A Simple Statistical Mechanical Approach to the Free Energy of the Electric Double Layer Including the Excluded Volume Effect

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Abstract. — A simple analytic statistical mechanical approach is applied to derive an expression for the free energy of a single electric double layer. Electrostatic interactions are considered by means of the mean electrostatic field while the finite size of particles constituting the electrolyte solution is considered by including the excluded volume effect. The calculated free energy of an univalent electrolyte is compared to the corresponding free energy obtained by the Poisson-Boltzmann theory. It is shown that the excluded volume effect considerably increases the energy of the electrostatic field while the corresponding decrease of the entropic contribution is less pronounced. As the entropic contribution is larger than the energy of the electrostatic field and as the effects on both contributions partially cancel, the free energy obtained by the Poisson-Boltzmann theory is an excellent approximation regarding to the excluded volume effect.

1. Introduction

If the electrolyte solution is in contact with the charged plane, counterions are accumulated near the plane and coions are depleted from this region, thereby creating a diffuse electric double layer. The electric double layer is used to describe the electrostatics of liquid crystals, cellular membranes, phospholipid bilayers and metals in contact with the electrolyte solution.

The simplest description of the electric double layer is obtained by the Poisson-Boltzmann theory [1,2] and its extensions such as the Stern-Gouy-Chapman model [3] which introduces the distance of closest approach of the ions to the charged plane. Within these theories ions are considered to be dimensionless point charges, surface charge is considered to be uniformly smeared over the plane, the electrolyte solution is described as a continuum with uniform dielectric constant, the potential of mean force is taken to be the mean electrostatic potential originating from charges of ions and the charged surface while direct ion-ion interactions are neglected. A quantity which is also of interest and is the scope of this work is the free energy of the system. The free energy is used to describe the interaction of the two electric double layers [4,5], and phase transitions of the lipid molecules [6]. Within the Poisson-Boltzmann theory electrostatic free energy of the electric double layer has been derived from thermodynamic

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grounds, applying either charging process or temperature integration of the energy of the electric field or by summing the energy of the electric field and the entropic contribution, all three expressions being equivalent [5].

In order to surmount the Poisson-Boltzmann theory, finite size of ions, image effects, direct interactions between ions, solvent structure and interactions, and discreteness of charge forming the charged plane were included in the description of the electric double layer. A statistical mechanical approach was initiated basing on the expression for a molecular Hamiltonian [7–9]. The theories of nonuniform fluids and of the bulk electrolytes were extended to the double layer problem resulting in the development of the modified Poisson-Boltzmann theory [10–12], cluster expansion theory of the double layer [13] and integral equation theories [14–17].

Comparison of theoretical predictions with computer simulations [18–29] indicates that the Poisson-Boltzmann theory satisfactorily describes the monotonous ion density and interface potential profiles of univalent electrolyte over a wide range of surface charge and electrolyte concentration [12, 16, 18, 19, 22–24] while oscillatory behavior of the ion concentration profile and charge inversion which may occur in highly charged surfaces, highly charged electrolyte and high electrolyte concentrations [20–22, 24] were explained by applying the theories based on the molecular Hamiltonian [11, 12, 16, 22, 23]. The interaction of the two electric double layers predicted by the Poisson-Boltzmann theory agrees well with the results of the Monte Carlo simulations for dilute univalent electrolyte, large separations and low surface charge [27], while oscillatory effects and attraction between like-charged surfaces which may occur in highly charged surfaces, highly charged electrolyte and high electrolyte concentrations [27, 29, 30] were obtained by integral equation theories [29, 32].

However, the theories based on the molecular Hamiltonian are often given a numerical, little transparent form. Therefore the Poisson-Boltzmann and related formalisms are due to simplicity and transparency still widely used for interpretation of the experimental data, often providing a remarkably good fit [33–37]. Also, it was determined that the Poisson-Boltzmann theory can describe the features of the double layer providing that the fitted parameters are not considered as the real physical parameters [38].

If the surface charge density is high, the counterions accumulate near the surface and the Poisson-Boltzmann theory may there overestimate the counterion concentration to an extent that it becomes unphysical [37]. In this work the corresponding corrections were accounted for by including an excluded volume effect within the electrostatic mean field approach. A simple statistical mechanical procedure is proposed in which the expression for the electrostatic free energy, consistently related to the electostatic potential and to ion and solvent distribution functions, is derived. The origin of individual contributing terms is transparent as the analytical form of the free energy is retained along the derivation. The obtained free energy is compared with the free energy of the Poisson-Boltzmann theory and the conditions for the validity of the latter are studied.

2. Theory

2.1. Minimization of the Free Energy of the Electrolyte Solution in Contact with the Charged Plane.

— A system is described in which a plane at $x = 0$ extending over an area A and bearing at its surface uniformly distributed charge with surface charge density σ is in contact with the electrolyte solution consisting of solvent molecules and M species of ions. The solution occupies a volume bounded by the area A in the $x = 0$ plane and extends in the positive x direction. Boundary effects are neglected. It is taken that the charged plane and the charges of ions in the solution create a mean electrostatic field in the volume occupied by the solution, while on the other side of the charged plane ($x < 0$) the electrostatic

field is zero.

