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## Displacement of voltammetric peaks with nanoparticles size: a nonextensive thermodynamic approach

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### Abstract

We show here that the concepts of *nonextensive thermodynamics* (NET), described previously (J. Phys. Chem. B, 2004, 108, 18980) and applied to redox behaviour of nanoparticles (J. Phys. Chem. C, 2008, 112, 12116) can be used to express by a power law the variations to the electrochemical kinetics of nanoparticles and in particular to voltammetry. We proposed here a generalization of Plieth's relationship for non-spherical aggregates by assuming that the interface between the particle and its environment is fuzzy. Thus, the relations of non-extensive thermodynamics can quantitatively account for the displacements of electro-oxidation potentials of metal nanoparticles deposited on electrodes, according to their measured size. Our approach also permits to formally justify the stability of the particles may increase as their size decreases, ( $\tau < 0$ ). This is usually found when the aggregates are in close contact with a matrix (in the case, for example, of embedded particles).

Keywords: nonextensive thermodynamics, size effect, electro-oxidation, nanoparticles

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## Introduction

Several recent experimental and theoretical studies on the electro-oxidation of metal nanoparticles deposited on electrodes show the complexity of the physico-chemical behavior of the material in a divided form. Indeed, a destabilization of the reduced species with a decrease in size [1], or rather a stabilization [2, 3], or sometimes, conditions of metastability [4] can be observed depending on the nature of the selected systems, the size of nanoparticles and the experiment conditions.

This diversity of behaviors is not specific to redox couples since it is found in other areas. Thus for indium nanoparticles, embedded in an aluminum matrix [5], there is, according to the method of preparation (melt-spinning and ball-milling) a decrease or an increase in the value of the melting point of particles with their size. For gaseous aggregates, it is shown that nanobubbles with an average radius of 50 nm are stable for more than two weeks, whereas conventional reasoning, based on the application of Laplace's law, provide for their almost immediate disappearance [6].

Obviously, all these changes cannot be described, let alone formalized by the classical (extensive) thermodynamics, which attaches great importance to the shape of the aggregate of nanometric size. The latter is usually assumed spherical, which is rarely the case in reality [7]. The particle shape is generally difficult to determine from standard geometrical dimensions (length, area, volume) and the concept of interfacial tension for material as a whole loses its meaning. It is for these reasons that we introduced in 2004 the bases of a "non-extensive" thermodynamics [8] adapted to the study of the reactivity of nanoparticles (NP) which does not involve the knowledge of the shape of the particle but only its mass. The interface between the particle and its environment is supposed to be fuzzy. The use of this approach to describe the reactivity of various interfacial systems [9-12], has been particularly fruitful.

The electrochemistry of surfaces is a field in constant evolution [13] and with regard to redox systems, we introduced in 2008, a study of the electrochemical properties of metal nanoparticles [14] at equilibrium. This work presented a generalization of the relationship proposed by Plieth [15] to non-spherical aggregates.

## 1. Theory

Without repeating all the bases of non-extensive thermodynamics, which can be found in detail in our previous publications, we present below some theoretical elements to easily follow our approach.

### 1.1 The conceptual bases of non-extensive thermodynamics, notion of fuzzy interface

In most cases, the nanoparticles are aggregates with geometric borders difficult to specify. Under these conditions, it is unrealistic to set that the interfacial energy relative to the aggregate is written as the product of interfacial tension,  $\gamma$ , by an area,  $A$ . Therefore, the use of the Laplace's law giving the pressure difference between the inside of the particle and its environment is artificial. In the approach we propose, we consider an aggregate of mass  $M$ , whose interface between the particle and its environment is not defined. By convention, we will name this type of interface a "*fuzzy interface*" [9, 16, 17]. The fact that we cannot describe the geometry of the object does not prevent it from having an interfacial energy,  $E$ . We agreed to write its variations as the product of a tension (intensive magnitude),  $\tau$ , and an "extensity",  $\chi$ , which varies with the mass of the system according to a homogeneous function (Euler's function) of degree equal to  $m$ ,  $m$  can be different from one.

$$dE = \tau d\chi \tag{1}$$

This is why our thermodynamic approach can be described as "nonextensive" as opposed to Gibbs thermodynamics, in which the extensities are Euler functions of degree one of the system mass. Gibbs thermodynamics is then called "extensive". The formal choice we have made is purely conventional. It has the advantage of using the same state functions as those involved in the classical thermodynamics, to give a simple operational form to the chemical potential, especially to admit the extensive classical thermodynamics as a particular case of the nonextensive thermodynamics.

