Abstract

A new tool for modeling electrochemical kinetics is presented. An extension of the Stochastic Simulation Algorithm framework to electrochemical systems is proposed. The physical justifications and constraints for the derivation of a chemical master equation are provided and discussed. The electrochemical driving forces are included in the mathematical framework, and equations are provided for the associated electric responses. The implementation for potentiostatic and galvanostatic systems is presented, with results pointing out the stochastic nature of the algorithm. The electric responses presented are in line with the expected results from the deterministic theory.
I. INTRODUCTION

Historically, chemical kinetics is formulated as a set of equations in order to predict the time evolution of the concentration of a number of species undergoing a set of reactions. With the assumption that the concentrations $Z = Z(t)$ can be well-described by a set of ordinary differential equations, the so-called Reaction Rate Equations (RRE) became an important and useful tool in chemistry. As more complex systems emerged, its studies demanded more mathematical tools, and several approximations were developed, from steady-state analytical solutions to spatial functions solved by numerical methods. Underlying it all is the understanding that, although all chemical processes are discrete and occur in the atomic and molecular scale, its macroscopic behavior can be reasonably explained and reproduced with continuous functions.

However, this macroscopic, continuous approach is ultimately just an approximation, albeit a very good one in most usual conditions (for noteworthy remarks on this point, see [1]). On a different front, it was pursued the microscopical, statistical formulation that would reduce to the RRE in the macroscopic limit (for a proper introduction and review on this topic, see [2]). In the framework of statistical mechanics, the stochastic approach to chemical kinetics was developed, where reactions are taken as random, discrete changes in the system, following a successful interaction between species. This approach is marked by the postulation of the chemical master equation (CME), a Fokker-Planck-type equation describing the time evolution of the probability density function of finding the system on a given configuration. Similarly to the RRE, if not worse, most systems of interest have no analytical solution to the master equation, and numerical methods proved inefficient for these systems.

This was partly solved by the development of the Stochastic Simulation Algorithm (SSA) by Gillespie [3]. Originally being a framework derived logically from statistical arguments, Gillespie went on to prove the connection of the SSA and the CME, providing a detailed derivation of the latter [4]. The SSA provides the time evolution of a system described by a CME, in a discrete-jump Markov-chain approximation. The result is a time trajectory in configuration space, noteworthy for producing results
statistically equal to the RRE. The SSA proved particularly useful for biological systems, where very low concentrations of enzymes and other macromolecules interact in complex mechanisms. However, certain systems presented large differences in the time scale of their various processes, significantly raising the computational cost for its simulation and reducing the usefulness of the exact approach. As the field progressed, several approximations and methods were developed, leading to a large array of algorithms enabling the simulation of diverse and complex systems. The development of the field led to the derivation of a chemical Langevin equation, and ultimately to a rigorous connection between both microscopic and macroscopic approaches, showing that the CME reduces to the RRE in the thermodynamic limit.

It must be noted, however, that the SSA was originally proposed for reactions in gas phase, and later on extended to diluted systems in a solvent, remaining apparently underused in fields outside biochemistry. As complex, non-linear systems are explored for a variety of objectives, and low concentrations are used in ever more sensitive systems, the deterministic results of the RRE fail to capture the intrinsic randomness of such systems. This is particularly striking for fields relying on interfacial systems, notably heterogeneous catalysis and electrochemistry. Nanometer-sized particles and complex feedback loops lead to systems sensitive to fluctuations, and advanced probing techniques respond accordingly, resulting in a “noise” mostly associated to thermal fluctuations (e.g. and references therein). The stochastic approach is, therefore, not only appropriate to study such systems, but one could argue that it is required in most of them, as the SSA proved to be in biological systems. A variety of frameworks and algorithms have been proposed to address this, however they are usually connected to advanced molecular dynamics and electronic structure methods, being cumbersome and unfamiliar to most experimental chemists. In this way, the main objective of this work is to propose an extension of Gillespie’s SSA to interfacial systems, in particular electrochemical ones, providing a straightforward framework to back up microscopic experiments. The remainder of this work is divided as follows. In Section it is provided the physical assumptions and justifications that lead to the master equation in an interfacial system. Section goes through the stochastic algorithm and the pro-
posed response for electrochemical systems, as well as the details of the implementation. Section IV shows some numerical results of the current implementation for simple electrochemical systems. Finally, Section V summarizes the work and some perspectives are pointed out.