The excluded volume effect is included in the description by requiring that the volume of the whole system is a sum of the volumes of all the constituting particles. Thereby in calculation of the entropy a lattice with an adjustable lattice constant is introduced. All sites in this lattice are occupied.

In deriving the expression for the free energy of the system F subject to the local thermodynamic equilibrium (Appendix A) the methods of statistical mechanics are used [39]. Starting from energies of individual particles and treating the particles as independent and indistinguishable the free energy of the system F is obtained (A.16),

$$F = W^{\text{el}} + kT \int_0^d \left(\sum_{j=0}^{M} n_j(x) \ln \frac{n_j(x)}{n_s q_j^0} \right) A \, dx, \tag{1}$$

where $W^{\text{el}} = \frac{1}{2} \epsilon \epsilon_0 \int_0^d E^2(x) A \, dx$ is the energy of the electrostatic field (A.17), k is the Boltzmann constant, T is the temperature, n_j is the density of the number of particles of the j-th species (A.13), where $j = 0$ denotes solvent molecules and $j = 1, 2, \ldots, M$ ions of the j-th species, n_s is the density of the number of lattice sites (A.14), q_j^0 is the partition function of the particle of the j-th species subject to no electrostatic variable (A.6-A.7), ϵ is the permittivity of the solution, ϵ_0 is the permittivity of the free space and E is the electrostatic field strength. Integrations are performed over the extension of the system in the x direction (d). At the distance d from the charged plane the effects of the charged plane can no longer be perceived by virtue of the screening of its electrostatic field by the counterions.

However, the explicit expressions for the functions $n_j(x)$, $j = 0, 1, 2, \ldots, M$ and $E(x)$ are not known. To derive explicit expressions for these functions, we use the condition for the free energy to be at its minimum in the thermodynamic equilibrium of the whole system, so that

$$\delta F = 0, \tag{2}$$

taking into account the following conditions:

- the conditions that the total number of the particles of each species in the whole system is constant while the variation is performed,

$$\int_0^d n_j(x) A \, dx = \Lambda_j, \quad j = 0, 1, 2, \ldots, M, \tag{3}$$

- the validity of the Gauss law at any x,

$$\epsilon \epsilon_0 \frac{\partial E}{\partial x} = e_0 \sum_{j=1}^{M} v_j n_j(x), \tag{4}$$

  where e_0 is the elementary charge and v_j valence of the ion of the j-th species,

- the condition, that all of the lattice sites are occupied (A.2). Using the density of the number of particles and lattice sites (A.13-A.14), it follows that for any x

$$n_s = \sum_{j=0}^{M} n_j(x). \tag{5}$$

Above isoparametric problem is reduced to the ordinary variational problem by constructing a functional

$$F + \sum_{j=0}^{M} \lambda_j \Lambda_j = \int_0^d L(\mathbf{n}(x), E(x)) A \; \mathrm{d}x, \tag{6}$$

where

$$L(\mathbf{n}(x), E(x)) = \frac{1}{2} \epsilon \epsilon_0 E^2(x) + kT \left(\sum_{j=0}^{M} n_j(x) \ln \frac{n_j(x)}{n_{\mathrm{s}} q_j^0} + \sum_{j=0}^{M} \lambda_j n_j(x) \right), \tag{7}$$

λ_j, $j = 0, 1, 2, \ldots, M$, are the Lagrange multipliers and $\mathbf{n} = (n_0, n_1, \ldots, n_M)$. Eliminating two of the variables from the constraints (4) and (5) the variation is performed by solving a system of Euler equations

$$\frac{\partial L}{\partial n_j} = 0, \quad j = 2, 3, \ldots, M, \tag{8}$$

$$\frac{\partial L}{\partial E} - \frac{\mathrm{d}}{\mathrm{d}x} \left(\frac{\partial L}{\partial \left(\frac{\partial E}{\partial x} \right)} \right) = 0. \tag{9}$$

At the distance d the average charge volume density as well as the mean electrostatic field are zero

$$E_d = - \left. \frac{\mathrm{d}\Phi}{\mathrm{d}x} \right|_d = 0, \tag{10}$$

and the potential Φ_d is constant. We chose

$$\Phi_d = 0. \tag{11}$$

Taking into account the above condition the solution of the system of equations (8) and (9) gives after some calculation the particle distribution functions,

$$n_0(x) = \frac{n_{\mathrm{s}}}{\left(1 + \sum_{i=1}^{M} (n_{id}/n_{0d}) \; \exp(-v_i e_0 \Phi(x)/kT) \right)}, \tag{12}$$

$$n_j(x) = \frac{n_{\mathrm{s}}(n_{jd}/n_{0d}) \; \exp(-v_j e_0 \Phi(x)/kT)}{\left(1 + \sum_{i=1}^{M} (n_{id}/n_{0d}) \; \exp(-v_i e_0 \Phi(x)/kT) \right)}, \quad j = 1, 2, \ldots, M, \tag{13}$$

