > |\chi_+|$. Therefore, the chemical reaction rate should here be identified as

$$\kappa = -\frac{1}{2}\, s_+(k=0) = -\frac{1}{2}\,\ln \chi_+(k=0) = \frac{\pi^2}{4L^2} + \mathcal{O}(L^{-3})\,. \tag{26}$$

On the other hand, the value

$$\kappa_{\mathrm{gap}} = -\frac{1}{2}\,\ln \mathrm{Max}\Big\{|\chi_+(k=0)|, |\chi_-(k=0)|\Big\} = \frac{\pi^2}{4L^2} + \mathcal{O}(L^{-4})\,, \tag{27}$$

which is the spectral gap of the reactive evolution operator, only provides a lower bound on the actual reaction rate κ [44]. Nevertheless, both values have the same leading asymptotic behaviour $\kappa \simeq \kappa_{\mathrm{gap}} \simeq \pi^2/(4L^2)$. This decrease of the reaction rate as $1/L^2$ where L is the distance between the catalysts is the signature of a one-dimensional diffusion-controlled reaction [14]. This is expected because the motion under the multibaker map is diffusive between the catalytic sites while the reaction occurs with unit probability as soon as a catalytic site is reached.

We may wonder which macroscopic equation would best correspond to the previous behaviour. In Ref. [43], it was proposed to directly use the dispersion relations to infer the macroscopic equations. However, these equations present cross-diffusive terms which have their origin in the fact that, on the largest spatial scales $l \gg L$, the density difference does not have a normal diffusive behaviour because of the changes of color at the catalytic sites.

Instead a local description on intermediate spatial scales, $1 \ll l \ll L$, can be provided by the following equations for the color densities, ρ_A and ρ_B,

$$\partial_t\, \rho_A = D\,\nabla^2 \rho_A - \kappa L \sum_{n=-\infty}^{+\infty} \delta(l-nL)\,(\rho_A-\rho_B)\,, \tag{28}$$

$$\partial_t\, \rho_B = D\,\nabla^2 \rho_B + \kappa L \sum_{n=-\infty}^{+\infty} \delta(l-nL)\,(\rho_A-\rho_B)\,, \tag{29}$$

as already proposed to model heterogeneous catalysis [15, 45]. In the local description, there is no cross-diffusive term because the colors normally diffuse with the diffusion coefficient $D = 1/2$ of the multibaker between the catalytic sites at $l = nL$. A further advantage of these equations is that the entropy production can be shown to be positive

$$\begin{aligned}
\frac{d_i S}{dt} =\ & \int D\left[\frac{(\nabla\rho_A)^2}{\rho_A} + \frac{(\nabla\rho_B)^2}{\rho_B}\right]dl \\
& + \kappa L \sum_{n=-\infty}^{+\infty}\left[(\rho_A-\rho_B)\ln\frac{\rho_A}{\rho_B}\right]_{l=nL} \geq 0\,,
\end{aligned} \tag{30}$$

for the standard expression of the entropy

$$S = \int\left(\rho_A\,\ln\frac{\rho_A^0}{\rho_A} + \rho_B\,\ln\frac{\rho_B^0}{\rho_B}\right)dl\,. \tag{31}$$

We should here emphasize that the deterministic multibaker map is area-preserving and time-reversal symmetric. It is therefore a priori surprising that irreversible properties like the diffusion and reaction-rate coefficients can be defined for such a model. As we mentioned, these irreversible coefficients are defined as Pollicott-Ruelle resonances, which describe exponential-type behaviours in the decay of the correlation functions. These resonances exist only as generalized eigenvalues of the evolution operator in the sense that the associated eigenstates are not functions but Schwartz distributions defined in the phase space [17, 36, 43]. It is the singular character of the eigenstates which opens the possibility of their exponential-type relaxation in spite of the area-preserving property of the map. Besides, a Pollicott-Ruelle resonance is only defined for either the forward or the backward semigroups of the time evolution. For the forward semigroup, the associated eigenstate is smooth along the unstable directions in phase space although singular along the stable directions, and vice versa for the backward semigroup. This singular character of the eigenstates along some privileged directions creates an inequivalence between the spectral decompositions of both

semigroups, which can be shortly referred to as a breaking of the time-reversal symmetry. This symmetry breaking does not preclude the existence of the time-reversed dynamics which always exists because the system is time-reversal symmetric, but it limits the use of the forward semigroup to strictly positive times, forbidding its extrapolation to negative times. An important remark is that the symmetry breaking is induced by the dynamical instability of the microdynamics.

IV. CONCLUSIONS

In this contribution, we have given an overview of possible connections between the microscopic chaotic dynamics and the macroscopic description of reactive systems.

