Statistical Approach to Fractal-Structured Physico-Chemical Systems: Analysis of non-Fickian diffusion

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Abstract

Competing styles in Statistical Mechanics have been introduced to investigate physico-chemical systems displaying complex structures, when one faces difficulties to handle the standard formalism in the well established Boltzmann-Gibbs statistics. After a brief description of the question, we consider the particular case of Renyi statistics whose use is illustrated in a study of the question of the "anomalous" (non-Fickian) diffusion that it is involved in experiments of cyclic voltammetry in electro-physical chemistry. In them one is dealing with the fractal-like structure of the thin film morphology present in electrodes in microbatteries which leads to fractional-power laws for describing voltammetry measurements and in the determination of the interphase width derived using atomic force microscopy. The fractional-powers associated to these quantities are related to each other and to the statistical fractal dimension, and can be expressed in terms of a power index, on which depends Renyi’s statistical mechanics. It is clarified the important fact that this index, which is limited to a given interval, provides a measure of the microroughness of the electrode surface, and is related to the dynamics involved, the non-equilibrium thermodynamic state of the system, and to the experimental protocol.

KEYWORDS: Complex structured systems, anomalous diffusion, fractal surfaces, unconventional statistics, Renyi’s statistics.
I. INTRODUCTION

A couple of decades ago Montroll and Shlesinger \[1\] stated that in the world of investigation of complex phenomena that requires statistical modeling and interpretation, several competing styles have been emerging, each with its own champions. Lately a good amount of efforts have been devoted to the topic. What is at play consists in that in the study of certain physico-chemical systems we may face difficulties when handling situations involving fractal-like structures, correlations (spatial and temporal) with some type of scaling, turbulent and chaotic motion, small size (nanometer scale) systems with eventually a low number of degrees of freedom and complicate boundary conditions, and so on. The interest has been nowadays enhanced as a result that such situations are present in electronics, opto-electronics, etc, devices of the present day point-first technologies, on which is so dependent our society, also in disordered systems, polymeric solutions, ion conducting glasses, microbatteries, and others. Most cases involve, what in the literature on the subject are called ”anomalous” physical properties (let them be transport, optical, hydrodynamical, etc. ones). As a rule what is noticed is that the observable experimental data can be theoretically adjusted by means of fractional-power laws in place of the standard ones. We can mention one type, related to the one presented here, consisting into ”anomalous” (non-Fickian) diffusion in micelles \[2, 3, 4, 5\], where the analysis of data used to be done introducing the so-called Lévy statistics. In this paper we present a closed statistical theory of a large scope in place of such approach.

In these situations the difficulties consist, as a rule, in that the researcher is impaired, for one reason or other, to satisfy Fisher’s criteria of efficiency and sufficiency \[6\] in the standard formalism to implement the conventional, well established, physically and logically sound Boltzmann-Gibbs statistics, meaning an impairment to correctly include the presence of large fluctuations (and eventually higher-order variances) and to account for the relevant and proper characteristics of the system, respectively. To contour these difficulties, and to be able to make predictions – providing and understanding, even partial, of the physico-chemical properties of the system of interest, for example, in analyzing technological characteristic of a device – there has been developed efforts along the line of introducing heterotypical statistics for providing an auxiliary method for fulfilling such purposes.

Among existing approaches it can be mentioned, what we call Generalized Statistical Me-
chanics as used by P.T. Landsberg showing that functional properties of the (informational) entropy (which is a generating functional of probability distributions) provides different types of thermodynamics, and rise the question of how to select a ”proper” one, that is, are some better than others? Superstatistics as used by C. Beck and E.G.D. Cohen for nonequilibrium systems with complex dynamics in stationary states with large fluctuations on long-time scales.

So-called nonextensive statistics based on Havrda-Charvat statistics applied to a number of cases are described in the Conference Proceedings of Ref.[11]. Renyi statistics has been introduced in the scientific literature, with T. Arimitsu and P. Jizba recently introducing an extensive analysis in a paper intitled ”The world according to Renyi; Kappa (sometimes called Deformational) statistics – a particular case of Sharma-Mittal statistics – was used in problems of plasma physics in celestial mechanics and by G. Kanadiakis in the case of relativistic systems.

The introduction of these alternative statistics resides on the fact, already stated, that the well established mechanical-statistical treatment via Boltzmann-Gibbs ensemble formalism, let it be around equilibrium (as in the usual response function theory) or for systems arbitrarily away from equilibrium, has its application impaired because of the complications set forth by the presence of spatial correlations, resulting for example in the illustration here presented from spatially varying microroughened boundaries showing a fractal structure. Such fractal structure introduces a degree of fuzziness in data and information, which consists in the lack of information on the space correlations imposed by the fractal-like microroughness of the electrode surface. Hence, as noticed, it is not satisfied Fisher’s criteria of efficiency and sufficiency in the characterization of the system, that is, the chosen description does not summarize the whole relevant information for the situation in hands. Hence the use of formulations based on unconventional statistics to perform calculations of average values and response functions in which the accompanying heterotypical probability distributions preferentially weight the probabilities of the states that contribute to the dynamics involved. We restate that the use of unconventional (index dependent) heterotypical statistical mechanicals for systems displaying correlation effects of one kind or other, is a circumventing way for overcoming the difficulty to assess such characteristics that should be incorporated in the conventional formulation within the well established Boltzmann-Gibbs theory.
We consider here Renyi statistics [12, 13] applied in statistical mechanics [15, 16, 23, 24], illustrating its use and utility in the case of a particular experiment, namely, observation and measurements using cyclic voltammetry in the study of fractal-structure electrodes in microbatteries. First, we begin again noticing that the advanced technologies that keep evolving nowadays present challenges for the associated physics which describes the phenomena that are in them involved thus, requiring a careful use of the accompanying theoretical physics to face the difficulties associated with the handling of these new situations. They involve aspects of the physics of soft-matter and disordered systems, complex structured systems, the already mentioned small systems, and others, as well as the question of functioning in far-from-equilibrium conditions and in the presence of ultrafast (pico- and femto-second time scales) relaxation and pumping effects. We are dealing in all these cases with condensed matter and then, we recall, it is inevitable for their study at the physico-chemical level to resort to statistical mechanics – in a sense it can be said that the physics of condensed matter is statistical mechanics by antonomasia. We consider here a particular situation which provides an excellent illustration of what can be called *Unconventional Statistical Mechanics* at work. We begin noticing that as a consequence of the nowadays large interest associated to the technological applications in displays, electrochromic windows and microbatteries (see, for example, Ref.[25]), the study of growth, annealing and surface morphology of thin film depositions has acquired particular relevance. These kind of systems involve the presence of microroughened surface boundaries in a geometrically constrained region, when fractal characteristics can be expected to greatly influence the physical properties [26]. It can be recalled that fractals display self-similarity, but the latter is said to come in two flavors: exact and statistical, the latter being the one with which we are dealing here. Moreover, fractals are characterized in terms of their, in general, fractional ”dimension” – as we shall see in the present case – which is a ”measure” of the complexity of the structure.

