

# Superstatistics in nanoscale electrochemical systems

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**Stochastic electrochemical reaction steps on nanosized electrodes are non-Markovian when externally driven by an applied voltage. We show that, compared to the Markovian case (when external driving is absent), nanoscale electrochemical systems obey a superstatistics characterized by a superposition of Tsallis'  $q$  indices. The distribution of Tsallis'  $q$  indices along stochastic trajectories can be calculated from the electrochemical master equation and normal distributions from Boltzmann–Gibbs thermostatics are recovered in the thermodynamic limit (the infinite electrode size limit). Although on the nanoscale the external control makes intricate correlations between the microstates, in the superstatistical frame one can still address the microstates as if they were uncorrelated. The resulting superstatistical entropic form is additive in this frame and Tsallis' indices have on the time-average values ( $q$ )  $\leq 1$ , which is, indeed, an example of a superstatistical system where no ad hoc distribution has to be assumed for the fluctuations; rather, the distribution is directly calculated from a mesoscopic master equation without freely adjustable parameters.**

chemical master equation | electrochemistry | electrode kinetics | Tsallis entropy | nonelectrodes

From a statistical point of view, electrochemical reaction events at the nanoscale possess uncommon features. On isolated nanoelectrodes, the electrode potential becomes a stochastic variable, because its value is affected by redox processes taking place at the interface. As a consequence (i) all electrochemical reaction steps are faster at the nanoscale and (ii) all rare reaction events are favored compared to macroscopic electrochemical kinetics (1). These findings were substantiated with an electrochemical master equation. The decisive difference to the chemical master equation is that the kinetic rate constants  $k$  depend on a fluctuating variable, and thus become time dependent. An extended Gillespie algorithm allows the electrochemical master equation to be solved, and simulations showed skewed and leptokurtic distributions for the instantaneous values of the electrode potential at the steady state, which were related to the stochastic enhancement of the kinetics (1). Fluctuation enhanced reaction rates are absent in purely chemical systems (assumed isothermal), which are well described by normal distributions coming from standard Boltzmann–Gibbs thermostatics (2). Because the increased rate constants at the nanoscale are caused by the stochastic nature of the charge transfer processes involved, it is natural to ask what might be the appropriate statistical framework to describe nanoscale electrochemical systems. In this article, we solve this question and we find the surprising result that the microscopic reaction events are indeed governed statistically by a generalized entropic form recently introduced in the literature (3–5), which constitutes a form of superstatistics (6–8): a Tsallis' entropy with a distribution of entropic  $q$  indices.

For a system in a nonequilibrium state, the following fluctuating, trajectory-dependent, nonequilibrium entropy has been introduced by Seifert (9); see also ref. 10:

$$s_{\text{traj}}(t) = -\ln p(x(t), t), \quad [1]$$

where  $p(x(t), t)$  is the probability of being in a point in phase space  $x(t)$  at time  $t$  on a stochastic trajectory  $R$ , obtained from

the solution of the master equation. If  $x_0 \equiv x(0)$  denotes a point on the initial ensemble, this probability satisfies (9)

$$\int p(x_0, 0) dx_0 = 1. \quad [2]$$

When averaging  $s_{\text{traj}}(t)$  over all possible trajectories, the non-equilibrium Gibbs entropy is obtained (9)

$$s_G(t) = - \int dx p(x, t) \ln p(x, t). \quad [3]$$

The introduction of the trajectory-dependent entropy  $s_{\text{traj}}(t)$  also allows Gibbs entropy for mesoscopic chemical systems to be calculated (2, 11). The state of a chemical system is given by the number of molecules  $N_i$  of each chemical species  $i$  in the system [i.e., by the vector  $\mathbf{N} = (N_A, N_B, \dots, N_M) \equiv x(t)$ , with  $M$  different chemical species that can fluctuate]. The dynamics of the system is completely specified by the chemical master equation

$$\frac{dP(\mathbf{N}, t)}{dt} = \sum_{\rho} [W_{\rho}(\mathbf{N} - \nu_{\rho}) P(\mathbf{N} - \nu_{\rho}, t) - W_{\rho}(\mathbf{N}) P(\mathbf{N}, t)], \quad [4]$$

