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Desorption transition at charged interfaces: Theoretical approach and experimental evidence

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A field theory is used to describe an ionic solution in contact with a charged and adsorbing wall. The Hamiltonian, a functional of the ionic density fields, contains the entropy, the electrostatic energy, a nonlocal Van der Waals type contribution preventing sharp density variations, and an adsorption potential. The mean-field equations are solved numerically. However, they can be recasted so as to put in evidence a one parameter Lie group structure, which is a generalization of the charge-translation symmetry present in the Gouy-Chapman theory. There is a region in the charge-adsorption parameter space where this symmetry is broken, which corresponds to a desorption transition for the ionic species. The properties of this transition are investigated. Finally, this desorption phenomenon provides a simple explanation for a general feature in the properties of metal-electrolyte interfaces: the branching pattern observed in the experimental capacitance curves for a series of electrolytes. The part of the capacitance curves which is independent of the nature of the ions is related to the absence of interaction of the ionic species with the wall once the desorption takes place.

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I. INTRODUCTION

The long range of the Coulombic potential is at the origin of very special behaviors such as the nonanalytic dependence of thermodynamic functions on ionic concentration or the existence of constraints on the correlation functions describing the structure of conducting phases. Due to this, Coulombic systems such as plasma, fused salts, electrolyte solutions, and charged colloidal systems have attracted attention of many theoreticians and experimentalists. In this paper we are interested in the theoretical description of a quite general experimental fact found at the metal-ionic solution interface. However, we believe that what is observed at this particular interface, may reveal some general behaviors for large classes of charged interfacial systems.

For a wide domain of applied potential the mercury-electrolyte interface may be considered as a pure capacitor. Then, for a given thermodynamic equilibrium, we can investigate the properties of the interface when changing, for instance, the nature of the solvent, the nature, and the concentration of the electrolyte or the charge of the electrode. For some solvents, we observe a range of potential where the capacitance is independent of the nature of the ions. A schematic representation of this behavior is given in Fig. 1. This kind of behavior is clearly visible for 0.1 M electrolytes in *N*-methylformamide [1] and formamide [2] but also distinguishable in *N*-methylacetamide [3], methanol [4], *N*,*N*-dimethylformamide [5], and dimethylsulphoxide [6]. The curves form a branching pattern in which there is a base curve from which branches are formed. From a mathematical view point this pattern implies nonanalyticity at the branching points.

To explain this behavior it is assumed that no ion is in contact with the electrode in this range of potential. In what follows, we first elaborate a model which predicts the existence of an ionic desorption transition when changing the electrical state of the interface. This is the first goal of this paper. After that we extend this model in order to investigate the experimental data observed at the mercury-solution interface. This is the second goal of this paper.

As we shall see, the differential equations describing the model have a special structure. We can thus generalize one property of the nonlinear Gouy-Chapman theory (NLGCT). In this theory there is only one generic profile for each quantity characterizing the interface (electric field, ionic densities, etc.). The profiles for a given charge on the surface is obtained by translating the origin of the coordinate system for

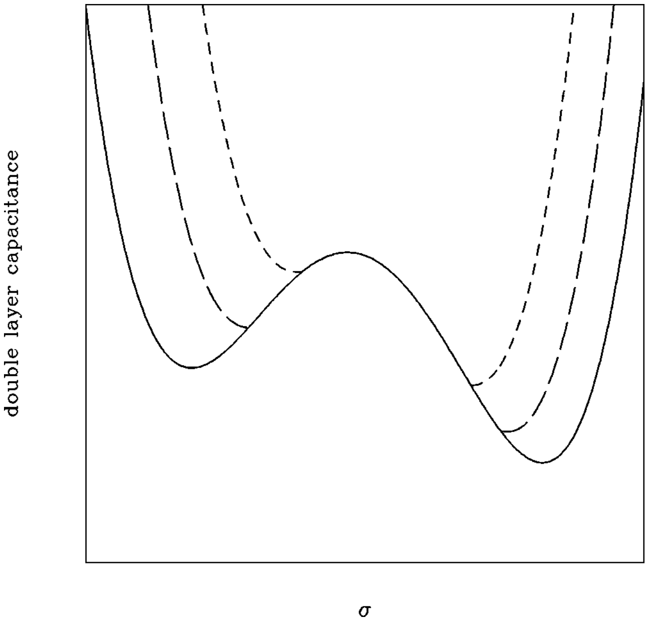

FIG. 1. Schematic representation of double layer capacitance of one of the typical solvents quoted in the text [3–6]. The branches correspond to different electrolytes.

the generic profiles. The third goal of this paper is to analyze and extend this charge-position symmetry. We will see that such a symmetry can be related to the existence of a one-dimensional Lie group.

