

## Free Energy of Electric Double Layer. Effect of Ion Size.

Klemen Bohinc<sup>1</sup>, Aleš Iglič<sup>1</sup>, Tomaž Slivnik<sup>1</sup>, Veronika Kralj-Iglič<sup>2</sup>

<sup>1</sup> University of Ljubljana, Faculty of Electrical Engineering, Laboratory of Applied Physics,  
Tržaška 25, SI-1000 Ljubljana, Slovenia

<sup>2</sup> University of Ljubljana, Medical Faculty, Institute of Biophysics,  
Lipičeva 2, SI-1000 Ljubljana, Slovenia

**Abstract.** An expression for the free energy of an electric double layer is derived. A method of undetermined multipliers is applied within a simple statistical mechanical approach. The electrostatic interactions are described by the mean electrostatic field while the finite size of particles, constituting the electrolyte solution, is considered by the excluded volume effect. The particles in the solution are distributed over a lattice with an adjustable constant. The free energy is derived for any composition of ions and any ion valency allowing the mean electrostatic field to vanish far from the charged plane.

**Key words:** electric double layer, method of undetermined multipliers, free energy, ion size

## Prosta energija električne dvojne plasti. Efekt velikosti ionov.

**Povzetek.** V tem delu izpeljemo izraz za prosto energijo električne dvojne plasti. Uporabimo metodo nedoločenih koeficientov v okviru preprostega statistično mehanskega pristopa. Elektrostatske interakcije opišemo s povprečnim poljem, končno velikost ionov pa s predpostavko, da se prostornine, ki jih zavzemajo posamezni delci, med seboj ne morejo prekrivati. Delci v raztopini so porazdeljeni v mrežo s nastavljivo mrežno konstanto. Izpeljemo prosto energijo za vsako kompozicijo in valenco ionov, ki ustrezajo pogoju, da je električno polje daleč od plošče enako nič.

**Ključne besede:** električna dvojna plast, metoda nedoločenih koeficientov, prosta energija, velikost ionov

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### 1 Introduction

We describe an electrolyte solution in contact with a charged plane. The solution is composed of  $M$  different species of ions and of solvent molecules. Due to the electrostatic force between the plane and the ions, the counterions (the ions with the charge sign opposite of that of the plane) are accumulated close to the plane and the coions (the ions with the charge of the same sign as that of the plane) are depleted from this region. A diffuse electric double layer is created. It can be used to describe the electrostatics of biological membranes, liquid crystals and metals in contact with the electrolyte solution [1, 2].

The first description of the electric double layer was obtained by the Poisson-Boltzmann theory [3, 4], con-

sidering, the ions as dimensionless (point) charges, surface charge as uniformly smeared over the plane, and describing the electrolyte solution as a continuum with a uniform dielectric constant. Though the electric double layer has been extensively studied [5], some features still need further clarification, one of them being the effect of the finite size of the particles that constitute the solution. Already in the 50's, Freise [6], and Eigen and Wicke [7, 8] introduced modifications into the Poisson-Boltzmann theory requiring that any ion in the solution occupies a finite volume of an equal extension. Eigen and Wicke [7, 8] multiplied the density of the number of particles in the Poisson-Boltzmann equation by a factor containing a number of vacant lattice sites. The calculation carried out by Freise [6] treated the problem by the thermodynamical method in which the space requirement of ions was introduced by the pressure dependent chemical potential. Recently, the excluded volume effect was further clarified [9, 10]. A theory was presented [11] where consistently related equilibrium free energy of the electric double layer, ion distribution functions and differential equation for the electric potential were obtained starting from a single particle energy. In this work we present an improved and more concise derivation of this theory by using the method of undetermined multipliers.

## 2 Theory

### 2.1 Free energy of the ionic solution in contact with a charged plane

We consider the case of a single planar surface at  $x = 0$  with uniformly distributed surface charge density  $\sigma$ . This charged plane of area  $A$  is in contact with an electrolyte solution, which extends in the positive  $x$  direction. The electrolyte solution is composed of  $M$  species of ions and of solvent molecules. All macroscopic quantities change only in the positive  $x$  direction. Boundary effects are neglected. The charges of ions and the charged plane create an electric field in the solution. It is assumed that there is no electric field on the other side of the charged plane ( $x < 0$ ).

