CARBON MONOXIDE OXIDATION 
ON IRIDIUM(111) SURFACES 
UNDER COLORED NOISE

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We study the effect of external noise on the catalytic oxidation of CO on an Iridium(111) single crystal under ultrahigh vacuum conditions. This reaction can be considered as a model of catalysis used in the industry. In the absence of noise, the reaction exhibits one or two stable stationary states, depending on the control parameters such as temperature and partial pressures. When noise is added, for instance, by randomly varying the quality of the influx mixture, the system exhibits stochastic reaction rate and switching. In this work, we present the theoretical predictions for the bistable situation using a number of colored-noise approximations that consider the intensity and correlation of the external fluctuations. As we will show, only some of these approximations are suitable for bistable systems.

Keywords: Surface reactions; bistability; stochastic processes; colored noise.

1. Introduction

The study of nonlinear dynamical systems usually rests on the implicit assumption that all the parameters are known with certainty and all the forcings are incorporated into the model. Now, when the quality of the substances or the couplings between different mechanisms have uncertainties, or there are external forcings that do not follow regular patterns, but seem to be random, one is forced to abandon the deterministic description in favor of a probabilistic one.

The study of nonlinear stochastic systems has shown that there are certain features of the random perturbations that are relevant for the dynamics. Some of these features are distribution, intensity, and autocorrelation. Here in this work we focus on the latter. Though the most important advances in the field of stochastic processes have been achieved using a correlation-free noise, there are many experimental and industrial situations where such assumption is untenable, and one should consider autocorrelated or colored noise.

The physical system that we consider in this work is a surface reaction on an Iridium plate that can be considered a laboratory version of the catalytic oxidation that finds widespread applications in the chemical industry and in the processing of gases generated in combustion engines.

243
Some notable examples of fruitful research on catalysis are the synthesis of ammonia developed by Fritz Haber (1868–1934) and the catalytic conversion of carbon monoxide explained by Gerhard Ertl (1936–). Haber and Ertl were awarded the Nobel Prize in Chemistry in 1918 and 2007, respectively. This article is based on mathematical modeling proposed by G. Ertl and collaborators, and considers external noise associated to random perturbations of pressure, temperature or concentrations.

For simplicity, we will assume that on the catalytic surface the reactants, oxygen and carbon monoxide, have homogeneous coverages i.e. do not depend on space, and thus the state of the system can be described by the surface concentrations only. These assumptions will allow us to use ordinary stochastic differential equations. The following assumption is also used: a good approximation is obtained by replacing the piecewise-constant noise used in experiments by an Ornstein–Uhlenbeck process.

In this work, we will review some theoretical tools that can be used for the analysis of nonlinear stochastic systems under colored noise with small but finite correlation time. These results should be contrasted first with numerical simulations and then with experimental data. This article builds on the work of Hayase et al. [2004], where the experimental setting was described and the basic model was elaborated. We will follow developments presented in the book by Horsthemke and Lefever [1984] and in the review of Hänggi and Jung [1995].

This article is structured as follows: In Sec. 2, we present the chemical model and its dynamics in the absence of noise. The deterministic vectorfield shows a clear separation of time scales, a fact that can be used to simplify both the deterministic and stochastic descriptions. In Sec. 3, we explain how noise is introduced in experiments. If the quality of the gas that feeds the oxidation varies randomly, the reaction rate will show stochastic behavior. The random perturbations can be characterized using two parameters: their intensity and autocorrelation. In Sec. 4, a white-noise approximation is used for the computation of relevant quantities assuming that the noise correlation is small. Section 5 is the main part of this work. We will consider the more general Ornstein–Uhlenbeck process and several approximate theories that have been developed for its analysis. Here, we used three of these theories and show some of their pitfalls and potentialities. In Sec. 6, we summarize the theoretical results of this work and comment on the experiments that should be performed to validate our predictions.

2. Reaction Model

2.1. Catalytic CO oxidation

The reaction mechanism of the catalytic CO oxidation on Platinum group metal surfaces under ultrahigh-vacuum conditions (UHV):

\[ 2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2, \]

is well established to be the Langmuir–Hinshelwood mechanism, which has been shown in 1978 by T. Engel and G. Ertl to be the mechanism for catalytic surface reactions [Engel & Ertl, 1978, 1979]. It consists of a sequence of three steps: (i) adsorption of the first reactant, (ii) adsorption of the second reactant and (iii) reaction between adsorbed particles and desorption of the product.