The microscopic chaos occurs on the short time scale of the collisions between the atoms and molecules composing the reactive systems. This short time scale has first been evaluated more than fifty years ago by Krylov [46] and has since then been more rigorously estimated by Sinai [47], Chernov [48] and very recently by Dorfman and coworkers [49]. At the macroscopic level, transport by diffusion occurs on a much longer time scale which depends on the spatial extension of the inhomogeneities in the densities of particles. In reactive systems, there exists furthermore the intermediate time scale associated with the reaction rates. This variety of time scales determine the way in which connections are established between the different phenomena.

In the escape-rate formalism, the variety of time scales explains why the irreversible coefficients are not directly related to either the Lyapunov exponents or the KS entropy, but to the difference between these quantities which characterize chaos. By taking such a difference, the connection is thus possible with a rate coefficient which is much smaller than the Lyapunov exponents or KS entropy. In this regard, the phenomenon of microscopic chaos differs from the mesoscopic and macroscopic rate processes, although the microscopic chaos plays an essential role because its dynamical randomness or stochasticity animates the irreversible processes.

The use of chaotic escape in the context of chemical reactions goes probably back to an early work by Eckmann et al. [50]. As it turns out, this idea can be generalized to several situations, including many-body systems, under the assumption that the underlying dynamics is classical, hyperbolic and chaotic. Moreover, the concept of Pollicott-Ruelle resonances appears very attractive in this context because it allows the rigorous definition of relaxation – and thus reaction – rates.

The problems of the nonequilibrium steady states and of the entropy production have already been solved in a diffusive system such as the multibaker [51, 52]. However, these problems are still open for the reactive multibaker model as well as for the reactive Lorentz gas.

The extension of the previous results to a quantum-mechanical description is of particular importance. Already, the relationship between the classical and quantal descriptions have been studied in several models of unimolecular reactions [41]. The classical escape rate has been shown to correspond to an average between the different decay rates of the quantum scattering resonances, although quantum lifetimes longer than the inverse classical escape rate exist [39]. In quantum many-body systems, the situation is more complicated because the concept of dynamical randomness has not yet found a firm foundation [53].

Therefore, we may conclude that many problems remain open in both the classical and quantal descriptions of reactive systems, which turn out to be conceptually far richer and more challenging than the nonreactive systems.

[1] J.-P. Eckmann, S. Oliffson Kamphurst, D. Ruelle, and S. Ciliberto, Phys. Rev. A **34** (1986) 4971.
[2] R. G. Harrison and D. J. Biswas, Nature **321** (1986) 394.
[3] L. F. Olsen and H. Degn, Quart. Rev. Biophys. **18** (1985) 165.
[4] L. Glass and M. C. Mackey, *From Clocks to Chaos: The Rhythms of Life*, Princeton University Press, Princeton, 1988.
[5] J.-C. Roux, R. H. Simoyi, and H. L. Swinney, Physica D **8** (1983) 257.
[6] S. K. Scott, *Chemical Chaos*, Clarendon Press, Oxford, 1991.
[7] M. T. M. Koper, P. Gaspard, and J. H. Sluyters, J. Chem. Phys. **97** (1992) 8250.
[8] R. Livi, A. Politi, and S. Ruffo, J. Phys. A: Math. Gen. **19** (1986) 2033.
[9] H. A. Posch and W. G. Hoover, Phys. Rev. A **38** (1988) 473; **39** (1989) 2175.
[10] Ch. Dellago and H. A. Posch, Phys. Rev. E **52** (1995) 2401; Ch. Dellago, H. A. Posch, and W. G. Hoover, Phys. Rev. E **53** (1996) 1485.

[11] P. Gaspard, M. E. Briggs, M. K. Francis, J. V. Sengers, R. W. Gammon, J. R. Dorfman, and R. V. Calabrese, Nature **394** (1998) 865.

[12] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74** (1995) 2694; J. Stat. Phys. **80** (1995) 931.

[13] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, Wiley, New York, 1961.

[14] S. Chandrasekhar, Rev. Mod. Phys. **15** (1943) 1; G. H. Weiss, J. Stat. Phys. **42** (1986) 3; B. J. Berne, M. Borkovec, and J. E. Straub, J. Phys. Chem. **92** (1988) 3711.

[15] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977); G. Nicolis and M. Malek Mansour, Prog. Theor. Phys. Suppl. **64** (1978) 249; F. Baras and M. Malek Mansour, Adv. Chem. Phys. **100** (1997) 393.

[16] P. Gaspard and X.-J. Wang, Phys. Reports **235** (1993) 291.

[17] P. Gaspard, *Chaos, Scattering, and Statistical Mechanics*, Cambridge University Press, Cambridge, 1998.

