# Dipolar Poisson-Boltzmann Equation: Ions and Dipoles Close to Charge Interfaces

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We present an extension to the Poisson-Boltzmann model where the dipolar features of solvent molecules are taken explicitly into account. The formulation is derived at mean-field level and can be extended to any order in a systematic expansion. It is applied to a two-plate system with oppositely charged surfaces. The ion distribution and profiles in the dipolar order parameter are calculated and can result in a large correction to the interplate pressure.

Charged objects (ions, interfaces, and particles) immersed in liquids play a central role in electrochemistry, colloidal science, and biology ranging from electrolyte applications, stabilization of colloidal suspensions, protein folding and its biological activity, and even in protein aggregation [1–5].

The most commonly used model—the Poisson-Boltzmann model (PB) [1,3]—assumes pointlike ions immersed in a continuum dielectric media and treats the system in a mean-field approximation. The medium is modeled by a homogeneous and isotropic dielectric constant. This model is simple, elegant, and efficient. It is in good agreement with experiments for monovalent ions up to energies of order of $k_B T$. However, careful measurements of the forces between two charged surfaces at nanometric scale show strong deviation from the simple PB picture [3]. In particular, the assumption that the continuum dielectric medium is homogeneous does not take into account the strong dielectric response of water molecules around charges. The discrete moments of water molecules will orient themselves close to charged ions and surfaces giving rise to hydration shells and to hydrophobic interactions, which can be measured at short distances, for example, between two charged plates (surface force balance apparatus). These hydration phenomena are very important in many biological processes such as protein folding, protein crystallization, and interactions between charged biopolymers inside the cell.

Most studies other than the PB rely on one of several theoretical techniques. Monte Carlo (MC) [6] or molecular dynamic (MD) [7] computer simulations take into account the discrete nature of the dipolar molecules. A second approach relies on liquid state theory, integral equation, and other methods [8,9]. In simple planar geometry the latter gives good agreement with the MC and MD simulations. However, all these methods are rather cumbersome and involve heavy computation resources. In addition, they lack the simple physical picture provided by a Poisson-Boltzmann type of approach.

In this Letter we propose another approach called the dipolar Poisson-Boltzmann (DPB). Unlike the PB model where the solution is characterized by a homogeneous dielectric constant, in the DPB model we coarse grain the interaction of individual ions and dipoles interacting together. This makes the DPB an analytic extension of the PB formalism. Although it is done on a mean-field level, it includes some aspects of the discrete nature of the dipolar solvent molecules and how they modify the ion–solvent interactions. We show that such corrections to the PB treatment are important in predicting dipolar profiles close to charged surfaces and result in a strong deviation from their average value. Furthermore, the DPB model can, in principle, be expanded to any desired higher order in a systematic expansion.

Consider a system composed of $N_d$ mobile dipoles each with a dipolar moment **p** and $I$ species of ions immersed in a continuum dielectric medium with a weak dielectric response (the justification for this system setup is elaborated below), $\epsilon \gtrsim \epsilon_0$, $\epsilon_0$ being the vacuum permittivity. Each ionic species has $N_j$ ions of charge $q_j e$, $j = 1, \ldots, I$, where $e$ is the electron charge. In addition, the system includes a fixed charge distribution $\rho_f(\mathbf{r})$. The charge density created by a point dipole **p** at point $\mathbf{r}_0$ is given by $\rho_d(\mathbf{r}) = -\mathbf{p} \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_0)$. Thus, the total charge density is

$$\rho(\mathbf{r}) = -\sum_{i=1}^{N_d} \mathbf{p}_i \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_i) + \sum_{j=1}^{I} \sum_{i=1}^{N_j} q_j e \delta(\mathbf{r} - \mathbf{R}_i^{(j)})$$
$$+ \rho_f(\mathbf{r}), \tag{1}$$

where $\mathbf{r}_i$ denotes the position of dipoles of moment $\mathbf{p}_i$ and $\mathbf{R}_i^{(j)}$ are the positions of ions of type $j$. The canonical partition function is given by

$$Z = \frac{1}{N_d! \prod_{j=1}^{I} N_j!} \int \prod_{i=1}^{N_d} d^3\mathbf{r}_i d^3\mathbf{p}_i$$
$$\times \prod_{j=1}^{I} \prod_{i=1}^{N_j} d^3\mathbf{R}_i^{(j)} e^{-(\beta/2) \int d^3r d^3r' \rho(\mathbf{r}) v_c(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')}, \quad (2)$$