This paper is organized as follows. In Sec. II we describe the main ingredients of our theoretical approach. In Sec. III we find the differential equations describing the interface in the mean-field approximation (MFA) and we perform a group analysis of these equations. In Sec. IV we describe the desorption transition. Sections II–IV describe a general model and its predictions for ionic solutions in contact with a charged hard wall. In Sec. V we discuss how to relate this model with the experimental data observed at the mercury-electrolyte interface. Finally in Sec. VI we present some concluding remarks.

II. THEORETICAL APPROACH

We describe the properties of an ionic solution in contact with a charged hard wall using a field theoretic approach already described in Ref. [7]. Since we focus on a phenomenon which depends explicitly on the ions we describe the system with the ionic density distributions only and we reduce the solvent to a dielectric continuum. The interfacial properties are determined by the Hamiltonian $\mathcal{H}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]$ which is a functional of two fields $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$, representing the distributions of cations and anions, respectively. We use for $\mathcal{H}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]$ the form investigated in Refs. [8–10]. For bulk ionic solutions with $\mathcal{H}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]$ truncated to a bilinear form in terms of the fields, the functional integration leads to the exact Debye limiting law but also to more general results [10,11]. For charged interfaces, if $\mathcal{H}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]$ is reduced to the sum of the ideal entropy and the coulombic part, the NLGCT is recovered in the MFA [8].

We consider a planar interface. Oz is the direction normal to the interface. We introduce a dividing surface located at $z=0$ where we assume the existence of a hard wall. In what follows we investigate the region $z\geqslant 0$. In the other half space $z<0$ we can have a bulk phase or the existence of another interface but till Sec. V the explicit properties of this region are not needed.

In order to describe the region $z>0$ we, first consider the same Hamiltonian $\mathcal{H}^{\text{bulk}}=\mathcal{H}^{\text{Coul}}+\mathcal{H}^{\text{ideal}}$ as for the bulk phase [10]. The Coulombic energy functional $\mathcal{H}^{\text{Coul}}$ corresponds to

$$\beta\mathcal{H}^{\text{Coul}}[q(\mathbf{r})]=\frac{K_D^2}{8\pi\rho_b}\int_{z\geqslant 0}\frac{q(\mathbf{r})q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \qquad (1)$$

where ε is the dielectric constant of the pure solvent, $\rho_b=2\rho$ and ρ is the electrolyte concentration, $K_D=(\rho_b e^2\beta/\varepsilon)^{1/2}$ the inverse Debye length, $\beta=(k_BT)^{-1}$ is the inverse temperature and e is the elementary charge. We consider a $1-1$ electrolyte and define the charge density as $q(\mathbf{r})=\rho_+(\mathbf{r})-\rho_-(\mathbf{r})$. The ideal entropy functional $\mathcal{H}^{\text{ideal}}$ is given by

$$\beta\mathcal{H}^{\text{ideal}}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]=\int_{z\geqslant 0}\left\{\rho_+(\mathbf{r})\left[\ln\frac{\rho_+(\mathbf{r})}{\rho_{\text{ref}}}-1\right]+\rho_-(\mathbf{r})\times\left[\ln\frac{\rho_-(\mathbf{r})}{\rho_{\text{ref}}}-1\right]\right\}d\mathbf{r}, \qquad (2)$$

where ρ_{ref} is an arbitrary reference density [10].

In order to avoid the large ionic density variations predicted by the NLGCT at the wall we introduce a nonlocal Hamiltonian defined according to

$$\beta\mathcal{H}^{\text{nonloc}}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]=\frac{1}{2}\sum_{i,j=+,-}\int_{z\geqslant 0}\tilde{b}_{ij}[\nabla\rho_i(\mathbf{r})]\times[\nabla\rho_j(\mathbf{r})]d\mathbf{r}. \qquad (3)$$

Since at a charged hard wall $\mathcal{H}^{\text{bulk}}$ leads to the NLGCT, at the same level of description we can assume that $\tilde{b}_{ij}$ coefficients do not contain ion specificity and then we have $\tilde{b}_{++}=\tilde{b}_{--}=\tilde{b}_{+-}=\tilde{b}$. This kind of term appears in the Van der Waals theory [12] and is commonly used in the Landau-Ginzburg Hamiltonian [13]. With this term each slice of the interface is correlated to its neigbhors.

