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Diffuse electric double layer in planar nanostructures due to Fermi-Dirac statistics

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ABSTRACT

A double nanocapacitor modelled by two equally charged planar surfaces that confine oppositely charged quanta subjected to Fermi-Dirac statistics is considered theoretically. A global thermodynamic equilibrium was found by minimization of the Helmholtz free energy satisfying constraints that require electroneutrality and fixed total number of confined quanta. The solution obtained by using the Euler–Lagrange method yields self–consistent quantities: distribution of quanta within the pore, electric potential, equilibrium free energy and differential capacitance. Within real values, a rigorous numerical solution and an approximate analytical solution for electrons in the low temperature limit was found. The Fermi–Dirac constraints on the wave functions in the nanopore induced an effect of a diffuse electrical double layer near both charged surfaces. This effect is comparable to the corresponding effect of entropy at finite temperatures and for classical particles, as described by the acknowledged Poisson–Boltzmann theory. At small distances and small surface charges, the electrons are almost evenly distributed within the pore, while at larger distances they condense to the charged surfaces, shielding the electric field. The force between the charged surfaces is repulsive and monotonously decreases with increasing distance between surfaces. The energies stored in the nanocapacitor are up to $\simeq 50\,\mathrm{eV/nm^2}$.

1. Introduction

The electric double layer (EDL) is a crucial phenomenon in many technological and biological applications. Primarily of interest in electrochemistry, the EDL has found use in understanding the interactions of biological membranes [1,2], while in recent years EDL also plays a pivotal role in energy storage technologies. Electrochemical nanocapacitors manufactured with nanoporous materials and a variety of electrolytes are yielding increasing energy and power densities, bridging the gap between batteries and classic capacitors [3–5]. Electric double layer nanocapacitors were composed from multiple layered (separated by a nanometer distance) carbon nanotubes in contact with electrolyte [6]. It was indicated that electrochemical double layer capacitors can store large amounts of energy and deliver high peak power [6].

It was found already a century ago that the capacitance of a system formed by the charged surface and an oppositely charged diffuse layer varies with electrolyte properties, its concentration, applied potential and charge on the surfaces [7,8]. Since then, the EDL theory was constantly advancing, incorporating ever novel ways of modelling [9]. One of the first things taken into account were steric effects induced by the finite sizes of ions [10–12], while later models include the dipole nature of water in the electrolyte solution leading to a coordinate-dependent dielectric permittivity [13,14]. Some models investigated a shift in the capacitance curve due to the asymmetric sizes of ions [15] and others considered the electron wave functions in the electrode interface [16].

Interest for nanostructured materials [17–20] requires that theoretical models of EDL are revisited with possible quantum effects taken into account. We attempt this in the present paper, where the effects of quantum statistics are studied through a simple model of charged quanta confined between two planar charged surfaces. For this purpose we generalize a previously developed density functional method for description of the electrical double layer with the local Helmholtz free energy of the system, and its minimization by solving the corresponding Euler–Lagrange variational problem [11].

2. Theory

The model system consists of a single type of negatively charged quanta (electrons) confined between two large planar yz surfaces at $x = 0$ and at $x = d$ (Fig. 1). Each surface carries a uniformly

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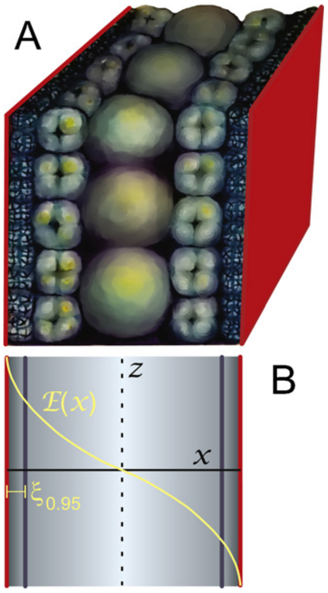