Hence, we do have that the dynamics or hydrodynamics involved in the functioning of such devices can be expected to be governed by some type or other of scaling laws [27, 28, 29]. Such characteristics have been experimentally evidenced and the scaling laws determined by researchers who resorted to the use of several experimental techniques, as atomic force microscopy [30] which allows to obtain the detailed topography of the surface – and then measuring the statistical fractal dimension – and cyclic voltammetry [31] which is an electrochemical technique used for the study of several phenomena, also allowing for the charac-
terization of the fractal properties (scaling laws) of the system. Particularly, through cyclic voltammetry it can be evidenced the property of the so-called ”anomalous” (more properly called non-Fickian) diffusion in these systems. It is our aim to present here a theory appropriate to deal with these kind of situations. For dealing with transport processes in electrochemical cells we introduce two different aspects of recent thermo-hydrodynamic theory: one is Informational Statistical Thermodynamics (IST for short [32, 33], which provides statistical foundations to Extended Irreversible Thermodynamics [34]), and a non-equilibrium ensemble formalism [21]. However, for the kind of experiments to be analyzed one needs, as noticed, to resort to a modified form of the standard formalism in the original and well established Boltzmann-Gibbs foundations of statistical mechanics. Originally, the relation between irreversible thermodynamics and transport laws, as Fick and Fourier laws, were well established – and kinetic and mechanical statistical foundations given – in the framework of classical (or Onsagerian) irreversible thermodynamics. But, it faces limitations since the theory is restricted to weak amplitudes of movement, with a linear relationship between fluxes (currents) and thermodynamic forces, smooth variation in space and time, locality in space and instantaneously in time (i.e. neglecting space and time correlations) and weak fluctuations, and then does not cover the case of fractal-structured systems. To remove these restrictions appeared a variety of approaches, a most convenient one is the already mentioned Extended Irreversible Thermodynamics and its statistical counterpart Informational Statistical Thermodynamics, and for a practical handling of fractal and nanometric systems one can resort to unconventional statistics. IST is founded on a non-equilibrium ensemble formalism which provides a generalized nonequilibrium grand-canonical ensemble [21, 35, 36]. On the other hand, unconventional statistics applies to systems displaying long-range interactions, persistent memory, evolution in a fractal space, etc [23, 24]. It has been applied to some kind of studies of ”anomalous” diffusion, as for example in Refs.[37-39], and we reconsider the question here, specified to the situation in fractal-structured electrodes of microbatteries leading to ”anomalous” results in experiments involving cyclic voltammetry.

II. THEORETICAL ANALYSIS

Within the variational approach to Statistical Mechanics [21] the use of unconventional (index-dependent) informational entropies (better called measure of uncertainty of informa-
tion, and not to be confused with the physical entropy which is a property of the thermodynamic state of physical systems, while the informational one is a property of any probability distribution \[23,24,40\) \[22\] leads to the construction of alternative Statistical Mechanics as described in Refs.\[23,24\]. Basically the process consists of two steps: (1) The choice of an heterotypical probability distribution \[22,23,24\], say \(\varrho_h\), and (2) the use of an escort probability \[41\] of order \(\gamma\) in terms of this heterotypical distribution, say \(\mathcal{D}_\gamma\{\varrho_h\}\); namely, in the calculation of average values it is used the definition

\[
\langle \hat{A} \rangle = \text{Tr} \left\{ \hat{A} \mathcal{D}_\gamma\{\varrho_h\} \right\},
\]

where the escort probability of order \(\gamma\) is given by

\[
\mathcal{D}_\gamma\{\varrho_h\} = \frac{\varrho^\gamma}{\text{Tr} \varrho^\gamma},
\]

where \(\gamma\) is a real positive number (see for example Ref.\[41\], where the name escort probability is used, and the concept generalized, and also in Chapter IX, pp. 569 et seq. of Ref.\[13\]). An in depth presentation and discussion is given elsewhere \[23,24\], here suffices to say that what the heterotypical distribution does is providing a weighting of the probabilities of the states involved, and the escort probability accounts for the influence of correlations and higher-order variances.

According to Beck and Schögl \[41\], the use of the escort probability introduces an increase in information (by incorporating self-consistently correlations and variances) in the sense that, for the case of index \(\alpha\)-dependent Renyi distribution \(\varrho_\alpha\) (see below)

\[
(1 - \alpha)^2 \frac{\partial I_\alpha}{\partial \alpha} = \text{Tr} \left\{ \mathcal{D}_\alpha\{\varrho_\alpha\} \left[ \ln (\mathcal{D}_\alpha\{\varrho_\alpha\}) - \ln (\varrho_\alpha) \right] \right\},
\]

where \(I_\alpha\) is the quantity of information (the negative of Renyi’s informational entropy in terms of \(\varrho_\alpha\)), and the right-hand side is interpreted as the information gain when using the escort probability \(\mathcal{D}_\alpha\) built in terms of the original one \(\varrho_\alpha\).