In order to introduce a coupling between the two sides of the interface we assume the existence of two external fields located at the dividing surface $z=0$. To compensate the charge distribution on the solution side we introduce a surface charge $e\tilde{\sigma}_0\delta(z)$, where $\tilde{\sigma}_0$ is the surface charge density on the wall. In order to work with an overall neutral system we redefine $\mathcal{H}^{\text{Coul}}$ with $q(\mathbf{r})=\tilde{\sigma}_0\delta(z)+\rho_+(\mathbf{r})-\rho_-(\mathbf{r})$. In addition, we consider a second external field which introduces a non-Coulombic coupling between the two sides of the interface. We assume that this potential has a very short range compared to the variation range of the ionic distribution and we represent its variation in space by a delta function localized in $z=0$. This leads to the following contribution $\mathcal{H}^{\text{surf}}$ to the Hamiltonian

$$\beta\mathcal{H}^{\text{surf}}[\rho_+(\mathbf{r}),\rho_-(\mathbf{r})]=\int_{z\geqslant 0}\tilde{h}_0[\rho_+(\mathbf{r})+\rho_-(\mathbf{r})]\delta(z)d\mathbf{r}. \qquad (4)$$

If $\tilde{h}_0$ is positive (negative) anions and cations are repelled (attracted) from (to) the wall. In what follows we investigate the total Hamiltonian defined by $\mathcal{H}=\mathcal{H}^{\text{bulk}}+\mathcal{H}^{\text{nonloc}}+\mathcal{H}^{\text{surf}}$.

III. MEAN FIELD EQUATIONS AND LIE GROUP DESCRIPTION

Instead of performing the functional integration we consider the MFA treatment of $\mathcal{H}$. It yields an integrodifferential system of equations for the ionic profiles [9]. To deal with these equations which have no analytic solution we can use any numerical method and discuss the solution for a given set of parameters. However, to have a better understanding of the physics behind these equations, it is possible to transform them in a form from which we can learn something about the system without having to solve them explicitly. Hereafter we follow this route. To find a useful transformation of the initial equations we take advantage of a very specific property of the NLGCT which corresponds to a special case of our Hamiltonian. For the NLGCT each interfacial property is described by a unique profile. Changing the charge on the wall is equivalent to translating the origin of coordinates. In order to analyze and to extend this charge-position symmetry it is very tempting to perform a group analysis of our equations. In what follows we transform the MFA equations into a system of differential equations where the existence of the Lie group is manifest.

Taking advantage of the symmetries of the Hamiltonian due to the existence of a common value of the parameter b and using the Poisson equation the integrodifferential system is transformed into two second order ordinary differential equations and then into four first order equations. In order to give a simple form to the equations we introduce the dimensionless quantities $\hat{z}=K_D z$, $g_{\pm}(\hat{z})=2\rho_{\pm}(z)/\rho_b$, $b^2=\rho_b K_D^2 \tilde{b}$, $h_0=2K_D\tilde{h}_0$, $v(\hat{z})=2\beta e V(\hat{z})$, and $\sigma_0=(2\beta e/\varepsilon K_D)\tilde{\sigma}_0=(2\beta e/K_D)E_0$, where $V(\hat{z})$ is the electric potential and E_0 is the electric field at the wall. Since no confusion is possible later we omit the hat on the reduced z variable. The interfacial free energy $\tilde{f}$ is calculated in reduced units according to $f=(4K_D\beta/\rho_b)\tilde{f}$. We define additional variables

$$\sigma(z)=-\frac{dv(z)}{dz}, \tag{5}$$

$$h(z)=b^2\frac{d}{dz}[g_+(z)+g_-(z)], \tag{6}$$

where $\sigma(z)$ is the electric field expressed in the dimensionless form and $h(z)$ is the rescaled gradient of ionic density. Then the system of four first order differential equations is written as follows:

$$\frac{d}{dz}g_+=\frac{\sigma g_+g_-+\frac{h}{b^2}g_+}{g_++g_-}, \tag{7}$$

$$\frac{d}{dz}g_-=\frac{-\sigma g_+g_-+\frac{h}{b^2}g_-}{g_++g_-}, \tag{8}$$

$$\frac{d}{dz}\sigma=g_+-g_-, \tag{9}$$

$$\frac{d}{dz}h=\ln(g_+g_-). \tag{10}$$

There are four boundary conditions. At $z=0$ we have one boundary condition related to electrostatics

$$\sigma(z)\Big|_{z=0}=-\frac{dv(z)}{dz}\Big|_{z=0}=\sigma_0. \tag{11}$$

The second boundary condition is set by $\mathcal{H}^{\mathrm{surf}}$:

$$h(z)\Big|_{z=0}=b^2\frac{d}{dz}[g_+(z)+g_-(z)]\Big|_{z=0}=h_0. \tag{12}$$

The two other boundary conditions state that we recover the bulk when $z\rightarrow\infty$:

$$g_+(z)\rightarrow 1 \quad \text{and}\ g_-(z)\rightarrow 1. \tag{13}$$

The above conditions imply that $\sigma\rightarrow 0$ and $h\rightarrow 0$ when $z\rightarrow\infty$.