In this expression,  $\tau$  can be positive or negative. One could be amazed at this possibility whereas the surface tension  $\gamma$  is always positive.

On the theoretical level, when a thermodynamics that is no longer based on the extensivity is developed, it is necessary to redefine all variables of the system and clarify its meaning. They may have the same mathematical definitions as in extensive thermodynamics but with different properties. Thus, in some developments of nonextensive thermodynamics, stemming from the work of Tsallis [18], the temperature is shown as a magnitude whose value depends on the system mass. In this case, this variable is not intensive (homogeneous function of degree 0 of

the system mass) [19]. This shows that it is always difficult to transpose to nonextensive approaches, patterns of thought inherited from the Gibbs thermodynamics.

Concerning  $\tau$ , there was no theoretical reason, *a priori*, to fix the sign and we did not do it. Experimentally, from the analysis of data from different fields of study, we showed that both situations ( $\tau > 0$  and  $\tau < 0$ ) are met. Thus, in terms of the change in melting points with the size of metal nanoparticles, we showed [10], from literature values, the relationships that we propose allow fully describing the evolution of considered systems. Most often, there is a decrease of the value of the melting point with decreasing particle size. This case corresponds to the evolution expected by the Gibbs-Thompson relation (ie, with  $\gamma > 0$ ), and regards us a positive value of  $\tau$ . However, when the considered particles are embedded or placed within a matrix, the opposite effect is observed. This corresponds in our approach to a negative value of  $\tau$ .

We can find another example of this feature of  $\tau$  considering the behavior of charged micelles [12]. In micellar solutions, the aggregates formed by the amphiphiles and their counter - ions can be treated as non-extensive interpenetrating phases. The activities of charged amphiphiles are fully described is by adopting a negative value of  $\tau$ . In contrast, the activities of the counter-ions against is represented by a positive value of  $\tau$ .

By convention, we assume that  $\chi$  is an Euler's function of degree  $m$  of the particle mass, or its volume,  $V$ . We recall here that in classical thermodynamics, the extensities are strictly extensive magnitudes, that is to say, by convention, an Euler's function of degree 1 of the mass. In our approach, the degree  $m$  can be different from 1 while being lower ( $m \leq 1$ ).

Among the possible Euler's functions, we chose to link  $\chi$  to the volume of the particle by a power law. The parameter  $m$  is called the "thermodynamic dimension" of the system.

$$\chi = aV^m$$

$$d\chi = maV^{m-1}dV = m \frac{\chi}{V} dV \quad (2)$$

The coefficient  $a$  characterizes the considered system. The variation of the interfacial energy is then written

$$dE = \tau d\chi = \tau m \frac{\chi}{V} dV \quad (3)$$

It can be introduced in the expression of the internal energy  $U$ . For a system defined by its content ( $n_1, n_2... n_i$  moles), in contact with an external phase at the pressure  $P$  and at the temperature  $T$ , we can write

$$dU = TdS - PdV + \sum \mu_i dn_i + \tau d\chi \quad (4)$$

Since  $\chi$  is not an extensive quantity,  $U$  is not either.

We have developed in detail the consequences of this property by posing as convention that  $T$  and  $\tau$  are intensive magnitudes (Euler's function of degree 0). The volume and numbers of moles are by definition extensive variables (which corresponds to Euler's function of degree one of mass). The result (relation 4) is that the entropy is no more extensive.

Pressure and chemical potentials are no more intensive magnitudes, that is to say that their values vary with the mass (or volume) of the considered system, at constant composition.

One of the most original results of this "non-extensive approach of thermodynamics" is to show that the value of the pressure,  $P^{NE}$ , in an aggregate made of  $n$  moles of a compound, considered as a non-extensive system, of volume  $V$ , of extensity  $\chi$ , and of dimension  $m$ , is different from that of its environment,  $P$ .

There is a relationship between the pressure of the non-extensive system and the external pressure, such as

$$(P^{NE} - P) = \tau \frac{d\chi}{dV} = m\tau \frac{\chi}{V} \quad (5)$$

According to the sign of  $\tau$ , this difference can be positive or negative.

