



## Ion adsorption and external electric field effects on isotropic liquids using a Fermi-like distribution

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### ABSTRACT

A Fermi-like distribution for charged particles is used to investigate adsorption and external electric field effects in a typical confined sample of an isotropic liquid. In the absence of adsorption, expressions for the reduced potential across the sample and for the specific differential capacitance of the double layer are established as a function of the applied dc voltage. In the presence of adsorption, without external field, the fundamental equations of the electrostatic model are analytically solved in the limit of small potential. Simple expressions for the reduced and chemical potential as well as for the specific differential capacitance of the double layer are established. The behavior of these quantities are analyzed as a function of the adsorption energy, the total density of ions in the bulk, and the potential drop between the electrode surface and the bulk.

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### 1. Introduction

Recently, a phenomenological Fermi-like distribution for the particles immersed in a fluid was proposed in order to describe the surface adsorption of charged or neutral particles in isotropic liquids [1,2]. The motivation for that new approach was to consider a statistical description for the adsorption phenomenon not limited to non-interacting adsorbate–adsorbate systems. The Fermi-like distribution, owing to the exclusion principle, naturally takes into account the occupation of the adsorption sites without the need to consider steric potentials with artificial cut-offs. For this reason, the saturation in the coverage of the surface by the adsorbed particles can be found also in the perfect gas approximation. A similar statistical distribution was employed to describe ionic liquids with particular emphasis on the behavior of the double-layer capacitance [3]. This theory resulted in a simple analytical expression for the double-layer capacitance, beyond the Gouy–Chapman formula [4], and has attracted the attention of other approaches [5–10]. When an external electric field is applied to a cell of an isotropic liquid, and the adsorption phenomenon is absent, a spatially dependent electric field distribution across the sample arises, in

view of the induced charge separation. On the other hand, the selective ion adsorption, that may occur in view of the existence of some electrochemical forces acting on the surface, also promotes a spatial redistribution of charges in the sample. However, while the external field produces an odd distribution of charges, the adsorption phenomenon is responsible for an even distribution of charges when identical surfaces are considered, as will be done here.

In this work, a Fermi-like description for mobile ions, in the hypothesis of fully dissociated positive and negative charges and in the continuum approximation, is used to face two different problems. The first problem considers the action of an external electric field (dc regime) assuming that the surfaces are perfectly blocking. In this framework, we present the fundamental equations of the model, with particular emphasis on the so-called Poisson–Fermi equation arising from the use of “Fermi” statistics for the distribution of particles in connection with the Poisson’s equation for the spatial profile of the electrical potential. These equations are solved, giving useful expressions for the electrical potential across the sample. Moreover, the double-layer capacitance is determined and its behavior is investigated as a function of the difference of potential across the sample, due to the external power supply. The second problem we consider deals with selective adsorption effects at the surfaces limiting the sample, but now in absence of external applied voltage. In this scenario, the surface density of adsorbed charges gives rise to a surface electric field whose intensity decays as we move away from the surface. To analyze the effects of this field,

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the fundamental equations are exactly solved in the limit of small potential. This procedure permits us to obtain analytical expressions for the specific differential capacitance of the double layer. It is a simple approach whose controlling parameters are limited to the number of sites in the bulk, the same quantity at the surface, and the adsorbing energy, which is a rather well known parameter. Furthermore, it allows to consider the density of possible adsorbed particles as a control parameter for the adsorption phenomenon. An approach of this kind is well tailored for isotropic liquids in the presence of high density of ions [11] but, in principle, can find applications in other contexts as, for instance, oriented nematic liquid crystals doped with charged particles [12–18].

This paper is organized as follows. In Section 2, the fundamental equations of the Fermi-like model are solved in the presence of an applied voltage to obtain the profile of the reduced potentials across the sample. These results allow us to obtain the electric field profile as well as the spatial dependence of the bulk density of positive and negative charges for significant values of the bias voltage. In addition, the behavior of the double-layer capacitance is investigated as a function of the applied voltage. In Section 3, selective adsorption effects are considered in the absence of external voltage. The equations of the model are solved in the limit of low potential, giving exact analytical expressions for the potentials (electrical and chemical). The double-layer capacitance in this limiting case is investigated as a function of the adsorbing energy and as a function of the number of ions per unit volume in the sample. Some concluding remarks are presented in Section 4.

## 2. Fermi-like model: external field effects

We first consider the ion distribution in an isotropic fluid limited by two nonadsorbing surfaces of thickness  $d$ , placed at  $z = \pm d/2$ , where  $z$  is the coordinate normal to the surfaces of the blocking electrodes limiting the sample in an essentially one-dimensional problem. The liquid is assumed as locally and globally neutral, containing  $n_+ = n_- = N$  ions, per unit volume, in the absence of external field. The densities of positive and negative ions are given by a Fermi-like distribution, in the form

$$n_{\pm}(z) = \frac{N_B}{1 + \exp(\pm\psi)}, \quad (1)$$

where  $N_B$  is the bulk density of sites. We indicate by  $\psi(z) = qV(z)/k_B T$  the reduced potential of a positive ion, of charge  $q$ , in  $k_B T$  units, where  $V(z)$  is the electrical potential,  $k_B$  is the Boltzmann constant, and  $T$  the absolute temperature. We assume that  $V(\pm d/2) = \pm U/2$ , where  $U$  is the difference of potential across the sample due to the external power supply. Hence,  $V(-z) = -V(z)$ .

