# Finite size effect of ions and dipoles close to charged interfaces*

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The modified dipolar Poisson–Boltzmann (MDPB) equation, where the electrostatics of the dipolar interactions of solvent molecules and also the finite size effects of ions and dipolar solvent molecules are explicitly taken into account on a mean-field level, is studied numerically for a two-plate system with oppositely charged surfaces. The MDPB equation is solved numerically, using the nonlinear Multigrid method, for one-dimensional finite volume meshes. For a high enough surface charge density, numerical results of the MDPB equation reveal that the effective dielectric constant decreases with the increase of the surface charge density. Furthermore, increasing the salt concentration leads to the decrease of the effective dielectric constant close to the charged surfaces. This decrease of the effective dielectric constant with the surface charge density is opposite to the trend from the dipolar Poisson–Boltzmann (DPB) equation. This seemingly inconsistent result is due to the fact that the mean-field approach breaks down in such highly charged systems where the counterions and dipoles are strongly attracted to the charged surfaces and form a quasi two-dimensional layer. In the weak-coupling regime with the electrostatic coupling parameter (the ratio of Bjerrum length to Gouy–Chapman length) $\Xi < 1$, where the MDPB equation works, the effective dielectric constant is independent of the distance from the charged surfaces and there is no accumulation of dipoles near the charged surfaces. Therefore, there are no physical and computational advantages for the MDPB equation over the modified Poisson–Boltzmann (MPB) equation where the effect of dipolar interactions of solvent dipoles is implicitly taken into account in the renormalised dielectric constant.

**Keywords:** dipole, Poisson–Boltzmann equation, charged interface, polarisation

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## 1. Introduction

The Poisson–Boltzmann (PB) equation is the most important continuum model for the study of the electrostatics of electrolyte solutions due to its simplicity and elegance.[1,2] Because of its simplicity, analytical solutions in simple geometries can be obtained which agree well with experiments. The PB equation has found wide applications in electrochemistry, colloidal science and biological science.[1−6] At low electric potential, the PB equation can be linearised, leading to the Debye–Huckel screening length describing the electrostatic screening of ions in electrolyte solutions.[7,8]

The PB equation is a mean-field model, assuming point-like ions immersed in a continuum dielectric media. The PB equation neglects the charge correlations and fluctuations, as well as non-electrostatic interactions between ions. Thus, it is not surprising that the PB equation cannot explain the physics satisfactorily in certain situations such as the adsorption of ions to highly charged surfaces, and the attractive interactions between two charged surfaces with the same sign of charge in the presence of multivalent counterions. Consequently, there have been many attempts to improve the PB equation by including the ion fluctuations and correlations.[9−16]

Because the PB equation does not take into account the finite size of ions, near a highly charged surface, the ion density is not bounded and can easily exceed the maximal allowed value by orders of magnitude. By taking into account the finite size effect of ions, Borukhov *et al.* derived a modified Poisson–Boltzmann (MPB) equation by using two different approaches, namely, a field-theoretical approach where the ions are placed onto a discrete lattice, and a phenomenological free energy formulation where the excluded volume effect is added through the entropy of the solvent molecules.[17,18] The MPB equation can correct the overestimation of the ion density near highly charged surfaces in the standard PB equation.

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The dipolar interaction of the dipolar solvent molecules has attracted much attention.[19−23] Recently, Abrashkin *et al.* derived a dipolar Poisson–Boltzmann (DPB) equation which explicitly takes into account the dipolar interactions of the dipolar solvent molecules.[24] It is argued that near a highly charged surface, the assumption in the standard PB equation that the continuum dielectric medium is homogeneous is inadequate to describe the strong dielectric response of dipolar water molecules. The DPB equation is obtained on the mean-field level by coarse graining the interactions of individual dipoles and ions. The DPB equation is applied to a two-plate system with oppositely charged surfaces. From the numerical solution of the DPB equation, it is found that there is a strong accumulation of dipoles between the two charged plates, which leads to a higher dielectric constant than the bulk. Like the standard PB equation for charged surfaces where the ion densities near the charged surfaces can exceed the close-packing values, the dipole density near the charged plates is unbounded in the DPB equation, which can reach an unphysical value above the close-packing one. To prevent the overcrowding of dipoles near the charged plates, they further derived a modified dipolar Poisson–Boltzmann (MDPB) equation which takes into account the finite sizes of ions and dipolar solvent molecules. In the derivation, the ions and dipoles are assumed to be of equal sizes and they are constrained on a discrete lattice, and the incompressibility condition is imposed on the lattice.