We divide the system into cells of equal volume [11],  $V^c = A\Delta x$ , where  $\Delta x$  is the dimension of the cell in the  $x$  direction. We assume that  $\Delta x$  is small compared to the distance over which macroscopic properties change essentially. In the cell we have  $N_j$  ions of the  $j$ -th species,  $j = 1, 2, \dots, M$ , and  $N_0$  solvent molecules. The finite size of particles is introduced by means of the excluded volume effect. A lattice is introduced with all sites occupied. The particles are distributed over  $N_s^c$  lattice sites of an equal volume in the cell

$$\sum_{j=0}^M N_j = N_s^c. \quad (1)$$

Any cell is open with respect to heat, and closed with respect to matter. The cell is therefore characterized by the variables: volume  $V^c$ , temperature  $T$  and number of the particles of all species  $N_j$ ,  $j = 0, 1, 2, \dots, M$ .

A particle in the cell is described by using the statistical mechanical approach. The canonical partition function  $q_{m_j j}$  of the  $m_j$ -th particle of the  $j$ -th species is

$$q_{m_j j} = \sum_i \exp(-\epsilon_{m_j j i}/kT), \quad m_j = 1, 2, \dots, N_j, \quad j = 0, 1, \dots, M, \quad (2)$$

where  $\epsilon_{m_j j i} = K_{m_j j i} + e_j(\Phi(\mathbf{r}_{m_j j}) - \Phi_{\text{ref}})$  is the energy state of the  $m_j$ -th particle, which consists of the electrostatic potential energy of the charged particles situated at  $\mathbf{r}_{m_j j}$ ,  $e_j(\Phi(\mathbf{r}_{m_j j}) - \Phi_{\text{ref}})$ , and other contributions  $K_{m_j j i}$  to the energy;  $\Phi(\mathbf{r}_{m_j j})$  is the potential of the electrostatic field,  $e_j$  is the charge of the ion of the  $j$ -th species,  $k$  is the Boltzmann constant and  $i$  is the index which runs through all possible energy states  $K_{m_j j i}$  of the  $m_j$ -th particle. The electric potential energy of the ion is calculated relative to the reference system in which the ions are infinitely far apart, so that the electrostatic field in this case vanishes and its potential is constant. For the reference potential we chose  $\Phi_{\text{ref}} = 0$ .

We assume that the electrostatic field in the system does not influence the contributions to the energy  $K_{m_j j i}$ .

Therefore, by inserting  $\epsilon_{m_j j i} = K_{m_j j i} + e_j\Phi(\mathbf{r}_{m_j j})$  into Eq.(2) and summing over all energy states of ions, the electrostatic potential energy can be written before the contribution of the sum,

$$q_{m_j j} = q_{m_j j}^0 \exp(-e_j\Phi(\mathbf{r}_{m_j j})/kT), \quad (3)$$

where  $q_{m_j j}^0 = \sum_i \exp(-K_{m_j j i}/kT)$ ,  $m_j = 1, 2, \dots, N_j$ ,  $j = 0, 1, 2, \dots, M$ .

The solution of the chosen cell is a system with a constant volume  $V^c$ , constant temperature  $T$  and constant number of particles of all species  $N_j$ ,  $j = 0, 1, 2, \dots, M$ . It is assumed that the particle-particle correlations are described by the effect of the mean electrostatic field and by the excluded volume effect so that the particles in the cell are explicitly considered to be independent. The particles of the  $j$ -th species are considered to be equal with respect to all energy states  $K_{m_j j i}$ ,  $q_{m_j j}^0 = q_j^0$ ,  $m_j = 1, 2, \dots, N_j$ ,  $j = 0, 1, \dots, M$ , where  $q_j^0$  is the particle partition function due to nonelectrostatic interactions. Further, it is assumed that the solution in the cell is in thermodynamic equilibrium. Taking into account all possible nonequivalent distributions of particles in the cell, the canonical partition function of the cell  $Q^c$  can be written as [12]

$$Q^c = \left( \prod_{j=0}^M \prod_{m_j=1}^{N_j} q_{m_j j} \right) \frac{N_s^c!}{\left( \prod_{j=0}^M N_j! \right)}. \quad (4)$$

All possible nonequivalent distributions of the particles in the single cell are taken into account by the factor  $N_s^c! / \prod_{j=0}^M N_j!$ . Using Eq. (3), the canonical partition function  $Q^c$  becomes

$$Q^c = \exp\left(-\frac{\Delta W^{\text{el}}}{kT}\right) \left( \prod_{j=0}^M (q_j^0)^{N_j} \right) \frac{N_s^c!}{\left( \prod_{j=0}^M N_j! \right)}, \quad (5)$$

where

$$\Delta W^{\text{el}} = \sum_k e_k \Phi(\mathbf{r}_k). \quad (6)$$

The summation is performed over all ions in the cell.