The right hand sides of Eqs. (7)–(10) are differentiable functions of σ, h, g_+, and g_-, for $g_+>0$ and $g_->0$ and do not contain z explicitly. This implies the existence of a four-variable one-parameter Lie group [14] which transforms the initial values, for $z=0$: σ_0, h_0, g_{0+}, g_{0-} into the solution of Eqs. (7)—(10) at the point z: $\sigma(z)$, $h(z)$, $g_+(z)$, $g_-(z)$.

If we change the wall parameters and contact values of the profiles according to the above transformation taking the values given for a new position z', we can see that this transformation amounts to a shift in space. The contact values are now given by $\sigma_0'=\sigma(z')$, $h_0'=h(z')$, $g_{0+}'=g_+(z')$,and $g_{0-}'=g_-(z')$. The profiles $[\sigma'(z),\ h'(z),\ g_+'(z),\ g_-'(z)]$ for the wall with the new contact values are simply related to the old ones by

$$\sigma'(z)=\sigma(z+z'),\quad h'(z)=h(z+z'),$$

$$g_+'(z)=g_+(z+z'),\quad \text{and}\ g_-'(z)=g_-(z+z'). \tag{14}$$

All the points $[\sigma(z),\ h(z),\ g_+(z),\ g_-(z)]$ transformed from one initial point define a trajectory in the four-dimensional space.

A four-variable one-parameter Lie group has three invariants [14]. We have found these invariants explicitly when all Eqs. (7)–(10) are linearized around their bulk values. The values of only two invariants, c_1 and c_2, are fixed by the bulk properties of the ionic solution. Using c_1 and c_2 we can express g_+ and g_- in terms of σ and h. The third invariant, c_3, establishes a relation between σ and h and selects a trajectory in the $(\sigma,\ h)$ plane. In general only one of the two first invariants is found explicitly:

$$\begin{aligned}c[g_+(z),g_-(z),\sigma(z),h(z)]&\\ =[2-\ln g_+(z)g_-(z)][g_+(z)+g_-(z)]+\frac{h^2(z)}{2b^2}&\\ -\frac{\sigma^2(z)}{2}=p,&\end{aligned} \tag{15}$$

where p is the bulk pressure in reduced units. The last equation yields the pressure as a function of interfacial properties at any point z across the interface. In particular, at the wall, it resembles the so called contact theorem for charged particles near a charged hard wall [15]. It recovers the form of the contact theorem in the NLGCT ($b=0$ and $h_0=0$).

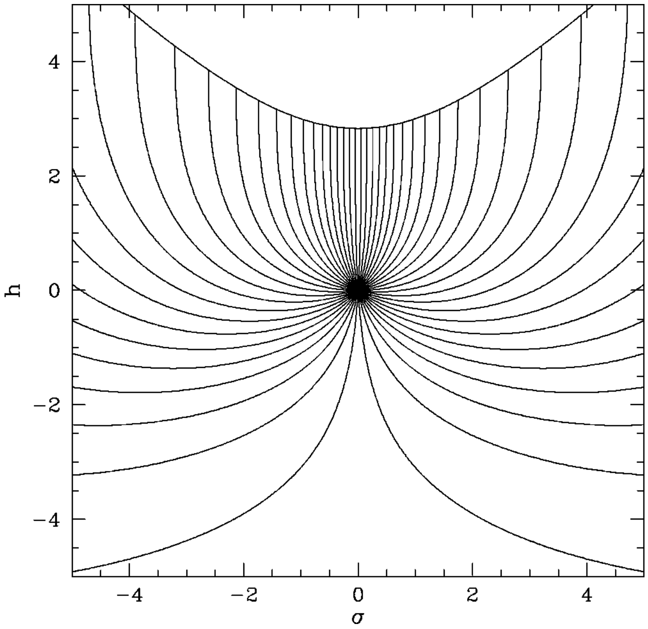

FIG. 2. Trajectories in the (σ,h) plane obtained by a numerical solution of Eqs. (7)–(10). $b=1$ in reduced units which corresponds to the Debye length in a given electrolyte.

IV. DESORPTION TRANSITION

Using the numerical method described in our previous papers [8,9] we can solve the system of differential equations for a given boundary condition. We find it useful to present the results first in the form of trajectories in the (σ,h) plane.