where  $P(\mathbf{N}, t)$  is the probability of having specific numbers of chemical species  $\mathbf{N}$  at a specific time,  $W_{\rho}(\mathbf{N})$  the stochastic reaction rate of reaction  $\rho$  and the elements of the vector  $\nu_{\rho} = \nu_{\rho} - \nu_{\rho}$  are the stoichiometric numbers of reaction step  $\rho$  (where  $\nu_{\rho}$  and  $\nu_{\rho}$  are vectors containing the number of molecules of products and of reactants, respectively, for each of the  $M$  fluctuating chemical species involved in a reaction step  $\rho$ ). Solving for the probability distributions  $P(\mathbf{N}, t)$  is in most cases an unfeasible task, but a trajectory  $\mathbf{N}(t)$  can be readily calculated, e.g., with Gillespie's First Reaction Method (12): For each reaction  $\rho$ , a random number  $p_{\rho}$  is drawn from the unit interval and a random time  $\tau_{\rho}$  is calculated according to

$$\tau_{\rho} = \frac{1}{W_{\rho}(\mathbf{N})} \ln \left( \frac{1}{p_{\rho}} \right). \quad [5]$$

The reaction  $\rho_j$  with the shortest waiting time  $\tau_j = \min\{\tau_{\rho}\}$  is then chosen to occur at time  $t + \tau_j$ . Thus, at time  $t + \tau_j$ , the trajectory evolves from state  $\mathbf{N}_j = \mathbf{N}(t)$  to state  $\mathbf{N}(t) + \nu_{\rho_j} = \mathbf{N}(t + \tau_j) = \mathbf{N}_{j+1}$ . Conversely, the probability that the reaction  $\rho_j$  has not yet occurred in the time interval between  $t$  and  $t + \tau_j$  is given by (12, 13)

$$p_{\rho_j} = e^{-W_{\rho_j} \tau_j}. \quad [6]$$

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A stochastic trajectory  $R$  is thus given by a series of discrete changes in time in the number of particles

$$\mathbf{N}_0 \xrightarrow{\rho_0} \mathbf{N}_1 \xrightarrow{\rho_1} \mathbf{N}_2 \xrightarrow{\rho_2} \dots \mathbf{N}_j \xrightarrow{\rho_j} \mathbf{N}_{j+1}, \quad [7]$$

$j$  counting the individual reaction events from the known initial state  $\mathbf{N}_0$  at  $j = 0$ . The probability  $p_j$  that no reaction  $\rho$  at all has occurred after a time interval  $\tau_j$  is given by

$$p_j = \prod_{\rho} p_{\rho}^j = \prod_{\rho} e^{-W_{\rho}^j \tau_j}, \quad [8]$$

and it coincides with the probability of being in a point of such trajectory during a time  $\tau_j$ . Note the difference between  $W_{\rho}^j$  and  $W_{\rho}^j$ : the former is the stochastic reaction rate after reaction event  $j$  of reaction  $\rho$ , while the latter is the one for the reaction  $\rho_j$ , which is then chosen to advance at reaction event  $j + 1$  at a later time  $t + \tau_j$ . The probability of residing on a trajectory of duration  $t = \sum_j \tau_j$  like in Eq. 7 is given by

$$p(x(t), t) = p(\mathbf{N}_0, 0) \prod_j p_j = p(\mathbf{N}_0, 0) \prod_{j, \rho} e^{-W_{\rho}^j \tau_j}. \quad [9]$$

The trajectories start from initial conditions  $\mathbf{N}_0$  sampling the initial ensemble and  $p(\mathbf{N}_0, 0)$  is an initial condition for the probability distribution satisfying the master equation. We assume in the rest of this paper that we are on the stationary state and this initial distribution is already the stationary distribution.