Fig. 1. A schematic of the model. (A) Probability densities of charged fermions trapped in a nanopore oppositely charged at its surfaces. (B) Two symmetrically positioned capacitors are formed, each consisting of a charged surface (at $x = 0$ and $x = d$, respectively), and a diffuse layer created by fermions of the opposite charge (represented by the hue). The light line represents the electric field profile, and parameter $\xi_{0.95}$ (a bound which encloses 95% of all the quanta of the respective half of the system) represents the effective thickness of the diffuse layer.

distributed positive charge with surface charge density $\sigma \geq 0$. Generalization to positively charged quanta and negatively charged surfaces is straightforward. The entire system is electrically neutral. The quanta are subjected to the constraint on available eigenenergy states implied in the Fermi-Dirac statistics while the effect of the electric field on the wavefunctions and on the energy states is not considered. These states can be either occupied or unoccupied, with the average number of quanta in the n-th energy state

$$\bar{s}_n = \frac{1}{1 + \exp((\varepsilon_n - \mu)/kT)}, \tag{1}$$

where μ is the Lagrange coefficient for the constraint requiring fixed total number of quanta in the ensemble, k is the Boltzmann constant and T is absolute temperature [21]. It is taken that each quantum is confined in an infinite three dimensional square potential well so that its energy is

$$\varepsilon_n = \frac{n^2 h^2}{8ma^2}, \quad n = 1, 2, 3, \ldots \tag{2}$$

Here, h is the Planck constant, m is the quantum mass and a is the extension of the potential well. As there are many quanta in the system, the energies are assumed to lie close together and the summation in the statistical averages can be replaced by integrals. The average number of quanta is

$$\overline{N} = 2 \cdot (1/8) \int_0^\infty \frac{4\pi n^2}{1 + \exp((\varepsilon - \mu)/kT)} \, \mathrm{d}n, \tag{3}$$

and the average energy is

$$\overline{E} = 2 \cdot (1/8) \int_0^\infty \frac{4\pi \varepsilon n^2}{1 + \exp((\varepsilon - \mu)/kT)} \, \mathrm{d}n. \tag{4}$$

The factor 2 comes from specifying quanta as electrons and considering their state degeneration.

The system is divided into thin slices with the area A and width δx, parallel to the yz plane and all fields are considered constant within the slice [11]. In the low temperature limit ($T \to 0$), only the lowest energies up to the Fermi energy μ are occupied. There is no entropy contribution and we calculate the Helmholtz free energy of a slice due to Fermi-Dirac wave function symmetry constraints to electrons δF_{sym} as

$$\delta F_{\text{sym}} = \delta \overline{E} = \frac{3}{5}\left(\frac{h^2}{8m}\right)\left(\frac{3}{\pi}\right)^{2/3}\left(\frac{\overline{N}}{V}\right)^{2/3}\overline{N}. \tag{5}$$

Summing all of the slices together we obtain

$$F_{sym} = \frac{3}{5}\left(\frac{h^2}{8m}\right)\left(\frac{3}{\pi}\right)^{2/3} A \int_0^d n^{5/3}(x) \, \mathrm{d}x. \tag{6}$$

Here, we introduced a volume density of quanta,

$$n = \frac{\overline{N}}{A\delta x}. \tag{7}$$

Charged particles and surfaces create an electric field that also contributes to the free energy of the system, namely the electrostatic energy

$$F_{\text{el}} = \frac{\varepsilon_0 A}{2} \int_0^d E^2(x) \, \mathrm{d}x, \tag{8}$$

where $E(x)$ is the magnitude of the electric field strength and ε_0 is the permittivity of vacuum. For simplicity we assumed that the electric field does not explicitly influence the solutions of the Schrödinger equation, therefore the total free energy is simply the sum

$$F = F_{\text{sym}} + F_{\text{el}}. \tag{9}$$

To obtain the global thermodynamic equilibrium, the latter function is minimized with respect to the unknown functions $n(x)$ and $E(x)$. The constraints of the system are the validity of Gauss law at each x,