Laplace's equation is a particular case of application of this equation for spherical systems. Thus, in the case of a liquid drop in contact with a gas, of Liquid-gas (Lg) interfacial tension  $\gamma^{Lg}$  and radius  $r$ , the pressure difference between the inner of the drop,  $P_g$ , ( $P^{NE} = P_g$ ) and the external pressure,  $P$  of the gas atmosphere (unlimited phase), is obtained by identifying  $\tau = \gamma^{Lg}$  and  $\chi = A^{Lg}$ . The area is an Euler's function of degree  $m = 2/3$  with respect to the mass or volume of the drop. This becomes

$$(P_g - P) = m \frac{\tau \chi}{V} = \frac{2}{3} \frac{\gamma^{Lg} A^{Lg}}{V} = 2 \frac{\gamma^{Lg}}{r} \quad (6)$$

In the case of using the Laplace's law, the surface tension is always a positive quantity, which means that the value of the pressure in the spherical particle is always larger than the one of the environment. This restriction is lifted in the case of the non-extensive thermodynamics,  $\tau$  can be negative. The fact that the pressure within an aggregate may be less than that of its surroundings may seem troubling in the case of nanoparticles, but it is an accepted concept in studies concerning the behavior of fluids separated by concave meniscus, for example in capillary systems [20].

This approach allows locating the origin of the change in behavior of the matter when finely divided. The pressure inside the nanoparticles is different from the ambient pressure, which

involves modifying the chemical potential of the species. The variation of the chemical potential of component  $i$  with pressure, at constant temperature and composition, satisfies the following relation

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_i} = V_i' \quad (7)$$

$V_i'$  is the partial molar volume of the species  $i$ .

This equation can be integrated between the pressure of the non-extensive phase,  $P^{NE}$ , and the ambient pressure,  $P$ , of the “unlimited phase” in contact, by supposing that the value of the partial molar volume of  $i$  does not vary with  $P$  (condensed phases)

$$\mu_i^{NE} = \mu_i^{un} + V_i' (P^{NE} - P) = \mu_i^{un} + V_i' \tau \frac{d\chi}{dV} \quad (8)$$

$\mu_i^{NE}$  is the chemical potential of  $i$  in the non-extensive phase,  $\mu_i^{un}$  is the chemical potential of  $i$  in the unlimited phase at the pressure  $P$ , *un* stands for unlimited.

The partial molar volumes of the species involved in these phenomena are most often positive. The extensity  $\chi$  varies in the same way that the volume. According to the sign of  $\tau$ , the chemical potential of  $i$  can be higher or lower than the chemical potential of the unlimited phase. When it is higher, the species is destabilized by the reduction in size and becomes more reactive. On the contrary, it is stabilized, then less reactive, when the value of  $\tau$  is negative. The value of the tension  $\tau$  can be small and then no effect of the size on the behavior of the particle will be observed.

Eq.8 allows justifying the variety of observed behaviors on the nanometric systems.

## 1.2. Conditions of the redox equilibrium

The behavior of redox couples is, by convention, referred to the couple  $H_2 / H^+$ . For a redox couple throwing in  $n$  electrons, the behavior is characterized by the conventional Nernst equation

$$ox + \frac{n}{2} H_2^R = red + nH^{+,R} \quad (9)$$

In order to simplify the notations, we do not show the number of charges ( $v+$ ) carried by the oxidized species. At the considered temperature, hydrogen,  $H_2^R$ , is taken in this standard state (perfect gas at the pressure of 1 bar,  $\mu_{H_2^R} = \mu_{H_2}^*$ ). The protons  $H^{+,R}$  are taken in their hypothetical

standard state at infinite dilution (values of activity and concentration are equal to one,  $\mu_{H^+,R} = \mu_{H^+}^\infty$ ). Let consider the case in which the reduced species is the non-extensive phase at the pressure  $P^{NE}$  and where the oxidized species is in the solution (the unlimited phase) at the external pressure  $P$ .

The free energy of the reaction, equilibrated in charge, is written as a function of the chemical potentials of the participating species

$$\Delta_{redox}G = n \mu_{H^+}^\infty + \mu_{red}^{P^{NE}} - \mu_{ox}^P - \frac{n}{2} \mu_{H_2}^* \quad (10)$$

In these conditions, the standard free energy of the conventional reaction of electronic exchange is written according to

$$\Delta_{redox}G^{0,P^{NE}} = n \mu_{H^+}^\infty + \mu_{red}^{0,P^{NE}} - \mu_{ox}^\infty - \frac{n}{2} \mu_{H_2}^* = -nFE^{0,NE} \quad (11)$$

By taking into account the previous relations, the standard chemical potential of the reduced species in unlimited phase can be introduced in this last expression.

$$\Delta_{redox}G^{0,P^{NE}} = n \mu_{H^+}^\infty + \mu_{red}^{0,un} + \tau V_{red}^0 \frac{d\chi}{dV} - \mu_{ox}^\infty - \frac{n}{2} \mu_{H_2}^* = -nFE^{0,NE} \quad (12)$$

For the redox reaction implying oxidized and reduced species in unlimited phase, the standard redox potential is

$$\Delta_{redox}G^{0,ill} = n \mu_{H^+}^\infty + \mu_{red}^{0,un} - \mu_{ox}^\infty - \frac{n}{2} \mu_{H_2}^* = -nFE^{0,ill} \quad (13)$$

The variation of the redox potential with the volume can be deduced

$$E^{0,NE} = E^{0,un} - \frac{V_{red}^0}{nF} \tau \frac{d\chi}{dV} \quad (14)$$

If the value of the tension,  $\tau$ , is positive, the standard redox potential decreases with the volume of the object and then the reduced species is more oxidizable.