The trajectories form a pattern symmetric with respect to the $\sigma=0$ axis reflecting the symmetry between ions (see Fig. 2). They do not intercept with each other as expected from the Lie group analysis but they diverge from the origin and terminate on a smooth curve in the upper halfplane. In Fig. 3 we present the set of trajectories in the (g_+,g_-) plane corresponding to those in Fig. 2. The pattern of lines is symmetric with respect to the $g_+=g_-$ axis because of the symmetry between ions and shows the existence of two focal points. All the trajectories diverge from the point corresponding to the bulk $(g_+=1,\ g_-=1)$ and converge towards the point $(g_+=0,\ g_-=0)$ corresponding to a desorption of the ions and also to the terminal curve in the (σ,h) plane. The right hand sides of Eqs. (7), (8), and (10) diverge when $g_+\to 0$ and $g_-\to 0$. For $g_+=0$ and $g_-=0$ we lose the Lie group condition for the equations. The invariant (15) taken in this limit yields

$$\frac{h^2}{2b^2}=p+\frac{\sigma^2}{2}. \tag{16}$$

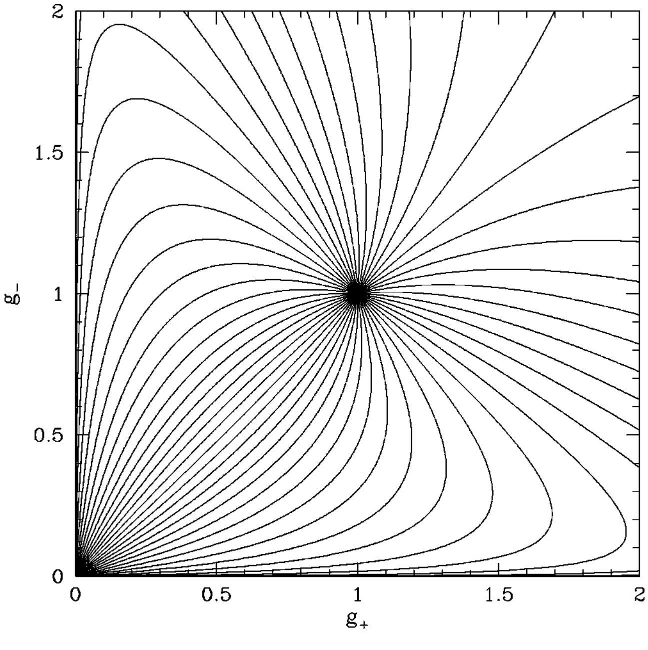

FIG. 3. Trajectories in the (g_+,g_-) plane corresponding to those in Fig. 2.

The limiting curve in the (σ,h) plane corresponds to the upper branch of the above hyperbola. The physical meaning of this result is the following. When the ionic densities vanish the pressure in the fluid is equal to $[\nabla(g_+ + g_-)]^2$. The value of this quantity is fixed, at the wall, by the desorbing potential h. Hence we see that the repulsion from the wall driven by h has to counterbalance both the electrostatic and bulk pressure which both have a tendency to bring ions close to the wall.

In contrast to the NLGCT, there is a continuous set of trajectories. Each of them corresponds, for each of the interfacial properties, to a different profile. Since every trajectory arrives at the limiting hyperbola at a point uniquely determined by its charge density it is convenient to parametrize the trajectories with this charge density σ_{limit}. The existence of this limiting point constitutes another difference with the NLGCT. At this point the Lie group symmetry, i.e., the charge-translation symmetry in the NLGCT, breaks down. From the Lie group parametrization with z, this point in the (σ,h) parameter space also corresponds to a position in real space. We can take this position as the origin of the coordinate system—a wall placed in this position is such that there is a complete desorption of the ions, the characteristic contact values are then completely determined by σ_{limit}. The generic profiles for this wall are written $g_+^*(\sigma_{\mathrm{limit}};z)$ and $g_-^*(\sigma_{\mathrm{limit}};z)$ with $g_\pm^*(\sigma_{\mathrm{limit}};z=0)=0$. In Fig. 4 we give an example of such generic profiles for various values of the charge density σ_{limit}. If we take an arbitrary wall characterized by (σ_0,h_0) we have to consider two cases. If $h_0 \geqslant b\sqrt{\sigma_0^2+2p}$, we are above the limiting curve, then the profile is identical to the generic profile for $\sigma_{\mathrm{limit}}=\sigma_0$ as we shall see below. If $h_0<b\sqrt{\sigma_0^2+2p}$ we have to find the trajectory passing through this point and determine in terms of the Lie group parametrization the distance z_0 from the limiting point to this point. Then the profiles are simply obtained from the generic profiles by a translation $g_+(z)=g_+^*(\sigma_{\mathrm{limit}},z+z_0)$ and $g_-(z)=g_-^*(\sigma_{\mathrm{limit}},z+z_0)$ for $z>0$.