II. THE CHEMICAL MASTER EQUATION

The aim of this section is to derive, heuristically, the CME that describes the time evolution of the probability density function of the population vector $\mathbf{X}(t)$ of a system representing the surface of a material and the chemical species adsorbed to it. In principle, there is no need to re-derive the master equation, since it is supposed to be able to describe any reasonably well-behaved chemical system. The actual point of this derivation is to provide justifications for the assumptions made, and therefore identify the physical meaning of the constraints required for it. The train of thought follows closely that of Gillespie’s in [4].

Consider a bi-dimensional system consisting of $N$ adsorbed chemical species $S_1, S_2, \ldots, S_N$, which interact through $M$ elementary reaction channels $R_1, R_2, \ldots, R_M$. Since it is the surface of a material, the different adsorption sites could be identified as “chemical” species, or “holes”, however the generality on the identity of species will be maintained. The system is, in general, open, consisting of a surface of area $A$, not necessarily flat, in thermal equilibrium at absolute temperature $T$. The system is described at any given time by the state vector $\mathbf{X}(t) = \mathbf{n}$, where:

$$X_i(t) \equiv \text{population number of species } S_i \text{ in the system at time } t, \text{ with } i \in [1, N],$$

(1)

$X_i(t)$ is connected with the species’ surface concentration by $\Gamma_i(t) = X_i(t)/A$.

To justify the Markov-chain approach to stochastic kinetics, two points are proposed. Unlike in gas-phase, the concept of a well-stirred mixture is not a necessary consequence of thermal equilibrium, as translation in the surface is usually dependent on hopping between energy barriers. The analogous situation can be given by a surface where
the energy barrier for site hopping has the same order of magnitude, or lower, than the thermal energy $k_B T$, where $k_B$ is Boltzmann’s constant. This would allow for an almost free translation, similarly to the scenario depicted by the linear adsorption isotherm, i.e. Henry’s law. This covers the homogeneity of the system and reaction channels that involves collision between species. For channels representing reactions with the surface, two approaches might be taken:

1. collision between the adsorbed species and the appropriate “hole”;

2. reaction coordinate incorporates vibrational and rotational degrees of freedom of involved species.

Approach #1 could be understood to reasonably justify the memory-less scenario if one accepts that translation is also sufficient to thermalize a system after an unsuccessful, reaction-less collision between two adsorbed species. On the other hand, approach #2 gives a different possibility for thermalization of the system after a tunneling attempt between adsorbed species and the surface, namely the vibrational and rotational modes of the adsorbed species. Either way, it is assumed that translational, in this case bi-dimensional, and/or vibrational and rotational modes are sufficient to thermalize the system, destroying any memory effect.

The thermalization of the system, as mentioned above, is necessary to enforce the following conditions: i) the position of a randomly selected molecule can be treated as a random variable of the system, being uniformly distributed over the surface; and ii) the energy of a randomly selected molecule can be treated as a random variable that follows Maxwell-Boltzmann statistics. The latter statement is broader than that originally given by Gillespie in [4], where the molecules’ momentum were taken as the random variable, hence only the kinetic energy was considered. However if we are to include the possibility of thermalization through vibrational and vibrational modes, solely considering the kinetic energy is insufficient to give an accurate physical picture of the system. The end point is the same, though, as Gillespie’s, i.e. that the molecular positions and internal energies are statistically independent of each other.
Having defined the system and its variables, it is now needed to establish its time evolution. It is defined the reaction probability:

$$\pi_\mu(t, dt) \equiv \text{probability that a randomly selected combination of } \mathcal{R}_\mu \text{ reactant molecules at time } t \text{ will react accordingly in the next infinitesimal time interval } [t, t+dt], \text{ with } \mu \in [1, M].$$ (2)