where $v_c(\mathbf{r})$ denotes the Coulomb potential. Using a standard Hubbard-Stratonovich transformation,

$$Z = \int \mathcal{D}\phi(\mathbf{r}) \exp\left(-\frac{\beta\epsilon}{2}\int d^3\mathbf{r}[\boldsymbol{\nabla}\phi(\mathbf{r})]^2\right.$$
$$+ \lambda_d \int d^3\mathbf{r}d^3\mathbf{p}e^{-i\beta\mathbf{p}\cdot\boldsymbol{\nabla}\phi} + \sum_{i=1}^{I}\lambda_i \int d^3\mathbf{r}e^{-i\beta q_i e\phi}$$
$$\left.- i\beta \int d^3\mathbf{r}\phi(\mathbf{r})\rho_f(\mathbf{r})\right), \qquad (3)$$

where $\epsilon = \epsilon_0\epsilon_r$ is the medium dielectric constant (in SI units) and $\beta = 1/T$ is the inverse temperature (where the Boltzmann constant $k_B$ is set to unity). The fugacities of the dipoles and $i$th ion species, $\lambda_d$ and $\lambda_i$, respectively, are derived from the relations: $N_d = \lambda_d\frac{\partial}{\partial\lambda_d}\log Z$ and $N_i = \lambda_i\frac{\partial}{\partial\lambda_i}\log Z$.

Assuming that each molecular dipole has a fixed magnitude, $|\mathbf{p}| = p_0$ we sum now over the $\{\mathbf{p}\}$ degrees of freedom and obtain the dipolar term in the form $\lambda_d \int d^3\mathbf{r}\sin(\beta p_0|\nabla\phi|)/\beta p_0|\nabla\phi|$.

The DPB equation is then obtained as the saddle point of the action (3) [where we have used $\Psi(\mathbf{r}) = i\phi(\mathbf{r})$ to denote the physical electrostatic potential]

$$-\epsilon\nabla^2\Psi = \sum_i\lambda_i q_i e\exp(-\beta q_i e\Psi) + \rho_f(\mathbf{r})$$
$$+ \lambda_d p_0\boldsymbol{\nabla}\cdot[(\boldsymbol{\nabla}\Psi/|\boldsymbol{\nabla}\Psi|)\mathcal{G}(\beta p_0|\boldsymbol{\nabla}\Psi|)] \quad (4)$$

and the function $\mathcal{G}(u) = \cosh u/u - \sinh u/u^2$ is related to the Langevin function $\mathcal{L}(u) = \coth u - 1/u$ by $\mathcal{G} = (\sinh u/u)\mathcal{L}$. One recognizes in (4) the usual terms of the Poisson-Boltzmann equation (the first two terms on the right-hand side), while the last term is the divergence of the polarization contributing to the induced charge density. The local polarization density (square brackets) in Eq. (4) is the product of the dipole density, $\sinh u/u$, and the average dipole moment given (on a mean-field level) by the Langevin function.

In the following we study a dipolar solvent with 1:1 salt confined between two *oppositely charged* planes [10]. While the spatial variation of the dielectric constant is pronounced near any charged surface, the dipolar contribution to the osmotic pressure is much larger for two antisymmetric plates than for equally charged ones (as will be explained below). Choosing the charge density to be $\mp\sigma$ for the two plates located at $z = \pm d/2$, the potential, ionic profiles and dipole density depend only on the $z$ coordinate perpendicular to the planes and (4) becomes

$$-\epsilon\Psi''(z) = -2c_s e\sinh\beta e\Psi + \sigma\delta(z + d/2)$$
$$- \sigma\delta(z - d/2) + c_d p_0\frac{d}{dz}[\mathcal{G}(\beta p_0\Psi')], \quad (5)$$

where we assume that the system is in contact with a reservoir containing a dipolar fluid of concentration $c_d$ and salt of concentration $c_s$ so that $\lambda_d = c_d$ and $\lambda_s = c_s$.

