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# Theoretical analysis of the competition between coulombic and specific interactions at charged interfaces

J. Stafiej<sup>2</sup>, D. di Caprio<sup>1</sup>, J. P. Badiali<sup>1x</sup>

<sup>1</sup>*Structure et Réactivité des Systèmes Interfaciaux,  
Université P. et M. Curie, Paris VI, Bât. 74, B.P. 52, 4. Place Jussieu,  
75230 Paris Cedex 05, France*

<sup>2</sup>*Department of Electrode Processes,  
Institute of Physical Chemistry of the Polish Academy of Sciences,  
ul. Kasprzaka 44/52, 01-224 Warsaw, Poland*

<sup>x</sup>To whom correspondence should be addressed

## Abstract

We present a model of an inhomogeneous electrolyte solution based on the Landau-Ginzburg approach. It contains coulombic interactions, ideal entropy contribution and non local specific interactions. With this model we can study the specific interaction of the electrolyte with the electrode surface. Numerical calculations of the ionic density, potential and charge density profiles have been performed assuming reasonable values of the phenomenological parameters. We also use numerical methods to obtain differential capacitance as a function of charge density and the magnitude of electrode/electrolyte specific interactions. It is a new aspect of this approach that ions can be excluded from the immediate vicinity of the electrode surface.

# Introduction

Electrified interfaces investigated in electrochemistry represent an example of complex systems. They have several components and a lot of phenomena take place *e. g.* solvation of ions, adsorption at the electrode surface. The existence of strong electric fields induces non linear phenomena when the charge of the interface is changed. In such systems we have to deal with several length scales. The coulombic interaction introduces the Debye length which depends on ionic concentration. The short range interactions between various components introduce the sizes of the species which are concentration independent. The interaction between the electrode and the solution side of the interface leads to another characteristic length. Taking into account the existence of these several length scales we introduce a simple model in order to investigate the competition between electrostatic and non electrostatic phenomena at a charged interface.

Our approach is based on a simple Landau-Ginzburg hamiltonian that we have already used to investigate several aspects concerning both the interfacial and bulk properties of ionic systems [1]-[4]. In these works we study a theoretical system in which we assume that the solvent has no relevant contribution. The basic ingredients are the distributions of cations  $\rho^+(\vec{r})$  and anions  $\rho^-(\vec{r})$  across the interface. In the spirit of a field theoretical approach we treat  $\rho^+(\vec{r})$  and  $\rho^-(\vec{r})$  as two fields [5]. The partition function of the interface is calculated via a functional integral in which all possible forms of  $\rho^+(\vec{r})$  and  $\rho^-(\vec{r})$  give a contribution weighted by the Boltzmann factor  $\exp\{-\beta\mathcal{H}[\rho^+(\vec{r}), \rho^-(\vec{r})]\}$  where the hamiltonian  $\mathcal{H}[\rho^+(\vec{r}), \rho^-(\vec{r})]$  is in fact a free energy functional of  $\rho^+(\vec{r})$  and  $\rho^-(\vec{r})$ .

If  $\mathcal{H}$  is restricted to the coulombic interaction and the ideal configurational entropy then, as we have shown [1], the mean field description leads to the non linear Gouy Chapman theory (NLGCT). By adding to the hamiltonian quadratic terms of the form  $\int a_{ij}\rho^i(\vec{r})\rho^j(\vec{r})d\vec{r}$ , where  $i, j = \pm$ , we introduce some specificity of the system via the coefficients  $a_{ij}$ . Quite surprisingly, such a simple model leads to qualitatively new behaviours compared to the NLGCT [2]. Near the point of zero charge and at low concentrations our results are identical to those of the NLGCT but at a higher concentration there can be a maximum or a minimum on the capacitance vs charge density

curve depending on the values of the parameters. For high values of charge density on the electrode we find two finite limits instead of the unlimited increase predicted by the NLGCT. If  $a_{++} \neq a_{--}$  the capacitance vs charge density curves are asymmetric with respect to zero charge density and otherwise they are symmetric.

The same kind of approach has been used to investigate the structure of bulk ionic solutions [4]. In this case an exact calculation has been performed. We have shown that the fluctuations around the mean field value of the ionic density lead to the exact Debye-Hückel limiting law. In addition, we have investigated the role of the symmetry between ions in the critical behaviour at low concentrations. In particular the Stillinger-Lovett conditions have been investigated near the critical point.

From our point of view the main interest in this kind of approach is to introduce physical ingredients with clear physical meaning. As we have seen already with very simple ingredients we can predict a large number of different behaviours.

For the charged interfaces only the electrostatic interaction between the electrode and the solution side has been considered. In this paper we go further and introduce a short range potential between the electrode and the solution. We assume that the effect of this potential is localized at the electrode surface. The magnitude of this potential can be positive or negative *i. e.* it can either favour adsorption or desorption.

This paper is organized as follows. In Section 1 we present the ingredients of the hamiltonian. In Section 2 the mean field theory (MFT) is considered. We give also the main points of the method of numerical solution of the MFT equations. In the last Section we present and discuss some results.

## 1 The hamiltonian

We define the system as a 1-1 mixture of ions carrying elementary charges  $\pm e$  of opposite signs at a given temperature  $T = k\beta^{-1}$  in a dielectric continuum with the dielectric constant  $\varepsilon$  equal to that of a pure solvent. The overall bulk ionic density  $\rho_b$  corresponds to twice the salt concentration. The electrolyte solution is limited to the halfspace,  $z > 0$ , by an impenetrable wall representing the electrode surface. We want to describe the gross features of the competition between the coulombic interaction with the other non coulombic interactions which may be present in this system. Therefore

we select the hamiltonian  $\mathcal{H}$  as simple as possible. It consists of the bulk part and the surface part:

$$\mathcal{H}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \mathcal{H}^{bulk} + \mathcal{H}^{surf} \quad (1)$$

The bulk part is further split into several contributions:

$$\mathcal{H}^{bulk}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \mathcal{H}^{coul} + \mathcal{H}^{entropic} + \mathcal{H}^{quad} + \mathcal{H}^{nloc} \quad (2)$$

described in detail in ref. [4] and the surface part of the hamiltonian is introduced in ref. [3]. Let us just briefly review the ingredients of the hamiltonian  $\mathcal{H}$ .