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

$$\frac{\mathrm{d}^2 \Phi}{\mathrm{d}x^2} = \frac{-e_0 n_{\mathrm{s}} \left(\sum_{j=1}^{M} v_j (n_{jd}/n_{0d}) \; \exp(-e_0 v_j \Phi(x)/kT) \right)}{\epsilon \epsilon_0 \left(1 + \sum_{j=1}^{M} (n_{jd}/n_{0d}) \; \exp(-e_0 v_j \Phi(x)/kT) \right)}, \tag{14}$$

where n_{jd} is the density of number of particles of the j-th species at $x = d$. According to (5) the density of the solvent molecules far from the charged plane is

$$n_{0d} = n_{\mathrm{s}} - \sum_{j=1}^{M} n_{jd}.$$ (15)

In order to obtain the explicit dependencies of n_j, $j = 0, 1, 2, \ldots, M$ and Φ on the distance x, the differential equation (14) subject to the conditions (10) and (11) is solved. The charged plane at $x = 0$ is taken into account by an additional boundary condition at $x = 0$,

$$\left.\frac{\mathrm{d}\Phi}{\mathrm{d}x}\right|_0 = -\frac{\sigma}{\epsilon\epsilon_0}.$$ (16)

2.2. EQUILIBRIUM ELECTROSTATIC FREE ENERGY OF THE ELECTRIC DOUBLE LAYER. —
In order to obtain the electrostatic free energy of the electric double layer a reference system should be defined. The reference system is required to contain the same amount of particles of each species homogeneously distributed over the solution.

In the electric double layer there is an excess of counterions over the coions. If the reference system were chosen to contain the same amount of particles of each species as the electric double layer described hitherto there would still be an electrostatic field in the solution, even if these particles were homogeneously distributed.

It seems therefore appropriate to consider the system to be in contact with a large reservoir for all species of particles corresponding to a bulk phase whose dimensions are much larger than the extension of the electric double layer d. Both, the electric double layer and the reference system are considered to be in contact with such reservoir. Therefore in the reference system the electrostatic field (which is the consequence of the excess of the counterions over the coions) is diminished to an extent which is negligible.

In describing the electric double layer the system and the reservoir are in thermal contact with the surroundings having a constant temperature, so that the temperature of the system and of the reservoir is kept constant as well. There is no mean electrostatic field in the reservoir and all species of particles are distributed uniformly over the reservoir; $n_{j,\mathrm{res}} = n_{jd}$, $j = 0, 1, 2, \ldots, M$, occupying the sites with the number density n_{s}. The solution in the reservoir is described by using the formalism derived in previous sections. Applying the expression for the Helmholtz free energy of the electrolyte solution (1), we obtain free energy of the reservoir

$$F^{\mathrm{res}} = kT \int_{V^{\mathrm{res}}} \sum_{j=0}^{M} n_{jd} \ln \frac{n_{jd}}{n_{\mathrm{s}}q_j^0} \mathrm{d}V,$$ (17)

where V^{res} is the volume of the reservoir.

The system and the reservoir together are referred to as a supersystem [39]. Free energy of the supersystem F^{sp} consists of the contribution of the solution under the influence of the electrostatic field and the contribution of the reservoir,

$$F^{\mathrm{sp}} = F + F^{\mathrm{res}}.$$ (18)

While deriving electrostatic free energy of the system, the requirement of thermodynamic equilibrium of the whole system should be taken into account by inserting the equilibrium distribution functions (12) and (13) and the equilibrium electrostatic potential (obtained by

solving the differential equation (14)) into the expression (1). After some rearranging we obtain

$$
\begin{aligned}
F^{\mathrm{sp}} = W^{\mathrm{el}} + kT \int_0^d \left(-\sum_{j=1}^M n_j v_j e_0 \Phi(x)/kT + n_{\mathrm{s}} \ln \frac{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}}}{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}} \exp(-v_j e_0 \Phi(x)/kT)} \right) A \, \mathrm{d}x \\
+ kT \sum_{j=0}^M N_{jT} \ln \frac{n_{jd}}{n_{\mathrm{s}} q_j^0},
\end{aligned}
\tag{19}
$$

where it is taken into account that the numbers of each of the M species of the particles in the supersystem are constant,

$$
N_{jT} = \int_0^d n_j(x) \, A \, \mathrm{d}x + \int_{V^{\mathrm{res}}} n_{jd} \mathrm{d}V, \quad j = 0, 1, 2, \ldots, M.
\tag{20}
$$

The electrostatic free energy of the electric double layer F^{el} is defined as the difference between the free energy of the supersystem F^{sp} and the free energy of the reference supersystem with the same number of particles of the same species N_{jT}, $j = 0, 1, 2, \ldots, M$, but in which the electrostatic field is negligibly small so that $\Phi = 0$,

$$
F^{\mathrm{el}} = F^{\mathrm{sp}} - F^{\mathrm{sp}}_{\mathrm{ref}}.
\tag{21}
$$

