Fluctuating Dynamics of Nanoscale Chemical Oscillations: Theory and Experiments

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ABSTRACT: Chemical oscillations are observed in a variety of reactive systems, including biological cells, for the functionality of which they play a central role. However, at such scales, molecular fluctuations are expected to endanger the regularity of these behaviors. The question of the mechanism by which robust oscillations can nevertheless emerge is still open. In this work, we report on the experimental investigation of nanoscale chemical oscillations observed during the NO₂ + H₂ reaction on platinum, using field electron microscopy. We show that the correlation time and the variance of the period of oscillations are connected by a universal constraint, as predicted theoretically for systems subjected to a phenomenon called phase diffusion. These results open the way to a better understanding, modeling, and control of nanoscale oscillators.

Chemical reactions are at the heart of a vast amount of self-organized phenomena found in both animate and inanimate systems. Such behaviors include, but are not limited to, the coexistence of multiple stationary states, the emergence of oscillations, and the chaotic evolution of concentrations in space and time. These emerging organizations play a central role in the dynamics of reactive systems ranging from tabletop experiments to industrial applications to biological cells.

The constructive role played by nonequilibrium reactions in the development of a macroscopic order has been clarified and put on a firm theoretical basis by Prigogine and co-workers.² Because of the intrinsically nonlinear character of their macroscopic kinetics, chemical reactions can destabilize the states emanating from equilibrium, which form the so-called thermodynamic branch. This destabilization can lead to the sudden appearance of new behaviors, among which one can encounter the aforementioned complex phenomena.

The above macroscopic approach has been used successfully to assess the origin of many nonlinear phenomena, including, in particular, oscillations observed in heterogeneous catalysis and in living cells.²⁻⁴⁻ In both of these cases, however, chemical reactions take place in extremely small systems. The diameter of catalytic particles ranges from a few to about a hundred nanometers, and that of a biological cell is typically on the order of the micrometer. At such a scale, the atomic structure of matter manifests itself in the form of important molecular fluctuations, which affect the time evolution of all observables. These fluctuations could in principle modify or altogether destroy the self-organized phenomena. It is thus crucial to understand the role that they play in nanoscale dynamics.

If much effort has been devoted to unveil the properties of fluctuations in systems at or close to thermodynamic equilibrium, much less is known about fluctuations in far-from-equilibrium systems, where the self-organization takes place. Theoretical studies of such noisy systems have been developed since the 1970s,⁷⁻⁹ and several effects have been investigated, such as noise-induced bistability,⁷ transitions between coexisting states induced by external or internal noise,⁶⁻¹² stochastic resonance,¹³⁻¹⁷ or variability and robustness in gene expression.¹⁸⁻²⁰ The studies performed thus far and the conclusions drawn from them rely almost exclusively on the use of stochastic approaches. In this framework, one assumes that the reactive processes can be modeled as random events, so that the statistics of the concentrations and their fluctuations is captured by a relatively simple evolution equation for the probability to find the system in a given state.

Experimental verifications of the validity of the stochastic approach for nanoscale reactions have lagged behind for a long time. Recent advances in experimental techniques have however allowed the study of far-from-equilibrium systems at the nanoscale. In particular, the discovery of nonlinear behaviors with field electron and field ion microscopes has opened new perspectives.¹¹⁻¹⁵ The metallic tip used in such microscopes has a radius of curvature of about 20 nm at the apex. The dynamics of reactions can be followed in regions...
comprising only a few hundred adsorption sites, a size for which molecular fluctuations are expected to play an important role.

The purpose of this work is to report on experimental results supporting fundamental assumptions of the stochastic theory used to describe nanoscale noisy oscillators. The question of the role played by fluctuations is pivotal for understanding the robustness of chemical clocks at the nanometric scale. We focus in particular on the phase diffusion induced by noise. According to this mechanism, the phase of the oscillator undergoes a random walk of Gaussian character, which is justified by the central limit theorem. Moreover, noisy oscillations are expected to lose their synchrony as periods repeat. This loss of synchrony can be characterized by the correlation time, which is defined as the damping time of the temporal autocorrelation function of the signal. Theory predicts a universal relationship between phase diffusion and the correlation time of oscillations, which we aim to test experimentally.