Seifert's entropy is obtained from Eq. 1 by using Eq. 9:

$$s_{\text{traj}}(t) = -\ln p(\mathbf{N}_0, 0) + \sum_{j, \rho} \ln \frac{1}{p_{\rho}^j}. \quad [10]$$

In chemical systems, the relationship between the latter entropy and the physical trajectory-dependent entropy, Eq. 1, is given by (11)

$$s(t) = s_{\text{traj}} + s^0, \quad [11]$$

where

$$s^0(t) = \sum_{k=A}^M \ln \frac{(\Omega/\omega_k)^{N_k(t)}}{N_k(t)!} \equiv \ln g_{\mathbf{N}} \quad [12]$$

is the internal entropy of state  $\mathbf{N}$  due to its degeneracy. Here the index  $k$  runs over the chemical species in the vector  $\mathbf{N}$ ,  $\Omega$  is the reaction volume (or system size), and  $\omega_k$  denote suitable normalizing volumes for each molecule, to match thermodynamics with a Hamiltonian description (see appendix A in ref. 11). We can now average over trajectory-dependent entropies by using Eq. 11 to obtain Gibbs entropy, Eq. 3, for chemical systems, which can be explicitly written as

$$\begin{aligned} s_G(t) &= -\sum_{\mathbf{N}} P(\mathbf{N}, t) \ln \left[ \frac{P(\mathbf{N}, t)}{g_{\mathbf{N}}} \right] = \sum_R p(x(t), t) s(t) \\ &= -\sum_R p(x(t), t) \ln \frac{p(x(t), t)}{g_{\mathbf{N}}} \\ &= \sum_R p(x(t), t) \left[ \ln \frac{g_{\mathbf{N}}}{p(\mathbf{N}_0, 0)} + \sum_{j, \rho} \ln \frac{1}{p_{\rho}^j} \right], \end{aligned} \quad [13]$$

where the latter sum runs over trajectories  $R$  starting on a specific initial condition  $\mathbf{N}_0$ .

## Results and Discussion

**Uncorrelated Dynamics Under Open Circuit Conditions.** We can consider now electrochemical redox reaction processes taking place on nanoelectrodes. The kinetic rate depends on the electrode potential of the nanoelectrode. Because a reaction transfer event changes the electrode potential of the nanoelectrode  $E$ , the kinetic constant of the reaction is affected and, therefore, it fluctuates. The mesoscopic state of an electrochemical system is thus given by the number of molecules  $N_i$  of each chemical species  $i$  as in a chemical system and the electrode potential  $E$ , a new mesoscopic fluctuating variable. We define now the vector  $\mathcal{N} = (N_A, N_B, \dots, N_M, E) = (\mathbf{N}, E) \equiv x(t)$  to describe a point in phase space. In [1] we have shown that fluctuations in  $E$  lead to fluctuations of the kinetic constant, which, in turn make all electrochemical reaction steps to be faster compared to macroelectrodes. In the latter, the electrode potential does not fluctuate and is constant and equal to the time-average of its instantaneous realizations  $\langle E \rangle$ : The stochastic behavior of the electrode potential vanishes for macroelectrodes because for them the fluctuations coming from single reaction events can be neglected. In Fig. 1A, the oxidation reaction step of a reversible redox reaction



is depicted. This reaction takes place on a nanoparticle, which plays here the role of the nanoelectrode, anchored to a metallic support through an ohmic resistive spacer (e.g., a thiol or a polymer electrolyte nanorod; see ref. 14). The system is in open circuit conditions: The nanoparticle can exchange electrons with the electrolyte through the oxidation or reduction steps of the above reversible redox reaction. A stationary state obeying detailed balance is attained after a transient. The probability that no reaction  $\rho$  at all has occurred in the time interval between  $t$  and  $t + \tau_j$  is given again by Eq. 8 but now with

$$W_{\rho}^j(\mathcal{N}_j) = W_{\rho}^j(\mathbf{N}_j, E_j) = W_{\rho}^{0j}(\mathbf{N}_j) e^{c_{\rho} E_j}, \quad [15]$$