In the study of the two-plate system of oppositely charged surfaces using the DPB equation, a background of a low dielectric solvent (e.g., either with dielectric constant of 4.5) is used for the salty aqueous solution, in order to prevent the dipoles from reaching unphysical values above the close-packing one.[24] Therefore, it is of particular interest to study the two-plate system with oppositely charged surfaces by numerically solving the MDPB equation directly without the need to use a background of a low dielectric solvent in the DPB equation. This motivated us and initiated the present work. The rest of the paper is organised as follows. In Section 2, the MDPB equation and the numerical details for solving the MDPB equation for the two-plate system using the nonlinear Multigrid method on one-dimensional finite volume meshes are presented. In Section 3, the numerical results from the MDPB equation are shown. The profiles of the polarisation and the effective dielectric constant across the two charged surfaces are displayed. It is found that at sufficiently high surface charge density, the effective dielectric constant decreases with the increase of the surface charge density. Also in this section, the applicability of the mean-field MDPB equation for highly charged systems is discussed. Finally in Section 4, the main conclusion of this work is summarised and the implication of the applicability of the MDPB equation for highly charged systems is discussed.

## 2. Model equation and numerical method

Using a mean-field field-theoretical approach, Abrashkin *et al.* derived the following dipolar Poisson–Boltzmann (DPB) equation[24]

$$\begin{aligned} & -\varepsilon_0 \nabla^2 \psi \\ = & -2C_{\mathrm{s}} e \sinh(\beta e \psi) \\ & + C_{\mathrm{d}} p_0 \boldsymbol{\nabla} \cdot \left[ \left( \frac{\boldsymbol{\nabla}\psi}{|\boldsymbol{\nabla}\psi|} \right) G(\beta p_0 |\boldsymbol{\nabla}\psi|) \right], \end{aligned} \tag{1}$$

where $\varepsilon_0$ denotes the vacuum permittivity; $\psi$ denotes the electric potential; $C_{\mathrm{s}}$ and $C_{\mathrm{d}}$ denote the 1:1 salt and dipole concentrations, respectively; $e$ is the elementary charge; $\beta = 1/(k_{\mathrm{B}}T)$ with $k_{\mathrm{B}}$ the Boltzmann constant and $T$ the absolute temperature; and $p_0$ is the magnitude of the dipolar moment of the dipolar solvent. In the above equation, the function $G(u) = \cosh(u)/u - \sinh(u)/u^2$. The above equation can be rewritten as

$$-\boldsymbol{\nabla} \cdot (\varepsilon_{\mathrm{eff}} \boldsymbol{\nabla}\psi) = -2C_{\mathrm{s}} e \sinh(\beta e \psi) \tag{2}$$

with the effective dielectric permittivity of the medium being

$$\varepsilon_{\mathrm{eff}} = \varepsilon_0 + C_{\mathrm{d}} p_0 G(\beta p_0 |\boldsymbol{\nabla}\psi|)/|\boldsymbol{\nabla}\psi|. \tag{3}$$

Taking into account the finite sizes of ions and dipoles, using a discrete lattice, Abrashkin *et al.* obtained the free energy of the salty dipolar solution

$$-\beta F = \frac{\beta\varepsilon_0}{2} \int \mathrm{d}^3\boldsymbol{r} \, |\boldsymbol{\nabla}\psi|^2 + \frac{1}{a^3} \int \mathrm{d}^3\boldsymbol{r} \log \left[ C_{\mathrm{d}} \frac{\sinh(\beta p_0 |\boldsymbol{\nabla}\psi|)}{\beta p_0 |\boldsymbol{\nabla}\psi|} + 2C_{\mathrm{s}} \cosh(\beta e \psi) \right], \tag{4}$$

where $a$ denotes the size of ions and dipoles, and $C_{\rm d} + 2C_{\rm s} = a^{-3}$. Minimizing the above free energy with respect to the electric potential, the modified dipolar Poisson–Boltzmann (MDPB) equation is obtained[24]

$$-\varepsilon_0 \nabla^2 \psi = \frac{C_{\rm d} p_0}{a^3} \boldsymbol{\nabla} \cdot \left[ \left( \frac{\boldsymbol{\nabla}\psi}{|\boldsymbol{\nabla}\psi|} \right) \frac{G\left(\beta p_0 |\boldsymbol{\nabla}\psi|\right)}{D} \right] - \frac{2C_{\rm s} e}{a^3} \frac{\sinh\left(\beta e \psi\right)}{D} \tag{5}$$

with

$$D = C_{\rm d} \frac{\sinh\left(\beta p_0 |\boldsymbol{\nabla}\psi|\right)}{\beta p_0 |\boldsymbol{\nabla}\psi|} + 2C_{\rm s} \cosh\left(\beta e \psi\right). \tag{6}$$