The experiments were carried out in a stainless steel field emission microscope with a base pressure of $10^{-10}$ mbar. Details about the setup and principles of the methods can be found elsewhere. The platinum field emitter tips were prepared by electrochemical etching and subsequently cleaned in a ultrahigh vacuum chamber by cycles of field evaporation, thermal annealing, and ion sputtering, as described in ref 27. Figure 1 shows an image of the surface of the resulting sample obtained by field ion microscopy at low temperature.

Field electron microscopy (FEM) was used to monitor the ongoing reaction. Typically, the procedure consisted of heating the sample to 390 K and then applying a field of about 4 V/nm$^{-1}$. A mixture of nitrogen dioxide (98% purity) and dihydrogen (99.9996% purity) was then admitted into the chamber. The partial pressures were measured by a Bayard–Alpert gauge. The values that we report take into consideration the gas correction factors. The dynamics of the reaction was followed by filming a phosphor screen, which collects the output of a multichannel plate used to amplify the electronic signal emitted from the tip sample. The video recording device has a time resolution of 40 ms digitized with a dynamic range of 8 bits.

The time series used for the statistical treatments correspond to variations of the brightness of the image as measured by the gray level over a fixed region of interest, from which the background brightness was subtracted. The region of interest that we followed corresponds to one of the {012} facets and extends over approximately 10 nm$^2$ (see Figure 1). The first return times were computed as the time it takes for the signal to cross its average brightness during an oscillation, on the way up. Statistics obtained with different definitions of the first return time (for example, the crossing time during a decrease of the intensity of the signal) were tested and shown to lead to no discernible differences with the results presented here. The histograms were obtained by using Scott’s normal reference rule$^{18}$ for the width of the bins. The (unbiased) autocorrelation functions were calculated with the corresponding Matlab built-in function. The correlation times (see later in the text) were obtained by a linear regression of the logarithm of the maxima of the autocorrelation function.

We started the experiments by setting a constant pressure of NO$_2$ and then increasing the pressure of H$_2$. The surface was in each case monitored for several minutes to detect kinetic instabilities. These experiments revealed that highly regular oscillations of the brightness could be observed above a critical pressure of H$_2$, $p_{H2}^c$ (see Figure 2a). FEM micrographs of the oscillating behavior are not shown here but can be found in previous publications (see, for example, ref 40). The first oscillations (i.e., those observed just beyond the critical pressure) have a relatively large amplitude and a low frequency. Both the amplitude and the period tend to fluctuate, however. This feature is not surprising in view of the very small size of the system under investigation. We will come back to this important point later on. As the distance from the critical pressure increases, the mean amplitude of the oscillations remains constant to some extent. The mean frequency increases, as pictured in Figure 2b. Note that when the NO$_2$ pressure is larger than the one used for the depicted results, the frequency presents a maximum that is observed at a well-defined pressure, and after which, it slowly decreases. In all cases, in the vicinity of the critical pressure, the mean frequency scales as $ν ∝ (cst - ln μ)^{-1}$, where $μ = (p_{H2} - p_{H2}^c)/p_{H2}$, which is consistent with the transition being a homoclinic bifurcation.$^{29}$

The oscillations that we observe are due to the fact that the catalytic surface is an open reactor, in which nonlinear chemical processes are taking place. Potential chemical mechanisms explaining these oscillations are discussed elsewhere.$^{27,40}$ Here, we want to assess in detail the variability of the oscillating process itself. More precisely, our objective is to verify whether the statistical properties of the fluctuating oscillations respect universal features, as predicted by stochastic theories.