In the case of a spherical particle of metal, of radius  $r$  and solid-liquid (SL) interfacial tension,  $\gamma^{SL}$ , the relationship proposed by Plieth (which comes from Gibbs-Thompson equation) is found

$$E^{0,NE} = E^{0,un} - \frac{V_{red}^0}{nF} \frac{2\gamma^{SL}}{r} \quad (15)$$

In this case, as  $\gamma^{SL}$  is always positive, a decrease of the standard redox potential with the particle radius is expected. These results can be used for analyzing the electrochemical behavior of redox couples in cyclic voltammetry.

## 2. Cyclic voltammetry

### 2.1. Unlimited phases

We may first recall the main relationships that characterize the behavior of a reversible redox couple studied in cyclic voltammetry for reactions in unlimited phases.

For a redox reaction involving  $n$  electrons, the half-peak potential  $E_{p/2}$  is simply expressed as a function of redox potential and the diffusion coefficients of the reduced and oxidized species.

$$E_{1/2} = E^{0,un} + \frac{RT}{nF} \ln \left( \frac{D_{red}}{D_{ox}} \right)^{1/2} \quad (16)$$

If for a given redox couple, the value of  $E^\circ$  varies with the state of confining of the compounds involved in the reaction, without changing the diffusion coefficients, then the current peak position changes.

### 2.2. Reversible reaction in non-extensive thermodynamics

Usually, the electrochemical behavior of metal nanoparticles with their size is characterized by studying their electro-oxidation after their deposition on electrodes.

#### 2.2.1. Position of the peak in unlimited phase

Suppose that the reduced species is a pure non-extensive phase on the electrode. The main consequence (eq. 14) is that the values of the peak and half-peak potentials will be modified according to the nanoparticle volumes.

$$E_{p/2}^{NE} = E^{o,NE} + \frac{RT}{nF} \ln \left( \frac{D_{red}}{D_{ox}} \right)^{1/2} = E^{0,un} + \frac{RT}{nF} \ln \left( \frac{D_{red}}{D_{ox}} \right)^{1/2} - \frac{V_{red}^*}{nF} \tau \frac{d\chi}{dV} \quad (17)$$

which can be also written

$$E_p^{un} - E_p^{NE} = E_{p/2}^{un} - E_{p/2}^{NE} = \frac{V_{red}^*}{nF} \tau \frac{d\chi}{dV} \quad (18)$$

By taking into account that the extensity is an Euler's function of order  $m$  of the mass (or of the volume), we show the general relationship

$$E_p^{un} - E_p^{NE} = E_{p/2}^{un} - E_{p/2}^{NE} = \frac{V_{red}^*}{nF} m \tau \frac{\chi}{V} \quad (19)$$

This relation can be applied when the aggregates are spherical particles of radius  $r$  and their interfacial tension,  $\gamma$ , is known.

$$E_p^{un} - E_p^{NE} = E_{p/2}^{un} - E_{p/2}^{NE} = \frac{V_{red}^*}{nF} \frac{2\gamma}{r} \quad (20)$$

In such a case, the peak potential varies with the inverse of the radius. The value of the peak potential will decrease with  $r$ . This relationship has been proposed by Plieth in 1982 [15]. It serves as a theoretical reference to current studies.

### 2.2.2. Peak position for non-extensive phases

By writing as previously that the extensity is an Euler's function of order  $m$  of the mass, we obtain

$$E_p^{un} - E_p^{NE} = E_{p/2}^{un} - E_{p/2}^{NE} = \frac{V_{red}^*}{nF} a m \tau V^{m-1} \quad (21)$$

The peak potential varies according to a power law of the volume (or of the mass) of the particles of reduced species. The relevance of this approach can be checked from the experimental results available in the literature.