It is shown in [4] that $\pi_\mu(t, dt)$ can be written in the form

$$\pi_\mu(t, dt) = c_\mu dt$$ (3)

for most, if not all, chemical reaction channels as a good approximation. The term $c_\mu$ is called the transition probability, or in Gillespie’s original terminology, the specific probability rate constant. This term is independent of $t$, and reflects the particularities of each channel $\mathcal{R}_\mu$. In Gillespie’s original work, it was sufficient to demonstrate that $\pi_\mu$ can be written as in Eq. 3. Here, it is important to elaborate it further. Firstly, if one considers that any surface reaction can be represented as a collision between molecules, similarly to the gas-phase, then the arguments given in [4] should be enough to justify the use of Eq. 3 with minor modifications due to reduced dimensionality. The same arguments are reasonably applied even in the circumstance where the vibrational or vibrational modes are the reaction coordinate, as one could interpret it as a single molecule reaction, driven by its own internal mechanism. Secondly, surface reactions actually take place in an interface between different phases, where a population-dependent difference in free energy arises. In electrochemistry, this is usually represented by the electrode potential, $E = E(X(t))$, being either a parameter or an observable in electrochemical experiments. In the case of $E$ as an variable, it is dependent on the population numbers, which makes $c_\mu = c_\mu(E(t))$, since the populations numbers are time-dependent. This is against the assumptions required to derive the master equation. The following reasoning is proposed to mend this apparent incompatibility. Following basic electrochemical theory[16], one starts by redefining the transition probability:

$$c_\mu(E(t)) = c_\mu^0 f(E(t))$$ (4)
where \( c^0_\mu \) is now the time-independent transition probability, and \( f(E(t)) \) is a function that gives the appropriate dependency on \( E \). This alone is not enough to mend the gap. To relax the dependency of \( E \) with \( t \), recall that the time dependency arises due to the population numbers \( X(t) \). However, \( X \) is actually a constant between reactions, i.e. within the interval \([t, t + dt]\), since its time evolution is given by discrete Markov jumps. Therefore, it is possible to establish that

\[
E(X(t)) = \text{constant}, \quad \text{for } t \in [t, t + dt),
\]

thus removing the dependency of \( c_\mu \) on \( t \) between reactions. The actual form of \( f(E) \), usually an exponential of \( E \), is not actually relevant, and can be modified according to the desired electrochemical kinetic model. However, it is important that \( E \) must either be a constant parameter or observable of the system, i.e. only potentiostatic (constant applied electrode potential) or galvanostatic (constant applied electric current) setups are relevant. To allow for time-dependent \( E \) as a parameter, it is necessary to resort to approximations.

Now, it should be noted that Eq. 3 defines the probability that a randomly selected combination of molecules react through channel \( R_\mu \). To calculate the actual probability of observing a reaction through channel \( R_\mu \), it is necessary to account for all possible combinations of molecules that might take part in it. This is done by defining the function

\[
h_\mu(n_1, \ldots, n_N) \equiv \text{the number of distinct combinations of } R_\mu \text{ reactant molecules in the system when there are exactly } n_i \text{ molecules of species } S_i, \text{ with } i \in [1, N]
\]

(6)

The actual form of \( h_\mu \) is given by the state change matrix \( \nu \), defined as

\[
\nu_{\mu i} \equiv \text{the change in } X_i \text{ caused by the occurrence of one } R_\mu \text{ reaction.}
\]

(7)

At this point we diverge somewhat from [4] by further describing it as:

\[
\nu = P - R
\]

(8)
where \( P \) and \( R \) are the products and reactants stoichiometric coefficients matrices, respectively. This implicitly defines all stoichiometric coefficients as positive integers, with the correct change in \( X \) given by the above definition of \( \nu \). This is done in order to provide a general definition for \( h_\mu \). By inspecting the form of elementary reaction steps, it is possible to generalize and write:

\[
h_\mu(n) = \prod_{i=1}^{N} \left( \frac{n_i}{R_{\mu i}} \right)
\]

\[
= \prod_{i=1}^{N} \frac{n_i!}{R_{\mu i}! (n_i - R_{\mu i})!}
\]

(9)

where it becomes clear why it is necessary that \( R \) consists only of positive integers. Finally, then, one finds that the total probability of a given combination of molecules reacting through channel \( R_\mu \) in the time interval \([t, t+dt]\) is given by the term \( c_\mu(E)h_\mu(n)dt \).

Having gone through the same development as Gillespie did in [4], one can use the same three theorems in order to conclude this derivation:

1. the probability of one reaction \( R_\mu \) to occur in the system in the time interval \([t, t+dt]\), given that \( X(t) = n \), is \( c_\mu(E)h_\mu(n)dt + O(dt^2) \);

2. the probability of no reaction occurring in the interval \([t, t+dt]\), given \( X(t) = n \), is \( 1 - \sum_{\mu=1}^{M} c_\mu(E)h_\mu(n)dt + O(dt^2) \);

3. the probability of an \( m \) number of reactions occurring in the system in the time interval \([t, t+dt]\) is \( O(dt^m) \).