Let us now proceed to deal with the problem on hands, when we make use of an unconventional statistics in Renyi approach in order to provide a statistical-thermodynamic treatment of the ”anomalous” diffusion law proposed to account for the experimental results obtained using cyclic voltammetry in the system of fractal-structured electrodes in microbatteries. It involves the process of motion of charges in the electrolyte bordered by a fractal-structured thin film on the electrode, motion which is usually considered that can be described as a
process of diffusion governed by Fick law [31]. But the use of standard Fick diffusion equation does not properly describe the experimental results, which show some kind of power law (see below) differing from the expected one. This is a consequence that in a constrained (nanometric scaled) fractal-like geometry, Fickian-diffusion does not apply because are not satisfied the quite restrictive conditions mentioned in the Introduction. A proper description using the conventional approach in statistical mechanics for providing foundations for hydrodynamics requires the use of a generalized higher-order thermo-hydrodynamics [42, 43, 44], that is, the description including as basic macrovariables the density of energy, the density of particles, \( h(r, t) \) and \( n(r, t) \), their fluxes of all orders, \( I_h(r, t) \), \( I_n(r, t) \), \( I_{hr}^r(r, t) \) with \( r = 2, 3, ... \) indicating the order of the flux and its tensorial rank; all the quantities are defined in Refs. [21] and [42]. To resort to this higher order hydrodynamics (which provides at the microscopic, i.e., statistical mechanical level, generalizations of super-Burnett and super-Gruyer-Krumhansl equations (see Refs. [45] and [38]), even in the linear approximation and neglecting fluctuations is a formidable task in the present case with spatially varying boundary conditions (in a nanometric scale and with a complex structure). Moreover, even though a contraction in the choice of the basic set of macrovariables can be introduced [21, 45], it is difficult to establish the order of the truncation. Therefore, what can be attempted in order to obtain a description of some properties of the system, is to introduce an unconventional statistics, leading to an unconventional hydrodynamics, in terms of a low-order truncation, in which one keeps only the variables

\[
\left\{ h(r, t), n(r, t), I_n(r, t) \right\}, \tag{4}
\]

that is, the energy density, the density of particles and the first-order flux (current). In that way we are led to obtain an ”anomalous” diffusion equation depending on a fractional-power which is determined by the dynamics, the fractality, the geometry and dimensions, and the thermodynamic state of the system (the unconventional generalized higher-order thermo-hydrodynamics is presented elsewhere [47, 48]). Let us proceed to derive their equations of evolution using Renyi approach to unconventional statistics [23, 24]. For that purpose, first we separate the Hamiltonian in the form

\[
\hat{H} = \hat{H}_0 + \hat{H}', \tag{5}
\]

where \( \hat{H}_0 \) is the kinetic energy and \( \hat{H}' \) contains all the interactions that are present in the system. Moreover, in a classical approach, the basic dynamic variables, whose average values
are those of Eq. (4), are

\[ \hat{h}(r|\Gamma) = \int d^3p \frac{p^2}{2m} \hat{n}_1(r, p|\Gamma) , \]  

(6)

\[ \hat{n}(r|\Gamma) = \int d^3p \hat{n}_1(r, p|\Gamma) , \]  

(7)

\[ \hat{I}_n(r|\Gamma) = \int d^3p \frac{p}{m} \hat{n}_1(r, p|\Gamma) , \]  

(8)

where \( m \) is the mass of the particles, \( p \) the momentum and \( \hat{n}_1 \) is the reduced single-particle density function

\[ \hat{n}_1(r, p|\Gamma) = \sum_{j=1}^{N} \delta(r - r_j) \delta(p - p_j) , \]  

(9)

with \( N \) being the number of particles, and \( \Gamma \) a point in phase space. The corresponding macrovariables are the average of those of Eqs. (6) to (8) using the indexed Renyi statistical approach, that is

\[ h(r, t) = \int d\Gamma \hat{h}(r|\Gamma) D_\alpha(\Gamma, t) , \]  

(10)

\[ n(r, t) = \int d\Gamma \hat{n}(r|\Gamma) D_\alpha(\Gamma, t) , \]  

(11)

\[ \hat{I}_n(r, t) = \int d\Gamma \hat{I}_n(r|\Gamma) D_\alpha(\Gamma, t) , \]  

(12)

where the integration is over the phase space. Moreover, according to the theory [13, 21, 23, 24] it is used the corresponding escort probability distribution (cf. Eq. (A11) in Appendix A)

\[ D_\alpha(\Gamma, t) = \frac{\rho_\alpha(\Gamma|t)}{\int d\Gamma \rho_\alpha(\Gamma|t)} , \]  

(13)

and it can be noticed that the order of the escort probability is the same of the index in Renyi’s distribution [13], so we keep only one parameter in the theory (the so-called infoentropic index \( \alpha \)), with Renyi’s heterotypical distribution of probability \( \rho_\alpha(\Gamma|t) \) given in Eq. (A13) after using Eq. (A14), both in Appendix A.
The equations of evolution for the basic variables associated to the material motion (the one of interest for us here) derived in the context of a nonlinear kinetic theory \[21, 42\] are

\[
\frac{\partial}{\partial t} n(r, t) = -\nabla \cdot I_n(r, t),
\]

(14)

\[
\frac{\partial}{\partial t} I_n(r, t) = -\nabla \cdot I_n^{[2]}(r, t) + J_{na}(r, t),
\]

(15)

with Eq. (14) being the conservation equation for the density, the terms with the presence of the divergence operator, \(\nabla \cdot \cdot \), arise out of the contribution resulting from performing the, in this classical case, Poisson bracket with the kinetic energy operator \(\hat{H}_0\) (i.e. \(\{\hat{n}, \hat{H}_0\}\), etc), and

\[
J_{na}(r, t) = \lim_{\epsilon \to +0} \frac{d\Gamma}{dt} \int_{-\infty}^{t} dt' e^{i(\omega t' - \epsilon)} \left\{ \left\{ \hat{n}(r|\Gamma), \hat{H}'(\Gamma|\Gamma) \right\} \hat{H}'(\Gamma) \right\} \mathcal{D}_\alpha(\Gamma, t),
\]