$$\varepsilon_0 \frac{\partial E}{\partial x} = -e_0 n(x), \tag{10}$$

and electroneutrality

$$e_0 \int_0^d n(x) \, \mathrm{d}x = 2\sigma, \tag{11}$$

where e_0 is the elementary charge. For convenience, dimensionless quantities marked by tilde are used:

$$\tilde{x} = x/d, \quad \tilde{n} = n/n_0, \quad \tilde{E} = E/E_0, \tag{12}$$

where

$$n_0 = \frac{2\sigma}{de_0}, \quad \phi_0 = \frac{\sigma d}{\varepsilon_0} \quad \textit{and} \quad E_0 = \frac{\sigma}{\varepsilon_0}. \tag{13}$$

With this substitution in place, we drop the tilde and subsequently consider all expressions devoid of dimension. The free energy density values are normalized with the area energy density of a parallel plate capacitor in a vacuum, which reads

$$f_0 = \frac{d\sigma}{2\varepsilon_0}. \tag{14}$$

The dimensionless Euler-Lagrange function of the system reads

$$\mathcal{L} = \alpha n^{\frac{5}{3}}(x) + E^2(x) - \lambda(x)\left(\frac{\partial E(x)}{\partial x} + 2n(x)\right) + \tilde{\lambda} n(x), \tag{15}$$

where $\lambda(x)$ and $\tilde{\lambda}$ are the local and global Lagrangian multipliers, respectively. The dimensionless constant α is equal to

$$\alpha = \frac{3}{5\sqrt[3]{2}}\left(\frac{3}{\pi}\right)^{2/3}\frac{h^2 \varepsilon_0}{m e_0^{5/3}}\frac{1}{\sqrt[3]{\sigma d^5}}. \tag{16}$$

The variational problem

$$\delta\left(\int_0^1 \mathcal{L}\left(n, E, \frac{\partial E}{\partial x}, x\right) \mathrm{d}x\right) = 0 \tag{17}$$

is expressed by the system of Euler–Lagrange equations

$$\frac{\partial \mathcal{L}}{\partial n} = 0, \tag{18}$$

$$\frac{\partial \mathcal{L}}{\partial E} - \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial \mathcal{L}}{\partial \frac{\partial E}{\partial x}}\right) = 0, \tag{19}$$

and the above constraints. Considering $E = -\,\mathrm{d}\phi/\mathrm{d}x$ reveals that the local Lagrange coefficient λ is the electric potential ϕ while the Gauss law yields the differential equation for the potential

$$\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\right)^{2/3} = \left(\frac{\beta\sqrt{5}}{4}\right)^2 (4\phi - \tilde{\lambda}). \tag{20}$$

Here,

$$\beta = 4\sqrt{\frac{2}{5}}\left(\frac{3}{5\alpha}\right)^{3/4}. \tag{21}$$

Electric field at the midline vanishes due to the symmetry of the system

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}\Big|_{x=1/2} = 0, \tag{22}$$

with electric potential there being constant. We set the constant value to zero at the midline

$$\phi(x = 1/2) = 0. \tag{23}$$

The other boundary condition follows from electroneutrality of the system

$$\frac{\mathrm{d}\phi}{\mathrm{d}x}\Big|_{x=0} = -1. \tag{24}$$

We consider only the real branch of Eq. (20),

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \left(\frac{\beta\sqrt{5}}{4}\right)^3 (4\phi - \tilde{\lambda})^{3/2}. \tag{25}$$

We make use of the identity

$$2\,\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2. \tag{26}$$

Introducing a new variable

$$u = 4\phi - \tilde{\lambda}, \tag{27}$$

multiplying both sides of this equation by $2\,\mathrm{d}\phi/\mathrm{d}x$, and integrating yields

$$\frac{\mathrm{d}u}{\mathrm{d}x} \approx -\beta\left(u^2 - u_{1/2}^2\right)^{1/2}, \tag{28}$$

where we approximated the power obtained from integration 5/2 by 2 by assuming that the above expression, which is analytically integrable, differs from the original function by a negligible amount. Here, $u_{1/2}$ is the reduced potential at $x = 1/2$. Considering that $u_{1/2}^{5/2} \leq u^{5/2}$, the simplified integral (Eq. (28)) can be solved analytically. The constant

$$u_{1/2} = \frac{1}{2\beta\sinh(\frac{\beta}{2})} \tag{29}$$

is determined by considering the reference value of the potential. The final result for potential in the nanopore yields

$$\phi(x) = \frac{1}{\beta\sinh(\frac{\beta}{2})}\left(\cosh(\beta(x - \frac{1}{2})) - 1\right). \tag{30}$$