The only remarks that might be reinforced is that trying to determine the time evolution of the species’ population vector \( X(t) \) is hopeless in most cases. Instead, one defines

\[
P(n, t|n_0, t_0) = \text{probability that } X(t) = n, \text{ given that } X(t_0) = n_0
\]

and \( t \geq t_0 \),

(10)

and try to determine its time evolution. Using the theorems above to account for the probabilities that the species’ population numbers be \( X(t) = n \), during a time interval
where $\nu_\mu$ is the state change vector for channel $R_\mu$. This equation indicates that, at first order in $dt$, two possibilities exist for the system to reach state $X(t + dt) = n$: i) the system is at state $X(t) = n$ and no reaction occurs, and ii) the system is at state $X(t) = n - \nu_\mu$ and one reaction $R_\mu$ occurs. Finally, one subtracts the probability at time $t$, divides by $dt$, and taking the limit $dt \to 0$, one obtains the following equation:

$$\frac{\partial}{\partial t} P(n, t|n_0, t_0) = \sum_{\mu=1}^{M} [c_\mu(E)h_\mu(n - \nu_\mu)P(n - \nu_\mu, t|n_0, t_0) - c_\mu(E)h_\mu(n)P(n, t|n_0, t_0)]$$  \hspace{1cm} (12)$$

subjected to the initial conditions

$$P(n, t = t_0|n_0, t_0) = \begin{cases} 1, & \text{if } n = n_0 \\ 0, & \text{if } n \neq n_0 \end{cases}$$  \hspace{1cm} (13)$$

This is the so-called chemical master equation, as derived by Gillespie in [4]. It follows then, by the arguments given by him, that the Stochastic Simulation Algorithm (SSA) [3] can also be applied to surface reactions, given that the above constraints are observed, particularly the low energy barrier for site hopping and that the electrode potential be constant between reactions.

III. THE STOCHASTIC SIMULATION ALGORITHM

A. Mathematical Framework

The SSA is deemed as a logic equivalent to the CME [4], differing by the fact that, while the CME describes the time evolution of the probability density function, the
SSA provides a time trajectory in population space. This is accomplished by sampling the joint probability distribution:

\[ P(\tau, \mu|n, t) \, d\tau \equiv \text{probability that the next reaction in the system will occur} \]
\[ \text{in the time interval } [t + \tau, t + \tau + d\tau) \text{ and will be an } R_\mu \text{ reaction.} \] (14)

To derive a formula for this joint probability, it is defined a given channel’s reaction propensity and the total reaction propensity functions:

\[ a_\mu(n, E) = c_\mu(E) \, h_\mu(n) \] (15)
\[ a_0(n, E) = \sum_{\mu=1}^{M} a_\mu(n, E) \] (16)

respectively, both with units of s\(^{-1}\). These functions are connected to Theorems #1 and #2: \( a_\mu \) representing the probability per unit time, to first order in \( dt \), that channel \( R_\mu \) will fire in the time interval \([t, t + dt)\); while the probability per unit time, also to first order in \( dt \), of no reaction occurring in the time interval \([t, t + dt)\) is given by \( 1 - a_0 \).

Considering this, it can be shown that the joint probability can be written as:

\[ P(\tau, \mu|n, t) = a_\mu(n, E) \exp[-a_0(n, E) \, \tau] \] (17)

In this way, the SSA proceeds by sampling the time for the next reaction, \( \tau \), and the channel that will subsequently fire, \( \mu \). This is done by noting that the time for any reaction to occur in the system is given by:

\[ P(\tau|n, t) = \sum_{\mu=1}^{M} P(\tau, \mu|n, n) \]
\[ = a_0(n, E) \exp[-a_0(n, E) \, \tau] \] (18)

and the probability of a given channel \( \mu \) firing is simply given by \( a_\mu/a_0 \). Details about the recommended implementation are described in [3].

As noted by the explicit dependency of the reaction propensity function in Eq. [4], the SSA works exactly the same way for surface reactions, electrochemical or not. This was noted in the beginning of the CME derivation. The interest now lies in providing
the associated electric response for the electrochemical reactions under the relevant conditions:

- Potentiostatic, with constant applied electrode potential $E$, the electric current $I = I(t; E)$.