These steps are depicted in Fig. 1, including also the diffusion of the species over the surface until the reactants meet and generate the product. The metal substrate acts as a catalyst: it does not participate as a reactant nor as a product, it is left unchanged when the product is released, but the reaction could not happen without the species being adsorbed first.

2.2. Mathematical model

Assuming that the concentrations inside the chamber can be perfectly controlled, the state of the oxidation can be described by the number of lattice sites covered by the reactant molecules. The kinetics of the reaction steps presented in the previous section, can be written as a set of partial differential equations that describe the evolution of the surface.

![Fig. 1. Schematic of the Langmuir–Hinshelwood mechanism showing the adsorption of the gaseous species, the diffusion over the surface and the reaction and production of gaseous carbon dioxide.](image-url)
concentration of oxygen $n_O$ and carbon monoxide $n_{CO}$:
\[
\frac{\partial n_{CO}}{\partial t} = d_{CO} \nabla^2 n_{CO} + Y_{\text{total}} n_{CO} \left( \frac{n_{\text{empty}}}{n_{Ir}} \right)^2
- n_{CO} n_{\text{Ir}} \nu_{\text{Ir}} \exp \left( -\frac{E_{\text{deso}}}{kT} \right)
- n_{CO} n_{O} \nu_{O} \exp \left( -\frac{E_{\text{rea}}}{kT} \right),
\]
(1)
\[
\frac{\partial n_{O}}{\partial t} = d_{O} \nabla^2 n_{O} + 2(1 - Y) Y_{\text{total}} n_{O} \left( \frac{n_{\text{empty}}}{n_{Ir}} \right)^3
- n_{CO} n_{\text{Ir}} \nu_{\text{Ir}} \exp \left( -\frac{E_{\text{deso}}}{kT} \right).
\]
(2)
Oxygen desorption could be neglected because of the temperature range considered here (see the article by Hayase et al. [2004] for more details on the model and the values of the constants). The diffusion of oxygen and carbon monoxide molecules over Iridium(111) surfaces is perfectly isotropic.

The available number of sites on the Iridium plate is constant:
\[
n_{Ir} = n_{\text{empty}} + n_{CO} + n_{O}.
\]
(3)
The parameter $Y$ is the molar fraction of CO in the total feed gas flux $\Phi_{\text{total}}$. In the first term of Eq. (1), the effective number of CO molecules in the gas that reach the surface (per unit of time) is $Y \Phi_{\text{total}}$. The probability for each CO molecule to get adsorbed is $s_{CO}(n_{\text{empty}}/n_{Ir})$. For the CO desorption, the number of molecules on the surface that can desorb is $n_{CO}$, and the rate is $\nu_{\text{Ir}}$ times the activation factor. The third term in Eq. (1) and the second one in Eq. (2) consider the reaction that takes place when an adsorbed molecule of CO meets an adsorbed O. The sticking coefficients $s_{CO}$, $s_{O}$ are nondimensional factors that can be interpreted as probabilities. For simplification $s_{CO}$ was taken to unity and the ratio $s_{O}/s_{CO}$ was adjusted from experimental data. The third power in the oxygen adsorption term comes from the fact that the action of three empty sites on the surface is required to destabilize an O$_2$ molecule (a more complete discussion is included in [Wehner et al., 2003b, p. 6829]).

For the observations, we should rely on the measurements of CO$_2$ gas flux measured by a quadrupole mass spectrometer:
\[
\text{CO}_2 \text{ rate} = \int n_{CO} n_{O} \nu_{\text{Ir}} \exp \left( -\frac{E_{\text{deso}}}{kT} \right) \text{d}x \text{d}y,
\]
(4)
or the oxygen coverage $n_O(x, y, t)$, measured using PEEM (photo-electron emission microscopy). This last technique has been used to monitor stochastic activity on Iridium [Wehner et al., 2005] as well as on Platinum crystals [Bodega et al., 2009] exhibiting complex spatiotemporal patterns for certain parameters.

Though there is a rich variety of spatial patterns generated by this reaction, in this work we will focus on stochastic behaviors that can be explained without using diffusion. We will assume from now on that $n_{CO}$ and $n_{O}$ depend on time only.