The coulombic interaction is given by:

$$\mathcal{H}^{coul}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \frac{1}{2} \frac{K_D^2}{4\pi\beta\rho_b} \int \frac{q(\vec{r})q(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' \quad (3)$$

where  $q(\vec{r}) = \rho^+(\vec{r}) - \rho^-(\vec{r})$  is the charge density expressed in the elementary charge units as the difference of the densities of univalent cations and anions, respectively.  $K_D^2 = e^2\beta\rho_b/\varepsilon$  is the square of the inverse Debye length. Let us note that

$$\frac{1}{e} \frac{\delta \mathcal{H}^{coul}}{\delta q(\vec{r})} = \frac{e}{4\pi\varepsilon} \int \frac{q(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = V(\vec{r}) \quad (4)$$

is just the electrostatic potential produced by the charge distribution  $eq(\vec{r}')$  at the point  $\vec{r}$ . The effect of the solvent on the Coulombic interaction is taken into account by the dielectric constant  $\varepsilon$ .

The configurational entropy gives the following contribution to the hamiltonian [1]:

$$\mathcal{H}^{entropic}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \frac{1}{\beta} \int \left\{ \rho^+(\vec{r}) \left[ -\ln \frac{\rho^+(\vec{r})}{\rho} + 1 \right] + \rho^-(\vec{r}) \left[ -\ln \frac{\rho^-(\vec{r})}{\rho} + 1 \right] \right\} d\vec{r} \quad (5)$$

where the meaning of the parameter  $\rho$  has been discussed in ref. [1].

The local quadratic contribution is given by:

$$\mathcal{H}^{quad}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \frac{1}{2\beta\rho_b} \int \{ a_{++}[\rho^+(\vec{r})]^2 + 2a_{+-}\rho^+(\vec{r})\rho^-(\vec{r}) + a_{--}[\rho^-(\vec{r})]^2 \} d\vec{r} \quad (6)$$

The quantities  $a_{++}$ ,  $a_{+-}$  and  $a_{--}$  already mentioned in the introduction are dimensionless parameters describing the correlations between ions. They contain the specific properties of the system. They are a part of the potential of mean force between ions

and thus they take into account implicitly some aspects of the short range ion-solvent interaction. The effect of the local quadratic term on the differential capacitance has been already discussed to some extent in our previous work [2]. In this term we focus on the interaction of the fields at a single point in the space.

The nonlocal term establishes a link between a point in the space and its neighbourhood. We write this term as:

$$\mathcal{H}^{nloc}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \frac{1}{2\beta\rho_b} \int \{b_{++}^2[\nabla\rho^+(\vec{r})]^2 + 2b_{+-}^2\nabla\rho^+(\vec{r})\nabla\rho^-(\vec{r}) + b_{--}^2[\nabla\rho^-(\vec{r})]^2\}d\vec{r} \quad (7)$$

To have the simplest hamiltonian possible in what follows we take the same value  $b$  for all  $b_{ij}$ 's,  $b_{++} = b_{--} = b_{+-} = b$ . Hence this non local term relates only to the total density of ions - the sum of the densities for the cation and anion. Note that there is already a nonlocal interaction associated with the charge distribution taken into account via the coulombic interaction. In principle, there should be no difficulty in considering the general case when  $b_{ij}$ 's are not necessarily the same but our simplification is greatly advantageous also for the numerical reasons. Note that  $b$  has a dimension of a length.

In addition to the above ingredients which enter  $\mathcal{H}^{bulk}$  and describe the bulk solution we introduce a specific surface hamiltonian for which we assume the following form:

$$\mathcal{H}^{surf}[\rho^+(\vec{r}), \rho^-(\vec{r})] = \frac{1}{\beta} \int h\delta(z)[\rho^+(\vec{r}) + \rho^-(\vec{r})]d\vec{r} \quad (8)$$

Thus in addition to behaving like a charged impenetrable wall with charge density  $\sigma$  we assume that the wall has a given affinity to adsorb ( $h < 0$ ) or desorb ( $h > 0$ ) ions with a strength  $h$ . We also assume that this effect is localized near the wall and that its range is sufficiently short compared with other lengths that we can represent it by a Dirac  $\delta$  function. This function is commonly used in the liquid state theory to represent short range potentials. When we use it we have in mind a narrow potential profile localized at the electrode surface and producing the effect equivalent to a step potential profile of magnitude  $1 kT$  over the distance  $h$  or the potential step profile  $h kT$  over the distance 1 in a given unit system. As above, for simplicity we assume that the wall behaves the same way for anions and cations. There is also no theoretical difficulty in considering a wall behaving in a different way for each kind of ions.

To summarize, we consider an interface described by the hamiltonian (1) in which there are several length scales involved: i) the Debye length  $K_D^{-1}$ , ii)  $b$  which controls the order of magnitude of the gradient of the total density and iii)  $h$  which, as will be seen below, eq. (12) determines the gradient of the total density profile in contact with the wall.

With the above hamiltonian one might attempt an exact calculation. However, as a first approximation, we stay on the level of the MFT.