The dynamics of reactive systems at the nanoscale is usually assessed on the basis of a chemical master equation.$^6$ In such an approach, the reactions are seen as Markovian stochastic processes satisfying well-defined physicochemical constraints. The study of oscillating reactions has shown that fluctuations can affect both the amplitude and the periodicity of the process. In the macroscopic limit, where the effects of fluctuations can be neglected, oscillating reactions define a limit cycle in the phase space spanned by the concentrations of the different species. One can then define a first return time as the time taken by the system to come back to a given point on the cycle.
The trajectories along (i.e., tangentially to) the limit cycle. As a consequence, the first return time is a statistically distributed quantity. Starting from the master equation for a homogeneous system, it has been shown that in the weak noise limit (where the master equation actually reduces to a Fokker–Planck equation), the first return time $T$ has a Gaussian distribution

$$P(T) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(T - \langle T \rangle)^2}{2\sigma^2}\right]$$

(1)

In this formula, $\langle T \rangle$ is the mean period of the noisy limit cycle and $\sigma^2$ the variance of the distribution. This prediction is valid for a fully developed cycle, in other words, when the system evolves far away from any bifurcation point. The variance of the first return time is related to the amplitude of the noise $\epsilon = 1/\Omega$, where $\Omega$ is proportional to the system size by $35$–$38$

$$\sigma^2 = cF$$

(2)

In this equation, $F$ is a function that critically depends on the details of the mechanism and on the rates of the reactions taking place in the system. It is thus highly system-specific.

The phase diffusion is also known to affect the shape of the temporal autocorrelation function

$$C(t - t') = \frac{\langle X(t)X(t') \rangle - \langle X(t) \rangle\langle X(t') \rangle}{\langle X^2(t) \rangle - \langle X(t) \rangle^2}$$

(3)

in which $X(t)$ is the brightness in the region of interest at a given time. The brackets represent averaging over time. This function measures how strongly correlated two measurements performed at a temporal distance $t - t'$ are during the oscillations. It has been predicted that $C(t - t')$ presents damped oscillations in the case of a noisy limit cycle, first for specific examples of simple reactions $32,39$ and then in a more general fashion. $36,37$ More precisely, it has been shown that the envelope of this function decreases exponentially as $e^{-t/\tau}$ with a decay rate given by

$$\tau = \frac{\langle T \rangle^3}{2\pi^2cF}$$

(4)

Like the variance of the first return time, this quantity depends on the details of the reactions through the system-specific function $F$. Despite these specificities, it appears that all of the fluctuating oscillations that comply with the hypotheses of the stochastic approach should be such that the product of their relative variance and their relative decay rate is a constant.

Table 1. Selected Experimental Time Series Summarizing the Conditions and the Measurements for the Experiments Retained in the Statistical Treatments

<table>
<thead>
<tr>
<th>experiment</th>
<th>$p_{NO_2}$ (mbar)</th>
<th>$p_{H_2}$ (mbar)</th>
<th>period (s)</th>
<th>$\tau$ (s)</th>
<th>$\sigma$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$5.43 \times 10^{-6}$</td>
<td>$3.48 \times 10^{-5}$</td>
<td>4.04</td>
<td>11.5</td>
<td>0.251</td>
</tr>
<tr>
<td>2</td>
<td>$5.43 \times 10^{-6}$</td>
<td>$1.91 \times 10^{-4}$</td>
<td>2.76</td>
<td>145.2</td>
<td>0.128</td>
</tr>
<tr>
<td>3</td>
<td>$5.43 \times 10^{-6}$</td>
<td>$4.45 \times 10^{-4}$</td>
<td>2.24</td>
<td>23.36</td>
<td>0.249</td>
</tr>
<tr>
<td>4</td>
<td>$5.36 \times 10^{-6}$</td>
<td>$1.57 \times 10^{-4}$</td>
<td>4.28</td>
<td>8.5</td>
<td>0.49</td>
</tr>
<tr>
<td>5</td>
<td>$5.36 \times 10^{-6}$</td>
<td>$2.41 \times 10^{-4}$</td>
<td>2.96</td>
<td>6.8</td>
<td>0.38</td>
</tr>
<tr>
<td>6</td>
<td>$3.64 \times 10^{-6}$</td>
<td>$1.05 \times 10^{-4}$</td>
<td>3.05</td>
<td>185.7</td>
<td>0.044</td>
</tr>
<tr>
<td>7</td>
<td>$3.64 \times 10^{-6}$</td>
<td>$1.46 \times 10^{-4}$</td>
<td>2.71</td>
<td>821.2</td>
<td>0.0230</td>
</tr>
<tr>
<td>8</td>
<td>$3.64 \times 10^{-6}$</td>
<td>$2.10 \times 10^{-4}$</td>
<td>2.36</td>
<td>109.4</td>
<td>0.057</td>
</tr>
<tr>
<td>9</td>
<td>$3.64 \times 10^{-6}$</td>
<td>$4.00 \times 10^{-4}$</td>
<td>5.900</td>
<td>87.5</td>
<td>0.322</td>
</tr>
<tr>
<td>10</td>
<td>$2.16 \times 10^{-6}$</td>
<td>$2.00 \times 10^{-4}$</td>
<td>8.90</td>
<td>49.2</td>
<td>0.73</td>
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<tr>
<td>11</td>
<td>$2.16 \times 10^{-6}$</td>
<td>$2.18 \times 10^{-4}$</td>
<td>10.42</td>
<td>26.8</td>
<td>1.03</td>
</tr>
<tr>
<td>12</td>
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<td>$2.44 \times 10^{-4}$</td>
<td>13.52</td>
<td>32.0</td>
<td>1.49</td>
</tr>
</tbody>
</table>