(16)

is a scattering integral accounting for the effects of the collisions generated by \(\hat{H}'\), and \(I^{[2]}\) is the second-order flux given by \[21, 36, 43\]

\[
I^{[2]}_n(r, t) = \int d^3p \frac{p p}{m^2} \hat{n}_1(r, p|\Gamma) \mathcal{D}_\alpha(\Gamma, t),
\]

(17)

where \([\ldots]\) stands for tensorial product of vectors, rendering a rank-two tensor. To solve the system of Eqs. (14) and (15) we need in Eq. (15) to express the right-hand side in terms of the basic variables. The scattering integral takes in general the form of a relaxation-time approach, namely (see Appendix B))

\[
J_{na}(r, t) = -\frac{\hat{I}_n(r, t)}{\tau_{Ia}},
\]

(18)

where \(\tau\) is the momentum relaxation time (see for example Ref.\[49\]). Transforming Fourier in time Eq. (15) we have, after using Eq. (18), that

\[
(1 + i \omega \tau_{Ia}) \mathbf{I}_n(r, \omega) = -\tau_{Ia} \nabla \cdot I^{[2]}_n(r, \omega),
\]

(19)

which in the limit of small frequency, meaning \(\omega \tau_{Ia} \ll 1\), reduces to

\[
\mathbf{I}_n(r, t) = -\tau_{Ia} \nabla \cdot I^{[2]}_n(r, t),
\]

(20)

and then, after using Eq. (20) in Eq. (15), we obtain that

\[
\frac{\partial}{\partial t} n(r, t) = \tau_{Ia} \nabla \cdot \nabla \cdot I^{[2]}_n(r, t).
\]

(21)
In order to close Eq. (21) we need to express the second-order flux in terms of the basic variables, \( n \) and \( I \), which after some calculus, described in Appendix A, results in that

\[
\nabla \cdot \nabla \cdot I_n^{[2]}(r, t) = \xi_{n\alpha} \nabla^2 n_\alpha^\gamma(r, t),
\]

where \( \xi_{n\alpha} \) is given in Eq. (A20) and where \( \gamma_\alpha \) is the \( \alpha \)-dependent fractional power

\[
\gamma_\alpha = \frac{5 - 3\alpha}{3 - \alpha},
\]

and consequently it follows the so-called ”anomalous” diffusion equation

\[
\partial_t n(r, t) + D_{n\alpha} \nabla^2 n_\alpha^\gamma(r, t) = 0,
\]

where \( D_{n\alpha} = \xi_{n\alpha} \tau_\alpha \) (it can be noticed that the dimension of \( D \) is \( \text{cm}^{3\gamma_\alpha - 1}/\text{sec} \)). Moreover, the possible values of \( \alpha \) having physical meaning (i.e. not leading to singularities) belong to the interval [see Appendix A]

\[
1 \leq \alpha < \frac{5}{3}.
\]

At this point we recall, and stress, that the ”anomalous” diffusion equation is an equation appropriate for approximately describing the hydrodynamic motion, being an artifact (thus the use of the word anomalous between quotation marks) of having applied an unconventional statistics in the truncated description as given in Eq. (4). As already noticed, in the conventional (well established and parameter free) formalism for satisfying the principle of sufficiency it must be used a higher-order hydrodynamics.

We proceed to analyze this question of ”anomalous” results in measurements using cyclic voltammetry in fractal-structured electrodes in terms of the previous results. Let us, for the sake of completeness, briefly summarize the case: The difference of chemical potential between an anode and a cathode with a thin film (nanometric fractal surface) of, say, nickel oxides, produces a movement of charges in the electrolyte from the former to the latter. In a cyclic voltammetry experiment, these charges circulate as a result of the application of a potential \( V(t) \), with particular characteristics: It keeps increasing linearly in time as \( V_0 + vt \), where \( v \) is a scanning velocity, during an interval, say \( \Delta t \), and next decreases with the same sweep rate, i.e. as \( V_0 + v \Delta t - vt \), until recovering the value \( V_0 \). A current \( i(t) \) is produced in the closed circuit, which following the potential \( V(t) \) keeps increasing up to a peak value \( i_p \), and next decreases. This current is the result of the movement of the
charges that keep arriving to the thin film fractal-like cathode. It is found that there follows a power law relation between the peak value, \(i_p\), of the current and the rate of change \(v\) of the electric field, namely \(i_p \sim v^\epsilon\). The value of the current to circulate in the cathode, \(i(t)\), is proportional to the charge at the interface, that is, the value at it of \(n(x, t)\), to be given by the solution of Eq. (26) which in one dimension, say, the \(x\)-direction normal to the electrode surface, is given by \[n(x, t) = b_\alpha t^{-\mu_\alpha} \left[a^2 + x^2 t^{-2\mu_\alpha}\right]^{1/\gamma_\alpha - 1},\] where \(a\) (which ensures the normalization) and \(b_\alpha\) are constants of no specific interest in what follows and then we omit to write them down, and

\[
\mu_\alpha = [\gamma_\alpha + 1]^{-1} = \frac{1}{4} \left[\frac{3 - \alpha}{2 - \alpha}\right]. \tag{27}
\]

Hence the charge at each given point \(x\) at the interface is given by Eq. (26), and the current to be produced in the electrode - motion of this charge arriving at it under the action of the field to be applied - is proportional to it, and then we have the law

\[I(t) = C_\alpha t^{-\mu_\alpha} \left[a^2 + x^2 t^{-2\mu_\alpha}\right]^{1/\gamma_\alpha - 1} \text{ at interface}, \tag{28}\]

where \(C_\alpha\) is a constant.