Defining the following nondimensional quantities:
\[
u \overset{\text{def}}{=} \frac{n_{CO}}{n_{Ir}} \quad \delta \overset{\text{def}}{=} \frac{n_{O}}{n_{Ir}}
\]
the ordinary differential equations can be scaled:
\[
du{t} = f_u(u, v) = \alpha Y(1 - u - v) - \beta u - \gamma uv,
\]
(5)
\[
dv{t} = f_v(u, v) = \delta (1 - Y)(1 - u - v)^3 - \gamma uv,
\]
(6)
where we have intentionally left the parameter $Y$ free so it can be used as a source of random variations. Representative values for the four parameters for a temperature $T = 500$ K are (in units of $1/$sec): $\alpha = 0.878205, \beta = 0.023692, \gamma = 6.640593, \delta = 0.193205$. These values are used without modification in the rest of the article.

### 2.3. Deterministic system

Depending on the value of parameter $Y$, the reaction has one stable steady state, or two stable and one stable steady states. The whole picture is represented in Fig. 2 which shows the solutions of $f_u(u, v) = f_v(u, v) = 0$ in Eqs. (5) and (6). When the parameter $Y$ is varied, these two states define two separate branches that we call upper rate (UR) and lower rate (LR). It has been shown experimentally in [Wehner et al., 2003a] that the coexistence of the two branches define an interval between $Y_L$ and $Y_S$ where the system is bistable (see Fig. 3). Inside the window, there is a hysteretic loop: as the control parameter $Y$ is slowly increased beyond $Y_U$, the reaction rate lies along the UR branch until it disappears at $Y_S$, then switches to LR. As $Y$ is decreased below $Y_L$, the reaction rate sticks to LR until the branch turns around at $Y_U$ and the reaction rate jumps to UR.

The existence and stability of steady states can be understood in phase plane (see Fig. 4), where
fixed points move and annihilate as parameter Y is varied beyond $Y_\ell \approx 0.073$ or $Y_h \approx 0.1215$ (these values correspond to the model). All the dynamics takes place inside the unit square ($0 \leq u \leq 1, 0 \leq v \leq 1$), regardless of the value of $Y$. The geometry of trajectories $(u(t), v(t))$ as they are repelled by unstable points and are attracted by stable points (LR and UR), reveals the existence of an attracting slow manifold that coincides with the unstable manifold of the saddle-point. Most trajectories (with the sole exception of the separatrix, stable manifold of saddle) get squeezed rapidly along this ‘slow’ manifold and then approach one of the nodes. The existence of this slow manifold allows one to simplify the analysis of both the deterministic system and its stochastic counterpart.

Besides the geometric features of the phase plane, there is a clear separation of time scales: almost any trajectory $(u(t), v(t))$ approaches the slow manifold (fast scale), then it stays close to this manifold (slow scale).

If one were able to approximate the shape of this manifold $v = \tilde{v}(u)$ then we could use the one-dimensional approximation:

$$\dot{u} = \tilde{f}(u) \equiv f(u, \tilde{v}(u)),$$

that captures the slow dynamics of the system and the existence of one or three fixed points depending on the value of $Y$. This reduction will be most useful in the stochastic case.

One direct consequence of the reduction is the change in time scales. If for the original two-dimensional system, the fastest time scale (associated to transients) can be estimated from the inverse of the stable eigenvalue of the saddle point $|1/\lambda_{st}| > 0.1 \text{s}$, in the reduced 1-d system the previous time scale is removed and the new fastest scale (for motion along the slow manifold) is given by $1/\lambda_{mat} \approx 10 \text{s}$, or the inverse of the maximum of $|f'(u)|$. 

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**Fig. 3.** Schematic experimental hysteretic loop for the CO oxidation. (Reproduced from Hoffmann, P., Wehner, S., Schmeisser, D., Brand, H. R. & Kuppers, J. [2006]. “Noise-induced spatiotemporal patterns in a bistable reaction-diffusion system: Photo-electron emission microscopy experiments and modeling of the CO oxidation reaction on Ir(111),” Phys. Rev. E 73, 056123, Copyright 2006 by the American Physical Society.)

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**Fig. 4.** Phase plane of deterministic system for CO oxidation Eqs. (5) and (6) for $Y = 0.1 \in [Y_\ell, Y_h]$. In this bistable scenario there are three fixed points, two stable nodes and one saddle, that lie on a slow manifold that attracts all trajectories.
3. External Noise

The CO oxidation on Ir(111) inside a UHV chamber is a reaction that can be controlled and measured in such a way that the intrinsic noise is severely limited [Hayase et al., 2004]. Now in the case of industrial settings, environmental fluctuations as well as uncertainties in parameter values force us to include random perturbations into the deterministic model presented in Eqs. (1)–(3).