## 2 MFT calculations

In MFT we assume that only the fields which minimize  $\mathcal{H}$  are important. This requirement gives us the MFT equations:

$$\begin{aligned} \left. \frac{\delta \beta \mathcal{H}[\rho^+(\vec{r}), \rho^-(\vec{r})]}{\delta \rho^+(\vec{r})} \right|_{\bar{\rho}_+(\vec{r}), \bar{\rho}_-(\vec{r})} &= \beta \mu_+ \\ \left. \frac{\delta \beta \mathcal{H}[\rho^+(\vec{r}), \rho^-(\vec{r})]}{\delta \rho^-(\vec{r})} \right|_{\bar{\rho}_-(\vec{r}), \bar{\rho}_+(\vec{r})} &= \beta \mu_- \end{aligned} \quad (9)$$

which yield the MFT profiles  $\bar{\rho}_+(\vec{r})$ ,  $\bar{\rho}_-(\vec{r})$  and  $F^{MFT} = \mathcal{H}[\bar{\rho}^+(\vec{r}), \bar{\rho}^-(\vec{r})]$  is identified with the free energy of the system. In our case these equations read for  $z > 0$ :

$$\begin{aligned} +\beta eV(z) + \log \frac{2\rho^+(z)}{\rho_b} + a_{++} \frac{\rho^+(z)}{\rho_b} + a_{+-} \frac{\rho^-(z)}{\rho_b} - \frac{b^2}{\rho_b} \frac{d^2}{dz^2} [\rho^+(z) + \rho^-(z)] &= \frac{1}{2}(a_{++} + a_{+-}) \\ -\beta eV(z) + \log \frac{2\rho^-(z)}{\rho_b} + a_{--} \frac{\rho^-(z)}{\rho_b} + a_{+-} \frac{\rho^+(z)}{\rho_b} - \frac{b^2}{\rho_b} \frac{d^2}{dz^2} [\rho^+(z) + \rho^-(z)] &= \frac{1}{2}(a_{--} + a_{+-}) \end{aligned} \quad (10)$$

where because of the symmetry of the system we consider the dependence only on one coordinate,  $z$ . We have eliminated the Lagrange multipliers  $\mu_+$ ,  $\mu_-$  taking care of the constant number of molecules in the system using the conditions for the bulk. For  $z = 0$ , where we place the wall, we obtain the following boundary conditions:

$$-\left. \frac{dV}{dz} \right|_{z=0} = \vec{E}(z=0) = \frac{\sigma}{\varepsilon} \quad (11)$$

$$\left. \frac{d}{dz} [\rho^+(z) + \rho^-(z)] \right|_{z=0} = \rho_b \frac{h}{b^2} \quad (12)$$

MFT equations (9) and (10) with (11) and (12) form a system of integro-differential equations which can be transformed into a system of differential equations which is in general much easier to handle.

## 2.1 MFT Differential Equations

It is convenient to introduce dimensionless reduced variables:

$$\hat{z} = K_D z \quad (13)$$

$$g_j(\hat{z}) = \frac{2\rho^j(z)}{\rho_b} \quad \text{where } j = +, - \quad (14)$$

$$v(\hat{z}) = 2\beta eV(z) \quad (15)$$

$$\hat{b} = bK_D \quad (16)$$

$$\hat{E}(\hat{z}) = \hat{\sigma}(\hat{z}) = -\frac{dv}{d\hat{z}} \quad (17)$$

$$\hat{h}(\hat{z}) = 2K_D h \quad (18)$$

They differ from their usual counterparts by conversion constants being combinations of the Debye inverse length  $K_D = e(\rho_b\beta/\varepsilon)^{\frac{1}{2}}$ , temperature  $T$ , concentration  $\rho_b$  and the universal constants. We use  $K_D^{-1}$  as a unit of length. From now on we will use reduced variables exclusively and we shall refer to  $g^+(\hat{z})$ ,  $g^-(\hat{z})$ ,  $v(\hat{z})$ ,  $\hat{\sigma}(\hat{z})$ ,  $\hat{h}(\hat{z})$  as ionic, electric potential, electric field and wall affinity ( $h$  field) profiles omitting the  $\hat{\phantom{x}}$  sign. Let us note that the boundary conditions set equivalence between the external wall parameter  $\sigma$  on the wall and the electric field at the position of the wall and also between the wall ionophobicity (or philicity) and the gradient of the overall ionic density at the position of the wall. Both fields *jointly* describe the effect of the wall which gradually diminishes away from the wall to vanish far in the bulk. By virtue of the Poisson equation and using the reduced variables we can transform the system of the two integro-differential equations into the following system of four non-linear first-order differential equations:

$$\left( \frac{2}{g^+(z)} + a_{++} - a_{+-} \right) \frac{dg^+(z)}{dz} - \left( \frac{2}{g^-(z)} + a_{--} - a_{+-} \right) \frac{dg^-(z)}{dz} = 2\sigma(z) \quad (19)$$

$$\frac{dg^+(z)}{dz} + \frac{dg^-(z)}{dz} = \frac{h(z)}{b^2} \quad (20)$$

$$\frac{d\sigma(z)}{dz} = g^+(z) - g^-(z) \quad (21)$$

$$\frac{dh(z)}{dz} = 2 \log(g^+(z)g^-(z)) + (a_{++} + a_{+-})g^+(z) + (a_{--} + a_{+-})g^-(z)$$



$$-(a_{++} + 2a_{+-} + a_{--}) \quad (22)$$

which have to be solved taking into account the boundary conditions. Two such conditions are imposed on the wall:

$$\sigma(z=0) = \sigma_0 \quad (23)$$

$$h(z=0) = h_0 \quad (24)$$

We also have infinitely far from the wall:

$$g^+(z \rightarrow \infty) = 1 \quad \text{and} \quad g^-(z \rightarrow \infty) = 1 \quad (25)$$

and then it follows that:

$$\sigma(z \rightarrow \infty) = 0 \quad (26)$$

$$h(z \rightarrow \infty) = 0 \quad (27)$$

## 2.2 Numerical methods

For a system of non linear differential equation we have no analytical solution in general. We resort to a numerical procedure and it is most straightforward to use a solver for the initial value problem. We cannot use it for the surface characterized by a given  $\sigma_0$  and  $h_0$  since for arbitrarily selected values of  $g_0^+ = g^+(z)$  and  $g_0^- = g^-(z)$  for  $z = 0$  we do not satisfy the conditions of the bulk phase at infinity. However far from the wall we can obtain the asymptotic solution of our problem by the linearization around the bulk values:  $g^+(z) \equiv 1$ ,  $g^-(z) \equiv 1$ ,  $\sigma(z) \equiv 0$  and  $h(z) \equiv 0$ . The linearized problem can be solved as discussed in our previous paper [2] for sufficiently small but otherwise arbitrary values of  $\sigma_a$  and  $h_a$  at an arbitrarily selected dividing point  $z_a > 0$  as if there were a wall just slightly affecting the bulk uniform profiles. The matching condition sets the initial values of the ionic profiles at the dividing point equal to those calculated from the linearized equations. Then we launch the numerical integration backwards. Of course, we cannot tell the values of  $\sigma_0$  and  $h_0$  before actually making the integration. However, we are sure to get the physical ionic profiles with the correct asymptotic behaviour corresponding to the wall characterized by the *calculated* values of  $\sigma_0$  and  $h_0$ . The above described approach is in fact essentially the same as that

discussed in ref.[2] for the case with no square gradient *i. e.*  $b = 0$ . In the present case, however, we have a two component group of transformations:

$$\sigma_0 = \sigma_0(\sigma_a, h_a, z_a) \quad (28)$$

$$h_0 = h_0(\sigma_a, h_a, z_a) \quad (29)$$

and then in contrast to the former case we can observe non monotonous ionic density profiles [3].

The quantity of a particular experimental interest is the differential capacitance. Assuming that the wall at  $z = 0$  does not change its ionophobicity (ionophilicity) when charged we can calculate the differential capacitance as:

$$C = \left( \frac{d\sigma_0}{dv_0} \right)_{h_0} \quad (30)$$

For the numerical calculation we use a simple shooting method [7] by which we apply a solver for an initial value problem to solve the boundary value problem.

## 3 Results

### 3.1 Choice of the parameters

To obtain meaningful results we have to specify the values of the phenomenological parameters related to the microscopic background of the studied phenomena. To mimic an aqueous electrolyte solution at room temperature we assume  $T = 298.15K$  and  $\varepsilon = 78$ . Since we concentrate on the effect of the competition between electrostatic and non electrostatic phenomena, we set the values of the local coupling constants  $a_{ij} = 0$ . The value of  $b$  in this case gives the correlation length for the non coulombic interaction. We set its value to a typical value of a molecular diameter in ionic solutions which is of the order of 0.3nm. This corresponds to  $b = 1$  in a 1M aqueous electrolyte solution for which  $K_D^{-1} = 0.3nm$  is also of the order of the molecular diameter. In a 1M solution the deviations in the ionic solution properties from the Debye-Hückel limiting law become already important which makes our selection reasonable. We consider the values of  $h$  of the order of 1 in reduced units which corresponds to the step potential profile  $1kT$  high and 0.15nm wide or  $1.5kT$  high and 1nm wide.

## 3.2 Ionic profiles

In Figures 1 and 2 we present two examples of profiles. They correspond to an electrode surface which is repulsive for both kind of ions. We choose the value of  $h$  such that both profiles vanish at the surface,  $g^+(z=0) = 0$  and  $g^-(z=0) = 0$ . Of course, for a higher value of charge density we need a higher value of  $h$  to make the counterion profile vanish. We can see that this behaviour is totally different from that of NLGCT already for reasonable values of  $h$  at the wall. For instance, if we interpret  $h$  as a height of the potential step profile extending 0.1nm from the electrode it is 4kT and 9kT for the cases presented in Figures 1 and 2 respectively. If the short range interaction dominates the coulombic interaction (Figure 1) the profiles increase monotonically from zero to their bulk values far from the wall. If, in contrast, the surface is strongly charged (Figure 2) we find a maximum in the distribution of counterions while the distribution of coions remains monotonic though exhibits an inflection point. The coions are excluded from the vicinity of the wall. Although the profiles in Figures 1 and 2 seem to have a simple spatial dependence a more detailed mathematical analysis shows that this is not true [8]. Near the wall the profiles exhibit a non-analytic behaviour.

In Figure 3 we present the profiles of the electric potential  $V(z)$  corresponding to the cases studied in Figures 1 and 2. These profiles are quantitatively different but otherwise both monotonic and there is no special feature from which to expect the qualitative difference in counterion profiles observed in the two cases. The potential profiles are also qualitatively similar to that of NLGCT. If we take, however, the second derivative of the potential profiles we obtain the charge density profiles which are non monotonous in contrast to NLGCT (Figure 4).

## 3.3 Differential capacitance

We expect that the differential capacitance dependence on charge density is more sensitive to the details of the present model than the corresponding dependence of the potential drop. The capacitance, as given by formula (30) may depend also on  $h$  *i. e.* the type of the surface in contact with solution. This is illustrated on Figure 5 where we present the capacitance curves calculated for  $b = 1$  and several values of  $h$ . For  $h = 0$  the capacitance at the pzc coincides with the Gouy-Chapman capacitance. In

this case the capacitance is determined by the response of the system to small values of  $\sigma$  keeping  $h = 0$ . Then the profiles deviate only slightly from the uniform bulk ones and are described by the linearized Gouy-Chapman theory. Away from the pzc and  $h = 0$  the effect of the gradient term couples with the non linear entropy term giving rise to a behaviour qualitatively different from that of the NLGCT. For non vanishing  $h$  it is interesting to discuss the results from the geometrical point of view. By integration of the Poisson equation we obtain the expression of the potential drop across the interface:

$$V(z = 0) = \frac{1}{\varepsilon} \int z q(z) dz = \langle z \rangle_{pzc} \frac{\sigma}{\varepsilon} \quad (31)$$