Taking into account that \(\mu_\alpha\) is positive (cf. Eqs. (27) and (25), and that \(0 < \gamma_\alpha \leq 1\), for not too-short times after application of the field we can expect that \(a^2 \gg x^2 t^{-2\mu_\alpha}\) and then there follows a power law in time for the current, namely

\[i(t) \approx t^{-\mu_\alpha} = t^{-\frac{1}{\gamma_\alpha - 1}} = t^{-\frac{3 - \alpha}{2 - \alpha}}. \tag{29}\]

But taking into account that the applied potential is \(V = V_0 + vt\) (where \(v\) is the scanning velocity), and then \(t = (V - V_0)/v\), Eq. (29) leads to the power law

\[i_p \approx v^\epsilon, \tag{30}\]

where \(\epsilon\) is \(\mu_\alpha\), that is,

\[\epsilon = (\gamma_\alpha + 1)^{-1} = \frac{1}{4} \left[\frac{3 - \alpha}{2 - \alpha}\right]. \tag{31}\]

In the conditions of the work of Pajkossy and Nyicos \(26\), the fractal power \(\epsilon\) is related to the fractal dimension \(d_f\) of the electrode rough surface by the relation \(\epsilon \simeq (d_f - 1)/2\), and
then in experiments when it holds, from the log-log plot of \( i_p \) vs \( v \) there follows the value of \( \epsilon \) and, consequently, the fractal dimension can be estimated. Using Eq. (31) we arrive to the relation between fractal dimension and the parameter \( \alpha \), namely

\[
\alpha = \frac{4d_f - 7}{2d_f - 3}.
\]

We can see that for \( d_f = 2 \) (a perfectly flat surface) we have \( \alpha = 1 \) as it should, while for the other possible extreme limit of \( d_f = 3 \), it follows \( \alpha = 5/3 \). As already noticed, the theory precisely restricts the values of \( \alpha \) to this interval; outside it the calculations present singularities. Then as a consequence the exponent \( \epsilon \) is also limited, and we can only expect for it values in the interval \( 0.5 \leq \epsilon < 1 \). Hence, we stress that these are the permitted limiting values of the indexes \( \alpha \) and \( \epsilon \): the value which adjusts the experimental data is to be contained between these limits, being dependent on the systems dynamics, geometry and size, macroscopic thermodynamic state, and the experimental protocol (in the present case depends on the scanning velocity \( v \), as shall be shown in the next section).

We can see that the three quantities, \( \alpha, \epsilon \) and \( d_f \) are related and give a kind of measure of the microroughness of the electrode surface. A perfect one (a totally smooth surface) corresponds to \( \alpha = 1, \epsilon = 0.5 \) and \( d_f = 2 \), and as the surface becomes more and more imperfect, these quantities increase, above those values, but with upper boundaries, being 1.666 for \( \alpha \), 1 for \( \epsilon \) and 3 for \( d_f \).

On the other hand, atomic force microscopy allows to obtain the fractal dimension and a kind of degree of microroughness of the surface. According to the method [29], it is calculated the so-called interface width, namely

\[
W(L) = \left[ \frac{1}{L} \sum_{j=1}^{L} (h_i - \bar{h})^2 \right]^{\frac{1}{2}},
\]

where \( L \) is the number of partitions in which the surface is divided and \( h_i - \bar{h} \) is the deviation, within each partition, of the height with respect to the average value. There exists a power law between \( W \) and \( L \), namely \( W \sim L^r \), where \( r \) is called the roughness exponent, which is related to the fractal dimension as \( d_f \simeq 3 - r \). Therefore, comparing with the theory developed for the case of cyclic voltammetry, we obtain relationships relating the different
quantities, namely

\[ r = 2(1 - \epsilon) \quad ; \quad r = \frac{1}{2} \left[ \frac{5 - 3\alpha}{2 - \alpha} \right] \quad ; \quad r = \frac{2\gamma\alpha}{\gamma\alpha + 1}. \] (34)

Recalling that, according to the theory, \( 1 \leq \alpha < 5/3 \), we have that \( r \) can only attain the values \( 0 < r \leq 1 \), comprising the conditions between highest roughness to a perfectly smooth surface, and thus can be used as a kind of "order parameter", or, better to say, "degree of fractality parameter".

III. THEORY AND EXPERIMENT

We apply the preceding theory to the study of a class of experiments [52]. In that work, the fractal dimension of nickel oxide thin films was analyzed by means of cyclic voltammetry and compared with the results obtained by atomic force microscopy (AFM).

Figure 1 shows the dependence of the peak current with the sweep-rate velocity \( v \). We can notice that the peak value of the current increases continuously with \( v \), and also that it can be identified two regions where the dependence is very approximately linear (one in the range \( 1 \leq v \leq 10 \text{ mV s}^{-1} \) with a more pronounced slope that the other in the range \( 20 \leq v \) up to \( \sim 100 \text{ mV s}^{-1} \)). Once we do have a log-log plot, consequently it can be identified two values of the exponent \( \epsilon \), in accordance with Eq.(30). Moreover, from equation Eq.(31) we obtain that

\[ \alpha = \frac{8\epsilon - 3}{4\epsilon - 1}, \] (35)

and two values of the infoentropic index \( \alpha \) can also be determined. The calculated values are presented in Table I. The associated statistical fractal dimension values \( (d_f, \text{Eq.(32)}) \) are also presented in this table. The larger \( d_f \) values are obtained in the slow-sweep ranges, in comparison with those obtained at faster scans. The fact that can be identified from this is that the fractal dimension depends on the observational scale, which is limited by the experimental protocol, here the scanning velocity range: At low values of \( v \), the ions are constrained in a spatial region close to the electrode (known as the diffusion layer), and are able to sense the fine details of the microroughness at the interface. On the other hand, increasing the scan rate also increases the length of the diffusion layer, and the global morphology of the electrode surface becomes predominant. This behavior is particularly
expected in the case of sensing by some experimental method the surface morphology of the thin film: this surface presents grains, and two distinct statistical processes are responsible either for the formation of the local surface morphology of individual grains or the global thin film surface morphology, formed by the assemblage of all grains. The experimental values determined in this work for the infoentropic index $\alpha$ are within the expected theoretical range ($1 \leq \alpha < 5/3$), and the $d_f$ values obtained by cyclic voltammetry (Table 1) indicate that a stronger asperity can be associated to the local grain morphology, in constrast to a smoother thin film global morphology.