Then the polarisation of the dipolar solvent can be found to be

$$\boldsymbol{P} = -\frac{C_{\rm d} p_0}{a^3} \frac{G\left(\beta p_0 |\boldsymbol{\nabla}\psi|\right)/|\boldsymbol{\nabla}\psi|}{D} \boldsymbol{\nabla}\psi. \tag{7}$$

The effective dielectric permittivity is

$$\varepsilon_{\rm eff} = \varepsilon_0 - \frac{\boldsymbol{P}}{\boldsymbol{\nabla}\psi} = \varepsilon_0 + \frac{C_{\rm d} p_0}{a^3} \frac{G\left(\beta p_0 |\boldsymbol{\nabla}\psi|\right)/|\boldsymbol{\nabla}\psi|}{D}. \tag{8}$$

It should be pointed out that in obtaining the DPB and MDPB equations, the degrees of freedom of the orientation of the dipoles are integrated out in the canonical partition function, assuming isotropic orientational distribution of the dipoles. Thus in the anisotropic two-plate system studied in DPB equation,[24] the tensorial properties of the dielectric response are lost.

In the one-dimensional two-plate system where the two oppositely charged surfaces are located at $z = \pm d/2$ with charge density $\mp\sigma$, the MDPB equation reduces to

$$\begin{aligned} -\varepsilon_0 \frac{{\rm d}\psi}{{\rm d}z} &= \frac{C_{\rm d} p_0}{a^3} \frac{\rm d}{{\rm d}z} \left[ \frac{G\left(\beta p_0 {\rm d}\psi/{\rm d}z\right)}{D} \right] \\ &\quad - \frac{2C_{\rm s} e}{a^3} \frac{\sinh\left(\beta e \psi\right)}{D}, \end{aligned} \tag{9}$$

where $D = C_{\rm d} \sinh\left(\beta p_0 {\rm d}\psi/{\rm d}z\right)/\left(\beta p_0 {\rm d}\psi/{\rm d}z\right) + 2C_{\rm s} \cosh\left(\beta e \psi\right)$. The boundary condition at the two charged surfaces is

$$-\varepsilon_0 \frac{{\rm d}\psi}{{\rm d}z} = \frac{C_{\rm d} p_0}{a^3} \frac{G\left(\beta p_0 {\rm d}\psi/{\rm d}z\right)}{C_{\rm d} \sinh\left(\beta p_0 {\rm d}\psi/{\rm d}z\right)/\left(\beta p_0 {\rm d}\psi/{\rm d}z\right) + 2C_{\rm s} \cosh\left(\beta e \psi\right)} + \sigma. \tag{10}$$

The above MDPB equation can be non-dimensionalised by rescaling the electric potential and the length using $\psi' = \beta e \psi$ and $z' = z/a$, respectively, resulting in the following dimensionless equation

$$\begin{aligned} -\frac{{\rm d}^2\psi}{{\rm d}z^2} &= B \frac{\rm d}{{\rm d}z} \left[ \frac{P\left({\rm d}\psi/{\rm d}z\right) \cosh\left(P {\rm d}\psi/{\rm d}z\right) - \sinh\left(P {\rm d}\psi/{\rm d}z\right)}{\left({\rm d}\psi/{\rm d}z\right) \sinh\left(P {\rm d}\psi/{\rm d}z\right) + 2RP \left({\rm d}\psi/{\rm d}z\right)^2 \cosh\left(\psi\right)} \right] \\ &\quad - \frac{RPB\left({\rm d}\psi/{\rm d}z\right) \sinh\left(\psi\right)}{\sinh\left(P {\rm d}\psi/{\rm d}z\right) + 2RP\left({\rm d}\psi/{\rm d}z\right) \cosh\left(\psi\right)}, \end{aligned} \tag{11}$$

where $B = \beta e^2/(a\varepsilon_0)$, $P = p_0/(ae)$ and $R = C_{\rm s}/C_{\rm d}$. Note that in the above equation, the primed quantities are changed back to un-primed quantities for the sake of convenience.

The above one-dimensional (1D) MDPB equation is numerically solved using the nonlinear Multigrid method.[25,26] The dimensionless equation is discretised on one-dimensional meshes using the finite volume method in which the node values are placed in the centres of the 1D meshes. The electric potential and the electric field are obtained for each node. Also the polarisation and the dielectric permittivity on each node are obtained numerically using the expressions in Eqs. (7) and (8).

## 3. Results and discussion

In Fig. 1, the polarisations of the pure dipolar solvent without the added salt for the two-plate system against the applied electric fields are displayed. It can be seen that at relatively high electric fields, due to the high surface charge densities, the increase of the polarisation with the electric field deviates from the linear fashion.

In Fig. 2, the effective dielectric constants ($\varepsilon_{\rm r} = \varepsilon_{\rm eff}/\varepsilon_0$) in different electric fields are shown, indicating its gradual decrease with increasing electric field.