The expression for the free energy of the solution in the cell can be obtained from the statistical mechanical relation  $\Delta F = -kT \ln Q^c$  [12],

$$\Delta F = \Delta W^{\text{el}} + kT \left( \sum_{j=0}^M n_j \ln \frac{n_j}{n_s q_j^0} \right) A\Delta x. \quad (7)$$

The Stirling approximation for large  $N_j$  was used while the density of the number of particles of the  $j$ -th species  $n_j$ ,  $j = 0, 1, \dots, M$  and the density of the number of sites  $n_s$  were introduced  $N_j = n_j A\Delta x$  and  $N_s^c = n_s A\Delta x$ .

Eq. (7) represents the free energy of the chosen cell. To obtain the free energy of the whole system, we sum up contributions of all the cells, i.e. perform the integration over the extension of the system in the direction perpendicular to the charged plane. For the upper bound we take the distance  $d$  where the influence of the charged plane can no longer be perceived. The expression for the electric potential energy of the system is calculated by taking into account that the potential at the site of a given ion is created by all other ions and the charged plane. We consider ions in the solution distributed with volume charge density  $\varrho_e(\mathbf{r})$  so that expression (6) can be transformed into  $W^{\text{el}} = \frac{1}{2}\epsilon\epsilon_0 \int_0^d E^2(x)Adx$ . Here,  $\epsilon$  is the permittivity of the solution,  $\epsilon_0$  is the influence constant and  $E$  is the electric field strength.

For the free energy of the whole system, subject to the local thermodynamic equilibrium, we therefore get

$$F = \int_0^d \left( \frac{1}{2}\epsilon\epsilon_0 E^2(x) + kT \sum_{j=0}^M n_j(x) \ln \frac{n_j(x)}{n_s q_j^0} \right) Adx. \quad (8)$$

## 2.2 Minimization of the free energy, the equilibrium distribution functions and the differential equation for the electric potential

The particle distribution functions  $n_j$ ,  $j = 0, 1, \dots, M$  and the electric field are in general not known. In the following, explicit expressions for the functions  $n_j(x)$ ,  $j = 0, 1, \dots, M$  and  $E(x)$  are obtained by using the condition for the free energy to be at its minimum in the thermodynamic equilibrium of the whole system. The free energy can be expressed by means of a functional  $L$ , that depends on the electric field strength  $E(x)$ , and the densities of the  $j$ -th species  $\mathbf{n}_j(x) = (n_0, n_1, \dots, n_M)$ ,

$$F = \int_0^d L(E(x), \mathbf{n}_j(x)) Adx, \quad (9)$$

where

$$L(E(x), \mathbf{n}_j(x)) = \frac{1}{2}\epsilon\epsilon_0 E^2(x) + kT \left( \sum_{j=0}^M n_j(x) \ln \frac{n_j(x)}{n_s q_j^0} \right). \quad (10)$$

The condition for the global equilibrium  $\delta F = 0$  is subject to a global constraint requiring that

- the total number of the particles of each species is constant

$$\int_0^d (n_j(x) - \Lambda_j) Adx = 0, \quad j = 0, 1, 2, \dots, M, \quad (11)$$

and two local constraints requiring

- the validity of the Gauss law at any  $x$

$$\epsilon\epsilon_0 \frac{\partial E}{\partial x} - e_0 \sum_{j=1}^M v_j n_j(x) = 0, \quad (12)$$

- and that all of the lattice sites are occupied

$$n_s - \sum_{j=0}^M n_j(x) = 0. \quad (13)$$

The valency of the ion of the  $j$ -th species is denoted by  $v_j$ ,  $j = 1, 2, \dots, M$ .