Figure 2 presents a typical AFM micrography. The presence of structured grains, with mean size $\approx 180$ nm, can be clearly seen. Figure 3 presents a log-log plot of the interface width $W(L)$ as a function of the partitions $L$. Two scaling regions (at short and medium $L$ ranges) are evidenced, separated by a transition $L$ value of $\approx 140$ nm, close to the mean grain size. The roughness exponent $r$ values calculated in accordance with Eq. (34), and the associated AFM images statistical fractal dimension values are listed in Table I. The calculated statistical fractal dimensions from both techniques are in good agreement. Returning to Fig.1, it is worth noticing that the full curve of dependence of $i_p$ with $v$, once we take into account Eqs. (30) and (31), can be approximated by the law

$$\alpha(v) \approx \frac{v + v_1}{v + v_2},$$

(36)

where $v_1 = 235 \pm 12$ and $v_2 = 145 \pm 8$ mV/s.

It can be noticed that this law in fact reproduces to a good degree of approximation (error smaller than 10%) the two straight lines in the given intervals described, and interpreted, above. We can also see that it is verified, as it should, a saturating behavior, namely, the infoentropic index $\alpha$ tends to the value 1 for large $v$, the minimum value it can take. Hence, according to Eq. (2) it follow that $d_f$ tends to 2, what can be interpreted, as already noticed, that as $v$ increases the charges keep "feeling" less and less the microroughness at the interface. Hence, for $v$ very large there follows that $d_f \approx 2$ (an averaged smooth surface), while the limit of $v$ going to zero would evidence the more detailed effect of the fractal topography, given in this case the values $d_f \approx 2.8$ (then near 3 and then indicating a strong roughness) and $\alpha \approx 1.62 \pm 0.08$, in accordance with the fact that $\alpha$ must remain in the interval as given by Eq. (25), and of course $2 \leq d_f < 3$. 

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IV. CONCLUDING REMARKS

We have considered in detail a quite interesting case consisting of a situation present in certain classes of systems where it becomes difficult for the researcher to apply the standard formalism in the conventional, well established, logically and physically sound Boltzmann-Gibbs statistics, because of the presence of inhomogeneous fluctuations which are "anomalous" in some sense and eventually, as in the case here, involving one type or other of fractality. In that cases – as already noticed – it may be convenient to depart from conventional statistics, introducing alternative ones. In other words, the appropriate use of the Boltzmann-Gibbs formalism may in some problems be quite complicated to apply or, and more fundamental, we may be faced with an inaccessible characterization constraints (information): thus, simplicity or the force of circumstances, respectively, would require setting on the use of other measures of informational entropies leading to heterotypical probability distributions [22] accompanied, as noticed, by the use of their associated escort probability [13, 23, 24, 41], and here we found convenient to use a physical statistical mechanics based on Renyi’s statistics [15, 16, 23, 24].

The matter has been illustrated in this paper by considering its application in a theoretical study of transport in electrodes in microbatteries, particularly cyclic voltammetry, which provides information on the fractal-like microroughened texture of them, providing an excellent illustration for the use and validation of such statistical theory. In ideal conditions (quite smooth surface) the peak current in the voltammetry experiment is proportional to the square root of the sweep-rate velocity, with which the applied field is changing. The standard theory relates this result to the diffusion of the charges that are going to reach the thin film electrode. But experimental data show that it is verified a power law, with a power different than 0.5, and this is referred to as resulting from a process of "anomalous" diffusion, as noted in the previous sections. As we have noticed, a description in terms of a process of diffusion does not apply, once the hydrodynamic motion that proceeds at the interphase electrolyte-electrode where is present a morphology with variations (asperity) ranging in the nano- to sub-nanometric scale. Hence, a proper description of the hydrodynamic motion requires to go well beyond the long-wavelength limit of classical (Onsagerian) thermo-hydrodynamics, being required to introduce an extended higher-order (sometimes referred-to as mesoscopic) thermo-hydrodynamics, together with the introduction of com-
complicated boundary conditions.

As shown in the Appendix, using Renyi’s statistics but ignoring the nano- to sub-nanometric-sized roughness of the thin film electrode, it is derived an ”anomalous” (non-Fickian) diffusion equation, which allows to describe the experimental results in cyclic voltammetry. The relevant point is that the index $\alpha$, that the Renyi statistics contains, determines the power law in the voltammetry experiment which allows to estimate the roughness of the electrode surface and, then, its quality and influence on the functioning of the device.

In section III has been presented a theoretical analysis of results in a given experiment (cyclic voltammetry and atomic force microscopy): in tables and figures are shown the results of the study of the index $\alpha$ of Renyi statistics, together with other power indexes (determined by the former) and the statistical fractal dimension, all depending on the experimental protocol.

Closing this section we notice that the use of an alternative statistics even though does not provide a complete physical picture of the problem in hands – once we do have an utter difficulty to handle the appropriate extended non-classical thermohydrodynamics to be applied – the sophistication of the formalism allow us to obtain a good insight into the physical aspects of the situation. On the one hand, as noticed, the use of the escort probability takes care of introducing correlations (fluctuations and higher-order variances), and on the other hand the heterotypical probability distribution (the one of Renyi here) modifies the weight of the Fourier amplitudes $|n(Q)|$ of the density in relation to their classical values in the linear Onsagerian regime \[^{47,48}\]. As previously noticed and discussed, classical thermo-hydrodynamics together with Fick’s diffusion equation is a satisfactory approach while $|n(Q)|$ has leading contributions for small Q (large wavelengths) and negligible for intermediate to large wavenumbers (intermediate to short wavelengths). When not only small wavenumbers but ever increasing ones become relevant for the description of the motion, i.e. associated to non-negligible amplitudes $|n(Q)|$ contributing in the Fourier analysis of the density, we need to introduce a higher-order thermo-hydrodynamics (with now equations of evolution of the Maxwell- Cattano-type, Burnett and super-Burnett-type, and so on) \[^{43,44}\]. In the case we have analyzed, Renyi heterotypical distribution, which leads to obtain the ”anomalous” diffusion equation of Eq.(24), and where $\alpha > 1$, in the restricted hydrodynamic description used, decreases what would be the values of $|n(Q)|$ in the stan-
standard treatment for short wavenumbers, that is, in the domain of classical hydrodynamics, while increases those amplitudes outside that region, i.e. in the regime of the higher order thermo-hydrodynamics.