- Galvanostatic, with constant applied electric current $I$, the electrode potential $E = E(X(t); I)$.

For the potentiostatic case, the most obvious solution would be to simply account for the number of electrons transferred in unit time at a given electrode potential, and then provide the electric current:

$$I = \frac{\delta Q}{\delta t}$$  \hspace{1cm} (19)

where $Q$ is the total charge transferred between the system’s population and the surface. However, in this way, there’s no clear way to simulate galvanostatic systems. To circumvent this, a different interpretation is proposed. For an ensemble, Eqs. [15] and [16] can be understood as the average number of reactions per unit time for channel $\mathcal{R}_\mu$ and all channels, respectively. By considering that electrochemical channels involve electron transfer to or from the electrode, it is straightforward, to connect these to the electric current for the ensemble:

$$I_\mu (n, E) = q_e \nu^e_\mu a_\mu (n, E)$$  \hspace{1cm} (20)

$$I (n, E) = \sum_{\mu=1}^{M} I_\mu$$

$$= q_e \sum_{\mu=1}^{M} \nu^e_\mu a_\mu (n, E)$$  \hspace{1cm} (21)

where $q_e$ is the fundamental charge, $\nu^e_\mu = \pm 1$ is the number of electrons transferred in channel $\mathcal{R}_\mu$. In this way, it is defined $\nu^e_\mu = 1$ for oxidation and $\nu^e_\mu = -1$ for reduction reactions, and therefore $I_\mu > 0$ and $I_\mu < 0$ for anodic and cathodic currents, respectively. Equation [21] directly provides the desired electric response in the case of potentiostatic setups, while providing the electrode potential through Eq. [4] in the case of galvanostatic setups. It is noteworthy that no electrochemical kinetic model has been assumed.
so far, so the form of \( f(E) \) is completely arbitrary, as long as it follows the required thermodynamical constraints.

The above ensemble can be shown to be consistent with the thermodynamic limit of the CME/SSA approach. It was shown in [10] that, through the conditions used in the \( \tau \)-leap method [7], it is possible to describe the time evolution of the population vector \( \mathbf{X}(t) \) through a Langevin-type equation. The \( \tau \)-leaping conditions are:

\[
a_{\mu}(\mathbf{n}, E) \approx \text{constant in } [t, t + \tau), \quad \forall \mu \quad (22)
\]
\[
a_{\mu}(\mathbf{n}, E)\tau \gg 1, \quad \forall \mu \quad (23)
\]

Assuming that both conditions be satisfied, the time evolution of the population vector can be written as:

\[
\mathbf{X}(t + dt) - \mathbf{X}(t) = \sum_{\mu=1}^{M} \nu_{\mu} a_{\mu}(\mathbf{X}(t), E) \, dt + \sum_{\mu=1}^{M} \nu_{\mu} \mathcal{N}_{\mu}(0, 1) \sqrt{a_{\mu}(\mathbf{X}(t), E)} \, dt \quad (24)
\]

where \( \mathcal{N}(0, 1) \) is a normally distributed random number with zero mean and unity standard deviation. Equation (24) is the chemical Langevin equation, as derived by Gillespie. It has been shown that the \( \tau \)-leap conditions can always be satisfied [11], given that the system be made “sufficiently large” [6], therefore Eq. (24) is always valid.

Taking the thermodynamic limit, that is, increasing the system such that \( A \to \infty \) with the constraint that the surface concentrations \( \Gamma = \mathbf{X} / A \) remains constant; the term on the left side of Eq. (24) grows linearly with system size, and so does the first term on the right side. The second term, the “noise”, grows with the square root of the size, being negligible in the thermodynamic limit. Hence, Eq. (24) reduces to

\[
\frac{d\mathbf{X}(t)}{dt} = \sum_{\mu=1}^{M} \nu_{\mu} a_{\mu}(\mathbf{X}(t), E) \quad (25)
\]

which is the usual, deterministic approach to chemical kinetics, the Reaction Rate Equation (RRE), more usually written using surface concentrations when dealing with
Electrochemical reactions:

$$\frac{d\Gamma(t)}{dt} = \frac{d}{dt} \left( \frac{X(t)}{A} \right) = \sum_{\mu=1}^{M} \nu_{\mu} a'_{\mu} (\Gamma(t), E)$$

(26)

where $a'_{\mu} = a_{\mu}/A$. Considering the possibility of electron transfer to or from the surface, one writes Faraday’s law of electrolysis:

$$I = q_e A \frac{d\Gamma(t)}{dt} = q_e \sum_{\mu=1}^{M} \nu_{\mu} e_{\mu} a_{\mu} (X(t), E)$$

(27)

which is the same as Eq. 21, thereby justifying the ensemble interpretation proposed above.