We can also consider that this integral introduces the first moment  $\langle z \rangle$  or the center of gravity of the charge distribution. From this last expression we can interpret the potential across the interface as equivalent to that of two charged planes separated by the distance  $\langle z \rangle$ . The integral capacitance is just  $\varepsilon / \langle z \rangle$  while the differential capacitance is given by:

$$\frac{1}{C} = \frac{\langle z \rangle}{\varepsilon} + \frac{\sigma}{\varepsilon} \frac{d \langle z \rangle}{d \sigma} \quad (32)$$

At the pzc,  $1/C = \langle z \rangle_{pzc} / \varepsilon$ . If  $h < 0$  the wall tends to adsorb both ions and we may expect that  $\langle z \rangle_{pzc}$  is smaller than the corresponding value in the NLGCT where we have  $\langle z \rangle_{pzc} = K_D^{-1}$ . Thus at the pzc for  $h < 0$  it is natural to find  $C(h < 0) > C_{GC} = \varepsilon K_D$ . In the case  $h > 0$  the wall tends to push ions away towards the bulk. Then  $\langle z \rangle_{pzc} > K_D^{-1}$  and, as expected,  $C(h > 0) < C_{GC}$ .

When we move away from the pzc the results are much more sophisticated. The differential capacitance is no longer given by  $\langle z \rangle$  but also by  $\sigma d \langle z \rangle / d \sigma$ . The case  $h = 0$  is no longer identical to the Gouy-Chapman theory since with (12) we fix as zero the derivative of the total density at the wall. This makes the center of gravity of the charge move away from the electrode. Then we may expect a decrease of the capacitance compared to NLGCT. In the domain close to pzc capacitance is not only smaller than that of the NLGCT but in contrast to the NLGCT decreases with charge forming a local maximum at the pzc surrounded by two minima. Then it starts to increase in the region where the contribution from  $\sigma \frac{d \langle z \rangle}{d \sigma}$  becomes important. A similar behaviour is observed for  $h = -1$ .

### 3.4 Conclusions

Already with a very simple hamiltonian we can describe various behaviours of the system which are qualitatively different from the Gouy-Chapman theory. We can have exclusion of both ions from the vicinity of the electrode surface. For a strongly charged electrode we have a competition between exclusion and electrostatic attraction of the counterion leading to the maximum of the counterion profile. We have also seen that the type of the electrode surface, given in our case by  $h$  as a measure of the electrode's ionophilicity or ionophobicity, influences the capacitance curve to a large extent if we adopt values reasonable from the point of view of a molecular description. We can hope that if we overcome the simplifications of the present treatment we will arrive at a more extensive description of the electrified interfaces.

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## Figure Captions

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Fig.1 Ionic profiles  $g^+(z)$  (dotted line) and  $g^-(z)$  (solid line) in a 1M solution at a charged wall. The characteristic length for specific non local interactions in the solution is  $b = 0.3\text{nm}$ . The values of the parameters characterizing the wall placed at  $z = 0$  are:

charge density  $\sigma_0 = 0.012\text{Cm}^{-2}$ ,

the ionophobicity parameter,  $h_0 = 2.7$  corresponding to a  $0.4\text{ nm} \times kT$  potential step.

Fig.2 Ionic profiles  $g^+(z)$  (dotted line) and  $g^-(z)$  (solid line) for a solution as in Fig.1 but at a different wall. The values of the parameters characterizing the wall placed at  $z = 0$  are:

charged density  $\sigma_0 = 0.16\text{Cm}^{-2}$ ,

the ionophobicity parameter,  $h_0 = 6.2$  corresponding to a  $0.9\text{ nm} \times kT$  potential step.

Fig.3 Potential profiles for the two cases:

- (1) of a weakly charged wall corresponding to Fig. 1
- (2) of a strongly charged wall corresponding to Fig.2

Fig.4 Charge density profiles for the two cases:

- (1) of a weakly charged wall corresponding to Fig. 1
- (2) of a strongly charged wall corresponding to Fig.2

Fig.5 Differential capacitance curves calculated according to the Gouy-Chapman theory (GC) and according to the formula (30) for  $b=1$  and with values of the ionophobicity parameter  $h$  indicated for each curve.