[18] P. Gaspard and G. Nicolis, Phys. Rev. Lett. **65** (1990) 1693.

[19] P. Gaspard, J. Stat. Phys. **68** (1992) 673.

[20] J.-P. Eckmann and D. Ruelle, Rev. Mod. Phys. **57** (1985) 617.

[21] R. Résibois and M. De Leener, *Classical Kinetic Theory of Fluids*, Wiley, New York, 1977.

[22] J.-P. Boon, D. Dab, R. Kapral, and A. Lawniczak, Phys. Reports **273** (1996) 55.

[23] L. Onsager and S. Machlup, Phys. Rev. **91** (1953) 1505; S. Machlup and L. Onsager, Phys. Rev. **91** (1953) 1512.

[24] P. Gaspard, Adv. Chem. Phys. **99** (1997) 369.

[25] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62** (1990) 251.

[26] P. Gaspard and F. Baras, Phys. Rev. E **51** (1995) 5332.

[27] J. R. Dorfman and P. Gaspard, Phys. Rev. E **51** (1995) 28.

[28] P. Gaspard and J. R. Dorfman, Phys. Rev. E **52** (1995) 3525.

[29] P. Szepfalusy and T. Tél, Phys. Rev. A **34** (1986) 2520; T. Tél, Phys. Rev. A **36** (1987) 1502.

[30] H. Kantz and P. Grassberger, Physica D **17** (1985) 75.

[31] G. Nicolis, *Introduction to Nonlinear Science*, Cambridge University Press, Cambridge, 1995.

[32] G. Nicolis and D. Daems, Chaos **8** (1998) 311.

[33] M. Pollicott, Invent. Math. **81** (1985) 413; D. Ruelle, Phys. Rev. Lett. **56** (1986) 405; D. Ruelle, J. Stat. Phys. **44** (1986) 281; D. Ruelle, J. Differ. Geom. **25** (1987) 99, 117.

[34] P. Cvitanović and B. Eckhardt, J. Phys. A: Math. Gen. **24** (1991) L237.

[35] P. Gaspard and D. Alonso Ramirez, Phys. Rev. A **45** (1992) 8383.

[36] P. Gaspard, Phys. Rev. E **53** (1996) 4379.

[37] S. K. Gray, S. A. Rice, and D. W. Noid, J. Chem. Phys. **84** (1986) 3745; S. K. Gray and S. A. Rice, Faraday Disc. Chem. Soc. **82** (1986) 307

[38] P. Gaspard, in: G. Casati, I. Guarneri, and U. Smilansky, eds., *Quantum Chaos*, North-Holland, Amsterdam, 1991, pp. 307-383.

[39] P. Gaspard and S. A. Rice, J. Chem. Phys. **90** (1989) 2225, 2242, 2255.

[40] D. M. Wardlaw and R. A. Marcus, Adv. Chem. Phys. **70** (1988) 231.

[41] P. Gaspard and I. Burghardt, Adv. Chem. Phys. **101** (1997) 491.

[42] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland, Amsterdam, 1981.

[43] P. Gaspard and R. Klages, Chaos **8** (1998) 409.

[44] In Ref. [43], the reaction rate was simply estimated with the spectral gap $\kappa_{\rm gap}$.

[45] P. Ortoleva and J. Ross, J. Chem. Phys. **56** (1972) 4397.

[46] N. S. Krylov, Nature **153** (1944) 709; N. S. Krylov, *Works on the Foundations of Statistical Physics*, Princeton University Press, Princeton, 1979.

[47] Ya. G. Sinai and N. I. Chernov, Russian Math. Surveys **42** (1987) 181.

[48] N. I. Chernov, Funct. Anal. Appl. **25** (1991) 204.

[49] H. van Beijeren and J. R. Dorfman, Phys. Rev. Lett. **74** (1995) 4412, *ibid.* **76** 3238E; H. van Beijeren, J. R. Dorfman, H. Posch, and Ch. Dellago, Phys. Rev. E **56** (1997) 5272; J. R. Dorfman, A. Latz, and H. van Beijeren, Chaos **8** (1998) 444.

[50] R. Kariotis, H. Suhl and J.-P. Eckmann, Phys. Rev. Lett. **54** (1985) 1106.

[51] S. Tasaki and P. Gaspard, J. Stat. Phys. **81** (1995) 935.

[52] P. Gaspard, J. Stat. Phys. **88** (1997) 1215.

[53] P. Gaspard, in: P. Cvitanović, I. Percival, and A. Wirzba, eds., *Quantum Chaos - Quantum Measurement*, Kluwer, Dordrecht, 1992, pp. 19-42; R. Alicki and M. Fannes, Lett. Math. Phys. **32** (1994) 75.