However, in most of the literature, we do not have the volume of aggregates, but an experimental size parameter,  $D$ , usually measured by spectroscopy. This can be a radius, a diameter, a length, a thickness, etc. We can transform the above equation by writing that the extensity,  $\chi$ , and the volume are both homogeneous functions of the variable  $D$ , such as

$$\begin{aligned} \chi &= \alpha D^p \\ V &= \beta D^q \end{aligned} \quad (22)$$

Then

$$\begin{aligned} d\chi &= \alpha p D^{p-1} dD \\ dV &= \beta q D^{q-1} dD \end{aligned} \quad (23)$$

which leads to

$$\frac{d\chi}{dV} = \frac{\alpha p}{\beta q} D^{p-q} \quad (24)$$

The variation of the peak (and half-peak) potential is written

$$E_p^{un} - E_p^{NE} = E_{p/2}^{un} - E_{p/2}^{NE} = \frac{V_{red}^*}{nF} \tau \frac{\alpha p}{\beta q} D^{p-q} \quad (25)$$

This relation shows that the potential difference ( $E_p^{un} - E_p^{NE}$ ) is linked to the measured size of the particles by a power law. Then, the use of experimental results can be realized graphically from the relationship

$$\ln( E_p^{un} - E_p^{NE} ) = \ln\left( \frac{V_{red}^*}{nF} \tau \frac{\alpha p}{\beta q} \right) + (p - q) \ln D \quad (26)$$

### 3. Discussion

There are, in the literature, many data on the variation of the peak potential with the nanoparticles size of the reduced species. Generally, these changes are interpreted from the Plieth's relationship that most often does not well describe the experimental reality, primarily for three reasons.

The first is that the value of the interfacial tension between the metal and its environment is not experimentally accessible. It must therefore be estimated from energy considerations, which makes it uncertain.

The second is that the Plieth's relationship relates to a homogeneous population in size and in shape of the nanoparticles. The micrographies reported in the literature show that it is rarely the case. The dispersions are sometimes very large.

The third reason is that nanoparticles are not spherical and thus the Plieth's relationship does not apply.

We extracted several examples from the literature to illustrate the relationships of the non-extensive thermodynamics outlined above. In particular, we will discuss two studies of Ivanova and Zamborini. The first considers silver particles [21]. These authors studied by voltammetry the oxidation of silver nanoparticles deposited on a glass electrode coated with indium-tin-oxide. The nanoparticles are characterized by microscopic techniques (AFM and SEM). The oxidations are carried out in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution. The values of the potential peaks are reported in Table 1 of their publication. We used the values in this table, adopting 799 mV/SHE as the redox potential value of silver in unlimited phase. To be consistent with the experimental values of potential referred to the Ag/AgCl electrode (172 mV/SHE according to the authors), we corrected the standard redox potential of silver and adopted the value of  $E^{0,un} = 627$  mV/Ag/AgCl to realize our exploitation.

Verification of the eq. 26 was made using the diameter values determined by SEM that lead to a consistent set of points.

The graphical evaluation leads to an excellent straight-line of slope -0.295 and intercept equal to 6.621.

Fig.1

From these data, the experimental variations of the potential can be properly described.

Fig.2

These results indicate that the decrease in standard potential with the size does not vary as assumed by Plieth's relation in  $1/d$  but in  $1/d^{0.295}$ . It is difficult to go further in the analysis, but if we assume that the volume is a quantity that varies as the particle size cubed (geometric dimension,  $q = 3$ ), this means that the extensity varies as the diameter to the 2.7<sup>th</sup> power. If the interface had the geometric dimension of a surface, it would vary according to the square of the size. This proves that the interface between the nanoparticles and their environment is much more complex than a simple surface, as microographies of particles also show.

The second study by the same authors, reported here, considers gold nanoparticles [22]. In this paper, the authors describe the electrochemical oxidation of an assembly of gold nanoparticles (Au NPs) attached to glass/indium-tin-oxide (ITO) electrodes as a function of particle size.

They show that the potential of electro-oxidation peak decreases of approximately 200 mV when the particle diameter decreases from 250 to 4 nm. The problem is more complex than previously because several oxidation degrees of gold are likely to be affected.

We have exploited data reported by these authors for the electrodeposition made at 0.8V, taking as the value of the peak potential, 926 mV, and as  $E^\circ$  those corresponding to the one-electron exchange (*i.e.*, 963 mV) [22]. The graphical exploitation of the eq. 26 leads to an excellent straight-line of slope -0.4428 and intercept 5.8984.

It was reported on Figure 3, the experimental data and the calculated curve. The agreement is excellent.

Fig.3

As before, the reduction in potential does not match that described by the Plieth's relation, probably because the particles are not spherical, as shown by the SEM images. The extensity varies with the measured particle diameter to the power of 2.5.

## Conclusion

The development that we described shows that the relations of non-extensive thermodynamics can quantitatively account for the displacements of electro-oxidation potentials of metals deposited as nanoparticles on electrodes, according to their measured size.