The preferred experimental method for adding external random perturbations is by controlling the CO fraction of gas flux $Y(t) = \Phi_{CO}/\Phi_{total}$ in a random manner, holding its value constant for fixed periods of time, as depicted in Fig. 5. For some $Y_0$ and $\Delta Y$ ($0 \leq Y_0 \leq 1$), the value of $Y(t)$ is updated every $\tau_n$ seconds following the distribution:

$$P(Y) = \left\{ \begin{array}{ll} \frac{N}{(\Delta Y)^2} \exp \left( -\frac{1}{2} \left( \frac{Y - Y_0}{\Delta Y} \right)^2 \right) & \text{if } |Y - Y_0| \leq \Delta Y, \\ 0 & \text{otherwise}. \end{array} \right. \quad (7)$$

The standard deviation of $Y$ is $\Delta Y_{\text{eff}}/2$ with $\Delta Y_{\text{eff}} \equiv \kappa \Delta Y$ where $\kappa \approx 0.88$ can be computed using the error function. The smallest value of $\tau_n$ that can be achieved in the current experimental setting is around one second. This limitation comes from the finite times required to open and close the valve that controls $Y$ and the time required for the gas to reach the chamber through a capillary.

Defining:

$$y(t) \equiv Y(t) - Y_0$$

one can verify that:

$$\langle y(t) \rangle = 0,$$

and,

$$\langle y(s)y(t) \rangle = \left\{ \begin{array}{ll} D \tau_n \left( 1 - \frac{|t - s|}{\tau_n} \right) & \text{if } |t - s| < \tau, \\ 0 & \text{otherwise}, \end{array} \right.$$ 

where:

$$D \equiv \frac{\tau_n}{2} \left( \frac{\Delta Y_{\text{eff}}}{2} \right)^2. \quad (8)$$

This noise has an intrinsic correlation time:

$$\tau \equiv \frac{\int_0^\infty \langle y(t)y(0) \rangle dt}{\langle y^2 \rangle} = \frac{\tau_n}{2}.$$

A full study of the influence of noise in the bistable system should consider all combinations of values of $\tau_n$ and $\Delta Y$, for $Y_0 \in (Y_1, Y_2)$. This study has not been performed yet. Here, we take the more modest goal of presenting some preliminary numerical simulations and evaluating approximation schemes that have been specifically developed for the study of nonlinear systems under colored noise.

In Figs. 6 and 7, some preliminary results are presented. They show stationary probability distributions (histograms) computed from the numerical integration of Eqs. (5) and (6) using the piecewise constant noise described by Eq. (7). The figures show how the stationary probability distribution depends on parameters $\tau_n$ and $\Delta Y$. Figures 6(a) and 6(b) show the small effect of increasing $\tau_n$ while keeping $D$ [defined in Eq. (8)] fixed; the peaks seem to become more narrow and the intermediate space becomes even less populated (as parameter $\Delta Y$ decreases). Figures 7(a) and 7(b) show the more noticeable effect of increasing $D$ when $\tau_n$ is large; the space between the peaks become more populated as more and more stochastic trajectories wander between the attractors. The effect is so big that the probability distribution becomes trimodal.

Now, in this article we focus on weak noise and weak correlation so Figs. 7(a) and 7(b) are not going to be explained by the approximations.

Figure 12 can be compared with Figs. 6(a) and 6(b). Though it is difficult to notice any shift of the peaks in the histograms, the peaks do become narrower and the intermediate range even more empty as $\tau_n$ increases.

We study the effects of the noise correlation on the reaction rate. The time scale that can be used
Fig. 6. Histograms that summarize long-time behavior of numerical simulations of Eqs. (5) and (6) and random perturbations given by Eq. (7) with $Y_0 = 0.094$. Their profiles should match the stationary probability distributions $p_u(u)$. The two figures correspond to small $\tau_n$ and share the same noise intensity $D = 0.028$: (a) $\Delta Y = 0.078$, $\tau_n = 1s$, (b) $\Delta Y = 0.035$, $\tau_n = 5s$. Though we used a long but finite time for the simulations, we verified that the results do not depend on initial conditions.

Fig. 7. Histograms that summarize long-time behavior of numerical simulations of Eqs. (5) and (6) and random perturbations given by Eq. (7) with $Y_0 = 0.094$. The two figures correspond to medium $\tau_n$ and show the effect of increasing noise intensity $D$: (a) $\Delta Y = 0.0215$, $\tau_n = 102.4s$, (b) $\Delta Y = 0.0375$, $\tau_n = 102.4s$. 
to compare with $\tau_a$ (or $\tau = \tau_a/2$), comes from the deterministic dynamics of the oxidation reaction. If one restricts the analysis to the slow manifold, this time scale is around 10 seconds.