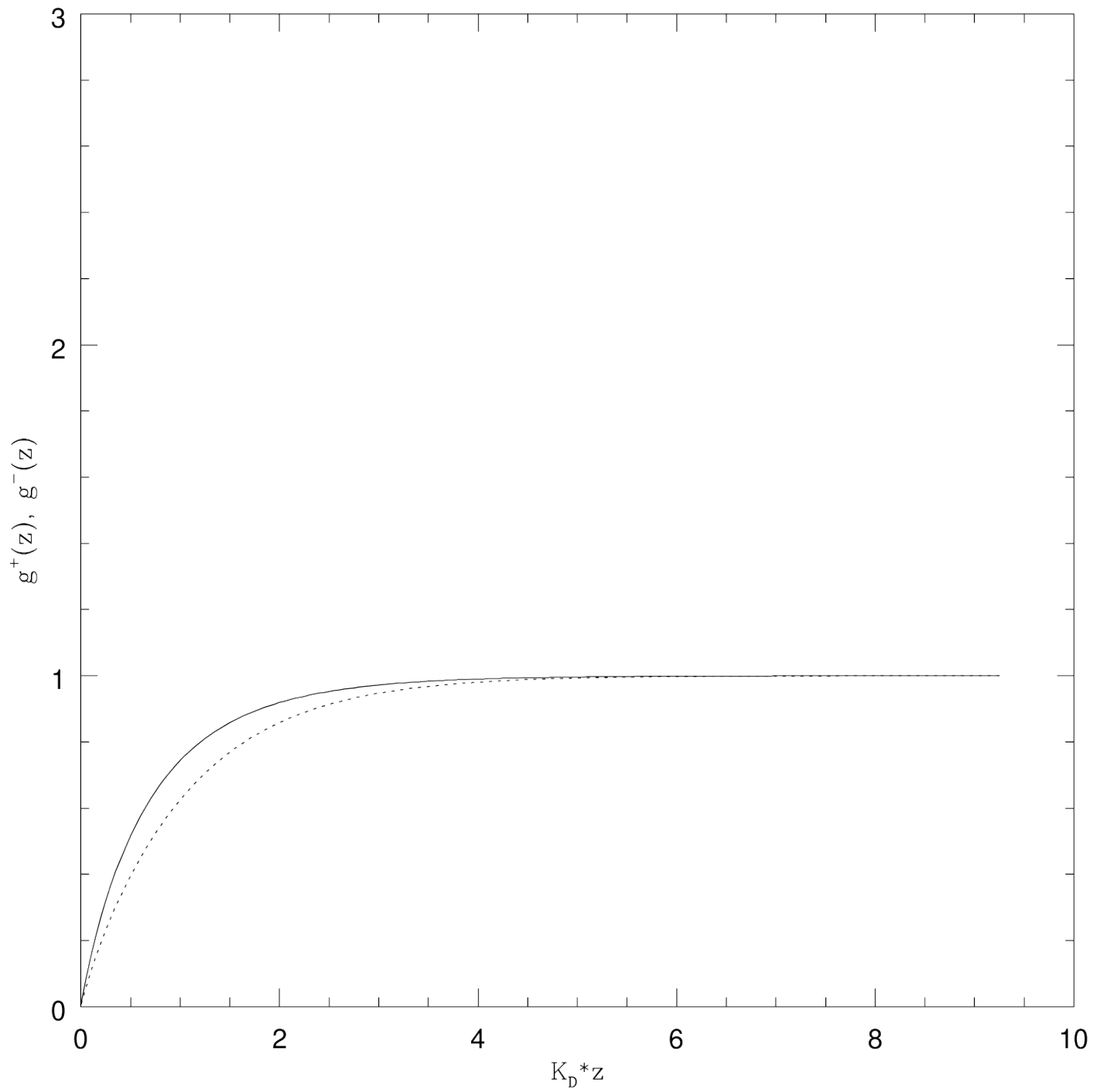


figure 1



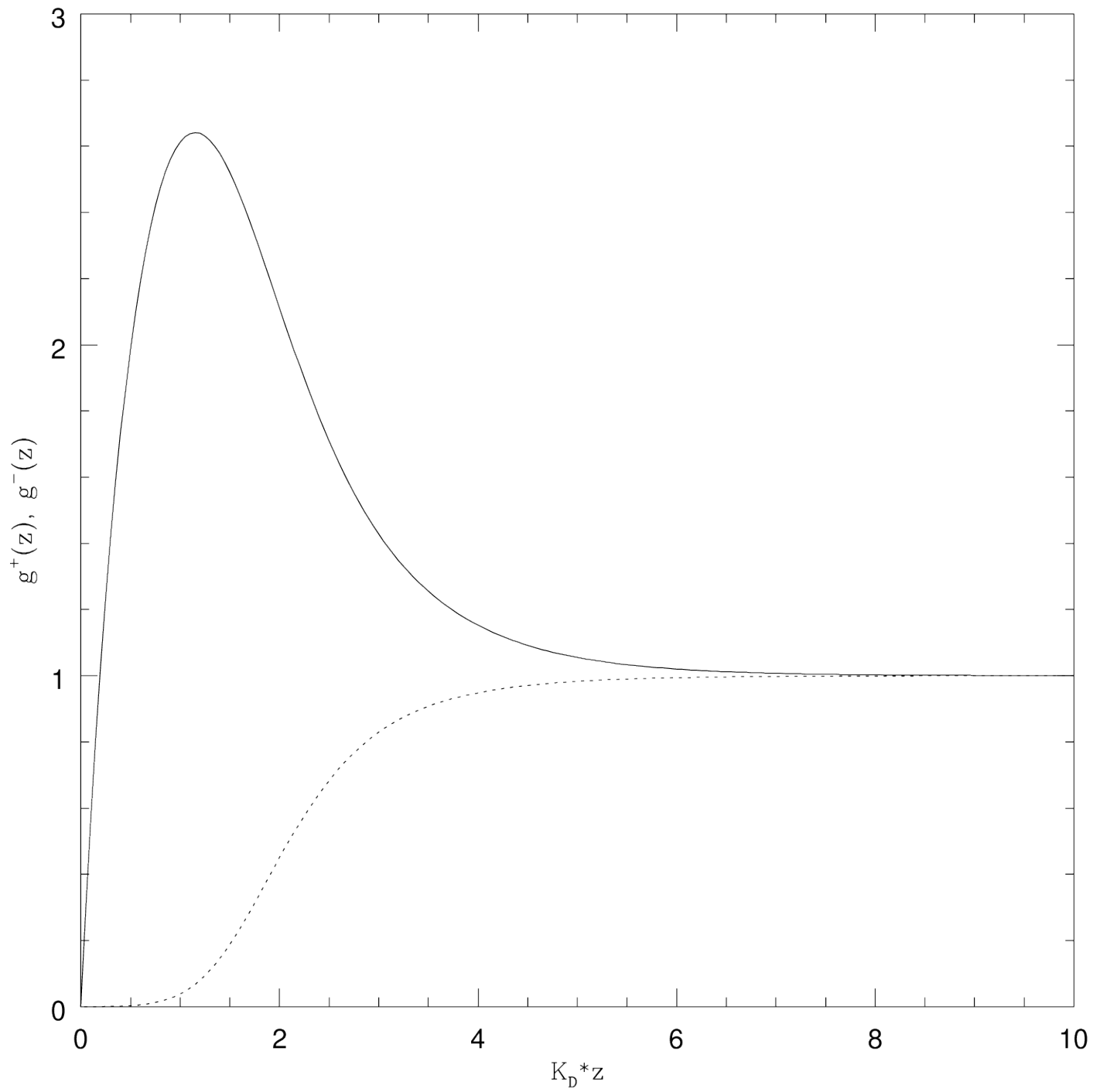