The variable parameters in β are the width of the nanopore d, the surface charge of the surfaces σ and the properties of the quanta, which we take to be electron mass and charge. Density of particles is derived from the Euler–Lagrange equations and is in direct relation to the potential,

$$n(x) = \frac{1}{2}\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{\beta}{2}\frac{\cosh(\beta(x - \frac{1}{2}))}{\sinh(\frac{\beta}{2})}. \tag{31}$$

3. Results and discussion

Eq. (25) was also solved rigorously by the shooting numerical method with Mathematica software (Wolfram Research, Inc., Mathematica, Version 9.0, Champaign, IL (2012)). Fig. 2 shows that potential monotonously decreases from the charged surface towards the midline ($x = 1/2$) (panel A) and that due to electrostatic attraction electrons accumulate near each of the charged surfaces (panel B). As they cannot all attain the same energy state near the surface, they are forced to states of higher energies or to locations further away from the charged surfaces. Holding the distance between the charged surfaces at a constant value and changing the surface charge, we find that at larger distances d and high surface charge densities σ the potential does not change much, while the particle densities are significant only near the surfaces. This particle accumulation accounts for effective screening of the electric field. At lower values of σ the electron density is almost constant throughout the pore (Fig. 2A), but variation of potential is larger due to the bulk charge accumulated between the surfaces (Fig. 2B). Differences between the numerical and analytical results are negligible (Fig. 2A, inset). Matching is best at $x = 1/2$.

Helmholtz free energy of the EDL is of considerable importance in colloid and surface sciences as it is used to describe phenomena such as the spreading pressure of charged monolayers and forces acting between the charged surfaces [22]. In our model system, the equilibrium free energy is the integral sum of the contribution due to symmetry restrictions upon the wave functions of the electrons and the contribution of the electrostatic field,

$$\frac{f}{f_0} = \int_0^1 \left(\alpha n^{5/3}(x) + E^2(x)\right) \mathrm{d}x \approx \int_0^1 \left(\alpha n^2(x) + \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2\right) \mathrm{d}x \tag{32}$$

The power approximation ($5/3 \rightarrow 2$) is used for purposes of convenient analytic treatment while exact rigorous integration was also performed numerically. Inserting Eq. (30) and Eq. (31) into Eq. (32) and integrating yields

$$\frac{f}{f_0} = \underbrace{\left(\frac{3}{5^{5/3}}\right)\left(\frac{2}{\beta}\right)^{1/3}\frac{\beta + \sinh\beta}{\sinh^2(\frac{\beta}{2})}}_{\text{sym.}} + \underbrace{\frac{\sinh\beta - \beta}{2\beta\sinh^2(\frac{\beta}{2})}}_{\text{el.}}. \tag{33}$$

For small β, we use series expansion to obtain $f/f_0 = \alpha$. Fig. 2C shows that the electrostatic energy increases as the surfaces are brought apart, and limits to zero at small distances. The energy due to symmetry constraints diverges towards positive infinity at small distances. The analytical results coincide well with their numerical counterparts.