Since the reservoir is taken to be very large, the presence of the electrostatic field causing redistribution of particles in the solution in the original system only negligibly changes the density of the number of particles in the reservoir n_{jd}, $j = 0, 1, 2, \ldots, M$, so that it follows from (19)

$$
F^{\mathrm{sp}}_{\mathrm{ref}} = kT \sum_{j=0}^M N_{jT} \ln \frac{n_{jd}}{n_{\mathrm{s}} q_j^0}.
\tag{22}
$$

By inserting $\sum_{j=1}^M v_j n_j(x)$ from (4) it follows from (19)-(22) that the electrostatic free energy of the solution under the influence of the electrostatic field is

$$
F^{\mathrm{el}} = W^{\mathrm{el}} + F^{\mathrm{ent}} .
\tag{23}
$$

where W^{el} is the energy of the electrostatic field and F^{ent} is the entropic contribution

$$
F^{\mathrm{ent}} = \int_0^d \left(\epsilon \epsilon_0 \frac{\mathrm{d}^2 \Phi}{\mathrm{d}x^2} \Phi(x) + kT n_{\mathrm{s}} \ln \frac{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}}}{1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}} \exp(-v_j e_0 \Phi(x)/kT)} \right) A \, \mathrm{d}x.
\tag{24}
$$

In order to calculate F^{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 (14). Electrostatic free energy F^{el} as well as the particle distribution functions (12) and (13) and the electrostatic potential depend on the density of the number of sites which can be occupied by the particles in the solution n_{s}. Note that the contribution $\int_0^d kT n_{\mathrm{s}} \ln \left(1 + \sum_{j=1}^M \frac{n_{jd}}{n_{0d}} \right) A \mathrm{d}x$

originates from the reference supersystem. It should be emphasized that the choice of the reference state is important for the expression for the free energy. The energy of the electrostatic field W^{el} reflects the strength and the distribution of the electrostatic field in the system while the entropic contribution F^{ent} accounts for the distribution of particles under the influence of the electrostatic field, the excluded volume effect and thermic motion of particles.

2.3. VERY DILUTE ELECTROLYTE SOLUTION IN CONTACT WITH THE CHARGED PLANE. — If it is assumed that the electrolyte solution is very dilute everywhere in the system, i.e. that for any x

$$\sum_{j=1}^{M} n_j(x) \ll n_0(x), \tag{25}$$

the ion distribution functions are obtained from equation (13) by neglecting the sum in the denominator and taking into account the approximation $n_{0d} \cong n_{\text{s}}$, to yield the Boltzmann distribution functions

$$n_j(x) = n_{jd} \exp(-v_j e_0 \Phi(x)/kT), \quad j = 1, 2, \ldots, M. \tag{26}$$

Considering the above condition (25), equation (14) transforms into the Poisson-Boltzmann equation

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} = -\frac{e_0}{\epsilon\epsilon_0} \sum_{j=1}^{M} v_j n_{jd} \exp(-v_j e_0 \Phi(x)/kT). \tag{27}$$

The electrostatic free energy F^{el} is obtained by considering the approximation $\ln(1+x) \cong x$ in the expressions (23, 24),

$$F^{\text{el}} = W^{\text{el}} + \int_0^d \left(\epsilon\epsilon_0 \frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} \Phi(x) - kT \sum_{j=1}^{M} (n_j(x) - n_{jd}) \right) A \,\mathrm{d}x. \tag{28}$$

The term $\int_0^d \sum_{j=1}^{M} kT n_{jd} \, A \,\mathrm{d}x$ in (28) originates from the reference supersystem. In order to calculate F^{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 Poisson-Boltzmann equation (27). The expression (28) is equivalent to the expressions proposed by Marcus [5].

In contrast to expressions for the electrostatic free energy (23, 24), particle distribution functions (12) and (13) and differential equation for the electrostatic potential (14), the corresponding Poisson-Boltzmann expressions (26-28) do not depend on the density of the number of sites n_{s}. This means that in the Poisson-Boltzmann theory the particles in the solution are considered as dimensionless and there is no upper limit of the concentration of particles. It should be kept in mind that this is strictly true only within the assumption (25) that the concentration of ions is very small everywhere in the system. If the surface charge density $|\sigma|$ is high, many counterions are attracted in the vicinity of the charged plane and therefore condition (25) may there be violated even if the concentration of ions far from the charged plane is very low.