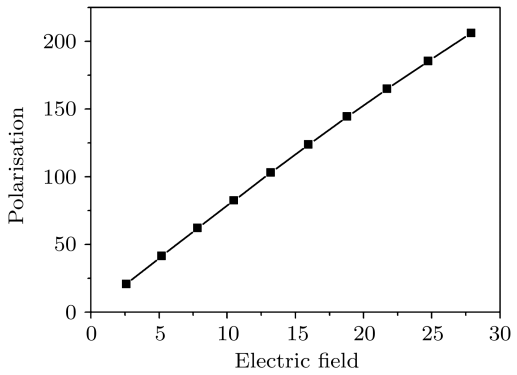



**Fig. 1.** Plot of the polarisations against electric field for a pure dipolar liquid between two oppositely charged plates at a separation of $d = 20$ Å (1 Å = 0.1 nm). The electric field and the polarisation are in units of $10^7$ V/m and $10^8$ C/m$^2$, respectively. In the following figures, the same units for the electric field and the polarisation are used. The corresponding surface charge densities are $e/872$ Å$^2$, $e/436$ Å$^2$, $e/291$ Å$^2$, $e/218$ Å$^2$, $e/174$ Å$^2$, $e/145$ Å$^2$, $e/125$ Å$^2$, $e/109$ Å$^2$, $e/97$ Å$^2$ and $e/87$ Å$^2$. In this paper, the magnitude of the dipolar moment of a water molecule is $p_0 = 1.62 \times 10^{-29}$ Cm, and the size of a water molecule is $a = 3.1$ Å, which corresponds to a dipolar concentration of $C_{\rm d} = 55$ M.

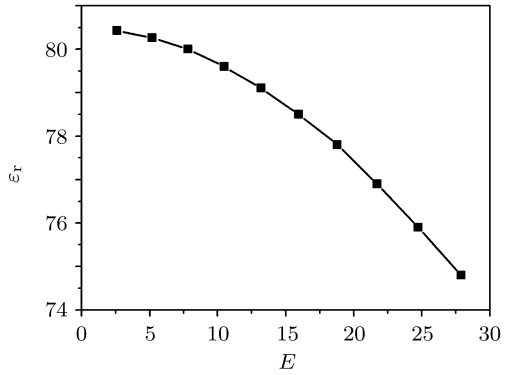



**Fig. 2.** Plot of the effective dielectric constants ($\varepsilon_{\rm r} = \varepsilon_{\rm eff}/\varepsilon_0$) of the pure dipolar solvent against the electric fields in the same systems as in Fig. 1.

In Fig. 3, the profiles of the effective dielectric constant across the two oppositely charged surfaces with different surface charge densities and salt concentrations are displayed. The four fairly straight lines correspond to a salt concentration of $10^{-5}$ M at different surface charge densities. The uppermost line obtained at a surface charge density of $e/436$ Å$^2$ corresponds to an effective dielectric constant of about 80.3, which is almost identical to the dielectric constant of 80.4 in the bulk. With the increase of the surface charge density above $e/436$ Å$^2$, the effective dielectric constant of the dipolar medium between the

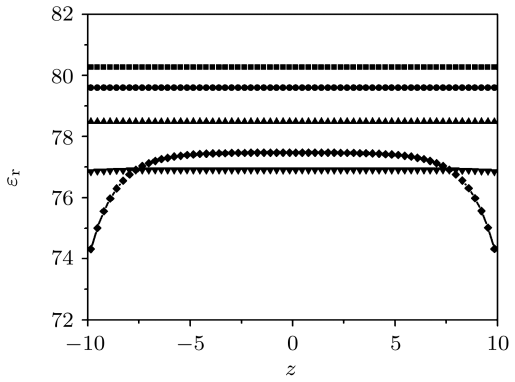



**Fig. 3.** The profiles of effective dielectric constants across two oppositely charged plates at a separation of 20 Å. The concentration of the 1:1 salt is $10^{-5}$ M for the four fairly straight lines, which respectively correspond to surface charge densities of $e/436$ Å$^2$, $e/218$ Å$^2$, $e/145$ Å$^2$ and $e/109$ Å$^2$. The curved profile corresponds to a surface charge density of $e/109$ Å$^2$ and a salt concentration of $10^{-3}$ M.