As mentioned in the introduction, a pivotal role concerning energy storage of EDL capacitors is resumed by the differential capacitance, resulting in many technological efforts which are directed towards maximizing its value [23,24]. In a classical approach, the differential capacitance of the EDL is defined as [25,26]

$$C = \frac{\mathrm{d}\sigma}{\mathrm{d}\phi(x = 0)}. \tag{34}$$

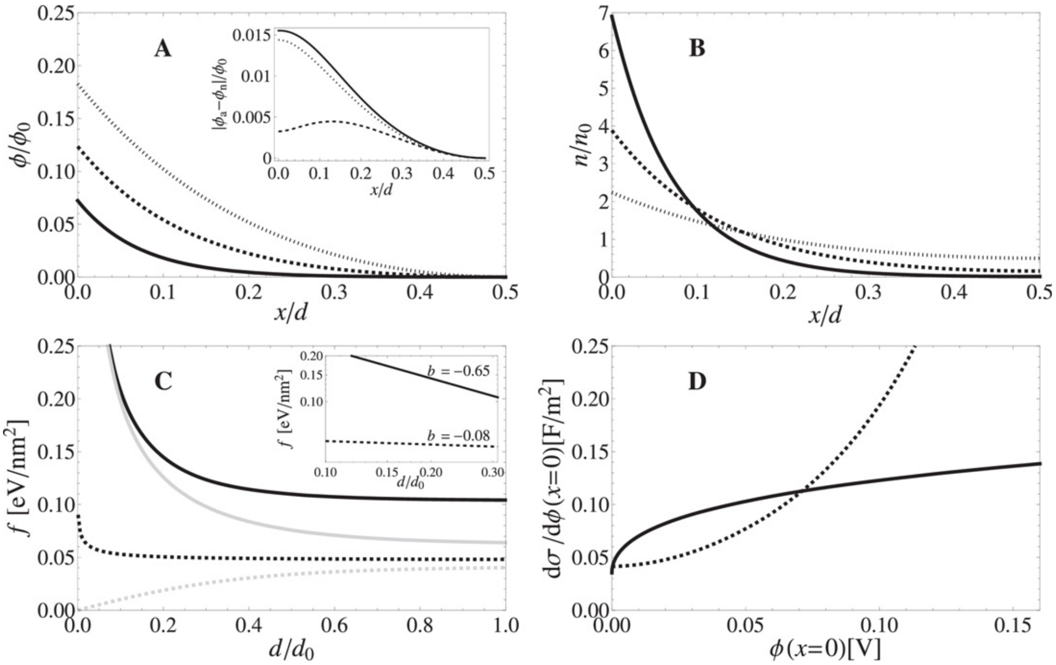

Fig. 2. (A) Normalized electric potential ϕ/ϕ_0 in dependence on x for pore size $d = 1$ nm and different values of surface charge density. Full line: 0.3 C/m^2, dashed line: 0.03 C/m^2, dotted line: 0.003 C/m^2. Inset (A) Absolute differences of analytical and numerical solutions. (B) Normalized electron number density n/n_0 in dependence on x corresponding to the parameter values in panel A. (C) Free energy of the system f (Eq. (33), full line) and its contributions: energy due to antisymmetric wavefunctions of electrons (full gray line) and electrostatic energy (dashed gray line). Also shown is free energy calculated using the Poisson-Boltzmann theory for $T = 300$ K (Eq. (43)), (dashed line). In both cases surface charge density is $\sigma = 0.03$ C/m^2. Inset (C) A detail of the full black and dashed curves in a log-log scale fitted with the function ax^b with specified power as indicated in the inset. (D) Analytic differential capacitance $\mathrm{d}\sigma/\mathrm{d}\phi(x = 0)$ (Eq. (38), full line) and the corresponding differential capacitance calculated by the Poisson - Boltzmann theory (Eq. (44), dashed line) at pore size $d = 1$ nm and $T = 300$ K. Electric potential and electron number density are shown for one half of the system, the dependencies are symmetric with respect to the midline.