2.4. CASE OF UNIVALENT ELECTROLYTE. — A system of univalent electrolyte is considered for illustration. In the solution there are solvent molecules, univalent counterions and univalent coions. Far from the charged plane the density of the number of counterions and the density of the number of coions are equal and are denoted by n_d while the density of the number of solvent molecules is denoted by n_{0d} .
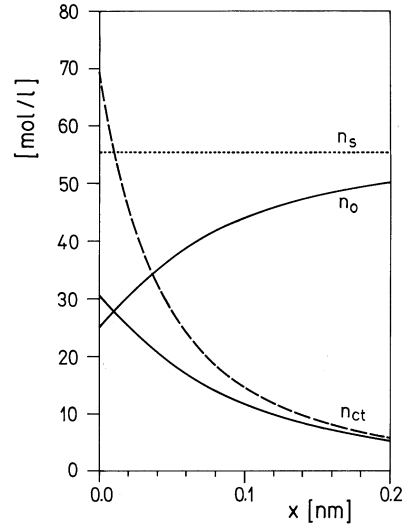
Fig. 1. — Density profile of counterions n_{ct} and of solvent molecules n_0 (full lines) and the corresponding counterion density profile calculated using the Poisson-Boltzmann theory (broken line). The density of number of available lattice sites n_s (calibrated to the concentration of pure water) is marked (dotted line). The values of model parameters are $|\sigma| = 0.4$ As/m^2, $T = 310$ K, $\epsilon = 78.5$, $M_{H_2O} = 18$ kg/kmol, $\rho_{H_2O} = 1000$ kg/m^3 .

The results are compared to the results of the Poisson-Boltzmann theory for univalent electrolyte where it is taken for the sake of simplicity that $d \rightarrow \infty$. This yields analytical expressions for the electrostatic potential and ion density profiles [4] as well as for the electrostatic free energy [6]. The density profiles of the counterions and of the solvent molecules are presented in Figure 1 (full lines). The corresponding density profile of the counterions calculated by using the Poisson-Boltzmann theory is also shown (broken line). Close to the charged plane there is a considerable excluded volume effect on the density profile of the counterions and on the solvent molecules. The concentration of the counterions is there comparable to the concentration of the solvent molecules so that the concentration of the solvent molecules deviates significantly from its value far from the charged plane. By using the Poisson-Boltzmann theory the counterion concentration is higher than the corresponding concentration where the excluded volume effect is considered. It can be noted that in the vicinity of the charged plane the counterion concentration calculated by using the Poisson-Boltzmann theory exceeds the concentration of available lattice sites thereby proving to be unphysical. The corresponding coion density profile attains the values which are due to strong repulsion by the charged plane at least two orders of magnitude smaller in the region considered so that the contribution of the coions to the excluded volume effect is negligible. The deviation of the ion and solvent density profiles as well as of the electrostatic field from the Poisson-Boltzmann theory can therefore be attributed mainly to steric effect of counterions and solvent molecules in a small region in the vicinity of the charged plane.

It can be seen in Figure 1 that the counterions which are accumulated near the charged plane strongly screen its electrostatic field. The screening can be described by introducing the effective thickness of the electric double layer $x_{1/2}$, which is the distance where the density of the number of counterions n_{ct} (calculated relative to its value far from the charged plane n_d)

drops to one half of its value at $x = 0$,

$$n_{\text{ct}}(x_{1/2}) - n_d = (n_{\text{ct}}(0) - n_d)/2, \tag{29}$$

where $n_{\text{ct}}(0)$ is density of the number of counterions at $x = 0$. The electrostatic free energy is calculated according to the expressions (23, 24),

$$F^{\text{el}} = W^{\text{el}} + \int_0^d \left(\epsilon \epsilon_0 \frac{\mathrm{d}^2 \Phi}{\mathrm{d}x^2} \Phi(x) + kT n_{\text{s}} \ln \left(\frac{1 + (2n_d/n_{0d})}{1 + (2n_d/n_{0d}) \cosh(e_0 \Phi/kT)} \right) \right) \ A \ \mathrm{d}x. \tag{30}$$

while the electrostatic potential is calculated by solving the differential equation

$$\frac{\mathrm{d}^2 \Phi}{\mathrm{d}x^2} = \frac{2e_0 n_{\text{s}} n_d \sinh(e_0 \Phi(x)/kT)}{\epsilon \epsilon_0 n_{0d} \left(1 + 2n_d/n_{0d} \cosh(e_0 \Phi(x)/kT) \right)}, \tag{31}$$

where according to (15)

$$n_{0d} = n_{\text{s}} - 2n_d. \tag{32}$$

Equation (31) is solved numerically using the Runge Kutta method, while the integration of F^{el} (Eq. (30)) is performed numerically by using the Simpson method. The extension of the system in the x direction d had been determined by the condition that its twofold increase did not increase the value of F^{el} beyond the prescribed error. The density of the number of sites n_{s} was determined by the concentration of pure water $n_{\text{s}} = \rho_{\text{w}} N_{\text{A}}/M_{\text{H}_2\text{O}}$, where ρ_{w} is the density of water, $M_{\text{H}_2\text{O}}$ is molar mass of water molecules and N_{A} is the Avogadro number.