*In each case, the temperature is 390 K.*
\[
\left( \frac{\sigma^2}{\langle T^2 \rangle} \right) \left( \frac{T}{\langle T \rangle} \right) = \frac{1}{2\pi^2} \tag{5}
\]

We extracted the statistics of numerous experiments in order to verify the above predictions. The oscillations observed just after crossing the critical pressure were discarded in order to account for the fact that the aforementioned results hold far from bifurcation points. The 12 selected experiments are listed in Table 1. Histograms of four of the chosen experiments are shown in Figure 3. The experiments correspond to different partial and total pressures and sometimes different platinum tips. The corresponding oscillations have different shapes, and their average periods differ. It nevertheless appears that in all cases, the first return time closely follows a normal distribution, as predicted by the Fokker–Planck equation.

The autocorrelation functions were also extracted from these experiments. They indeed consist of damped oscillations, as reported earlier. The correlation time was obtained by fitting each of the decaying envelopes of these oscillations with an exponential function. By combining these results with the variance and the mean of the first return times, \( \sigma^2/T^2 \) and \( \tau/T \) were calculated. Figure 4 shows a plot of the logarithm of the relative variance of the period of oscillations. The points correspond to the selected periodic behaviors (see Table 1). The dashed line is the best linear fit of the data. Its intercept and slope are consistent with the proposed scaling, as discussed in the text.

Figure 4. Logarithm of the relative lifetime as a function of the logarithm of the relative variance of the period of oscillations. The points correspond to the selected periodic behaviors (see Table 1). The dashed line is the best linear fit of the data. Its intercept and slope are consistent with the proposed scaling, as discussed in the text.

The variance and the mean of the exponential function. By combining these results with the first reported evidence that stochastic approaches can indeed be used to assess the noisy behavior of chemical clocks. They confirm that phase diffusion is a key phenomenon affecting the regularity and hence the robustness and the controllability of chemical reactions at such scales.

We plan to assess the universal character of these results by studying other oscillating reactions with the same technique (such as the \( \text{NO}_2 + \text{H}_2 \) or the \( \text{O}_2 + \text{H}_2 \) reactions on rhodium). Future work should also address the issue of the determination of nonuniversal aspects of such systems. Besides the understanding of the reaction mechanism at the origin of oscillations, several issues remain open, in particular, the determination of the noise amplitude \( \epsilon = \Omega^{-1} \), which is related to the system size. One of the basic assumptions of the theoretical results that we used is that the system under consideration is well-mixed. The robustness of the oscillations that we observed suggests that the number of particles involved in the phenomenon is larger than what can be found on the single monitored facet. This observation implies that a mechanism of synchronization exists, which is able to couple different parts of the sample so that \( \epsilon \) is effectively small. The nature and the efficiency of such coupling should be investigated in detail.

The variance and the correlation time of oscillations are determined by the function \( \epsilon \), which depends on the chemical mechanistic details of the oscillations. Our results suggest that information on these nonuniversal features can be extracted using time series analysis. The validity of proposed chemical mechanisms could be assessed not only from the predictions that they lead to concerning the average behavior of the system but also from the very structure of the fluctuations around such an average.

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\subsection*{Notes}
The authors declare no competing financial interest.

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