When $\tau \ll 10\text{ s}$, a white-noise approximation can be used. From the Langevin equation and the associated Fokker–Planck equation, one can compute the stationary probability distribution, that changes with the average of $Y(t)$ and the power of the noise $D$.

When $\tau \gg 10\text{ s}$, one can try to use a quasi-stationary approach that assumes $u(t)$ essentially follows the attractors of the deterministic system, that are moved by $Y(t)$.

For intermediate values of $\tau$, i.e. colored noise, there are several approximation approaches that can be evaluated.

4. White-Noise Approximation

It can be shown [Cisternas et al., 2009] that a white-noise approximation can be used to account for most of the experimental findings in the bistable regime $Y_0 < Y < Y_f$. This approach uses the reduction to the slow manifold described in Sec. 2, that can be extended to stochastic systems [Knobloch & Wiesenfeld, 1983]. For the reduced system, a noise correlation time $\tau < 10\text{ s}$ can be considered fast and can be approximated by white noise. Assuming that the noise is weak, the reduced equation is transformed into a stochastic equation for a given $Y_0 = Y(t)$:

$$
\dot{u} = \tilde{f}(u, Y(t))
\approx \tilde{f}(u, Y)|_{Y_0} + (Y(t) - Y_0) \left. \frac{\partial \tilde{f}(u, Y)}{\partial Y} \right|_{Y_0} 
\approx a(u) + y(t) b(u),
$$

(9)

where we have used:

$$
a(u) \equiv \tilde{f}(u, Y_0),

b(u) \equiv \left. \frac{\partial \tilde{f}(u, Y)}{\partial Y} \right|_{Y_0},

y(t) \equiv Y(t) - Y_0.
$$

Then it can be proved that in the limit of $\tau \to 0$ the random term $y(t)$ can be approximated by $\sqrt{D}$ times the white-noise $\xi(t)$:

$$
\langle \xi(t) \rangle = 0, \langle \xi(s) \xi(t) \rangle = 2\delta(t - s).
$$

Thus we can use a Stratonovich stochastic differential equation:

$$
\dot{u} = a(u) + \sqrt{D} \xi b(u),
$$

(10)

and its associated Fokker–Planck equation for the evolution of the probability distribution:

$$
\frac{\partial p(u, t)}{\partial t} = -\frac{\partial}{\partial u} [a(u)p(u, t)]
+ \frac{D}{2} \left\{ \frac{\partial}{\partial u} [b(u)p(u, t)] \right\}.
$$

(11)

The stationary solution of this equation can be found analytically:

$$
p_s(u) = \frac{N}{b(u)} \exp \left[ \frac{2}{D} \int^u a(v)b(v) dv \right].
$$

(12)

The functions $a(u)$ and $b(u)$ used in these formulas (as well as in the rest of this article) were
presentation of both functions, that approximate the along the slow manifold. See Fig. 8 for a graphic representation of diffusion around the attractors. As we increase \( \Delta Y \) ranging from 0 to 0.094, \( \tau_n = 3 \) s, and values of \( \Delta Y \) ranging from 0.002 (red dashed curve) to 0.05. For larger values of \( \Delta Y \), the support of \( p_t (u) \) spreads out and the peaks shift to the endpoints of the unit interval. These figures should be compared with Figs. 6(a) and 6(b).

extracted from numerical simulations (small \( \Delta t \)):

\[
a(u) = \frac{\Delta u}{\Delta t}, \quad b(u) = \frac{1}{D} \left( \frac{\Delta u - a(u)\partial_t p}{\Delta t} \right),
\]

where the averages are taken for many independent realizations, but for a given \((u, v)\) initial condition along the slow manifold. See Fig. 8 for a graphic representation of both functions, that approximate the dynamics of the oxidation for a value of \( Y_0 = 0.094 \). The function \( a(u) \) indicates the presence of two stable fixed points and one unstable saddle in between. The function \( b(u) \) shows the relative magnitudes of diffusion around the attractors. As we increase \( D \) (either by increasing \( \Delta Y \) or \( \tau_n \)), the stationary probability density (computed from the Fokker–Planck equation) changes its shape as it can be seen in Fig. 9; it becomes less concentrated around the stable fixed points (UR and LR), spreading its support over the whole interval \((0, 1)\), and shifting the location of the peaks.