The boundary condition at the $z = -d/2$ charged plane is $-\epsilon\Psi'_s = c_d p_0\mathcal{G}(\beta p_0\Psi'_s) + \sigma$ and the electric field $E = -\Psi'$ is the same, for the antisymmetric system, as on the other plane. Note that the usual Neumann boundary conditions for the PB equation include now the polarization induced surface charges. We find that for strong enough surface charge densities, the induced charge can be substantial and corresponds to a large modification of the standard boundary condition.

From (5) we obtain the first integral which is equivalent to the contact theorem expression for the pressure difference $\Pi = P_{\text{in}} - P_{\text{out}}$

$$\Pi = -\frac{\epsilon}{2}\Psi'^2(z) + 2c_s T(\cosh\beta e\Psi - 1)$$
$$- c_d p_0\Psi'\mathcal{G}(\beta p_0\Psi') + c_d T\left(\frac{\sinh\beta p_0\Psi'}{\beta p_0\Psi'} - 1\right). \quad (6)$$

This equation allows us to express $\Psi(z)$ as a function of $\Psi'$ and thus solves (5) by a simple quadrature. The first two terms in $\Pi$ are the usual PB contributions, the first being the electric field and the second the mixing entropy of the ions. The other two terms are the specific terms of the DPB model. The first is the enthalpic contribution related to the orientation of the dipoles in a local electric field. The last term is the rotational entropy of the dipoles. The pressure at any point $z$ is calculated with respect to the pressure exerted by the bulk reservoir outside the plates.

Another way to interpret (5) is to write it as a PB equation with an effective field-dependent dielectric constant $\epsilon^{\text{eff}}(E) = \epsilon_0\epsilon_r^{\text{eff}}(E)$ replacing the $\epsilon$ on the left-hand side. The nonlinear dielectric response is given by

$$\epsilon^{\text{eff}}(E) = \epsilon + \frac{c_d p_0}{E}\mathcal{G}(\beta p_0 E). \quad (7)$$

For weak fields one can expand the function $\mathcal{G}$ to first order and obtain the standard PB equation $\epsilon^{\text{eff}}\Psi''(z) \approx 2c_s e\sinh\beta e\Psi$ with an effective homogeneous dielectric constant $\epsilon^{\text{eff}} = \epsilon + \beta c_d p_0^2/3$.

This result for dielectric response of molecules with intrinsic dipoles in dilute systems is well known. Since we are interested in aqueous solutions, we have chosen as a fit parameter the molecular dipole moment of water to be $p_0 = 4.86$ D (instead of the physical value $p_0 = 1.85$). This allows us to obtain $\epsilon_r^{\text{eff}} = 80$ for $\epsilon = \epsilon_0$ (vacuum permittivity) and $c_d = 55$ M.

When the dipolar effects are strong (see below) there is a crowding of dipoles and ions between the plates, and their densities can reach values higher than close packing. To avoid this problem, we can generalize our theory to take into account the finite molecular size [11]. Assuming that the 1:1 ions and dipoles are constrained on a lattice of spacing $a$ (roughly equal to their molecular size), and imposing the condition that each site of the lattice is occupied by only one of the three species (incompressibility condition), the free energy becomes

$$-\beta F = \frac{\beta \epsilon}{2} \int d^3\mathbf{r}[\boldsymbol{\nabla}\Psi(\mathbf{r})]^2$$

$$+ \frac{1}{a^3} \int d^3\mathbf{r} \log\left(c_d \frac{\sinh\beta p_0|\boldsymbol{\nabla}\Psi|}{\beta p_0|\boldsymbol{\nabla}\Psi|}\right.$$

$$\left. + 2c_s \cosh(\beta e \Psi)\right), \qquad (8)$$

where $c_d + 2c_s = a^{-3}$. Minimizing the above free energy, the modified dipolar Poisson-Boltzmann (MDPB) equation is obtained

$$-\epsilon\Psi''(z) = \sigma\delta(z + d/2) - \sigma\delta(z - d/2)$$

$$+ \frac{c_d p_0}{a^3} \frac{d}{dz}\left[\frac{\mathcal{G}(\beta p_0 \Psi')}{\mathcal{D}}\right] - \frac{2c_s e}{a^3} \frac{\sinh\beta e \Psi}{\mathcal{D}}, \qquad (9)$$

where $\mathcal{D} = c_d \sinh(\beta p_0 \Psi')/\beta p_0 \Psi' + 2c_s \cosh(\beta e \Psi)$. The presence of the denominator $\mathcal{D}$ in (9) leads to saturation of the local ionic and dipolar densities, which is quite important close to charged boundaries. Without the dipolar effect $p_0 = 0$, the MDPB equation reduces to the modified PB equation which also displays an ionic saturation effect because of solvent entropy [11].