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APPENDIX A: "ANOMALOUS" (NON-FICKIAN) DIFFUSION

Let us consider first the conventional case of diffusion, when the principle of sufficiency is satisfied, meaning that the several stringent restrictions its validity requires are met, namely, local equilibrium, linear Onsager relations and symmetry laws, condition of movement with long wavelengths and very low frequencies, and weak fluctuations, are verified. A specific criterion of validity is given in Ref.[46], where it is considered a system composed of two ideal fluids in interaction between them. The continuity equation for the flux \( I_n(r, t) \) [cf. Eq.(19)], after transforming Fourier in time, takes the form:

\[
(1 + i \omega \tau_{n1}) I_n(r, t) + \tau_{n1} \nabla \cdot I^{(2)}_n(r, t) = 0 ,
\]  

(A1)

where \( \tau_{n1} \) is the momentum relaxation time. But, at very low frequencies \( \omega \tau_{n1} \ll 1 \), and then

\[
I_n(r, t) \simeq -\tau_{n1} \nabla \cdot I^{(2)}(r, t) ,
\]

(A2)

and a direct calculation tell us that

\[
\nabla \cdot I^{(2)}(r, t) = \frac{k_B T}{m} \nabla n(r, t) ,
\]

(A3)

Replacing Eq.(A3) in Eq.(A2), and the latter in the conservation equation for the density, (Eq.(14)) we obtain the usual Fick’s diffusion equation

\[
\frac{\partial}{\partial t} n(r, t) + D \nabla^2 n(r, t) = 0 ,
\]

(A4)
where $D = \frac{1}{3} v_{th}^2 \tau_n$, with $\frac{1}{2} m v_{th}^2 = \frac{3}{2} k_B T$; $v_{th}$ is the thermal velocity and $D$ is the diffusion coefficient, with dimensions cm$^2$/sec, and $m$ is the mass of each particle.

Let us now go over the unconventional treatment, which is required once one is looking forward for an analysis of data on the basis of a description in terms of a diffusive movement, when this is not possible, as a consequence that diffusion in the microroughened region is governed by not too long wavelengths (up to nanometric ones, i.e., $10^{-7}$ cm, while the limitation of the diffusive region is of the order of $D/v_{th}$, say, typically $10^{-2}$ to $10^{-4}$ cm). A higher-order thermo-hydrodynamics needs be introduced, but if the lower order description including only the density and its flux is kept, then sufficiency is not satisfied and we need to introduce auxiliary Statistical Mechanics. Let us consider the auxiliary statistical operator which for this system of identical free particles is in Renyi statistics given by

$$\overline{\eta}_\alpha(\Gamma|t) = \frac{1}{\eta_\alpha(t)} \left[ 1 + (\alpha - 1) \int d^3 r \int d^3 p \varphi_\alpha(r, p; t) \Delta \hat{n}_1(r, p, t|\Gamma) \right]^{-\frac{1}{\alpha - 1}}, \quad (A5)$$

where

$$\Delta \hat{n}_1(r, p; t) = \hat{n}_1(r, p; |\Gamma) - \langle \hat{n}_1(r, p; t) \rangle_\alpha,$$  \quad (A6)

with

$$\langle \hat{n}_1(r, p; t) \rangle_\alpha = \int d\Gamma \hat{n}_1(r, p; |\Gamma) D_\alpha(\Gamma|t), \quad (A7)$$

and where $\varphi_\alpha(r, p, t)$ is the associated Lagrange multiplier, $\overline{\eta}$ ensures its normalization, $\hat{n}_1$ is given in Eq.(9), and

$$D_\alpha(\Gamma|t) = (\overline{\eta}_\alpha)^\alpha / \int d\Gamma (\overline{\eta}_\alpha)^\alpha,$$  \quad (A8)

is the accompanying escort probability (cf. Eq.(1)).

Introducing the modified Lagrange multiplier

$$\tilde{\varphi}_\alpha(r, p, t) = \varphi_\alpha(r, p, t) \left[ 1 - (\alpha - 1) \int d^3 r \int d^3 p \varphi_\alpha(r, p, t) \langle \hat{n}_1(r, p; t) \rangle_\alpha \right]^{-1}, \quad (A9)$$

we find that

$$\overline{\eta}_\alpha(\Gamma|t) = \frac{1}{\overline{\zeta}(t)} \left[ 1 + (\alpha - 1) \int d^3 r \int d^3 p \tilde{\varphi}_\alpha(r, p, t) \hat{n}_1(r, p, t|\Gamma) \right]^{-\frac{1}{\alpha - 1}}, \quad (A10)$$
with $\tau(t)$ ensuring the normalization condition. At this point we introduce for $\tilde{\varphi}$ the form
\[\tilde{\varphi}_\alpha(r, p, t) = F_h(r, t) \frac{p^2}{2m} + F_n(r, t) + F_n(r, t) \cdot \frac{P}{m}, \quad (A11)\]
for, in such a way, keeping as basic variables the three of Eqs.(10) to (12), and thus arriving to the statistical operator of Eq.(13).