where  $E_j$  is the electrode potential between successive instants at which reaction events occur, labeled  $j$  and  $j + 1$ ,  $c_{\rho} = \frac{-\alpha n_{\rho} F}{RT}$  for reduction reactions and  $c_{\rho} = \frac{(1-\alpha) n_{\rho} F}{RT}$  for oxidation reactions ( $\alpha$  is the transfer coefficient,  $n_{\rho}$  the number of electrons transferred,  $F$  the Faraday constant,  $R$  the ideal gas constant, and  $T$  the temperature). In this paper, we consider  $\alpha = 0.5$  and  $T = 300$  K. We also have

$$W_{\rho}^{0j}(\mathbf{N}_j) = \Omega k_{\rho}^0 e^{-c_{\rho} E^0} \prod_{i=A}^M \prod_{m=1}^{j_{\rho}} \frac{N_{i,j} - m + 1}{\Omega}. \quad [16]$$

Here  $E^0$  is the redox potential of the reaction, the preexponential factor  $k_{\rho}^0$  does not depend on the electrode potential but contains possible concentrations of species that do not change in time during the reaction. After the reaction event, the electrode potential changes as

$$E_{j+1} = E_j - \frac{n_{\rho} e}{CA}, \quad [17]$$

where  $e$  is the electron charge and  $C$  is the double layer capacitance per unit area ( $A = \Omega a_0^2$  being the area of the nanoelectrode and  $a_0$  the lattice constant). In the macroscopic limit,  $A \rightarrow \infty$  and Eq. 17 yields  $E_{j+1} = E_j$  (i.e., the electrode potential does not fluctuate any longer).

In open circuit conditions, the Gibbs and Seifert entropies have the same form as in chemical systems. In a reaction network

composed of reversible reactions, as in Eq. 14, we can calculate the total entropy production along a trajectory as follows:

$$\sigma = \ln \frac{p(\mathcal{N}_0, 0)}{p(\mathcal{N}(t), t)} + \sum_j \ln \frac{W_{\rho_j}^j(\mathcal{N}_j)}{W_{-\rho_j}^j(\mathcal{N}_{j+1})}, \quad [18]$$

where  $-\rho_j$  corresponds to a backward (forward) reaction step provided that  $\rho_j$  denotes a forward (backward) reaction step, the latter leading from a point  $\mathcal{N}_j$  to a point  $\mathcal{N}_{j+1}$  in phase space. For a long trajectory at the stationary state, the first term in the right-hand side of Eq. 18 is negligible compared to the second one and we obtain the trajectory fluctuation theorem (9, 11)

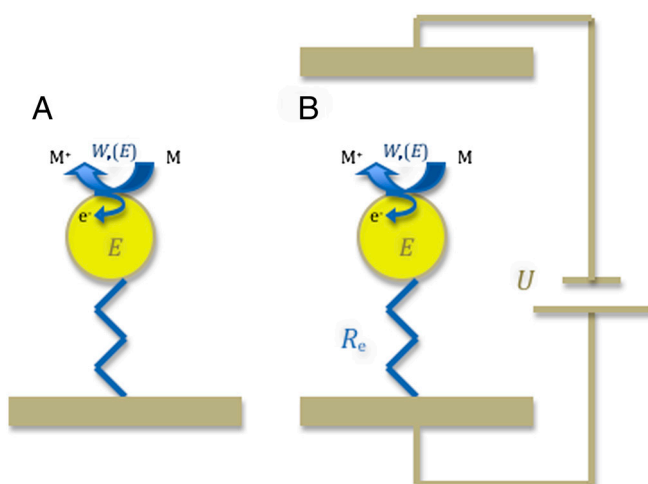
$$\frac{p(-\sigma)}{p(\sigma)} = e^{-\sigma}, \quad [19]$$

where (under appropriate renormalization)  $p(\sigma) = \prod_j W_{\rho_j}^j(\mathcal{N}_j)$  and  $p(-\sigma) = \prod_j W_{-\rho_j}^j(\mathcal{N}_{j+1})$  are the probabilities of measuring a positive or a negative entropy production, respectively (along a single trajectory followed either in the forward or in the backward directions).