Within the Poisson-Boltzmann theory the effective thickness of the electric double layer can be obtained analytically

$$x_{1/2} = \frac{1}{\kappa} \ln \left(\frac{(\sqrt{(1 + \exp(-e_0 \Phi(0)/kT))/2} + 1)(1 - \exp(e_0 \Phi(0)/2kT))}{(\sqrt{(1 + \exp(-e_0 \Phi(0)/kT))/2} - 1)(1 + \exp(e_0 \Phi(0)/2kT))} \right). \tag{33}$$

where $1/\kappa$ is the Debye length

$$\kappa = \sqrt{\frac{2n_d N_{\text{A}} e_0^2}{\epsilon \epsilon_0 kT}}, \tag{34}$$

$$\Phi(0) = -\frac{2kT}{e_0} \ln \left(\sqrt{1 + (|\sigma|/c)^2} + |\sigma|/c \right), \tag{35}$$

$$c = 8kT \epsilon \epsilon_0 N_{\text{A}} n_d. \tag{36}$$

The effective thickness of the electric double layer $x_{1/2}$ in dependence on the absolute value of the charge area density of the $x = 0$ plane $|\sigma|$ is shown in Figure 2 (full line). The corresponding dependence of $x_{1/2}$ on $|\sigma|$, calculated by using the Poisson-Boltzmann theory is also shown (broken line). Both curves are decreasing for small $|\sigma|$ since the plane bearing higher charge attracts in its vicinity larger number of counterions and the screening is therefore more effective.

Within the presented theory where the excluded volume effect is taken into account, the thickness of the diffuse layer is increased with respect to the Poisson-Boltzmann case. However, the excluded volume imposes an upper limit on the density of the number of counterions, which becomes especially significant near the charged plane where counterions are accumulated (Fig. 1). This imposes a limit also on the screening of the electrostatic field. As more counterions are attracted near the charged plane with further increase of $|\sigma|$, the influence of the excluded volume effect increases with increasing $|\sigma|$, so that $x_{1/2}$, after reaching its minimal value, begins to increase with increasing $|\sigma|$ (Fig. 2). In the Poisson-Boltzmann model, there
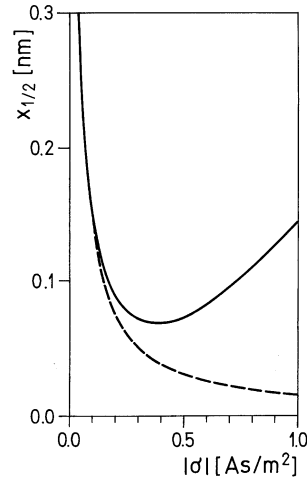
Fig. 2. — The effective thickness of the electric double layer $x_{1/2}$ in dependence on the absolute value of the charge area density of the $x = 0$ plane $|\sigma|$ for $n_d = 0.1$ mol/l considering the excluded volume effect (full line) and the corresponding dependence calculated using the Poisson-Boltzmann theory (broken line). The values of other parameters are the same as in Figure 1.

is no upper limit of the density of the number of ions and there is a monotonous decrease of $x_{1/2}$ with the increase of $|\sigma|$. For high values of $|\sigma|$ the use of Poisson-Boltzmann theory for calculating the ion concentration profile is not justified. Namely, the condition (25) is not fulfilled in the vicinity of the charged plane.

It can also be seen in Figure 2 that $x_{1/2}$ using both models are very small meaning that the behavior far from the charged plane is almost insensitive to the details near the charged plane. The way the counterions electrostatically condense near the charged plane (with or without the finite volume constraint) does not affect the effective potential far from the surface. This can be also seen in Figure 1 where the difference in counterion density profiles calculated with both models rapidly decreases.

Figure 3 shows the electrostatic free energy F^{el} (a) and both contributions to F^{el} : energy of the electrostatic field W^{el} and the entropic contribution F^{ent} (b) in dependence on the absolute value of the charge area density of the $x = 0$ plane $|\sigma|$ (full lines). The corresponding dependencies calculated by using the Poisson-Boltzmann theory are also shown (broken lines). All the curves are increasing with increasing $|\sigma|$ as electrostatic field in the system is stronger if $|\sigma|$ is higher. Since the screening of the electric field is less effective when the excluded volume effect is taken into account, the field protrudes further into the solution and the energy of the electrostatic field W^{el} is higher than the corresponding energy calculated by using the Poisson-Boltzmann theory. The entropic contribution F^{ent} reflects rearranging of ions in the solution. When the excluded volume effect is considered, the rearrangement of ions is extended further into the solution as the electrostatic field extends further into the solution. However, the rearrangement of the ions near the charged plane is much less pronounced than in the Poisson-Boltzmann model, where the concentration of counterions is much higher in the vicinity of the charged plane, the latter effect prevailing. The excluded volume effect on W^{el} is therefore contrary to this effect on F^{ent}, so that the effect on the free energy of the electric double layer F^{el} (which is the sum of W^{el} and F^{ent}) partly cancels itself (Fig. 3a).
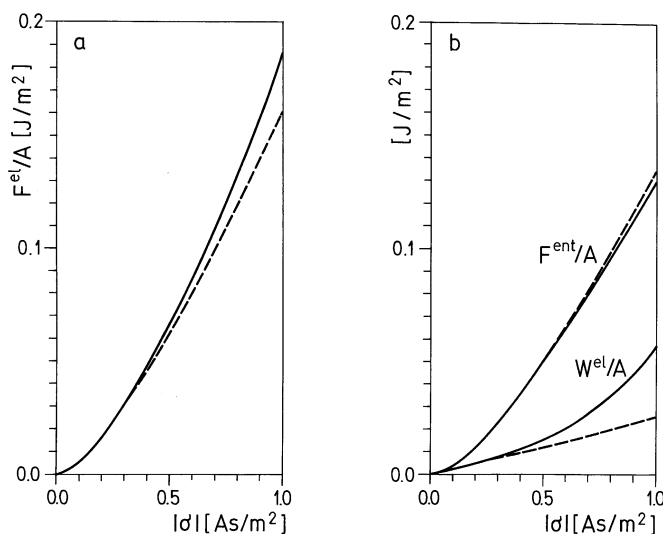
Fig. 3. — The electrostatic free energy of electric double layer $F^{\mathrm{el}} = W^{\mathrm{el}} + F^{\mathrm{ent}}$ (a) and both contributions: energy of the electrostatic field W^{el} and the entropic contribution F^{ent} (b) calculated per unit area in dependence on the absolute value of the charge area density of the $x = 0$ plane $|\sigma|$ for $n_d = 0.1$ mol/l considering the excluded volume effect (full lines). The corresponding dependencies calculated by using the Poisson-Boltzmann theory are also shown (broken lines). The values of other parameters are the same as in Figure 1.