figure 2

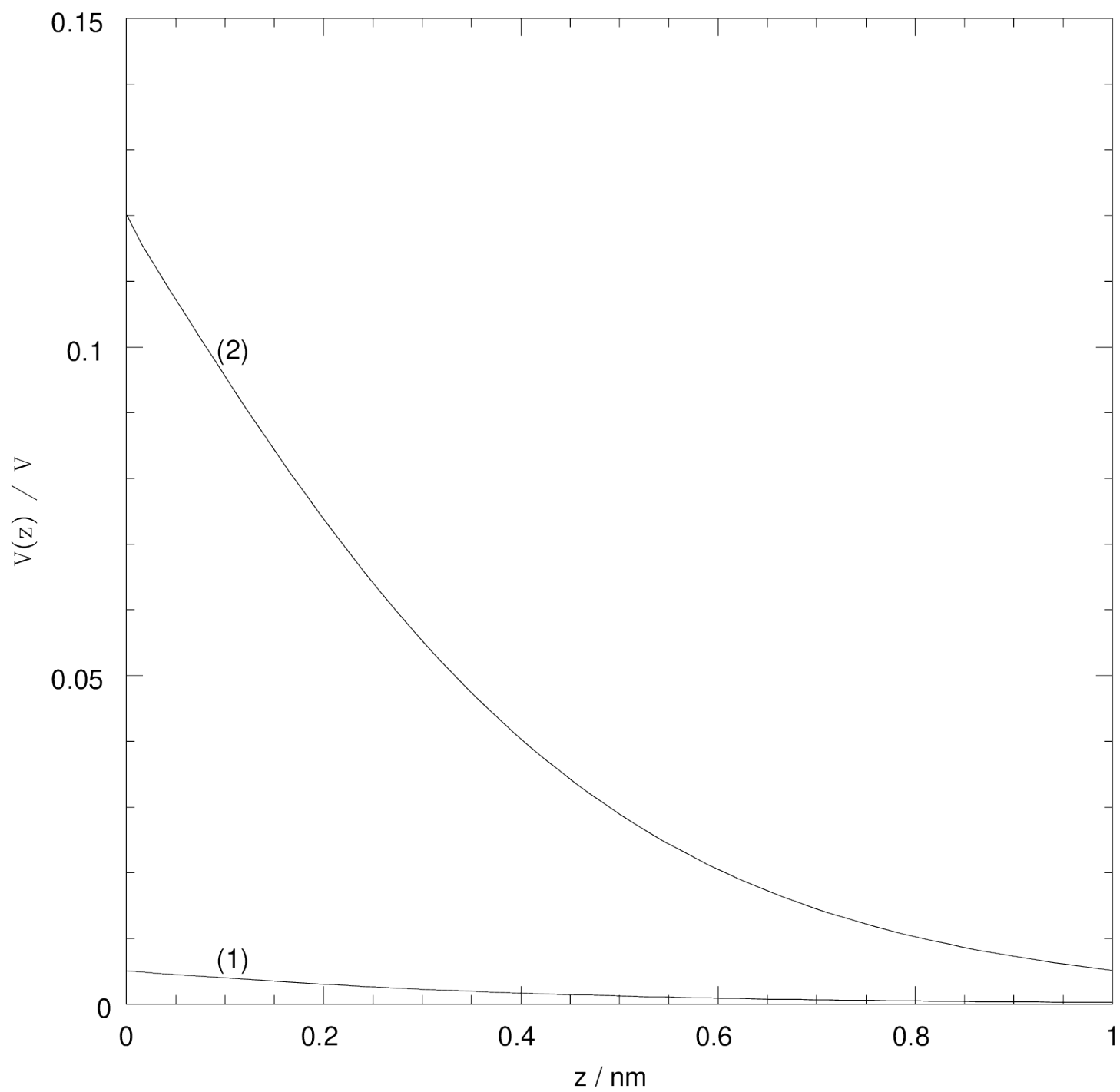


figure 3