**Correlated Dynamics Under External (Potentiostatic) Control.** A different situation arises when the electrostatic potential of the metallic support to which the nanoparticle is anchored is controlled externally, as shown in Fig. 1B. The electrode potential  $E$  of the nanoparticle remains a degree of freedom that can fluctuate because a series resistance  $R_e$ , which for simplicity we assume to be ohmic, appears through the resistive spacer anchoring the nanoparticle. If  $\tau_j$  denotes, as before, the time spent between reaction events  $j$  and  $j+1$ , the electrode potential changes now as (1)

$$E_{j+1} = E_j - \frac{n_{\rho_j} e}{CA} + \frac{U - E_j}{R_e CA} \tau_j, \quad [20]$$

where  $U$  is the externally applied potential of the support. The external control renders the process non-Markovian. Thus, the last term makes explicit that  $E$  is driven toward the external voltage  $U$  through the control, which has profound consequences on the stochastic dynamics. In [1], we showed that the waiting time for each reaction  $\rho$  now obeys



**Fig. 1.** (A) Nanoparticle anchored to a metallic support under open circuit conditions. A reversible redox reaction takes place on the nanoparticle at a stochastic rate that depends on the surface potential  $E$  of the nanoparticle. (B) The same system under an externally applied voltage  $U$ . The resistive spacer anchoring the nanoparticle behaves now as an ohmic series resistance  $R_e$ .

$$\tau_\rho = \frac{R_e CA}{c_\rho(U - E_j)} \ln \left[ 1 + \frac{c_\rho(U - E_j)}{R_e CA W_\rho^j} \ln \left( \frac{1}{\tilde{p}_\rho} \right) \right]. \quad [21]$$

We can solve this latter equation for the probability that reaction  $\rho$  has not yet occurred in a time interval  $\tau_j$  (after which the next reaction  $\rho_j$  with the minimal waiting time  $\tau_j$  will occur). We have

$$\tilde{p}_\rho^j = \exp \left( - \frac{\exp[(1 - q_\rho^j) W_\rho^j \tau_j] - 1}{1 - q_\rho^j} \right) \quad [22]$$

(the tilde denotes here the probability of an event in the new experimental setup and is introduced to describe the probability of *correlated* events through the external driving). Here we have defined

$$q_\rho^j = 1 - \frac{c_\rho(U - E_j)}{R_e CA W_\rho^j}, \quad [23]$$

which can take any real value. If  $q_\rho^j = 1$ , then  $\tilde{p}_\rho^j = p_\rho^j = \exp(-W_\rho^j \tau_j)$  and we recover the behavior found in chemical systems or electrochemical systems under open circuit conditions (i.e., Eq. 8). However, if  $q_\rho^j > 1$  and  $\tau_j \rightarrow \infty$ , Eq. 22 implies

$$\tilde{p}_\rho^j(\tau_j \rightarrow \infty) = \exp \left( \frac{1}{1 - q_\rho^j} \right). \quad [24]$$

This surprising result means that, because of the external potentiostatic control, it can happen that a specific reaction never occurs from a specific point in phase space (specified by the vector  $\mathbf{N}$ ) (i.e., there is a finite probability for a reaction not having occurred over an infinite time period). When, in contrast,  $q_\rho^j < 1$  and  $\tau_j \rightarrow \infty$ , the decay of the probability  $\tilde{p}_\rho^j$  to 0 is faster than in the exponential case  $q_\rho^j = 1$  and, therefore, such a reaction will also occur faster. Of course, because the reactions that are faster are the ones selected to occur, there will be regions in phase space that will never be accessed (usually the ones for which  $q_\rho^j > 1$ ), and the ones that are accessed will be privileged by the stochastic dynamics (the ones with  $q_\rho^j < 1$ ). The external driving deforms the accessibility of points in phase space and, as a result, the mesoscopic fluctuations accelerate the dynamics in the accessible parts in phase space and create inaccessible regions.