3. Conclusions

The procedure is derived starting with the energies of individual particles and yielding expressions for particle distribution functions, differential equation for the electrostatic potential and free energy of the system. The energies of the individual particles are therefore incorporated in these expressions in a consistent way. The origin of individual terms in the expression of the free energy is elucidated. In order to do this the reference state with respect to which the free energy is calculated is introduced. The choice of the reference state proves to be important since some terms in the expression for the free energy originate from this reference state.

It was shown before on different levels why in some cases the Poisson-Boltzmann theory and its modifications work so well in predicting the ion concentration profile [31, 34, 38, 40]. Our analysis shows that the electrostatic field is stronger and protrudes further into the solution if the excluded volume effect is included. The electrostatic field causes redistribution of ions and solvent molecules which is also extended further into the solution. On the other hand, the redistribution of counterions very close to the charged plane is more pronounced in the Poisson-Boltzmann theory. Due to superposition of these effects and due to the fact that the excluded volume affects only a small region near the charged plane we can also establish that regarding the excluded volume effect the free energy for univalent electrolyte calculated with the Poisson-Boltzmann theory is an excellent approximation in a rather large interval of the values of surface charge density, even beyond the validity of the requirement that the concentration of ions in the solution should be very low everywhere in the system. However, as $|\sigma|$ increases, the significance of the excluded volume effect increases.

Appendix A

Free Energy of the Electrolyte Solution in Contact with the Charged Plane

Assuming local thermodynamic equilibrium and taking into account energies of the individual particles in the solution the expression for the free energy within the mean field approximation is derived.

The system is divided into cells of equal volume,

$$V^{\mathrm{c}} = A\,\Delta x \tag{A.1}$$

where Δx is the dimension of the cell in the x direction. It is assumed, that Δx is small comparing to the distance over which macroscopic properties of the system change appreciably.

In the particular cell chosen, there are N_0 solvent molecules and N_j ions of j-th species, $j = 1, 2, ..., M$. The excluded volume effect is included in the description so that the particles are distributed over $N_{\mathrm{s}}^{\mathrm{c}}$ sites of equal volume in the cell, all sites being occupied,

$$\sum_{j=0}^{M} N_j = N_{\mathrm{s}}^{\mathrm{c}}. \tag{A.2}$$

In accordance to (A.2) the volume of the cell is proportional to the number of the sites $N_{\mathrm{s}}^{\mathrm{c}}$. It is also assumed, that the volume of the particles is conserved while the particles mix.

The solution in the cell is described using the methods of statistical mechanics [39]. The particle partition function q of the m_j-th particle of the j-th species is

$$q_{m_j j} = \sum_i \exp\left(-\varepsilon_{m_j j i}/kT\right), \quad m_j = 1, 2, \ldots, N_j, \quad j = 0, 1, 2, \ldots, M, \tag{A.3}$$

where k is the Boltzmann constant and T is the temperature. Index i runs through all possible energy states of the m_j-th particle $\varepsilon_{m_j j i}$.

Since an individual ion is charged, there is a contribution of its electrostatic potential energy to the energy of the given state,

$$\varepsilon_{m_j j i} = K_{m_j j i} + e_j \left(\Phi(\mathbf{r}_{m_j j}) - \Phi_{\mathrm{ref}}\right), \quad m_j = 1, 2, \ldots, N_j, \quad j = 1, 2, \ldots, M, \tag{A.4}$$

where e_j is the charge of the ion of the j-th species, $\Phi(\mathbf{r}_{m_j j})$ the potential of the electrostatic field, $e_j \left(\Phi(\mathbf{r}_{m_j j}) - \Phi_{\mathrm{ref}}\right)$ the electrostatic potential energy of the ion situated at $\mathbf{r}_{m_j j}$, and $K_{m_j j i}$ all other contributions to the energy of a given state. The electrostatic potential energy of the ion is calculated relative to the reference potential energy $e_j \Phi_{\mathrm{ref}}$. In the reference system chosen the ions are infinitely distant apart so that the electrostatic field in this case vanishes and its potential is constant. We chose $\Phi_{\mathrm{ref}} = 0$.