Our approach generalizes the one proposed by Plieth to particles with non-spherical shape and it allows describing by power laws the experimental variations of peak potential with the aggregate size. The non-extensive thermodynamics also permits to formally justify the stability

of the particles may increase as their size decreases, ( $\tau < 0$ ). This is usually found when the aggregates are in close contact with a matrix (in the case, for example, of embedded particles). We cannot be certain that the particle/matrix interaction is not largely responsible for this behavior.

Our thermodynamic approach has also its application limits. Thus, there is in the literature many data that we have not been able to exploit, especially those published in the works Brainina *et al.* Indeed, in order to have a thermodynamic meaning, our relations can only be applied on homogeneous populations of particles. Even if we admit that their shape is fuzzy, this shape must be “uniform” with similar characteristics in size and structure. Brainina *et al.* studies [23-28] show very well the shifts of the peaks that are consistent with the positive values of the tension,  $\tau$ . But the considered systems are usually too widely polydisperse for properly applying eq. 26.

In the examples that we have exploited and given here, the SEM images showed that the particles were geometrically ill-defined. But this may not be always the case. Indeed, an abundant literature reports nanoparticles with well-defined interfaces in terms of crystallography, such as the (111) plane of gold or copper [29]. The non-extensive thermodynamic approach also allows describing such systems, assuming that the particle exhibits to the environment several different types of interfaces. The pressure difference between the non-extensive phase and unlimited phase is then written

$$P^{NE} - P = \sum_i \tau_i \frac{d\chi_i}{dV} = \sum_i m_i \tau_i \frac{\chi_i}{V} \quad (27)$$

Each interface is characterized by extensity,  $\chi_i$ , a dimension,  $m_i$ , and a tension,  $\tau_i$ , which can account for the anisotropy of the studied crystal. This is the way we used to treat the equilibrium conditions of a liquid drop put onto a substrate [9]. It would be interesting to have quantitative studies of well-defined particles according to their structural characteristics and size.

Another limitation that we have not mentioned is the assumption that we implicitly do on the fact that the value of  $\tau$  does not vary with the mass of the nanoparticle. This may not be true for the particles of weaker masses. Probably, the non-extensive thermodynamics has the same limitations as classical thermodynamics.

On this point, we must recall the remark we made in our study about the redox potential whose the lower limit of validity is placed around the nanometer. We can assume that below this size, particle stability essentially involves quantum phenomena [30]. However, we used measures of Tang *et al.* [31, 32] on the electrochemical stability of platinum nanoparticles of very small size

in acidic medium. The experimental values published by these authors respond to the depression of standard redox potential proposed in eq. 26 with a power law in  $1/r^{0.7}$  and not  $1/r$  as assumed by Plieth's relation.

We have plotted on Figure 4 the experimental data extracted from the figure of ref [31] and the calculated values. The agreement is excellent.

Fig.4

The exploitation of voltammetry data and more generally of electrochemistry at equilibrium shows that, as in other areas, the relations of non-extensive thermodynamics can adequately describe the change in the behavior of matter when it is in the shape of nanoparticles. This reinforces our belief that the behavior of "small systems" and in particular that of nanoparticles does not respond to classical extensive thermodynamics as assumed by Du [33], and it is necessary to introduce the non-extensivity to account for it.

Another way of expressing this conclusion is to say that thermodynamics, in general, is not extensive and the extensivity is a particular case, which allows accounting for the behavior of unlimited systems.

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## Lists of Captions

Figure 1 : application of eq. 26 to the data of table 1 of ref [21]. The sizes correspond to the one measured by SEM (diameter  $D$  in nm). The redox potential value ( $E^{un}$ ) against Ag/AgCl is taken equal to 0.627V.

Figure 2 : experimental variation of peak potentials for the system (points) described in ref. [21]. The solid curve is calculated from eq. 26.

Figure 3 : experimental of peak potentials for the system (solid points) described in ref. [22]. The solid curve is calculated from eq.26.