A large deviation of the DPB treatment from the standard PB one may occur in the strong $E$ field regime. Such a case is presented now by solving numerically Eq. (5) with its boundary condition for a system composed of two planar surfaces located at $z = \pm d/2$, with opposite surface charge densities $\mp\sigma$ and with small amounts of 1:1 salt to avoid strong screening effects. In this antisymmetric system the potential at the midplane vanishes, while the electric field there is nonzero. The DPB pressure, in turn, deviates substantially from its corresponding PB value due to the coupling between the dipole density and the nonzero electric field. This is in contrast with a symmetric planar system where the electric field vanishes at the midplane.

Had we modeled the water solvent as dipoles in vacuum ($\epsilon = \epsilon_0$), the dipole density in the midregion (see Fig. 1) would have reached unphysical values above the close packing ones, because nothing in our model prevents overcrowding. In order to avoid this artifact we use a background of low dielectric solvent (e.g., $\epsilon_r = 4.5$ for ether) and treat *explicitly* the strong water dielectric response by the dipolar term in the DPB Eq. (5). In this fashion the water bulk density is lower than its close packing value, yielding a dipole profile density which is higher than the bulk value but below the close packing one. Note that all other mixture enthalpic and entropic terms are not considered at present [12].

In Fig. 1 we present the DPB profiles for the dipole density and local dielectric constant between two charged plates with separation of $d = 20$ Å. The figure shows a strong accumulation of dipoles between the charged plates leading to high effective dielectric constant. The profile of the dipole density (dashed line) is rescaled by its bulk value. It can be seen that in the surface vicinity (up to
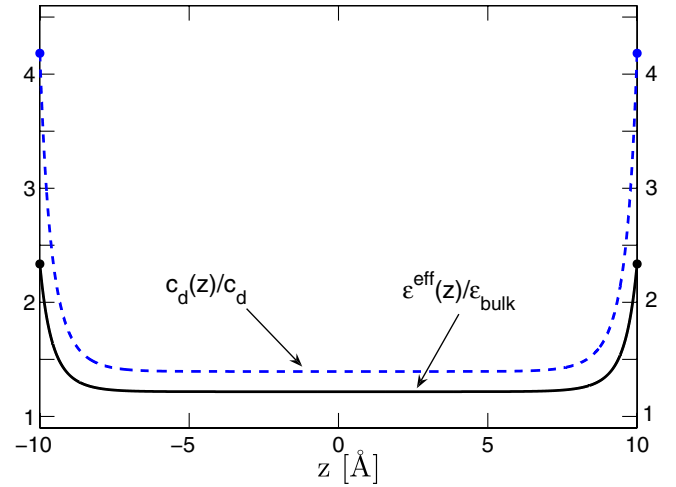


FIG. 1 (color online). The DPB rescaled dielectric constant $\epsilon^{\mathrm{eff}}(z)/\epsilon_{\mathrm{bulk}}$ and the dipole density $c_d(z)/c_d$ profiles between two oppositely charged plates at separation $d = 20$ Å. The surface charge density is $\sigma = \mp e/50$ Å$^2$. The reservoir contains 1:1 salt of concentration $c_s = 10^{-5}$ M and dipoles of density $c_d = 10$ M. The dielectric constant is rescaled with respect to its bulk value $\epsilon_{\mathrm{bulk}} = 18.2$. The profiles have a strong variation in the vicinity of the plates (up to 2 Å) and then saturate to a value that is somewhat higher than their bulk values.

about 2 Å), the density rises to above 4 times its bulk value due to the strong attraction with the charged surface. In the midregion the density saturates at about 1.4 times its bulk value. The corresponding local effective dielectric constant (solid line in the figure) can be calculated from (7). The profile resembles that of the dipole density. In rescaled units, it saturates at a value of about 1.2 in the midregion and reaches about 2.3 at the surfaces.

Compared to a PB theory with the *same* bulk and homogeneous $\epsilon^{\mathrm{eff}}$ taken as constant throughout the system, the DPB demonstrates strong deviations, not only in the surface proximity but also in its saturated midrange value (for strong enough $\sigma$ and/or small $d$).