**New Entropy Function and Its Universality Class.** By using Eq. 22 and  $p_\rho^j = \exp(-W_\rho^j \tau_j)$ , we obtain Seifert's entropy on a trajectory as

$$s_{\text{traj}}(t) = -\ln p(\mathbf{N}_0, 0) + \sum_{j,\rho} \ln \frac{1}{\tilde{p}_\rho^j} = -\ln p(\mathbf{N}_0, 0) + \sum_{j,\rho} \ln_{\{q_\rho^j\}} \frac{1}{p_\rho^j}. \quad [25]$$

In the last expression, we have introduced the Tsallis' deformed  $q$ -logarithm function

$$\ln_{(q)}(x) \equiv \frac{x^{1-q} - 1}{1 - q}. \quad [26]$$

We observe that, if one accepts Seifert's form for the entropy on each segment of a trajectory in the *correlated* frame (as it should be the case because Seifert's entropy applies also to non-Markovian processes), it has the form of a Tsallis' microcanonical entropy in the *uncorrelated* frame. Tsallis' microcanonical entropy arises naturally on fractal phase spaces (see equation 16 in ref. 8, note that  $\Gamma$  there is equal to  $1/p_\rho^j$  here), where the minimum number of available microstates is reduced compared to a situation described by Boltzmann entropy, which describes a situation where the whole available phase space is densely filled with a

uniform distribution. In ref. 8, it was found that fractal phase spaces are well described in the microcanonical ensemble by Tsallis' entropy with an entropic index  $0 \leq q \leq 1$ , which is fully consistent with the above statements made on the accessibility in phase space of electrochemical systems.

Recently, a rigorous classification of entropy functionals has been given in terms of umbral calculus and universal formal groups by Tempesta (15). Such classification has profound and intriguing connections with number theory and Zeta Riemann functions. According to ref. 15, entropic forms can be classified under universality classes in terms of the so-called formal group exponential defined over the polynomial ring  $\mathbb{Q}[c_1, c_2, \dots]$  by

$$G(y) = \sum_{k=0}^{\infty} c_k \frac{y^{k+1}}{k+1}, \quad [27]$$

with  $c_0 = 1$ . Because Seifert's entropy is compatible on ensemble averaging with the Gibbs entropy, both fall, after normalization, in the universality class (15)

$$G(y) = y. \quad [28]$$

Following the treatment given in ref. 15, we can calculate the universality class of our entropy Eq. 25. We find that it is given by Eq. 27 with

$$c_k = \frac{1}{\mathcal{M}} \sum_{j,\rho} \frac{(1 - q_\rho^j)^k}{k!} \quad [29]$$

with  $\mathcal{M} = \sum_{j,\rho} 1$ . When all segments and all reactions in the trajectory have the same index  $q$ , we obtain from Eqs. 27 and 29

$$G(y) = \frac{e^{(1-q)y} - 1}{1 - q}, \quad [30]$$

which coincides with the Tsallis' universality class (15).

Averaging Eq. 25 over trajectories, we can derive the corresponding ensemble entropy, which reads

$$s_{TS}(t) = \sum_R p(x(t), t) \left[ \ln \frac{g_N}{p(\mathbf{N}_0, 0)} + \sum_{j,\rho} \ln_{\{q_\rho\}} \frac{1}{p_\rho^j} \right], \quad [31]$$

an entropic form which corresponds indeed to a generalized Tsallis' entropy arising from a distribution of  $q$  indices (see equation 7 in ref. 5). Such an entropy is consistent with a wide class of superstatistics (6). The distribution of  $q_\rho^j$  indices for each random jump event from time  $j$  is given explicitly by Eq. 23. This result is the most important one of our paper, and it constitutes an example of a superstatistical system where the distribution of  $q$  indices can be a priori known.

The values of  $q_\rho^j$  are usually lower than one, and from Eq. 22 we see that this fact implies that all reaction events are enhanced on the average, as we found in ref. 1 [the effect (i) mentioned in the Introduction]. When the system size  $A$  or the resistance  $R_e$  tend to infinity, all  $q_\rho$  tend to one and we recover the Gibbs' entropy, Eq. 13, from Tsallis' generalized entropy, Eq. 31. In such limits, standard Boltzmann-Gibbs thermostatics (i.e., extensivity of the uncorrelated frame) is regained. Eq. 31 describes a genuine nanoscale situation out of the thermodynamic limit, under an external control which correlates the events in time.