Figure 4 : redox potential of Pt/ Pt<sup>2+</sup> couple in respect with the nanoparticle radius according to ref. [31]. The solid line curve corresponds to  $E = 1.188 - \exp(-0.9656) * r^{-0.7}$

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Fig. 1

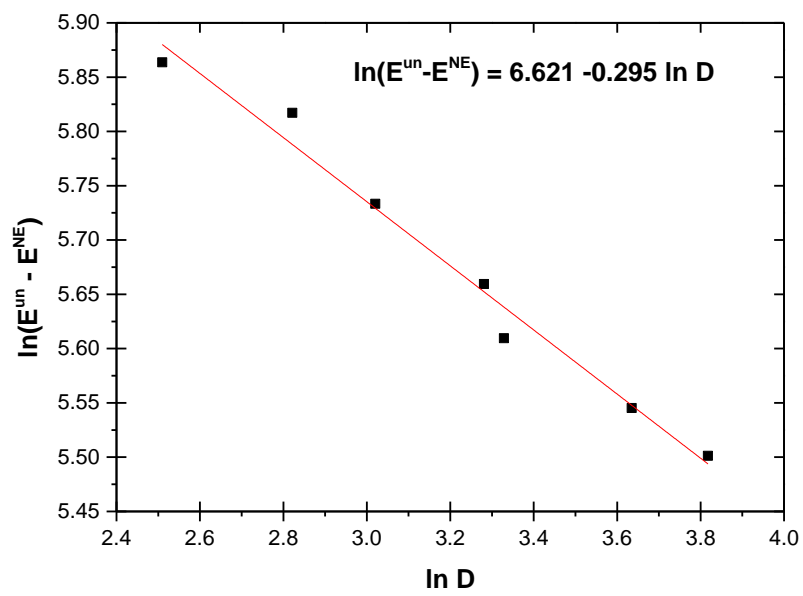


Fig.2

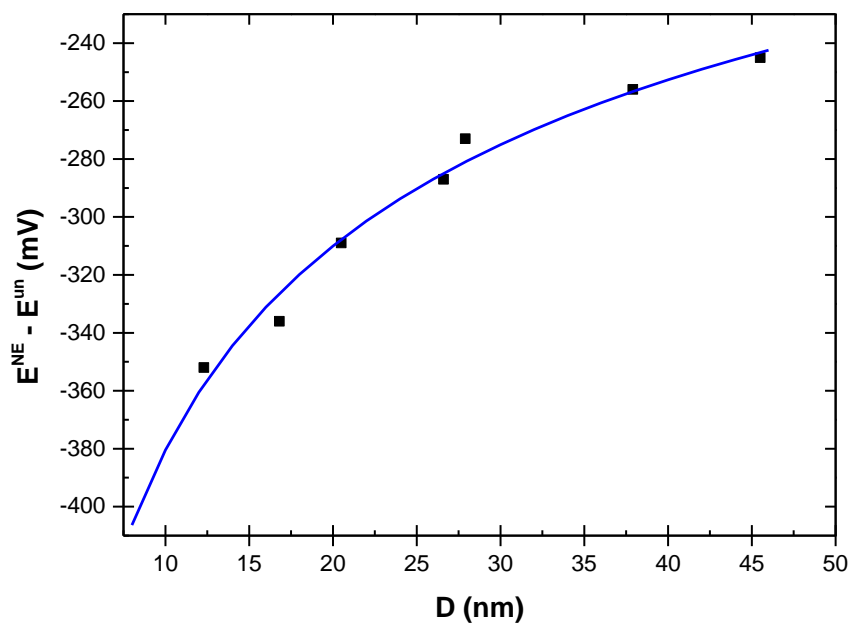


Fig. 3

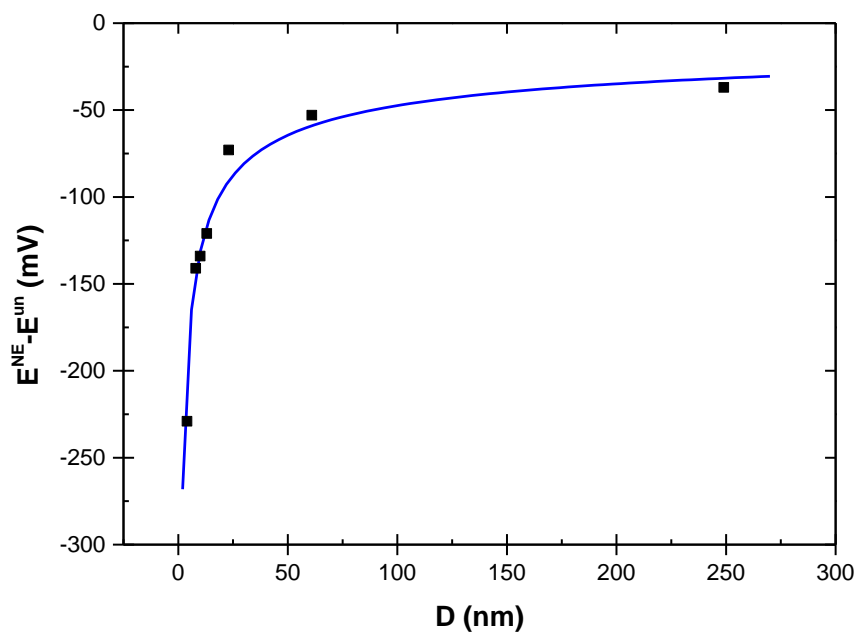
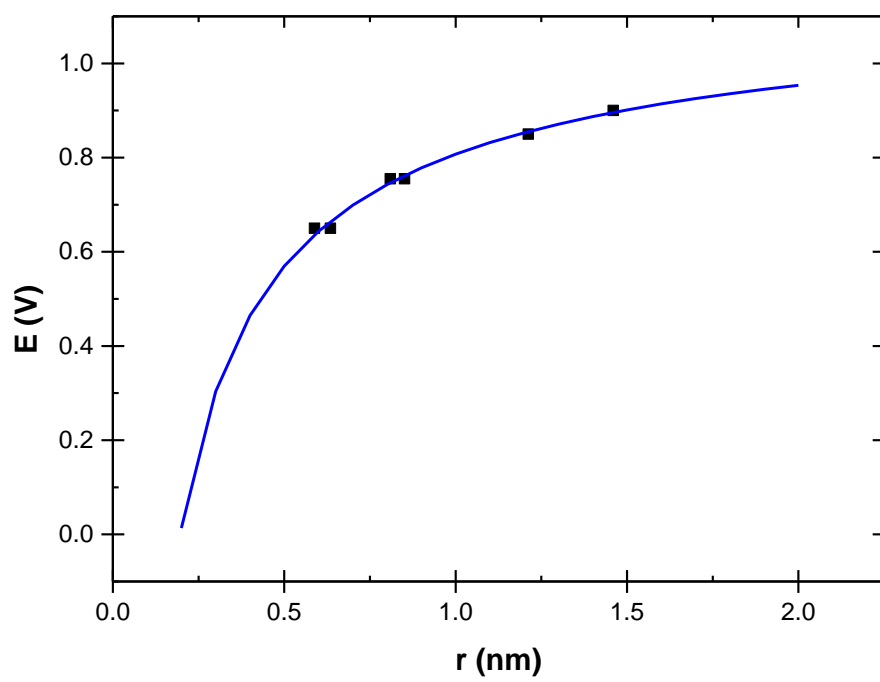