### B. Implementation

For the results shown in Section IV, a MATLAB® 2012a script was written. As an example, the Butler-Volmer model of electrochemical kinetic is used to define $f(E)$. The macroscopic derivation for the model can be found in [16]. In the present framework, it is implemented as:

$$f(E) = \exp \left[ \alpha_{\mu} \frac{\nu_{\mu} q_e}{k_B T} \left( E - E_{0'}^{\mu} \right) \right]$$

(28)

where $\alpha_{\mu}$ is the transference coefficient and $E_{0'}^{\mu}$ is the formal potential of channel $R_{\mu}$. The usually employed Faraday’s constant, $F$, and the universal gas constant, $R$, have been exchanged for its molecular counterparts, $q_e$ and $k_B$ respectively, in order to maintain coherence. Hence, the reaction propensity function is completely defined as

$$a_{\mu} (n, E) = c_{\mu}^{0} h_{\mu} (n) \exp \left[ \alpha_{\mu} \frac{\nu_{\mu} q_e}{k_B T} \left( E - E_{0'}^{\mu} \right) \right]$$

(29)

and consequently, the associated individual and total currents. For potentiostatic systems, the implementation is quite straightforward, with the current in Eq. 21 possessing
a parametric dependence on $E$:

$$I(n; E) = q_e \sum_{\mu=1}^{M} \nu_{\mu} a_{\mu}(n; E)$$

(30)

For galvanostatic systems, a simple minimization of Eq. 21, coupled to Eq. 29, is sufficient:

$$\sum_{\mu=1}^{M} \nu_{\mu} a_{\mu}(n, E) - \frac{I}{q_e} = 0$$

(31)

In the current implementation, the minimization is carried through the Newton-Raphson method, with a relative tolerance of $10^{-6}$. Another point worth noticing is that function $h_{\mu}(n)$ is not implemented using the definition given in Eq. 9 but using individual forms to reactions up to order 3 for a given species. Figure 1 shows the core of the implementation.

FIG. 1: Flowchart of the current implementation of the electrochemical SSA.
IV. NUMERICAL RESULTS

As illustration of the framework and the current implementation, first consider the simple redox pair:

\[ S_1 + e^- \rightleftharpoons S_2 \]

which is implemented as two different reactions:

\[ S_1 + e^- \rightarrow S_2 \quad (32a) \]
\[ S_2 \rightarrow S_1 + e^- \quad (32b) \]

being the forward and backward reactions, respectively. Figure 2 presents a few superimposed time evolutions, and associated electric responses, for both potentiostatic and galvanostatic systems. The parameters used are \( \alpha_f = \alpha_b = 0.5 \) and \( E_f^0 = E_b^0 = 0.36 \) V. The electrode potential used for Fig. 2a is \( E = 0.4 \) V, while the electric current used for Fig. 2b is \( I = 2 \times 10^{-17} \) A. The initial conditions for both systems is \( X_1(t=0) = 0 \) for species \( S_1 \) and \( X_2(t=0) = 1000 \) for \( S_2 \).

It can be seen from Fig. 2a that the potentiostatic setup results in a time evolution quite similar to that of a simple chemical equilibrium. That is expected from the effect of the electrode potential as given in Eq. 29. The electric response is also what is expected from the current decay of a potential-step chronoamperometry\[16\], i.e. a high current surge followed by a fast decrease to zero at equilibrium. These results are mainly the result of the electrochemical kinetics model chosen, which is known to correctly reproduce most experimental results\[16\]. The main feature here would be the current oscillations around zero, which are the result of the dynamical, and stochastic, nature of chemical equilibrium.