5. Ornstein–Uhlenbeck Noise and Approximation Theories

When the noise has nonzero autocorrelation, one is forced to use approximation schemes to estimate the stationary probability and other statistical quantities. In this section, we apply three different approaches to the simplified CO oxidation model:

\[
\dot{u} = a(u) + \sqrt{D} \xi, \quad \dot{\xi} = \frac{1}{\tau} (-\xi + \xi)
\]

where \( a(u) \) and \( b(u) \) are the functions presented in the previous section and \( \xi(t) \) is a white noise process. The statistics of the colored noise \( \zeta(t) \) are:

\[
\langle \zeta(t) \rangle = 0, \quad \langle \zeta(s)\zeta(t) \rangle = \frac{1}{\tau} \exp \left( -\frac{|t-s|}{\tau} \right).
\]

For \( D \) defined in Eq. (8) and \( \tau = \tau_n/2 \), the function \( Y(t) = Y_0 + \sqrt{D} \xi(t) \) has the same correlation time and standard deviation used by the piecewise-constant \( Y(t) \) in experiments and defined in Eq. (7). In Fig. 10 we show a realization of the colored noise process \( Y(t) \) for finite \( \tau \).

5.1. Standard small correlation approximation

The standard small \( \tau \) approximation is by far the most used small correlation approximation. It considers a Fokker–Planck-like evolution equation:

\[
\frac{\partial p(u, t)}{\partial t} = -\frac{\partial}{\partial u} \left[ a(u)p(u, t) \right] + \frac{D}{2} \left( \frac{\partial}{\partial u}b(u) \right) b(u) \left[ 1 + \tau b(u) \frac{a(u)}{b(u)} \right] p(u, t) \bigg|_{t=0}^{t=\tau}.
\]

(where the prime indicates differentiation with respect to \( u \)) proposed first by Stratonovich [1963]. It captures the long-term evolution of the probability distribution when the noise correlation time \( \tau \) is small.

This equation has a similar structure as a Fokker–Planck equation and its stationary solution
can be solved analytically:

\[ p_\epsilon(u) = \left. \frac{N}{b(u)} \left\{ 1 + \tau b(u) \frac{a(u)}{b(u)} \right\} \right\}_w^1 \exp \left\{ \frac{2}{D} \right\} \]

\[ \times \int \frac{a(w)}{b'(w)} \left\{ 1 + \tau b(w) \frac{a(w)}{b'(w)} \right\} dw. \]

(16)

Equation (15) and similar variants have been derived following a variety of methods, for instance, the one presented by Lindenberg and West [1983] and Fox [1996]. Now the small differences between these derivations give sometimes totally different answers revealing the fact that Eq. (15) does not come from a consistent expansion in powers of \( \tau \) (see [Hänggi & Jung, 1995] for a detailed discussion on this specific point).

The main limitation of Eq. (16) comes from its very narrow applicability. It only works when \( \tau \ll 1 \). When \( \tau \) is small but finite, the denominators of Eq. (16) often become zero in the neighborhood of fixed points. For instance, when \( a(u) = 0 \) and \( a'(u) < 0 \) (stable fixed point), there is an upper bound for the parameter \( \tau \). In our case, starting from the base situation \( Y_0 = 0.094 \) and \( \Delta Y = 0.015 \), this limit is \( \tau < 0.02s \). Now for such small \( \tau \) the white-noise assumption is still a good approximation so the improvements offered by this small \( \tau \) approximation should be negligible.

5.2. Wideband perturbation expansion

Another approximation approach is the so-called wideband perturbation expansion presented by Horsfield and Lefever [1984]. It considers the Fokker–Planck equation of the extended system \( (u, \zeta) \), captures the probability distribution for both \( u \) and \( \zeta \):

\[ p_\epsilon(u, \zeta) = p_\epsilon(\zeta)p_\epsilon(u + \epsilon r_1(u, \zeta) + \epsilon^2 r_2(u, \zeta)), \]

where the expansion parameter \( \epsilon = \sqrt{\tau} \) is small but \( \sigma^2 = D/\tau \) is finite.

