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 behavior 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).

1. 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.

2. 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.

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2.1. 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, γ, 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), τ, and an "extensity", χ, 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, τ can be positive or negative. One could be amazed at this possibility whereas the surface tension γ 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 τ, 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 τ. 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 τ.

We can find another example of this feature of τ 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 τ. In contrast, the activities of the counter-ions against is represented by a positive value of τ.

By convention, we assume that χ 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 χ to the volume of the particle by a power law. The parameter m is called the "thermodynamic dimension" of the system.

$$\chi = aV^m$$
$$d\chi = maV^{m-1}dV = m\frac{\chi}{V}dV \tag{2}$$

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

$$dE = \tau d\chi = \tau m \frac{\chi}{V} dV \tag{3}$$

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

$$dU = TdS - PdV + \sum \mu_i dn_i + \tau d\chi \tag{4}$$

Since χ 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 τ 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 χ, 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

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

According to the sign of τ, this difference can be positive or negative. This point was widely discussed for melting point of metal NP for which we showed that for embedded NP in matrix the behavior of NP was well described with a negative value of the tension, τ [10].

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 γ^{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

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

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, τ 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