Here $\phi(x = 0)$ is the potential at $x = 0$ in unit V. By inserting $x = 0$ into Eq. (30), we obtain the dependence of $\phi(x = 0)$ on β. Since we want to differentiate by σ, we write

$$\beta = \tilde{A} d^{5/4} \sigma^{1/4}, \tag{35}$$

where $\tilde{A}$ is defined by universal constants,

$$\tilde{A} = 4\sqrt{\frac{\pi}{15}} \left(\frac{2 m e_0^{5/3}}{h^2 \varepsilon_0} \right)^{3/4}. \tag{36}$$

The potential at $x = 0$ (in unit V) is

$$\phi(x = 0) = \frac{K_1 \sigma^{3/4}}{K_2 \sinh(\frac{K_2 \sigma^{1/4}}{2})} \left(\cosh(\frac{K_2 \sigma^{1/4}}{2}) - 1 \right). \tag{37}$$

Here, $K_1 = d/\varepsilon_0$ is in unit V, while $K_2 = \tilde{A} d^{5/4}$. We make use of implicit differentiation by $\mathrm{d}/\mathrm{d}\phi(x = 0)$,

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\phi(x = 0)} = \frac{16 K_2 \cosh^2(\frac{K_2 \sigma^{1/4}}{4}) \sigma^{1/4}}{6 K_1 \sinh(\frac{K_2 \sigma^{1/4}}{2}) + K_1 K_2 \sigma^{1/4}}. \tag{38}$$

Numerically, we transpose the dependency $\phi(x = 0)(\sigma)$ and differentiate.

We compare the results with the results of the acknowledged Poisson-Boltzmann theory where at finite temperature the quanta are distributed over the energies according to the Boltzmann distribution [21] $\bar{s}_n = \exp(-\varepsilon_n/kT)$ and the entropic term is considered in the free energy. This is reflected in the partition functions and, accordingly, the Lagrange function of the system. Using an analogous approach and the same constraints upon the system as above we derive the differential equation for the electric potential

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} - B \exp(\frac{4\phi}{\gamma}) = 0, \tag{39}$$

where

$$\gamma = \frac{4kT\varepsilon_0}{d e_0 \sigma}, \tag{40}$$

and B is a constant. We do not present the procedure to solve Eq. (39) in detail here as a very similar formalism has previously been considered in an electrolyte [27]. The dimensionless electric potential in this case is

$$\phi(x) = \frac{\gamma}{4} \ln \left(1 + \tan^2(\kappa(\frac{1}{2} - x)) \right), \tag{41}$$

where it was chosen that $\phi(x = 1/2) = 0$. The constant κ was determined from the boundary condition at the charged surface, which yields the equation

$$\frac{\kappa}{2} \tan(\frac{\kappa}{2}) = \frac{2}{\gamma}, \tag{42}$$

which was solved numerically for κ. The equilibrium free energy is

$$\frac{f}{f_0} = \gamma \ln \left(\frac{\kappa K}{e^2 \sin\kappa} \right) + \left(\frac{\kappa\gamma}{2} \right)^2 \tag{43}$$

where $K = (h^2/2\pi mkT)^{3/2} \sigma/ede_0$. The differential capacitance is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\phi(x = 0)} = \frac{e_0}{kT} \left(\tan(\frac{\kappa}{2}) \frac{\mathrm{d}\kappa}{\mathrm{d}\sigma} \right)^{-1}. \tag{44}$$

In need of a measure of particle density near the charged surface, we define an effective thickness of the electric double layer at ξ_ω within which there is ω% of all electrons. Since the number density function $n(x)$ is symmetrical to the midline $x = 1/2$, the effective thickness is calculated by finding the upper bound of the integral ξ_ω. We chose $\omega = 0.95$ in line with the definition of electronic orbitals,