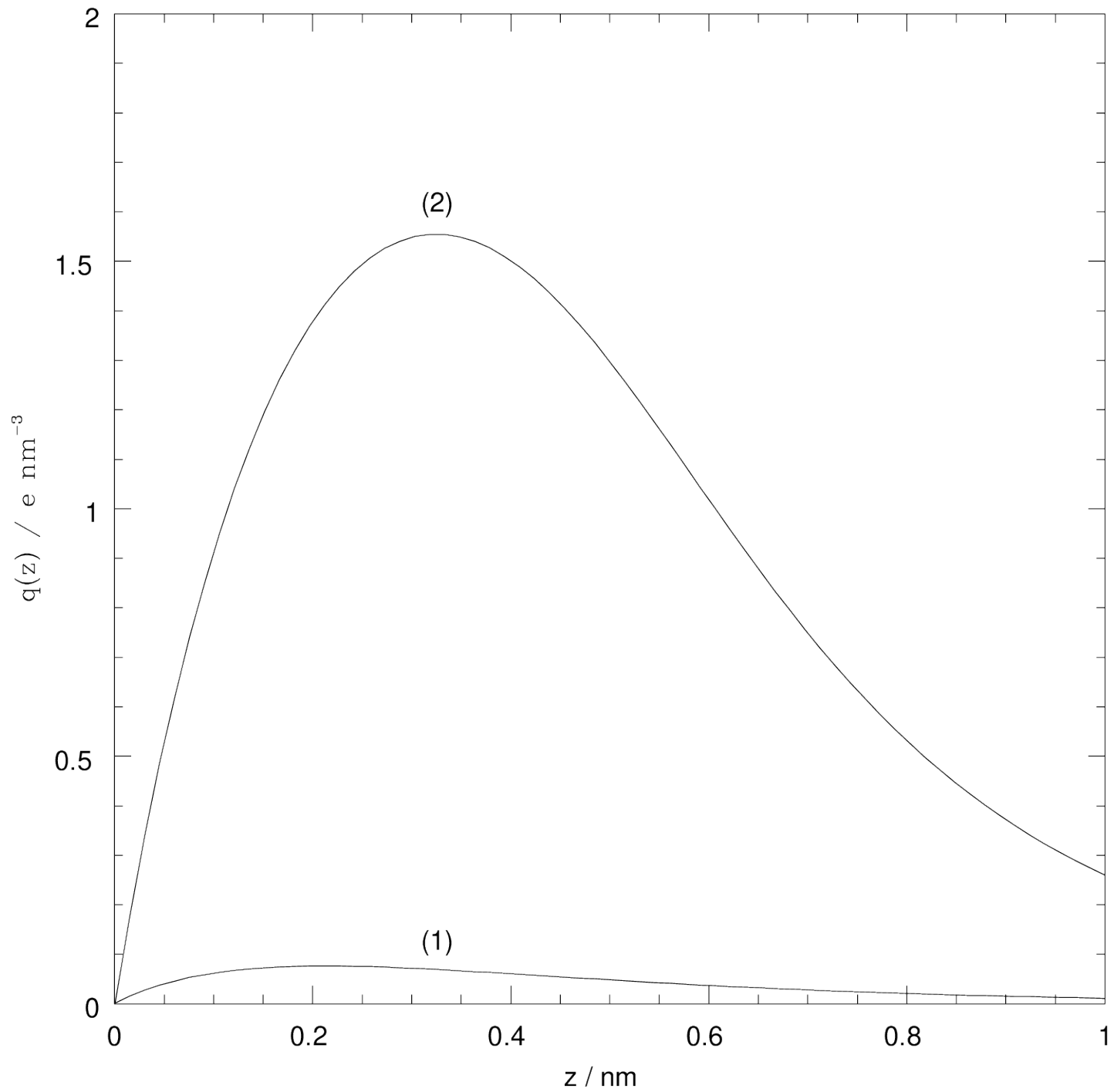


figure 4

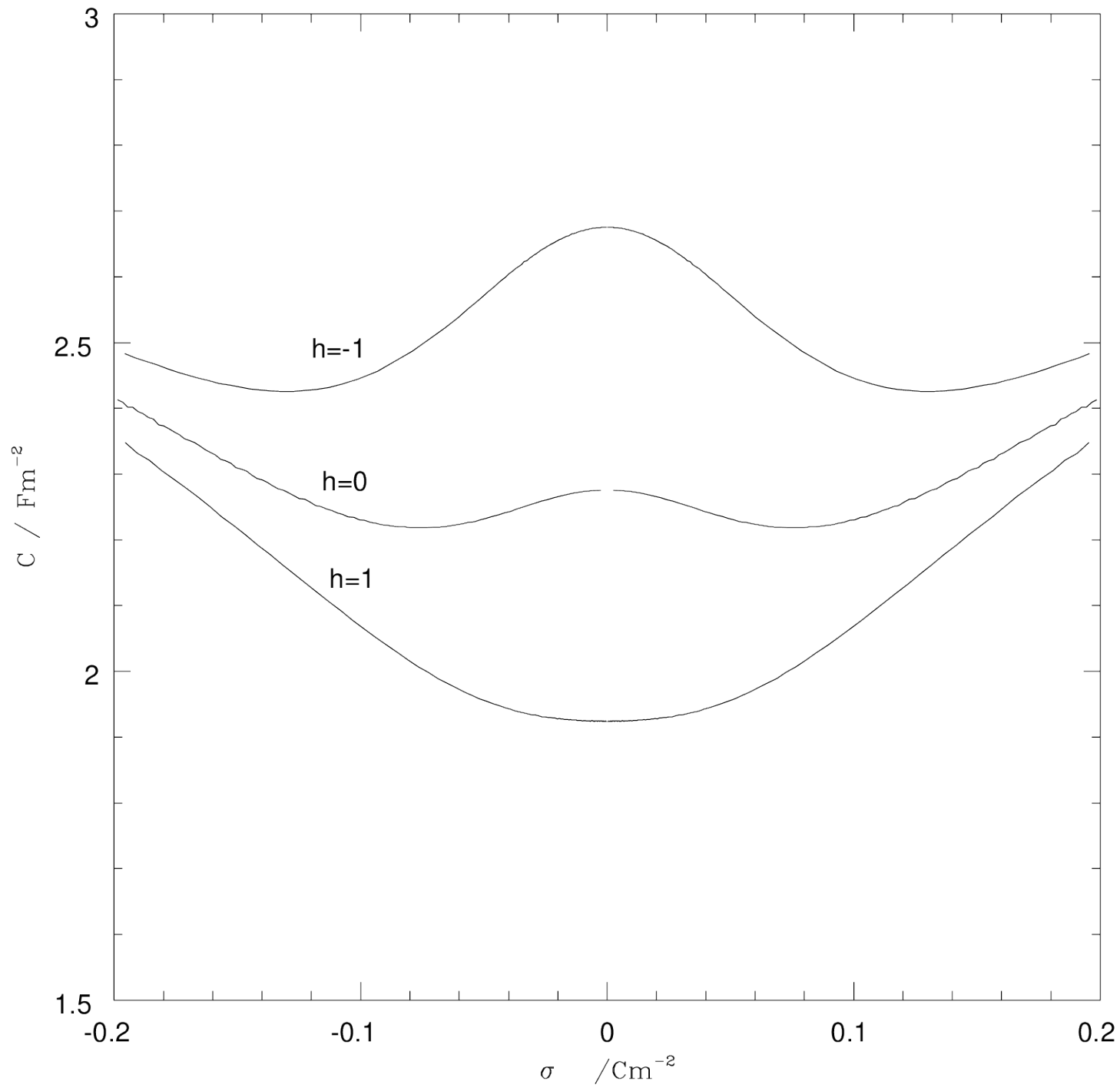


figure 5