In the vicinity of the completely desorbing wall $(h_0=b\sqrt{\sigma_0^2+2p}$ and $\sigma_0=\sigma_{\mathrm{limit}})$, $z\approx 0$, from Eqs. (7)–(10) we can see that the profiles show a nonanalytic dependence on z:

$$\left(\frac{h_0}{b^2}z+z^2\ln z\right). \tag{17}$$

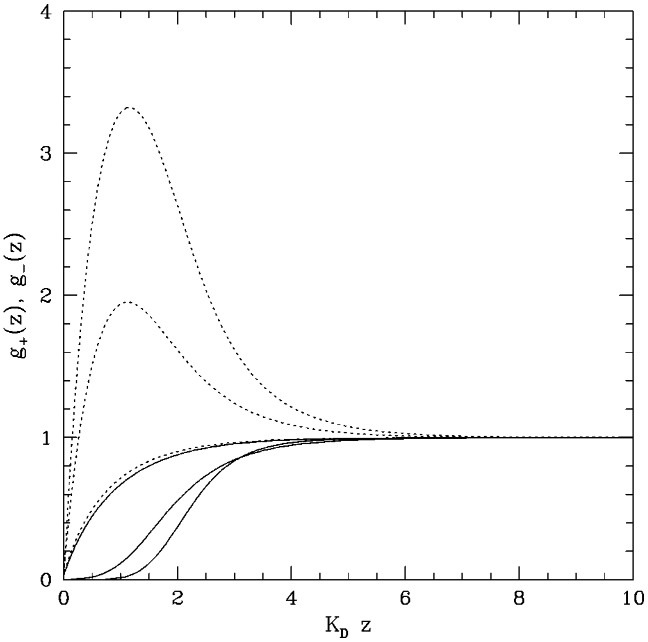

FIG. 4. Generic profiles of ions for the values of charge density at the limiting curve $\sigma_{\rm limit}=0.014$, 0.05, and 0.1 C/m^2 from lower to uppermost dotted line for anions and from the upper to lowermost solid line for cations.

If $z\approx 0$ the trajectory in the (σ,h) plane is given by a scaling law of the form

$$|h-h_0|\approx|\sigma-\sigma_0|^{1/2}\ln|\sigma-\sigma_0|. \tag{18}$$

It is seen that the trajectory approaches the terminal curve with an infinite slope. Similar scaling relations can be found for other pairs of variables $g_\pm\propto|\sigma-\sigma_0|^{1/2}$ and $|h-h_0|\propto g_\pm \ln g_\pm$.

When the wall characterized by $h_0\geqslant b\sqrt{\sigma_0^2+2p}$ is put in contact with the solution the effect of the wall is the same as for $h_0=b\sqrt{\sigma_0^2+2p}$. The ions are already pushed out of the range of the repulsive potential and do not feel any further increase. Thus all the region $h_0\geqslant b\sqrt{\sigma_0^2+2p}$ corresponds to the condition $g_+=g_-=0$. The natural prolongations of the trajectories above the limiting curve are vertical lines $\sigma=\text{const}$ consistent with the limit $dh/d\sigma\rightarrow\infty$ when approaching the terminal curve from below.

The interfacial free energy depends on the wall parameters $f=f(\sigma_0,h_0)$. From Ref. [9] we know:

$$\left(\frac{\partial f}{\partial \sigma}\right)_{h_0}=v \quad \text{and} \quad \left(\frac{\partial f}{\partial h}\right)_{\sigma_0}=g_+ + g_-, \tag{19}$$

where v and $g_+ + g_-$ refer to the electric potential and total density contact values, in reduced units, for the wall characterized by σ_0 and h_0. We can verify that $(\partial f/\partial h)_{\sigma_0}$ and higher order derivatives continuously vanish when approaching complete desorption ($\sigma_0\rightarrow\sigma_{\rm limit}$). However, the free energy is nonanalytic on the terminal curve because $(\partial f/\partial h)_{\sigma_{\rm limit}}=0$ for $h\geqslant b\sqrt{2p+\sigma_{\rm limit}^2}$ and $(\partial f/\partial h)_{\sigma_{\rm limit}}>0$ otherwise. The crossing of the limiting curve can be considered as a kind of phase transition. We have nonanalyticity, scaling relations and Lie group symmetry breaking at the crossing point. The peculiarity of this transition is that the free energy is continuously differentiable up to an arbitrary order but nonanalytic at this point.