charged plates begins to decrease. The highest surface charge density used in the numerical solution of the MDPB equation for the dipolar solvent with added salt is $e/109$ Å$^2$, which is about half of that used in Ref. [24]. With further increase of the surface charge density, the convergence of our nonlinear Multigrid solver begins to deteriorate. This is due to difficulty in the proper implementation of the boundary conditions shown in Eq. (10), which is a mixed Neumann/Dirichlet boundary condition. With such a mixed boundary condition, the electric potential and the electric field at the boundary are coupled, and it is impossible to obtain their explicit values from such a single boundary condition. For the node closest to the left boundary (half a mesh size away from the boundary in the finite volume method), its first order derivative, i.e.,$\mathrm{d}\psi/\mathrm{d}z$, should in principle be computed from the second order accurate finite difference scheme $\mathrm{d}\psi/\mathrm{d}z = (\psi|_{\rm e} - \psi|_{\rm bc})/\Delta z$, where $\Delta z$ is the size of the 1D mesh, and the subscripts e and bc refer to the values on the east and west (of the boundary) faces, respectively. Because of the difficulty associated with the mixed boundary condition, its first derivative is instead obtained by the extrapolation from the first derivatives of the interior nodes. For the node closest to the right boundary, the same extrapolation scheme is used to obtain its first derivative. At a surface charge density higher than $e/109$ Å$^2$, the inaccuracy of the implementation of the mixed Neumann/Dirichlet boundary condition leads to the deterioration of the convergence of the numerical solution of the highly nonlinear MDPB equation. Like

the pure dipolar solvent without the added salt, the effective dielectric constant of a salty dipolar solution also decreases with increasing surface charge density. It is apparent from Fig. 3 that the profile for the higher salt concentration is much more curved than that corresponding to the lower salt concentration. The effective dielectric constant corresponding to the higher salt concentration attains a maximal value in the middle point between the two charged surfaces, while it reaches minimal values on the charged surfaces.

The decrease of the effective dielectric constant with the increase of both the surface charge density and the salt concentration at sufficiently high surface charge density can be qualitatively understood by careful inspection of the expression of the effective dielectric permittivity shown in Eq. (8). At the salt concentration of $10^{-5}$ M, it is fairly safe to neglect the contribution of salt ions, then the effective dielectric permittivity becomes

$$\varepsilon_{\rm eff} = \varepsilon_0 + \frac{C_{\rm d} p_0}{a^3} \frac{G\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)/\left|\boldsymbol{\nabla}\psi\right|}{C_{\rm d} \sinh\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)/\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)}. \quad (12)$$

In the limit of $\beta p_0 \left|\boldsymbol{\nabla}\psi\right| \to 0$, the effective dielectric permittivity reduces to that shown in Eq. (3) with $\varepsilon_{\rm eff} = \varepsilon_0 + \beta C_{\rm d} p_0^2/3$. However, in the limit of $\beta p_0 \left|\boldsymbol{\nabla}\psi\right| \gg 1$, equation (12) can be rewritten as

$$\begin{aligned}
\varepsilon_{\rm eff} &= \varepsilon_0 + \frac{\beta p_0^2}{a^3} \frac{\cosh\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)/\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right) - \sinh\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)/\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)^2}{\sinh\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)} \\
&= \varepsilon_0 + \beta C_{\rm d} p_0^2 \left[\frac{1}{\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)\tanh\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)} - \frac{1}{\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)^2}\right] \\
&\approx \varepsilon_0 + \beta C_{\rm d} p_0^2 \left[\frac{1}{\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)} - \frac{1}{\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)^2}\right] \\
&\approx \varepsilon_0 + \frac{\beta C_{\rm d} p_0^2}{\left(\beta p_0 \left|\boldsymbol{\nabla}\psi\right|\right)}. \quad (13)
\end{aligned}$$

Because the strength of the electric field $\left|\boldsymbol{\nabla}\psi\right|$ is proportional to the surface charge density, for sufficiently high surface charge density, the effective dielectric constant decreases with the increase of the surface charge density. The polarisation of the pure dipolar solvent without the added salt in the two-plate system in the limit of $\beta p_0 \left|\boldsymbol{\nabla}\psi\right| \gg 1$ can also be obtained

$$\begin{aligned}
\boldsymbol{P} &= -\left(\varepsilon_{\rm eff} - \varepsilon_0\right)\boldsymbol{\nabla}\psi \\
&\approx -\frac{\beta C_{\rm d} p_0^2}{\beta p_0 \left|\boldsymbol{\nabla}\psi\right|}\boldsymbol{\nabla}\psi \\
&= C_{\rm d} p_0 \boldsymbol{e}, \quad (14)
\end{aligned}$$

which corresponds to completely perfect alignment of the dipoles along the electric field line $\boldsymbol{e}$. The effect of the salt on the effective dielectric constant at sufficiently high surface charge density can also be qualitatively analysed by the inspection of Eq. (8). The effect of the salt is manifested inside the expression of $D$ which is proportional to $2C_{\rm s}\cosh\left(\beta e\psi\right)$. The dimensionless electric potentials $\beta e\psi$ at the two different salt concentrations with the same surface charge density of $e/109$ Å$^2$ are shown in Fig. 4. It can be seen that the absolute slope of the electric potential which corresponds to the magnitude of the electric field (see also Fig. 5 for the electric field) is lower for the higher salt concentration, and at the middle point between the two surfaces, the electric potential is zero. Thus the term $2C_{\rm s}\cosh\left(\beta e\psi\right)$ reaches a minimum in the middle between the two surfaces, and attains a maximal value at the boundaries. Therefore, the effective dielectric constant reaches a maximum in the middle between the two surfaces, and attains a minimal value at the boundaries, which is corroborated by the nu-