The net charge density of the system is  $\rho = q(n_+ - n_-)$  which, with the help of Eqs. (1), can be written as

$$\rho = -qN_B \tanh\left(\frac{\psi}{2}\right). \quad (2)$$

A simple calculation shows that

$$\int_{-d/2}^{d/2} \rho dz = -qN_B \int_{-d/2}^{d/2} \tanh\left(\frac{\psi}{2}\right) dz = 0, \quad (3)$$

stating the global neutrality of the system

$$Nd = \int_{-d/2}^{d/2} n_+(z) dz. \quad (4)$$

The charge distribution and the electrical potential are connected by Poisson's equation  $d^2V/dz^2 = -\rho/\epsilon$ , which, by using the definition of  $\psi(z)$  and Eq. (2), can be put in the form

$$\frac{d^2\psi}{dz^2} = \frac{1}{\lambda^2} \tanh\left(\frac{\psi}{2}\right), \quad (5)$$

where  $\lambda^2 = 2N\lambda_0^2/N_B$ , in which the intrinsic parameter is  $\lambda_0 = \sqrt{\epsilon k_B T / (2Nq^2)}$ , i.e., the usual Debye's length [2]. Notice that, for a diluted system, in general  $N < N_B$ . It is possible to have an idea about the order of magnitude of  $N_B$  if we consider that typical values of  $\lambda_0 \approx 1 \mu\text{m}$ ,  $q = 1.6 \times 10^{-19} \text{ C}$  (monovalent ions),  $\epsilon \approx \epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ , and  $k_B T \approx 4 \times 10^{-21} \text{ J}$ . This gives  $N \approx 7 \times 10^{17} \text{ m}^{-3}$ .

By Eq. (5) we get

$$\frac{d\psi}{dz} = \frac{2}{\lambda} \sqrt{\ln[\cosh(\psi/2)] + k}, \quad (6)$$

where  $k$  is an integration constant to be determined by the boundary conditions:

$$\psi(\pm d/2) = \pm u = \pm \frac{1}{2} \frac{U}{V_T}, \quad (7)$$

where  $V_T = k_B T/q$  is the thermal potential. By using (7), we can rewrite Eqs. (4) and (6) in the form

$$I(k, u) = \int_{-u}^u \frac{d\psi}{\sqrt{\ln[\cosh(\psi/2)] + k}} = \frac{2d}{\lambda} \quad (8)$$

and

$$J(k, u) = \int_{-u}^u \frac{d\psi}{[1 + \exp(\psi)] \sqrt{\ln[\cosh(\psi/2)] + k}} = \frac{N}{N_B} \frac{2d}{\lambda} \quad (9)$$

From Eqs. (8) and (9), we obtain

$$I(k, u)J(k, u) = 2 \left( \frac{d}{\lambda_0} \right)^2. \quad (10)$$

Using Eqs. (6) and (10), one can determine  $\psi$ , when the other parameters characterizing the sample are given. As can be seen from Eqs. (8) and (9),  $\lambda = \lambda(k)$ , and, hence,  $\lambda = \lambda(U)$ , i.e., the effective Debye's screening length depends on the applied voltage. These equations constitute a simple and complete framework to investigate the effect of external electric field on an isotropic fluid when "Fermi" statistics is considered. The spatial profile of the electrical potential in  $V_T$  units (i.e. the reduced potential) is shown in Fig. 1 for a typical value of  $\lambda_0$ , consistent with the hypothesis that  $N < N_B$ .

To complete the presentation of the main results of the model, the electric field profile inside the sample can be analyzed. It is easily determined from (6), in the form  $E(z) = -V_T d\psi/dz$ . In Fig. 2, the profile of the electric field is exhibited for two different values of  $u$ . In Fig. 3, the spatial distribution of positive and negative ions are shown for two different values of the applied potential. As expected, there is an increasing accumulation of charges near the electrodes with the increasing of the bias voltage that reaches a saturation for large enough values of  $u$ . However, this saturation is more pronounced for "Fermi" statistics than the "classical" Maxwell-Boltzmann case (see e.g., Ref. [1]). For this reason, the present approach can be the more suitable one when we consider densely packed ionic liquids.

### 2.1. The double-layer capacitance

The specific differential capacitance of the double layer is defined as [19]:

$$C = \frac{d\sigma}{dU}, \quad (11)$$

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