This desorption transition is an exact consequence of the MFA treatment of our Hamiltonian. However, there are two points to consider. First, is MFA sufficient to describe the above transition and second, is the Hamiltonian sufficient to describe a real system? From the literature it is known that MFA is generally qualitatively correct as a first approximation to describe a phase transition (the famous exception is the one-dimensional Ising model) [16]. Concerning the second point we see from Eq. (17) that the second derivative of the profiles diverges as $\ln z$ at $z=0$. It might suggest that the square gradient term is not enough to describe this transition. Strictly speaking this is right. However, the region where the second derivative becomes large is extremely localized near $z=0$ and the divergence is integrable. If we exclude the immediate vicinity of $z=0$ we are already in the region where the two profiles tend to vanish. A more refined Hamiltonian would change the scaling laws but not the existence of this transition which indeed has a very clear meaning. At a point (σ_0,h_0) above the hyperbola the wall repels ions from its vicinity. If we increase the absolute value of σ_0 keeping h_0 constant we may expect a critical value of σ_0 for which the electrostatic attraction compensates the repulsion due to h_0. For higher values of σ_0, counterions will be forced back in contact with the wall. This is the simple physics that our model describes.

V. COMPARISON WITH EXPERIMENTS

In order to compare the predictions of our model with experimental results observed at the mercury electrolyte-interface we have to calculate the differential capacitance. Since we assume that h_0 is independent of σ_0 the capacitance is defined according to

$$\frac{1}{C}=\left(\frac{\partial v}{\partial \sigma}\right)_{h_0}, \tag{20}$$

where the potential drop across the interface v and the capacitance C are calculated numerically. If $h_0<b\sqrt{2p}$ we have a nonvanishing contact value for the density profiles whatever σ_0. If $h_0\geqslant b\sqrt{2p}$ then the line $h_0=\text{const}$ crosses the hyperbola. In this case we pass from the region below the hyperbola to the region above it when changing σ_0 along the $h_0=\text{const}$ line. In the upper region the value of the potential for a given charge density corresponds to the value of the potential at the limiting point on the hyperbola for the same charge density and the capacitance is calculated moving along the limiting hyperbola. The results are given in Fig. 5 for several values of h_0. In our case we associate h_0 to the nature of the electrolyte. Immediately we see that the stronger repulsion from the wall, i.e., larger h_0, corresponds to the wider region of desorption.

This result is reminiscent of Fig. 1. The main difference between Fig. 1 and Fig. 5 is that the ''experimental desorption'' takes place in a region shifted with respect to the point of zero charge. This is not surprising taking into account the

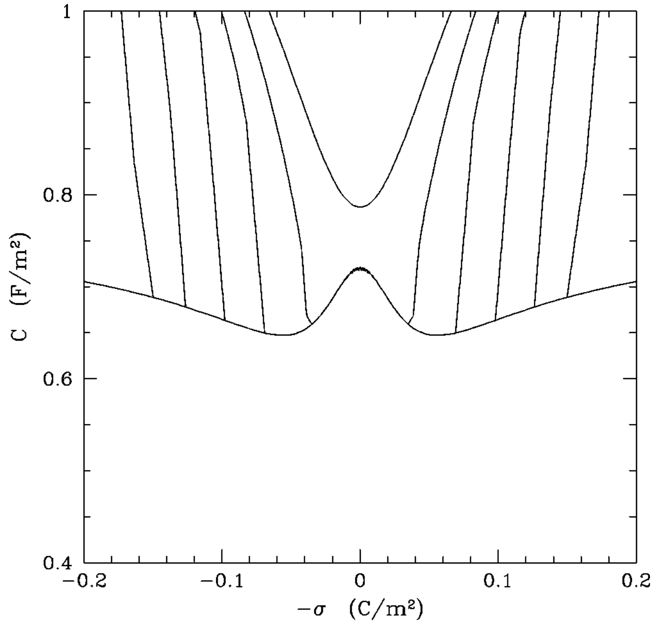

FIG. 5. Capacitance curves calculated from our model using parameters for 0.1 M solutions in *N*-methylformamide [1]. In reduced units $b=1$ and $h=2$, 4, 6, 8, 10, and 12. The capacitance curve for $h=2$ displays no desorption region. For higher values of h the desorption region gradually increases. The apparent nondifferentiability at the branching point results from numerical inaccuracy and the scale of the figure.