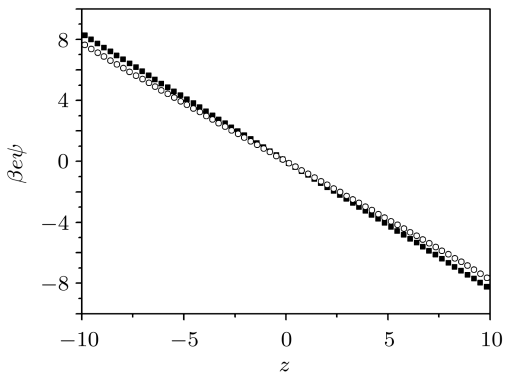



**Fig. 4.** Plots of the dimensionless electric potential ($\beta e\psi$) across two oppositely charged surfaces for two different salt concentrations ($10^{-3}$ M and $10^{-5}$ M) at a surface charge density of $e/109$ Å$^2$. The line with open circles corresponds to higher salt concentration.

merical results shown in Fig. 3. Also, with a higher salt concentration, the profile of the effective dielectric constant is curved more severely because $D$ is proportional to the salt concentration.

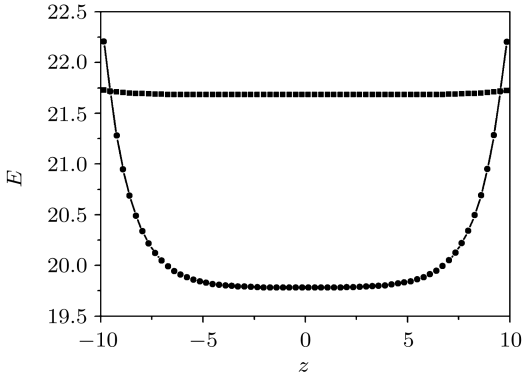



**Fig. 5.** Profiles of the electric fields across the two oppositely charged surfaces for the two different salt concentrations at a surface charge density of $e/109$ Å$^2$. The curved profile corresponds to the higher salt concentration.

In Fig. 6, the profiles of the polarisation of the dipolar solvent across the two charged plates at two different salt concentrations are shown. It can be easily seen that the polarisation at the higher salt concentration is lower for the same surface charge density.

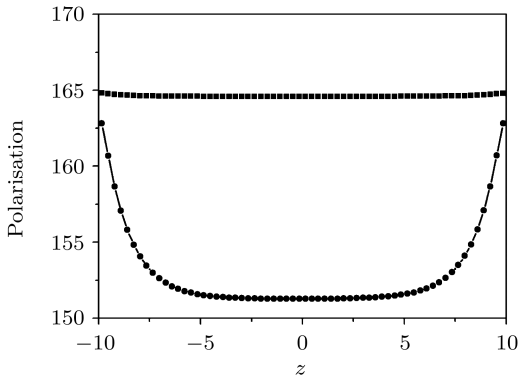



**Fig. 6.** Profiles of the polarisations across the two plates for the same systems as in Fig. 5. The curved profile corresponds to the higher salt concentration.

The decrease of the effective dielectric constant of the dipolar solution with the increase of the surface charge density at sufficiently high surface charge density inferred from the MDPB equation is in sharp contrast to the result from the DPB equation, where the opposite trend is found. As pointed out by Abrashkin *et al.*,[24] the DPB equation may overestimate the dielectric response in strongly charged systems, resulting in a crowding of dipoles and ions close to the charged surfaces with their densities exceeding the close-packing values. Whereas in the MDPB equation the finite size effect of ions and dipoles is taken into account, the presence of the denominator in Eq. (5) leads to the saturation of the densities of local ions and dipoles close to charged surfaces. Figure 3 clearly shows that there is no accumulation of dipoles between the two charged surfaces and the effective dielectric constant keeps the bulk value for surface charge densities up to $e/436$ Å$^2$. The subsequent decrease of the effective dielectric constant with further increase of the surface charge density revealed in the numerical solution of the MDPB equation seems to be inconsistent with the opposite trend in the DPB equation. This seemingly inconsistent dielectric response to high surface charge densities between the DPB and MDPB equations, in fact, has a much deeper physical origin. In the following, the different length scales involved in the charged system studied in this paper will be examined and the physical origin of the inconsistency of the dielectric response to the highly charged surfaces between the DPB and MDPB equations will be elucidated.