The integration in the noise variable gives \( p_\epsilon(u) = \int p_\epsilon(u, \zeta)d\zeta \):

\[ p_\epsilon(u) = p_\epsilon^0(u) \left\{ 1 + \epsilon^2 \left[ C - a'(u) \right] \right\} \]

\[ + a \left( \frac{b'(u)}{b(u)} - \frac{1}{\sigma^2} \frac{a'^2(u)}{b'(u)} \right) \]

(17)

where the constant \( C \) is:

\[ C = -\frac{1}{\sigma^2} \int_0^1 p_\epsilon^0(w) b^2(w) dw, \]

and \( p_\epsilon^0(u) \) is the probability density for the white-noise approximation \( (\epsilon = 0) \).

This method does not break down when applied to a bistable system such as ours. But it has some limitations. If the quantity between square brackets in Eq. (17) becomes negative in some neighborhood, for instance, where \( a(u) = 0 \) and \( a'(u) > 0 \) (unstable point), there will be a limitation on the value of \( \tau \) that gives non-negative probability distributions \( p_\epsilon(u) \). In Fig. 11, we can appreciate that the function \( p_\epsilon(u) \) becomes negative between the peaks for \( \tau > 5s \). It should be emphasized that this approach assumes that \( D \) rescales with \( \tau \); other approximations assume that \( D \) is fixed, so some caution should be taken when comparing results.

For large \( \tau \) and constant \( \sigma \), the system should follow quasi-statically the motion of the attractors: as can be seen in Fig. 11 (for the largest value of \( \tau \)) the probability \( p(u) \) looks like a bimodal distribution with the width of each peak depending on \( \sigma \).

5.3. Unified colored noise approximation

A totally different approach is the unified colored noise approximation (UCNA), presented by Jung and Hänggi [1987] and reviewed in [Hänggi & Jung, 1995, Section V.C.]. Briefly speaking, it consists of
the combination of Eqs. (13) and (14) and the writing of a new Langevin equation that resembles a nonlinear oscillator under white-noise forcing. Following [Jung & Hänggi, 1988b], we first transform Eq. (13) into a new system with additive noise:

\[
\frac{dz}{ds} = h(z) + \sqrt{2D} \xi_s,
\]

where:

\[
h(z) = \frac{a(u(z))}{b(u(z))}, \quad z = \int_0^s \frac{1}{b(u)} dw,
\]

and a new time scale \( s \equiv t/\tau \) is used. The stochastic equation now looks like:

\[
a \frac{d^2z}{ds^2} + \gamma(z) \frac{dz}{ds} - h(z) = \frac{D^{1/2}}{\tau^{1/2}} \xi(s),
\]

where the nonlinear damping term is defined by:

\[
\gamma(z) \equiv \tau^{-1/2} + \tau^{1/2} - h'(z).
\]

Assuming that the damping that multiplies the velocity \( dz/ds \) is large, one can eliminate the acceleration and derive a new Markovian stochastic equation with white noise, that contains implicitly most of the effects of noise correlation \( \tau \). Now this approach is valid for both large and small correlation time \( \tau \). Writing the reduced Stratonovich stochastic equation in the original variable \( u \) and time \( t \):

\[
\dot{u} = \frac{a(u)}{1 - \tau b(u)} \left[ a'(u) - \frac{a(u) b'(u)}{b(u)} \right] \\
+ \sqrt{D} \frac{b(u)}{1 - \tau b(u)} \left[ a(u) - \frac{a(u) b'(u)}{b(u)} \right] \xi(t). \quad (18)
\]

The Fokker–Planck equation for the probability reads:

\[
\frac{\partial p(u,t)}{\partial t} = -\frac{\partial}{\partial u} \left[ \frac{a(u) b_{\text{wna}}(u)}{b(u)} p(u,t) \right] \\
+ \frac{D}{2} \left\{ \frac{\partial}{\partial u} \frac{a(u) b_{\text{wna}}(u)}{b(u)} \cdot \frac{\partial}{\partial u} \frac{a(u) b_{\text{wna}}(u)}{b(u)} p(u,t) \right\}, \quad (19)
\]

with an effective multiplicative noise function:

\[
b_{\text{wna}}(u) \equiv \frac{b(u)}{1 - \tau b(u)} \left[ \frac{a(u)}{b(u)} \right].
\]

The stationary solution of Eq. (19):

\[
p_s(u) = \frac{N}{b(u)} \left[ 1 - \tau b(u) \left[ \frac{a(u)}{b(u)} \right] \right] \\
\times \exp \frac{2}{D} \int a(u) \left( 1 - \tau b(u) \left[ \frac{a(u)}{b(u)} \right] \right) dw.
\quad (20)
\]

This method presents a number of positive features: its analytic solution does not become singular for finite \( \tau \); the probability is always non-negative given that \( b_{\text{wna}}(u) \) is positive; and it has been proved that the method gives exact results for very small and very large values of \( \tau \). So for intermediate values, chances are that it gives good answers too.