It is assumed, that the electrostatic field in the system does not influence the contributions to the energy $K_{m_j j i}$. Therefore, by inserting (A.4) into (A.3) and summing over all energy states of ions, the electrostatic potential energy can therefore be written before the sum,

$$q_{m_j j} = q_{m_j j}^0 \exp\left(-e_j \Phi(\mathbf{r}_{m_j j})/kT\right), \tag{A.5}$$

where

$$q_{m_j j}^0 = \sum_i \exp\left(-K_{m_j ji}/kT\right), \quad m_j = 1, 2, \ldots, N_j, \quad j = 1, 2, \ldots, M. \tag{A.6}$$

Partition function of the solvent molecule is

$$q_{m_0 0} = q_{m_0 0}^0 = \sum_i \exp\left(-K_{m_0 0i}/kT\right), \quad m_0 = 1, 2, \ldots, N_0. \tag{A.7}$$

The solution in the chosen cell is considered to be a system with the constant volume V_s^c and constant number of all species of particles $N_0, N_1, N_2, \ldots, N_M$, which is immersed in a heat bath, so that its temperature T is constant. Since it is assumed, that the particle-particle correlations are described through effect of the mean electrostatic field and the excluded volume effect, the particles in the cell are explicitly considered to be independent. The particles of a chosen species are also considered to be equal with respect to all energy states $K_{m_j ji}$,

$$q_{m_j j}^0 \equiv q_j^0, \quad m_j = 1, 2, \ldots, N_j, \quad j = 0, 1, 2, \ldots, M \tag{A.8}$$

and indistinguishable. Assuming that the system is in the "local" thermodynamic equilibrium and taking into account all possible nonequivalent distributions of the particles in the cell, the canonical partition function of the cell is

$$Q^c(V^c, \mathbf{N}, T) = \left(\prod_{j=0}^{M} (q_j)^{N_j}\right) \frac{N_s^c!}{\left(\prod_{j=0}^{M} N_j!\right)}, \tag{A.9}$$

where $\mathbf{N} = (N_0, N_1, N_2, \ldots, N_M)$. Using (A.5)-(A.8), equation (A.9) can be written as

$$Q^c(V^c, \mathbf{N}, T) = \exp\left(-\Delta W^{el}/kT\right) \prod_{j=0}^{M} (q_j^0)^{N_j} \frac{N_s^c!}{\left(\prod_{j=0}^{M} N_j!\right)}, \tag{A.10}$$

where

$$\Delta W^{el} = \sum_l e_l \Phi(\mathbf{r}_l), \tag{A.11}$$

summing over all ions (of all the species) in the cell.

Knowing the canonical partition function Q^c, we obtain the Helmholtz free energy of the solution in the chosen cell ΔF,

$$\Delta F = -kT \ln Q^c. \tag{A.12}$$

Inserting (A.10) into (A.12), using (A.1) and (A.2), applying the Stirling approximation and introducing the density of the number of particles of the j-th species n_j as well as the density of the number of sites n_s,

$$n_j = \frac{N_j}{V^c}, \quad j = 0, 1, 2, \ldots, M, \tag{A.13}$$

$$n_s = \frac{N_s^c}{V^c}, \tag{A.14}$$

we obtain

$$\Delta F = \Delta W^{\mathrm{el}} + kT \sum_{j=0}^{M} n_j \ln \frac{n_j}{n_{\mathrm{s}} q_j^0} A \, \Delta x. \tag{A.15}$$

Equation (A.15) gives the expression for the Helmholtz free energy of the solution in the chosen cell, where the densities of the number of ions are functions of position, i.e. $n_j = n_j(x)$, $j = 0, 1, 2, \ldots, M$.

The contributions of all the cells which constitute the system are summed, i.e. the integration over the extension of the system d is performed to obtain the free energy in the mean field approximation

$$F = W^{\mathrm{el}} + kT \int_0^d \left(\sum_{j=0}^{M} n_j(x) \ln \frac{n_j(x)}{n_{\mathrm{s}} q_j^0} \right) A \, \mathrm{d}x. \tag{A.16}$$

While calculating W^{el}, it is taken into account that the potential at the site of a given ion is created by all other ions and the charged plane as well. The ions are assumed to be immersed in a medium with permittivity ϵ. To avoid the problem regarding to the infinite self energy of point charges, we consider ions in the solution distributed with volume charge density $\rho_{\mathrm{e}}(\mathbf{r})$ so that expression (A.11) can be transformed into

$$W^{\mathrm{el}} = \frac{1}{2} \epsilon \epsilon_0 \int_0^d E^2(x) A \, \mathrm{d}x, \tag{A.17}$$

where ϵ_0 is the permittivity of the free space and E is the electric field strength. Thus the free energy of the system expressed by (A.16) includes interactions of ions with the mean electrostatic field due to all the charges in the system and the entropy of mixing of all the particles in the system.

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