On the other hand, the galvanostatic setup (Fig. 2b) shows a linear time evolution for the population numbers. Such result is relatively unfamiliar even in electrochemistry textbooks (e.g. \[16\] and \[18\]), but it can be predicted for simple systems, such as Eq. 32 using Eq. 31. The electrode potential, on the other hand, is the textbook
FIG. 2: Time evolution of the system described by Eq. (32) a) potentiostatic setup, $E = 0.4 \text{ V}$; b) galvanostatic setup, $I = 2 \times 10^{-17} \text{ A}$. Parameters used for both setups: $c_f^0 = c_b^0 = 1 \text{ s}^{-1}, \alpha_f = \alpha_b = 0.5, E_f^{0'} = E_b^{0'} = 0.36 \text{ V}$ and $X(t=0) = [0, 1000]$. Each figure shows 5 superimposed independent runs.

example for a current-step galvanostatic transient, loosely called a chronopotentiometry, showing the inflection point approximately at $0.36 \text{ V}$ and $X_1 \approx X_2$. The fluctuations are more evident than in the potentiostatic case, although being mostly due to the forced condition of the galvanostatic setup. This is reflected as large differences in the electrode potential, due to the exponential nature of the Butler-Volmer model.

A major advantage of the SSA is the possibility of obtaining statistics on the system under study, for instance average values and expected standard deviation. This allows a rigorous comparison with experimental results, but also provides a picture on the effects of random fluctuations in the system. Figure 3 shows the average and standard deviation of the electric current for 100 runs of the potentiostatic setup for Eq. (32) for two different initial population for species $S_2$. In this way, it is possible to establish if differences between a model and the experimental results are significant, given a certain statistical power. This becomes particularly important for “small” systems, as
FIG. 3: Average current associated with Eq. 32 with one standard deviation shown as the shaded area: Top: $X(t = 0) = [0, 1000]$, with inset showing a zoom in the $y$ axis; Bottom: $X(t = 0) = [0, 100]$. Statistics for each figure performed over 100 runs.

can be seen comparing the top and bottom graphs in Fig. 3. The currents differ by the size of the system, by one order of magnitude, as is noticed by the scales of the current. As expected, the behavior of the average current is basically the same for both systems. However, the standard deviation associated with the smaller system is significantly higher, relative to its peak current values, being roughly the same as for the larger system ($\delta I \approx 0.5 \times 10^{-17}$ A).

The simple model represented by Eq. 32 do not exhibit many of the effects commonly seen in electrochemical systems, most notably diffusion. Being a stochastic process, diffusion is readily incorporated in the current framework. However, the differences in time scales that arise lead to oversampling of the diffusion, greatly increasing the computation times for similar sampling of the reaction events when neglecting diffusion. A diffusional propensity function, although approximate, has been developed[9]. Its implementation, however, requires further development of the present framework, which
FIG. 4: Time evolution of the system described by Eq. 33: 
(a) potentiostatic setup, \( E = 0.4 \text{ V} \); (b) galvanostatic setup, \( I = 6 \times 10^{-17} \text{ A} \). Parameters used for both setups: 
\( c_{b,f}^0 = c_{b,b}^0 = 1 \text{ s}^{-1} \), \( \alpha_f = \alpha_b = 0.5 \), \( E_f^0 = E_b^0 = 0.36 \text{ V} \), \( c_a^0 = c_c^0 = 250 \text{ s}^{-1} \) and 
\( X(t = 0) = [0, 1000] \). The figures shows 5 superimposed independent runs.

are under pursue. On the other hand, the following model shows similar effects:

\[
\begin{align*}
\emptyset & \rightarrow S_2 & (33a) \\
S_2 & \rightleftharpoons S_1 + e^- & (33b) \\
S_1 & \rightarrow \emptyset & (33c)
\end{align*}
\]

where the empty set means a connection with a species reservoir, with no interest to the simulation. The redox reaction is the same as Eq. 32, and the parameters used are the same. For the diffusion channels, only the potential-independent specific transition coefficients are needed, being set up as \( c_a^0 = c_c^0 = 250 \text{ s}^{-1} \). Figure 4 presents the time evolution for both potentiostatic and galvanostatic setups.

The noteworthy effect of including the diffusion channels in the system is achieving a non-zero stationary current, in the potentiostatic setup (Fig. 4a). This is expected from the physical scenario and the deterministic theory. However, the decay in
current does not follow the prediction of Cottrell’s equation\cite{16}, which predicts a decay with $t^{-1/2}$, while the observed behavior is roughly proportional to $t^{-1}$. This is probably due to the fact that actual diffusion depends on the gradient of species’ population, unlike what has been used in this system. For the galvanostatic setup (Fig. 4b) no significant changes are seen, only the increased lifetime of species $S_2$, as noted by the higher value of applied current used. It is expected that more complex systems do require diffusion in order to accurately simulate them, demanding approximations in order to be able to perform it efficiently.