A characteristic length scale in ionic solutions is the so-called Bjerrum length $l_{\rm B}$, at which the Coulomb interaction between two elementary charges is comparable to the thermal energy $k_{\rm B}T$. Thus we have

$$l_{\rm B} = \frac{e^2}{4\pi\varepsilon_{\rm eff}k_{\rm B}T}. \tag{15}$$

For aqueous solutions at room temperature, the Bjerrum length $l_{\rm B} \approx 7$ Å. The second length scale is the so-called Gouy–Chapman length $\mu$, at which the thermal energy equals the counterion-charged surface electrostatic interaction. For the case of two oppositely charged surfaces, the counterion-charged surface interaction is $U(z) = \sigma e^2 z/\varepsilon_{\rm eff}$, where $z$ is the distance from the surfaces. Thus the Gouy–Chapman length is

$$\mu = \frac{1}{4\pi l_{\rm B}\sigma}. \tag{16}$$

The ratio of these two length scales defines the so-called dimensionless electrostatic coupling parameter $\Xi$[27,28]

$$\Xi = \frac{l_{\rm B}}{\mu} = 4\pi l_{\rm B}^2\sigma. \tag{17}$$

For small coupling parameter $\Xi \ll 1$, the Gouy–Chapman length is relatively large, indicating a loosely bound counterion cloud at the charged surface. Thus in this weak-coupling regime, mean-field theories such as the PB equation are applicable.[27] For large coupling parameter $\Xi \gg 1$, the Gouy–Chapman length is relatively small, which indicates that the

counterions are strongly attracted to the charged surface. For counterions localised near the charged surface, the local charge neutrality implies a typical lateral separation distance

$$a_{\perp} \sim \sqrt{\frac{1}{\sigma}}. \tag{18}$$

This length scale is related to the Gouy–Chapman length as

$$\frac{a_{\perp}}{\mu} \sim \sqrt{\Xi}. \tag{19}$$

For large coupling parameter $\Xi \gg 1$, the counterions essentially form a quasi two-dimensional (2D) layer as their lateral separation at the surface is much larger than the Gouy–Chapman length. In such a quasi 2D layer, the mutual repulsions between counterions freeze out the lateral degrees of freedom. Thus, the counterions become laterally correlated. Therefore, in the strong-coupling regime, the mean-field approximations, such as the Poisson–Boltzmann equation, break down.[27]

Using the parameter in Fig. 3, the coupling parameter $\Xi$ can be estimated. For the lowest surface charge density of $e/436$ Å$^2$ used in Fig. 3, it can be easily found that $\Xi \approx 1.4$, whereas for the highest surface charge density of $e/109$ Å$^2$, the coupling parameter $\Xi \approx 5.6$. Then it is apparent that at a surface charge density as high as $e/109$ Å$^2$, the mean-field theory is incapable of describing the electrostatics of such a highly charged system. The surface charge density of $e/436$ Å$^2$ at which the coupling parameter $\Xi \sim 1$ would be the highest surface charge density at which the mean-field theory is applicable. The effective dielectric constant for pure water confined between two oppositely charged plates, obtained from the DPB equation[24]

$$\varepsilon_{\rm r} = \frac{\varepsilon_{\rm eff}}{\varepsilon_0} = 1 + C_{\rm d} p_0 \frac{G\left(\beta p_0 \left|\boldsymbol{E}\right|\right)}{\varepsilon_0 \left|\boldsymbol{E}\right|} \tag{20}$$

is plotted against the dimensionless electric field $\beta p_0 |\boldsymbol{E}|$ in Fig. 7. It can be easily seen that, at the surface charge density of $e/436$ Å$^2$ at which the coupling parameter $\Xi \sim 1$ with $\beta p_0 |\boldsymbol{E}| \approx 0.2$, the effective dielectric constant is virtually the same as that in the bulk dipolar solution.

Based on the above discussion concerning the applicability of mean-field theories in charged systems, the curve in Fig. 3 corresponding to a salt concentration of $10^{-3}$ M and a surface charge density of $e/109$ Å$^2$ ($\Xi \approx 5.6$) should be read with caution. For large electrostatic coupling parameter $\Xi$ and relatively high salt concentrations, the effect of counterions is pronounced, and the counterions are strongly attracted to the charged surface and become laterally correlated.