To find the extremum of the functional (9) taking into account the constraints (11)-(13), the method of undetermined multipliers [13] is used. The function  $L^*(x)$  is constructed,

$$\begin{aligned} L^*(E(x), \mathbf{n}_j(x), \frac{\partial E(x)}{\partial x}, \eta_1(x), \eta_2(x)) &= \\ &= L(E(x), \mathbf{n}_j(x)) + \sum_{j=0}^M \lambda_j (n_j(x) - \Lambda_j) - \\ &- \eta_1(x) \left( \epsilon\epsilon_0 \frac{\partial E}{\partial x} - e_0 \sum_{j=1}^M v_j n_j(x) \right) + \\ &+ \eta_2(x) \left( n_s - \sum_{j=0}^M n_j(x) \right), \end{aligned} \quad (14)$$

and examined for the extrema. Here,  $\lambda_j$ ,  $j = 0, 1, \dots, M$  are the global Lagrange multipliers, while  $\eta_1(x)$  and  $\eta_2(x)$  are the local Lagrange multipliers. The variation is performed by solving a system of Euler equations

$$\frac{\partial L^*}{\partial E} - \frac{d}{dx} \left( \frac{\partial L^*}{\partial (\frac{\partial E}{\partial x})} \right) = 0, \quad (15)$$

$$\frac{\partial L^*}{\partial n_j} = 0, \quad j = 0, 1, 2, \dots, M, \quad (16)$$

The first boundary condition is given by the Gauss law applied in the vicinity of the charged plane, while the second boundary condition states that the electric field far away from the charged plane is zero. Eqs. (15) and (16) and boundary conditions give after some calculation the particle distribution functions

$$n_j(x) = \frac{n_s (n_{jd}/n_{0d}) \exp(-v_j e_0 \Phi(x)/kT)}{1 + \sum_{i=1}^M (n_{id}/n_{0d}) \exp(-v_i e_0 \Phi(x)/kT)} \quad j = 0, 1, 2, \dots, M \quad (17)$$

and the differential equation for  $\Phi(x)$

$$\frac{d^2\Phi(x)}{dx^2} = \frac{-e_0 n_s}{\epsilon\epsilon_0} \cdot \frac{\left(\sum_{i=1}^M v_i (n_{id}/n_{0d}) \exp(-v_i e_0 \Phi(x)/kT)\right)}{\left(1 + \sum_{i=1}^M (n_{id}/n_{0d}) \exp(-v_i e_0 \Phi(x)/kT)\right)}, \quad (18)$$

where  $n_{jd}$  is the density of the number of particles of the  $j$ -th species at  $x = d$ . The local Lagrange multipliers are

$$\eta_1(x) = \Phi(x), \quad (19)$$

$$\begin{aligned} \eta_2(x) &= kT \left( \ln \frac{n_0}{n_s q_0^0} + 1 + \frac{\lambda_0}{kT} \right) = \\ &= kT \left( \ln \frac{n_j}{n_s q_j^0} + 1 + \frac{\lambda_j}{kT} \right) + e_0 v_j \Phi(x), \end{aligned}$$

$$j = 1, 2, \dots, M. \quad (20)$$

The local Lagrange multiplier  $\eta_1(x)$  is equal to the electrostatic potential.

The chemical potential for the  $j$ -th species of ions can be calculated from the relation [12]

$$\mu_j = -kT \frac{\partial \ln Q^c}{\partial N_j} \Big|_{T, N_{j \neq i}, V}. \quad (21)$$

After some calculation we obtain the chemical potential of the particles of the  $j$ -th species of the ions

$$\mu_j = kT \ln \frac{n_{jd}}{n_{0d}}, \quad j = 1, 2, \dots, M. \quad (22)$$

To obtain the equilibrium free energy of the ionic solution in contact with the charged plane  $F$ , the requirement of the thermodynamic equilibrium of the whole system is taken into account by inserting the equilibrium distribution function (17) into Eq. (8). The constraint (11) regarding the density of the number of the particles is considered. After some rearranging we obtain

$$\begin{aligned} F &= W^{\text{el}} + kT \int_0^d \left( - \sum_{j=1}^M n_j v_j \frac{e_0 \Phi(x)}{kT} \right. \\ &+ n_s \ln \left( \frac{1}{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}} \exp(-v_j e_0 \Phi(x)/kT)} \right) \Big) Adx + \\ &+ kT \sum_{j=0}^M \Lambda_j Ad \cdot \ln \left( \frac{n_{jd}}{q_j^0 n_{0d}} \right). \end{aligned} \quad (23)$$

The equilibrium electrostatic free energy of the electric double layer is defined as the difference between the free energy of the system under consideration  $F$  and the free energy of the reference system  $F^{\text{ref}}$

$$F^{\text{el}} = F - F^{\text{ref}}. \quad (24)$$

In the reference system of the same extension  $d$  as the system under consideration, there is no electric field while  $\Phi = 0$ . If the electric double layer is very large, it can be taken that the total number of the particles of  $j$ -th species per volume of the original system ( $\Lambda_j$ ) is equal to the total number of the particles of  $j$ -th species per volume of the reference system.