Despite the limitations on constant applied electrode potential or electric current, more elaborated setups can be achieved by combining different applied parameters and sampling the associated response. The potentiostatic setup, for instance, can be used to simulate a more commonly used experimental approach, which consists of sampling the current at a given time, for several values of the applied electrode potential. Such current-sampled voltammogram, as it is called, is presented in Figure 5 for both Eqs. 32 and 33. The results presentation differs by showing a graph of $I$ as a function of the applied electrode potential $E$, resulting in a richer source of qualitative and quantitative information. The simulated results follow the deterministic response\cite{16}: a peak current value associated to $E$ values higher than the formal potential $E_0^{0'}$; and a non-zero current after the peak, for the system of Eq. 33. This so-called diffusional plateau is a noteworthy feature of diffusion-limited electrochemical processes, and it is seen to be well-reproduced in the present framework, in contrast to the near-zero current for the diffusion-less system of Eq. 32. The actual peak shape features, for instance the value of applied $E$ for the peak current and the peak asymmetry, are likely to differ from the deterministic theory, for the same reason given for the potential-step chronoamperometry.

Despite the simplicity of the models shown, it is straightforward to simulate more complex systems, as well as increase the complexity of the simulations by sweeping the applied parameter and sampling the associated response. The limitations of the algorithm restricts the current range of application, in particular for time-dependent parameter (e.g. cyclic voltammetry). However it should be possible to simulate a wide
FIG. 5: Current-sampled voltammograms with sampling time $t \approx 0.5 \, s^{-1}$, for the systems of Eqs. 32 (○) and 33 (□). Parameters are the same as described in Figs. 2 and 4 for Eqs. 32 and 33, respectively. Statistics performed over 25 samples at each potential step, with error bars representing one standard deviation. Black dashed line shows the formal equilibrium potential $E^0' = 0.36 \, V$.

variety of surface reactions and setups, without having to resort to approximations or analogies to circuit models.

V. SUMMARY

The use of the Stochastic Simulation Algorithm (SSA) has been explored for interfacial systems, particularly electrochemical ones. Following Gillespie’s original work, the Chemical Master Equation (CME) has been obtained for such systems. The assumptions needed have been discussed, namely the low-energy barrier between surface adsorption sites and the use of translational as well as vibrational and rotational degrees of freedom for thermalization of the system. The role of the electrochemical potential, or more specifically the electrode potential, has been shown to satisfy the requirements
for the CME, as long as it remains constant in the time interval between reactions.

Having a CME describing the system, the SSA being deemed a logically equivalent\cite{4}, it is assumed the possibility of its application to simulate a time trajectory in population space. It is shown that, aside from the associated electric response, the algorithm proceeds exactly as originally proposed\cite{3}. For electrochemical systems, potentiostatic and galvanostatic setups are described, and equations for each setup’s electric driving force and response are given based on an ensemble argument. This argument is backed by the macroscopic limit of the CME/SSA approach\cite{11}, where the thermodynamic limit of a Langevin-type equation (CLE)\cite{10}, together with Faraday’s law of electrolysis\cite{16}, is shown to result in the proposed equations.

Finally, it is shown the results of using the SSA for electrochemical systems, with the electrical response being given by the Butler-Volmer model of electrochemical kinetics\cite{16}. A simple redox system is used for examples, with and without a diffusion-like process. The usual, well-described differences between the two systems are pointed out for potentiostatic setups, together with galvanostatic results. It is shown that the current framework reproduces the expected behaviors, with the major advantage of enabling a rigorous quantitative comparison with experimental results through statistical analysis, for both current and potential-controlled techniques.

The conditions assumed and the requirements needed for the derivation of the CME constraints the algorithm for constant current and potential-controlled systems. The implementation of the approximations and methods developed for the original SSA should allow the study of more complex electrochemical systems, including both time-dependent current and potential control and diffusion processes. It is expected that, in this way, the whole behavior of the so-called electric double layer can be simulated using the framework presented and its future improvements.

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