$$\int_0^{\xi_\omega} n(x)\,\mathrm{d}x = \frac{\omega}{2}. \tag{45}$$

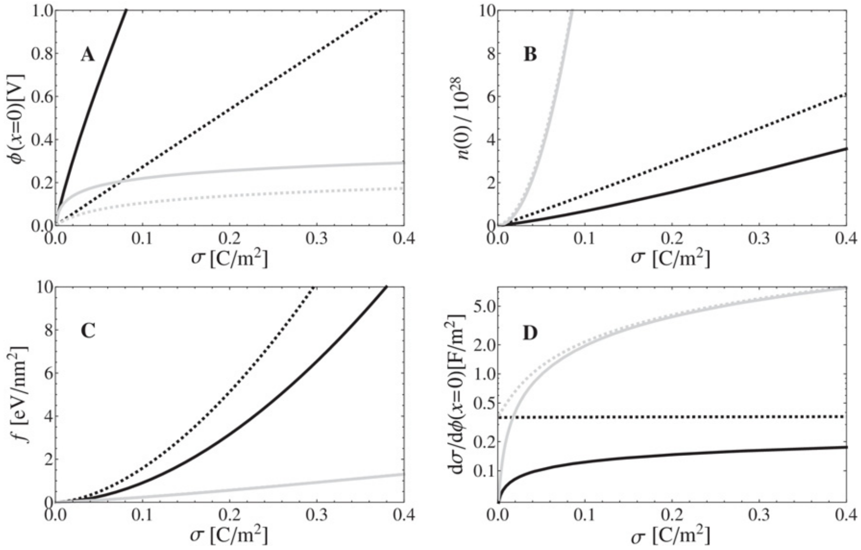

Fig. 3. (A) Electric potential at the charged surface $\phi(x=0)$ (in units V), (B) number density of electrons at the charged surface $n(x=0)$, (C) free energy of the electric double layer f and (D) differential capacitance of the electric double layer $d\sigma/d\phi(x=0)$, in dependence on the area density of charge σ. All quantities are calculated for two pore sizes (($d=1$ nm) - full lines and ($d=0.1$ nm) - dotted lines). Black lines pertain to the model taking into account the quantum statistics and gray lines pertain to the Poisson - Boltzmann theory at $T=300$ K.

It can be seen in Fig. 2C that the values of free energy of the system subjected to quantum statistics in the low temperature limit are of the same order of magnitude as the corresponding values obtained by the Poisson-Boltzmann theory at room temperature. Moreover, the quantum statistics effects indicate higher energy stored in the capacitor. Due to quantum constraints, the electrons are less effective in shielding the electric field so that the effective thickness of quantum EDL is larger and the electric field in the capacitor is on average larger. The differential capacitance of the two models shows a monotonous increase with the potential at the charged surface (Fig. 2D) and values within the same order of magnitude in both models, however, the curves have different shapes due to different dependencies of the electric field on the surface charge density and the distance between the surfaces.

Fig. 2C shows that the electrostatic energy increases as the surfaces are brought apart, and approaches zero at zero distance. The energy due to symmetry constraints behaves differently: at $d=0$ it diverges towards positive infinity. The analytical results coincide well with their numerical counterparts (Fig. 2). Both analytical and numerical functions are symmetric around the midplane $x=1/2$. For small β, we use series expansion of the hyperbolic sine to obtain $f/f_0=\alpha$. For large β, the expression limits to zero. However, at chosen d, the slope of the $f(d)$ curve is different in both models (inset of Fig. 2C).

Fig. 3C shows dependencies of the electric potential at the charged surface $\phi(x=0)$ (in units V) (Panel A), number density of electrons at the charged surface $n(x=0)$ (Panel B), free energy of the electric double layer f (Panel C) and differential capacitance of the electric double layer $d\sigma/d\phi(x=0)$ (Panel D), in dependence on the surface charge density σ. All these quantities monotonously increase with increasing surface charge density. The antisymmetry of the wavefunctions imposes stronger constraints upon the accumulation of the quanta near the charged surface and consequently prevents them to shield the electric field. Therefore, the electric field protrudes further in the direction from the charged surface (Fig. 4). As larger surface charge means larger number of electrons in the system (to satisfy electroneutrality), also the energy of the system increases with increasing σ.

It can be seen in Figs. 3B, C and D that the curves pertaining to the Poisson-Boltzmann theory are almost identical, owing to the condensation of quanta to the surfaces. As almost all quanta are in the near vicinity of the charged surface, shielding of the charged surface is very effective and the contribution of the space around the midplane (if enlarged beyond certain distance) to the relevant quantities is negligible.