crudeness of our model. For mathematical convenience and to show the existence of the desorption transition we describe the solution side with only one parameter b. All the interfacial specificities are represented by h_0 so far assumed independent of σ_0. As mentioned in Sec. II next to the wall we may expect a specific interfacial region. Electrochemists often assume that this region, $z<0$, is formed by a monolayer of solvent molecules covering the mercury. Then h_0 introduced in Eq. (4) represents the coupling between this monolayer and the remaining part of the solution. This coupling is short ranged and only the contact values of the ionic profiles may have an influence on it. Of course, the value of h_0 depends on the structure of the solvent monolayer (number of solvent molecules, their orientation, etc.) which must be charge dependent. In other words charging the electrode will affect h_0. To describe experiments we have to introduce an extra relation between h_0 and σ_0. When we calculate the capacitance, we integrate equations along the trajectories up to a point on this $h_0(\sigma_0)$ curve. Now the capacitance is given by

$$\frac{1}{C}=\frac{dv}{d\sigma}=\left(\frac{\partial v}{\partial\sigma}\right)_{h_0}+\left(\frac{\partial v}{\partial h}\right)_{\sigma_0}\frac{dh}{d\sigma}. \tag{21}$$

On Fig. 6 we have plotted the capacitance for a given choice of $h_0(\sigma_0)$ relations. The asymmetry between positive and negative charge densities observed in the experimental data is now recovered.

Note that the monolayer gives its own contribution to the experimental capacitance. The resulting capacitance is expected to depend on the contribution we calculate from our model in a complicated way but as far as the dependence is continuous it will not change the topological character of the branching pattern observed.

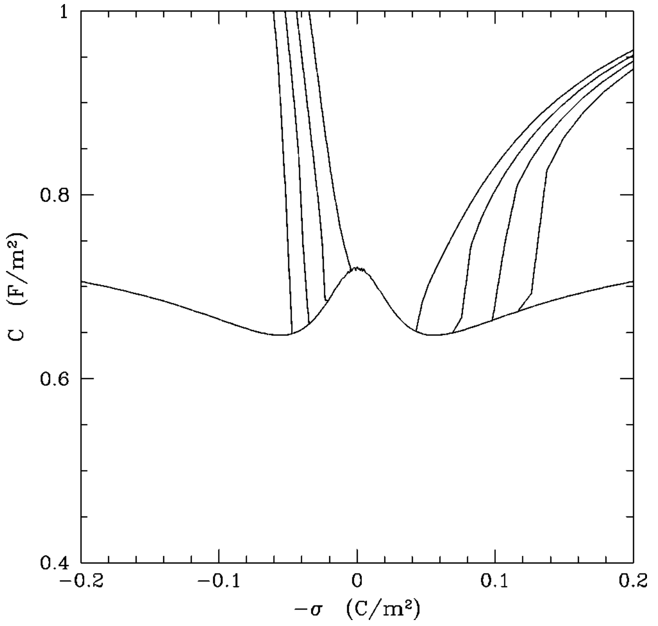

FIG. 6. Capacitance curves as in Fig. 5 calculated for several $h_0(\sigma_0)$ taken in a linear form $h_0=a_1\sigma_0+a_0$, where $a_1=0.4$ and $a_0=3$, 4, 5, and 6. The higher value of a_0 corresponds to the wider desorption region.

VI. CONCLUSIONS

In this paper we consider a simple model for an electrolyte solution in contact with a charged and adsorbing wall. The model differs from the NLGCT in the following aspects. First, we take into account a nonlocal interaction which prevents a too steep variation of the ionic density at the interface. Second, there is a nonelectrostatic external potential located at the wall h_0. Its effect is to attract or repel ions from the immediate vicinity of the wall. The perturbation induced in the solution side by h_0 and the external charge density σ_0 propagates via two modes—electric field and the gradient of density. With just one parameter b characterizing the solution side we obtain a sort of phase diagram in the (σ,h) plane. The plane is divided into two regions by a limiting curve. In the upper region the contact values of ionic profiles vanish. On the limiting curve the free energy is regular but not analytic. Thus we have found a peculiar ionic desorption transition with nonanalytic behavior of the free energy, scaling laws, and symmetry breaking.

This desorption transition leads to a branching pattern in the capacitance curves and can provide a simple explanation for the non-ion-specific feature observed in the experimental curves for a series of electrolytes. However, to describe a real electrode surface we need an extra relation $h_0=h(\sigma_0)$. It represents a coupling between electrostatic and nonelectrostatic properties of the wall expected in a real interface. Then the asymmetry of the experimental data can be reproduced. Note that in the usual description of the electrochemical interface the inner layer and the diffuse layer are coupled only by the electric field, here a nonelectrostatic coupling between the two layers has been introduced. The desorption transition described in this paper is driven by simple physics and we think it ought to appear in a larger class of charged interfaces than the mercury-electrolyte interface.

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