A limitation of this approach, it assumes that \( \gamma(u) \) is always negative. This is not true close to saddle points where \( a(u) = 0 \) and \( a'(u) > 0 \). Now Eq. (20) does not break close to these unstable points, suggesting that the inaccuracies of Eq. (20) are under control.

In Fig. 12, we see \( p_s(u) \) computed with this last method, for a variety of values of the correlation time \( \tau \). As \( \tau \) increases, the rightmost peak moves to the left, closer to the location of the fixed point \( u \approx 0.8 \) and the intermediate range between the peaks becomes deserted. Figure 12 should be compared with Figs. 6(a) and 6(b). Though it is difficult to notice any shift of the peaks in the histograms,
Fig. 13. Nonlinear damping function $\gamma(u)$ for different values of $\tau$ ranging from zero to 51 s (curve with the lowest valley). In the unified colored noise approximation, this function is assumed to be positive and large, but for the bistable system studied in this work, this assumption is not valid beyond $\tau \approx 10$ s.

The peaks do become narrower and the intermediate range even more empty as $\tau_n$ increases.

In Fig. 13, we see the function $\gamma(u)$ for different values of $\tau$. The nonlinear damping term $\gamma(u)$ becomes negative beginning at a value $\tau \approx 10$ s. The UCNA theory is not valid beyond that point.

Now for very large $\tau$ and constant $D$, the variable $Y(t)$ takes values that are concentrated around $Y_0$, so the probability $p(u)$ should look like two deltas located at the attractors. In Fig. 12, we see that this behavior is qualitatively captured by the UCNA approximation.

There are other methods that can be used for colored noise, for instance, the matrix continued fraction method presented by Risken [1989] that computes the probability in the extended phase space $(u, \zeta)$ for arbitrary noise correlation time $\tau$, but here we restricted our analysis to methods that offer an analytic solution for the stationary probability distribution $p_s(u)$.

6. Conclusions and Outlook

We have studied the CO oxidation on an Iridium(111) surface and the influence of random fluctuations. Assuming that the surface is covered homogeneously at all times, the dynamics of this system is described by two stochastic differential equations, that can be further reduced if one is willing to neglect transients.

Neglecting the time correlation of the noise, a white-noise approximation can be used to estimate quantities such as the stationary probability distribution.

Now in the experimental setting the noise has finite correlation time, that is neither very small nor very large, so other methods should be considered.

In this work, we explicitly show how the standard small correlation approximation, the wideband perturbation expansion, and the unified colored noise approximation, work for a concrete physical system, namely the CO oxidation on Iridium(111) surfaces, that we modeled as a dynamical system under colored noise. As it turned out, selecting the right approximation scheme is of utmost importance in the study of bistable systems.

Although the colored-noise approximations predict qualitative features that are correct, they have a number of problems. The first theory becomes singular even for small but finite correlation times. The second predicts negative probabilities. The third, unified colored noise approximation, does not have these pitfalls and offers exact answers for very small and very large correlation times, so in principle, it should give good approximations in the intermediate range. But this last method relies on an assumption that is not always true for bistable systems. In this work, we found that there is a limit on the correlation time for which the approximations give meaningful results.

None of these methods was able to compute probabilities for large values of the correlation time, for which a number of noise-induced transitions have been observed in numerical simulations. Further work should be devoted to the intermediate and large correlation regimes. To our knowledge, the only colored-noise approximation method that does not restrict its analysis to small correlations is the eigenfunction expansion, a method that becomes intractable when the potential is not symmetric or there is multiplicative noise.

Some of the problems faced by the colored-noise approximations could be expected in advance. For instance, close to the saddle point and for weak noise the probability is small, so any correction is going to be large and inaccurate. If the probability distribution vanishes around the saddle, switching between stable attractors will not take place and the long term behavior will depend on the initial condition.

Before trying to confirm the findings of this work in experiments, one should extend this work and consider spatial heterogeneities and the role of spatial correlation of the random perturbations. It
would be most interesting to understand when and how the homogeneous description developed here breaks down, and the spatiotemporal patterns that may arise. These patterns should be observable in experiments using PEEM technology. The influence of noise on spatiotemporal behavior has been studied in other physical systems (see [Sagués et al., 2007] for a recent review) so probably similar phenomena is going to be observed through the surface reaction studied in this article.

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