The ionic concentration is much less affected by the presence of the dipoles. We have computed the ion densities as a function of the distance to the surface. Because of the different boundary condition the ionic density is strongly suppressed at the surface with respect to PB (to about half of its original value). However, it comes back to its PB value at distances as close as 0.5 Å from the surface.

In Fig. 2 we plot the relative osmotic pressure difference $(\Pi_{\mathrm{DBP}} - \Pi_{\mathrm{PB}})/\Pi_{\mathrm{PB}}$ as a function of the surface separation $d$. The pressure is a global quantity, and is sensitive to the strength of the electric field throughout the system rather than to its value on the surface. As a result, $\Pi_{\mathrm{DPB}}$ deviates strongly from $\Pi_{\mathrm{PB}}$ for small $d$, while $\Pi_{\mathrm{DPB}} \approx \Pi_{\mathrm{PB}}$ at larger separation.

We have presented an analytical modification of the PB equation by including the dipole degrees of freedom. We calculated the correction to the potential, electric field and densities for a system of two oppositely charged plates
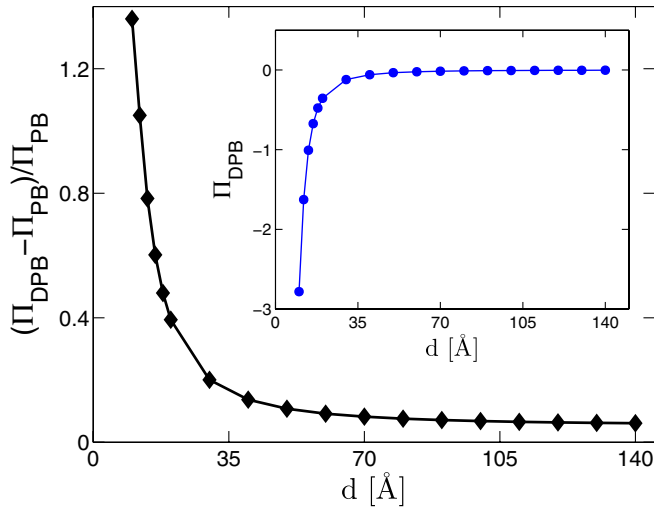
FIG. 2 (color online). The DPB calculated pressure $\Pi$ as a function of the interplate separation $10 \leq d \leq 140$ Å for two oppositely charged plates. All other system parameters are as in Fig. 1. We compare the DPB with the usual PB models by plotting their relative difference $(\Pi_{DBP} - \Pi_{PB})/\Pi_{PB}$. In the inset the DPB pressure is plotted in units of $10^{-2}k_B T/\text{Å}^3$.

(Fig. 1). The results are compared with those of the usual PB equation with an effective dielectric constant. We find that when the electric field is strong ($p_0 E \approx k_B T$), there are strong deviations from the PB model. The spatial dependence of the dielectric constant signals an ordering of the dipoles at the surfaces. This spatial dependence is also a signature of nonlinearity in the dielectric response. The interplate pressure is sensitive to the value of the electric field at the midplane and can deviate considerably from the PB results for small enough separation and/or large surface charges (Fig. 2).

The formalism presented here is general and opens up the way to several interesting applications. Even on a mean-field level, as used in this Letter to compute profiles and osmotic pressure, we find large deviations from the corresponding PB results. However, this treatment has several limitations: it lacks correlation effects and it does not treat correctly the finite size of ions and dipoles, whose densities can reach unphysical high values in high $E$ fields. The former limitation can be removed by considering a systematic higher-order loop expansion of the free energy, taking into account correlation effects. The latter can be remedied by including the hard core of ions and dipoles as appeared in Eq. (9). It will be of interest to compare the outcome of these refinements [12] with other models such as hypernetted-chain and computer simulations, as they include correlation effects and show an oscillatory density profile in the vicinity of charged surfaces.

The results presented in this Letter can be verified experimentally by using, for example, the surface force balance (SFB) apparatus. Recent SFB experiments [13] have been performed on asymmetrically charged surfaces. The range of intersurface separations that we used can be explored using the SFB technique. What is needed, however, are careful studies of mixtures of different dielectric solvents in order to extract the dipole contribution to the osmotic pressure. This systematic set of experiments may shed light on the short-range hydrophobic effect and hydration forces.

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