**Extended Fluctuation Theorem.** By keeping all the definitions introduced above for stochastic rate constants, we can derive an extended fluctuation theorem for a long trajectory around the stationary state by using Eqs. 18, 20, and 23 as

$$\frac{p(-\sigma)}{p(\sigma)} = e^{-\sigma} e^{\sum_j (1 - q_\rho^j) W_{\rho_j}^j \tau_j} = e^{-\sigma} e^{\mathcal{A}t} = e^{-\sigma} (1 + \mathcal{A}t + \dots), \quad [32]$$

which has the form of a superstatistical fluctuation theorem (16). Here we have defined the time-averaged quantity

$$\mathcal{A} \equiv \frac{\sum_j (1 - q_\rho^j) W_{\rho_j}^j \tau_j}{\sum_j \tau_j}, \quad [33]$$

whose inverse gives a characteristic time constant for the effect of the superposition of Tsallis' indices to be significant on the entropy production along the trajectory. Most importantly, because  $W_\rho^j$  and  $\tau_j$  are both positive and  $q_\rho^j < 1$ , the exponential factor depending on all these quantities is larger than one. The probability of observing a trajectory with negative entropy production is higher in mesoscopic electrochemical systems compared to a situation where one can neglect the non-Markovian fluctuations of the electrode potential. Rare events are thus enhanced through fluctuations, proving statistically our statement (ii) in the Introduction.

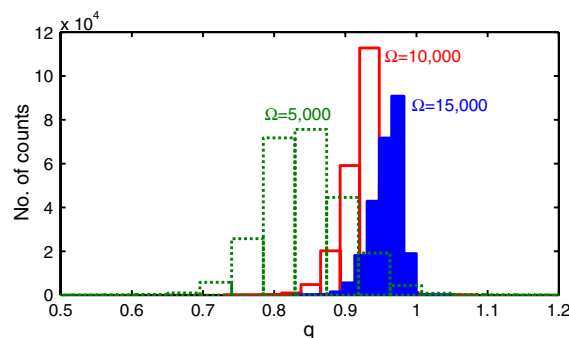
The quantity  $\mathcal{A}$  is in general an *observable*. We consider the reaction events coming from a single irreversible oxidation reaction (for a reduction reaction the treatment is the same)



We assume that there are no fluctuating numbers of chemical species (the reservoirs keep constant  $M$  and  $M^+$ ) and only the electrode potential fluctuates because electrons are transferred to the electrode. The electrochemical master equation can be simulated following the algorithm in ref. 1. After hundreds of thousands of iterations, a stationary state is reached. In Fig. 2, the distribution of instantaneous values of  $q_\rho^j$  indices in time is shown for a single trajectory around the stationary state. These histograms do not change when longer trajectories are considered, after normalization to the total number of counts and, therefore, they correspond to stationary probability distributions. The distributions have a well-defined time-averaged value  $\langle q \rangle \approx q_{av}$ , and we can express the observable  $\mathcal{A}$  as

$$\mathcal{A} \approx (1 - q_{av}) \langle W_{\rho_j}^j \rangle = \frac{c_\rho (U - \langle E \rangle)}{R_e C A}, \quad [35]$$

which solely depends on the time average of the electrode potential  $\langle E \rangle$  at the stationary state and can therefore be directly obtained from an experimental time series. Possible electrode



**Fig. 2.** Histograms for the distributions of instantaneous values of  $q_\rho^j$  indices for one irreversible oxidation reaction. Results shown for different system sizes, with  $a_0 = 0.27$  nm indicated in the figure. Other parameter values:  $R_e A = 0.3 \Omega \text{ cm}^2$ ,  $C = 0.05 \text{ F m}^{-2}$ ,  $k = 10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$ ,  $U = 0.3 \text{ V}$ .