To obtain free energy of the reference system, we insert for the electrostatic potential  $\Phi = 0$  into Eq. (23). Thereby, the first term and the second term vanish to give

$$\begin{aligned} F^{\text{ref}} &= kT \int_0^d \left( n_s \ln \frac{1}{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}}} \right) Adx + \\ &+ kT \sum_{j=0}^M \Lambda_j Ad \cdot \ln \left( \frac{n_{jd}}{q_j^0 n_{0d}} \right). \end{aligned} \quad (25)$$

Taking the difference between the expressions (23) and (25) and inserting  $\sum_{j=1}^M v_j n_j(x)$  from (12), we get the equilibrium electrostatic free energy of the electric double layer

$$\begin{aligned} F^{\text{el}} &= W^{\text{el}} + \int_0^d \left( \epsilon\epsilon_0 \frac{d^2\Phi}{dx^2} \Phi(x) + kT n_s \cdot \right. \\ &\cdot \ln \left( \frac{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}}}{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}} \exp(-v_j e_0 \Phi(x)/kT)} \right) \Big) Adx. \end{aligned} \quad (26)$$

The contribution  $\int_0^d kT n_s \ln(1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}}) Adx$  in Eq. (26) originates from the reference system. The energy of the electrostatic field  $W^{\text{el}}$  represents the strength and the distribution of the electrostatic field in the system while the entropic contribution, *i.e.* the last two terms in Eq. (26), express the distribution of particles under the influence of the electrostatic field, the excluded volume effect and thermic motion of particles.

If we want to calculate  $F^{\text{el}}$ , the dependence of the electrostatic potential on the distance from the charged plane  $\Phi(x)$  should be known. This is obtained by solving the differential equation (18).

### 3 Discussion and conclusion

We used the canonical ensemble lattice statistics to derive the particle distribution functions, differential equation for the electric potential and the free energy of the electric double layer. The local and the global constraints were considered by the corresponding terms in the Lagrange function subject to the variational problem. In minimization of the free energy we used the method of undetermined multipliers. The presented derivation offers a consistent and transparent way to incorporate the same basic predictions into the distribution functions, the electric potential and the free energy.

We have used the canonical ensemble to represent the system. The canonical statistics requires a fixed num-

ber of the particles of all species in every cell composing the solution although in reality the particles are free to move over the solution. Fluctuations of the densities of the particles and of the volume can in general be non-negligible thus making the choice of the ensemble important [12, 14]. In our model the volume fluctuations are forbidden due to the lattice while the fluctuations of the number of the particles are negligible as we are describing the equilibrium state [12].

Using the canonical ensemble yields the chemical potential of the particles. The condition of the chemical potential equality is equivalent to the condition of the minimal free energy of the system and may sometimes be more convenient. It is interesting to note that the local Lagrange multiplier subject to the constraint expressing the Gauss law  $\eta_1(x)$  is shown to be the electric potential (19).

Employing two derivations, a systematic path integral approach, where the ions were put on a discrete lattice, and a phenomenological free energy formulation, where the excluded volume effect was introduced through the entropy of the solvent, Borukhov et al. [9] also obtained the same expressions for the distribution functions, for the differential equation for the electrostatic field and for the chemical potential as the ones presented in this work. Their formalism is however less general than ours as it does not apply to an arbitrary choice of the valencies of the counterion and coion combinations within the condition  $\sum_{j=1}^M v_j n_{jd} = 0$ . There is also a slight difference in the respective expressions for the free energy. Our contribution to the free energy  $\int_0^d kT n_s \ln(1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}}) Adx$  that originates from the reference system does not appear in [9] where the reference system is not explicitly defined.

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**Klemen Bohinc** received his M. Sc. degree in physics in 1998 and Ph. D. degree in electrical engineering in 2001.

**Aleš Iglič** received his Ph. D. degree in physics in 1995 and Ph. D. degree in electrical engineering in 1996. He is an assistant professor at the Faculty of Electrical Engineering in Ljubljana.

**Tomaž Slivnik** received his Ph. D. degree in electrical engineering in 1975. He is a professor at the Faculty of Electrical Engineering in Ljubljana.

**Veronika Kralj-Iglič** received her Ph. D. degree in physics in 1993. She is an assistant professor at the Faculty of Medicine in Ljubljana.