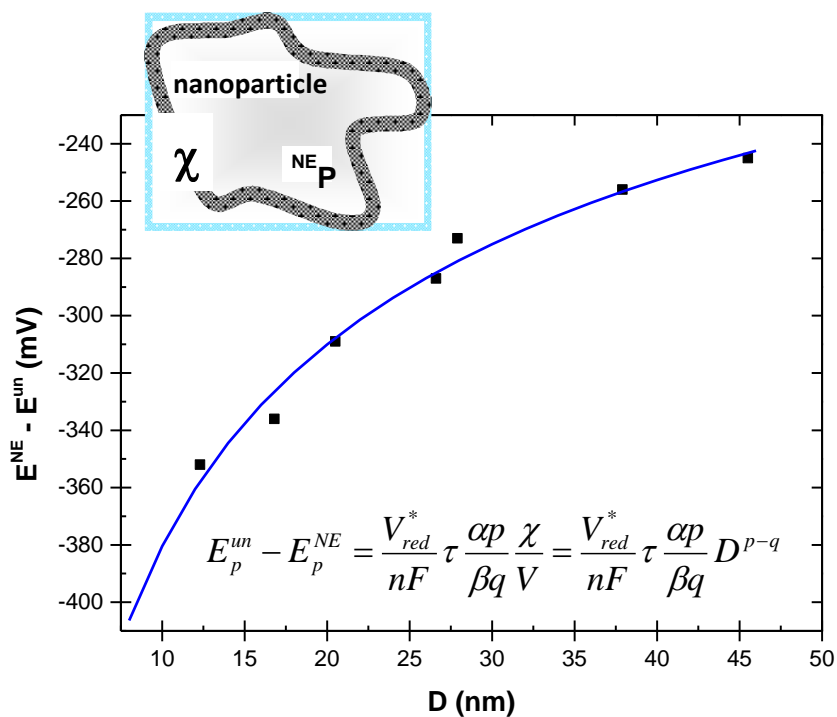


Fig. 4



## Graphical Abstract



The nonextensive thermodynamic approach is applied to the electro-oxidation of metal nanoparticles to describe the displacement of voltammetric peaks. We showed that, for many examples, the interface can be characterized by a function  $\chi$  which varies according to a power law. The interface of the nanoparticle is then defined as “fuzzy”.