configurations are discussed in ref. 14. A suitable irreversible electron transfer reaction is, for example, the reduction of peroxodisulfate and  $\mathcal{A}$  is obtained from a measurement of the total faradaic current and the determination of  $R_e$  and  $c_p$ . The value of the index  $q_{av}$  is thus entirely dependent only on the features of the stationary state. We observe that almost all  $q_p^j < 1$  and, therefore, we have  $q \approx q_{av}$  lower than unity: All reaction events are enhanced on the average. As the system size increases, the distribution of instantaneous values tends to lump around  $q = 1$  indicating the passage to Boltzmann–Gibbs thermostatics and normal distributions. For smaller systems, the distribution gets broader and displaced to values of  $q$  lower than one. Note however, that there is also a nontrivial dependence of the shape of the distribution on  $R_e$ ; thus, we recover normal distributions ( $\langle q \rangle = 1$ ) for three different conditions: (i) under galvanostatic (i.e., constant current) conditions ( $U \rightarrow \infty, R_e \rightarrow \infty, U/R_e = ct$ ); (ii) for  $R_e = 0, U = \text{cnst}$ ; and (iii) under open circuit conditions (14).

The characteristic timescales between two microscopic events at which values of  $q < 1$  are observed fall in the interval 2.5–5.5  $\mu\text{s}$  for the system with  $\Omega = 5,000$  and 10–65 ns for the system with  $\Omega = 15,000$  in Fig. 2. These are the same orders of magnitude as the time intervals found in simulations of purely chemical systems (i.e., in the absence of correlations) and, therefore, the phenomenon of the superposition of Tsallis' indices predicted in our paper is a mesoscopic observable effect at roughly the same timescales as when the superposition is absent.

We see then that non-Markovian linear stochastic processes as found in nanoscale electrochemical systems lead to superstatistical behavior. There is no need to introduce nonlinear Fokker–Planck equations (17), which are sometimes not well justified from the nature of stochastic processes, to generate superstatistical behavior. A chemical master equation with fluctuating time-dependent reaction rate constants leads in a straightforward manner to superstatistics.

## Conclusions

In this paper, we have shown that nanoscale electrochemical systems obey in general a superstatistics characterized by a superposition of Tsallis' entropic indices. These systems have a fluctuating electrode potential that is subject to a potentiostatic control. The electrode potential constitutes, therefore, a slowly

varying external driving force. The (mesoscopic) electrochemical master equation allows for a derivation of an analytical expression for an observable quantity which captures the effects of the Tsallis' distributions displayed by the mesoscopic dynamics. The distribution of entropic indices  $q_p^j$  can be calculated and there are no freely adjustable parameters. Although this superstatistics is relevant on the mesoscopic scale, it reduces to standard Boltzmann–Gibbs thermostatics in the large system limit (because there, the stochastic correlations caused by the driving are negligible). In Tsallis' statistics, the averaging is always performed over the uncorrelated events, and the complexity is removed by means of the deformation of the uncorrelated events through the index  $q_p$ . The idea of using the uncorrelated events is central to Tsallis' formalism because in many complex systems it is not always possible to know what causes the correlations. Sometimes, a time-dependent driving created by the system itself superimposes to the dynamics governed by a master equation. In mesoscopic electrochemical systems, the correlations can be explicitly calculated and the way the driving creates superstatistics is elucidated.

We have also derived an extended version of the fluctuation theorem for stochastic trajectories which generalizes Seifert's fluctuation theorem to mesoscopic electrochemical systems. We observe that because the existence of correlations, there is a higher probability of observing trajectories with a negative entropy production compared to a dynamics where these correlations are not present.

In fact, the results seem to be of much wider reach. We have corroborated that the superstatistical properties are linked to the exponential dependence of the stochastic rate constants on the fluctuating electrode potential. This observation suggests that all systems described by mesoscopic master equations in which the stochastic reaction rates  $W_p^j$  are proportional to the Boltzmann factor of a fluctuating quantity—which is slowly driven externally compared to the timescale of the fluctuations—obey a superstatistics characterized by a superposition of Tsallis' indices.

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