Unlike in the ideal gas model, where the particles are explicitly considered independent, the particles in a system obeying quantum statistics are necessarily interacting: fermions are subjected to the Pauli exclusion principle due to the asymmetry of the wavefunctions, which has been taken into account in the model by the formulation of the free energy. In the model, the electrostatic interaction is considered within the mean field approximation. This means that the charged surfaces as well as the spatially distributed charges have effects through the solution of the variational problem including the Gauss law and the boundary conditions. The effect of the electric field on the wavefunctions is not taken into account. As we wanted to focus on the effect of quantum statistics, we considered the electric interaction by simplest possible means. This enabled almost analytical and therefore transparent solution of the problem as regards the dependencies of the relevant quantities on the surface charge, distance between the charged surfaces and quanta mass. The next step would be consideration of the effect of the electric field on the solution of the Schrödinger equation, other possible confinement potentials and finite temperatures.

By using a square well model we have shown that nano - sized diffuse electric double layer which stores energy can be formed due to constraints on the eigenfunctions of fermions (electrons). Consideration of antisymmetry of wave functions expands the electric double layer, causes the electric field to protrude further from the charged surface, evens the distribution of quanta and increases the effective thickness of the electric double layer. The effect on the differential capacitance is however more complex and depends also on other model parameters. Including anisotropy of the potential well, effects of the electric field on the solution of the Schrödinger equation and finite temperatures would improve the description but would not change this major qualitative result.

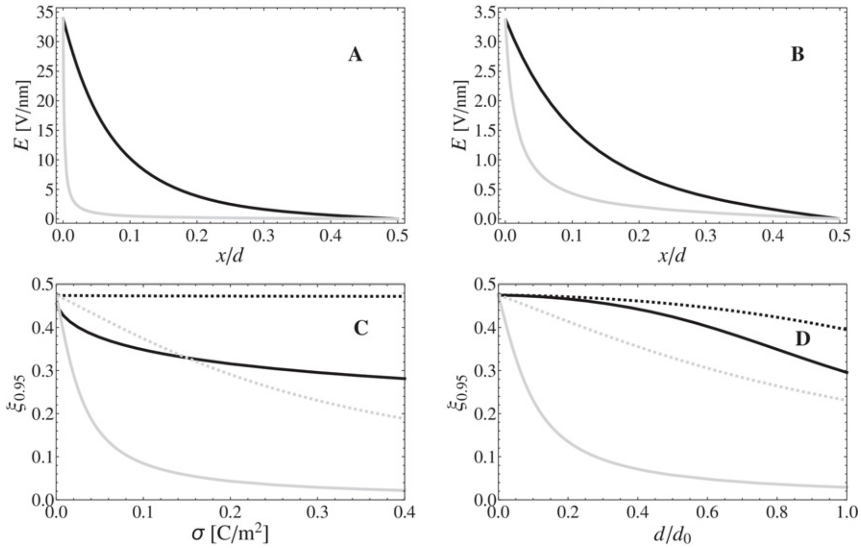

Fig. 4. Electric field in the direction perpendicular to the charged surface E in dependence on x for (A) $\sigma = 0.3\,\mathrm{C/m^2}$ and (B) $\sigma = 0.03\,\mathrm{C/m^2}$, where in both cases, $d = 1$ nm. Effective thickness of the electric double layer $\xi_{0.95}$ in dependence on (C) surface charge density σ for two pore sizes (($d = 1$ nm) - full lines and ($d = 0.1$ nm) - dotted lines), and on the distance between charged surfaces (D) for two surface charge densities (($\sigma = 0.3\,\mathrm{C/m^2}$) - full lines and ($\sigma = 0.03\,\mathrm{C/m^2}$)- broken lines). Here, $d_0 = 1$ nm. Black lines pertain to the model taking into account the quantum statistics and gray lines pertain to the Poisson - Boltzmann theory at $T = 300$ K. Electric field is shown for one half of the system, the dependencies are antisymmetric with respect to the midline (see Fig. 1).

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