Using Eqs. (A.5) to (A.14), after some lengthy but straightforward calculations, it follows for the energy density that
\[h(r, t) = \int d^3p \frac{p^2}{2m} \int d\Gamma \hat{n}_1(r, p|\Gamma) \mathcal{D}_\alpha(\Gamma, t) = u(r, t) + n(r, t) \frac{1}{2} m v_\alpha^2(r, t), \quad (A12)\]
i.e., composed of the energy associated to the drift movement (the last term) and the internal energy density
\[u(r, t) = \frac{3}{5 - 3\alpha} \frac{C_\alpha(r, t)}{\beta_\alpha(r, t)} n^{\gamma_\alpha}(r, t), \quad (A13)\]
where
\[C_\alpha(r, t) = \left\{ \frac{2 \pi N}{(\alpha - 1)^{3/2} \tau_1(t)} \left[ \frac{2m}{\beta_\alpha(r, t)} \right]^{3/2} \mathcal{B}(\frac{3}{2}; \alpha - 1 - \frac{3}{2}) \right\}^{\frac{1}{3-\alpha}}. \quad (A14)\]
$\mathcal{B}(\nu, x)$ is the Beta function, we have written $F_{n\alpha}(r, t) = \tilde{\beta}_\alpha(r, t)$; $F_{n\alpha}(r, t) = m \tilde{\beta}_\alpha(r, t) v(r, t)$ (introducing a "drift velocity" field $v(r, t)$); moreover
\[\gamma_\alpha = \frac{5 - 3\alpha}{3\alpha - 5}, \quad (A15)\]
and the values of $\alpha$ are restricted to the interval $[54]$
\[1 \leq \alpha < \frac{5}{3}, \quad (A16)\]

Finally, the second order flux is given by
\[I_n^{[2]}(r, t) = \int d^3p \left[ \frac{pp}{m^2} \right] \int d\Gamma \hat{n}_1(r, p|\Gamma) \mathcal{D}_\alpha(\Gamma, t) = n(r, t) [v_\alpha(r, t) v_\alpha(r, t)] + \frac{2}{3m} u(r, t) 1^{[2]}, \quad (A17)\]
where $1^{[2]}$ is the unit second-rank tensor, $[...]$ stands for the tensorial product of vectors, and it can be noticed that
\[P^{[2]}(r, t) = m I_n^{[2]}(r, t) - m n(r, t) [v_\alpha(r, t) v_\alpha(r, t) = m I_n^{[2]}(r, t) - m n(r, t) [v_\alpha(r, t) v_\alpha(r, t)], \quad (A18)\]
is the pressure tensor. Neglecting the terms quadratic in the drift velocity, combining the above equations we obtain that

\[ I_{n}^{[2]}(r, t) = \xi_{n\alpha}(r, t) n^{\gamma\alpha}(r, t) 1^{[2]}, \]  

(A19)

where

\[ \xi_{n\alpha}(r, t) = \frac{2}{3 m} \frac{5}{5 - 3 \alpha} \frac{C_{\alpha}(r, t)}{\beta_{\alpha}(r, t)}, \]  

(A20)

is the quantity present in Eq.(22).

**APPENDIX B: FLUX RELAXATION**

The scattering integral of Eq.(16) depends, through the statistical operator \( D_{\alpha} \), on the non-equilibrium thermodynamic quantities \( F_{h}, F_{n}, \) and \( F_{n} \) (related to the Lagrange multipliers that the variational method introduces; cf. Appendix A). But the latter are related to the basic variables, \( h, n \) and \( I_{n} \), by means of Eqs.(10) to (12), which are considered as being equations of state in the associated nonequilibrium thermodynamics [21, 32, 33]. Hence \( J_{n\alpha}(r, t) \) is a functional of these basic variables. But we do have, on the one hand, that \( n(r, t) = n_{0} + \Delta n(r, t) \) and \( h(r, t) = h_{0} + \Delta h(r, t) \), namely their constant global values modified by a small variation, that is \( \Delta n \ll n_{0} \) and, on the other hand, \( I \) being also small we can write a series expansion in it but retaining only the first (linear) contribution

\[ J_{n\alpha}(r, t) \simeq \left[ \Theta_{\alpha}^{[2]} \right]^{-1} \otimes I_{n}(r, t), \]  

(B1)

where \( \left[ \Theta_{\alpha}^{[2]} \right]^{-1} \) is the second-rank tensor (playing the role of the inverse of a tensorial Maxwell-characteristic time [32]) of components \( \delta J_{i}/\delta I_{j} \), dependent only on \( n_{0} \) and \( h_{0} \). Writing

\[ \left[ \Theta_{\alpha}^{[2]} \right]^{-1} = \frac{1}{\tau_{I\alpha}} + \left[ \Theta_{\alpha}^{[2]} \right]^{-1}, \]  

(B2)

where

\[ \frac{1}{\tau_{I\alpha}} = \frac{1}{3} Tr \left\{ \left[ \Theta_{\alpha}^{[2]} \right]^{-1} \right\} \]  

(B3)

and the last term on the right of Eq.(B2) being then the traceless part of Maxwell characteristic time tensor, neglecting it Eq.(B1) becomes Eq.(18).
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| Cyclic Voltammetry |   |   |   |
|-------------------|---|---|---|
|                   | \(\epsilon\) | \(\alpha\) | \(d_f\) |
| slow scan rates   | 0.85 | 1.58 | 2.70 |
| fast scan rates   | 0.63 | 1.34 | 2.26 |

| Atomic Force Microscopy |   |   |
|-------------------------|---|---|
|                         | \(r\) | \(d_f\) |
| short L ranges         | 0.76 | 2.24 |
| medium L ranges        | 0.27 | 2.73 |

TABLE I: Exponent \(\epsilon\), Infoentropic index \(\alpha\) and fractal dimension \(d_f\) obtained from cyclic voltammetry experiments performed at slow and fast scan rates. The values of the roughness exponent \(r\) and fractal dimension \(d_f\) obtained from Atomic Force Microscopy images at short and medium L ranges are also presented.
**Figure Captions**

*Figure 1-* Log-log plot of peak current $i_p$ *versus* sweep rate $v$.

*Figure 2-* AFM micrograph, 1000 nm $\times$ 1000 nm $\times$ 23 nm.

*Figure 3-* Log-log plot of interface width $W(L)$ *versus* partitions L.
FIG. 1: Log-log plot of peak current $i_p$ versus sweep rate $v$. 

\[ \log(i_p, \text{mA}) \]

\[ \log(v, \text{mV/s}) \]
FIG. 2: AFM micrograph, 1000 nm × 1000 nm × 23 nm.
FIG. 3: Log-log plot of interface width $W(L)$ versus partitions $L$. 