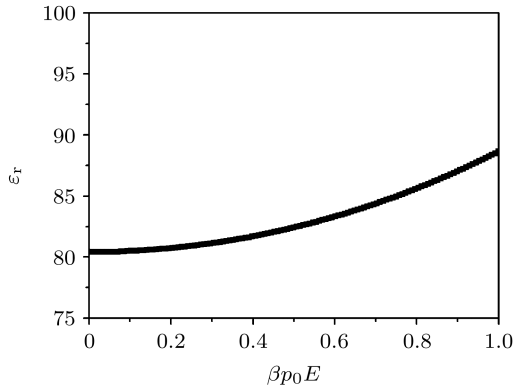



**Fig. 7.** Plot of the effective dielectric constant against the dimensionless electric field $\beta p_0 |\boldsymbol{E}|$ for pure water confined between two oppositely charged surfaces from the DPB equation.

For salty dipolar solutions, there are two additional length scales associated with the salt ions. The first one is the mean distance between the salt ions in the bulk, which is denoted as $a_{\rm s}$ and is related to the salt concentration $C_{\rm s}$ via $C_{\rm s} \sim a_{\rm s}^{-3}$. The second one is the electrostatic screening length of the salt ions, which is denoted as $\kappa$ and is related to the salt concentration via $\kappa^{-2} = 8\pi l_{\rm B} C_{\rm s}$. For a salt concentration of $10^{-5}$ M, $a_{\rm s} \approx 550$ Å, and $\kappa \approx 960$ Å. Clearly, the mean distance between the salt ions is much larger than the separation between the two oppositely charged surfaces studied in Fig. 3. Thus, it is more appropriate to have a much higher salt concentration in order for the continuum field approach such as the dipolar Poisson–Boltzmann equation to be applicable.

Now, it is very clear that in the weak-coupling regime with $\Xi < 1$, where the mean-field PB, MPB, DPB and MDPB equations work well, the effective dielectric constant in the two-plate system is the same as the bulk value of the dipolar solution, and the nonlinear dielectric response of the dipolar solvent near the charged surface is very weak. Then, it suffices to use the MPB equation with the effective dielectric constant of the bulk solution instead of the MDPB equation to study the electrostatics and ion adsorption in charged systems with interfaces where the finite size effect of ions near the charged surfaces is important.

Very recently, an extension of the DPB model, called the Yukawa Langevin Poisson–Boltzmann

(YULP) model was proposed to study the organisation of water molecules around bio-molecules.[29] Unlike the DPB and MDPB equations, in the YULP model, an additional attractive field at each position on the lattice, which is derived from a Yukawa potential, is introduced. However, the regime in which the organisation of water molecules around bio-molecules is studied corresponds to electrostatic coupling parameter $\Xi > 10$. Clearly, this does not fall into the weak-coupling regime. Furthermore, as shown in Fig. 1 in Ref. [29], the two water layers around the protein surface cannot be clearly identified because the water radial density profiles do not present a significant trough between the two water layers. Thus, the lack of molecular details of water dipoles around the charged surface and the breakdown of the mean-field theory in the YULP model imply that the YULP model presents no advantage over the MPB equation. It is clear from this work that continuum mean-field theories based on the PB equation are unable to show molecular details and the nonlinear response of water dipoles near charged surfaces. To study the molecular organisation and the nonlinear response of water dipoles near charged surfaces, it is more appropriate to use other types of models, such as the mean sphere approximation theory,[30] reference hyper-netted chain model[31] and the density functional theory.[32]

## 4. Conclusions

In this work, the MDPB equation, where the dipolar features of solvent molecules and also the finite size effects of ions and dipolar solvent molecules are explicitly taken into account on a mean-field level, is studied numerically for a two-plate system with oppositely charged surfaces. In the system, a 1:1 salt aqueous solution is confined between two oppositely charged planes. In the MDPB equation, the free energy of the system is derived from the assumptions that the ions and water dipoles are constrained on a lattice with equal sizes and the system is incompressible. The MDPB equation is solved numerically using the nonlinear Multigrid method on 1D finite volume meshes. From the numerical results, the profiles of the polarisation and the effective dielectric constant across the two oppositely charged surfaces are obtained.

The numerical results from the MDPB equation show that at low salt concentration, the effective dielectric constant remains a constant across the two charged surfaces. The flatness of the profiles of the effective dielectric constant at high surface charge densities indicates that there is no accumulation of dipoles between the charged surfaces. Whereas in the DPB equation where the finite size effects of ions and dipoles are not taken into account, the previous study has shown that there is a strong accumulation of dipoles between the charged surfaces and a dielectric constant jump is found close to the charged surfaces. As expected, the MDPB equation prevents the overcrowding of dipoles near the charged surfaces.

For a high enough surface charge density, numerical results from the MDPB equation reveal that the effective dielectric constant decreases with the increase of the surface charge density, which is unexpected. Furthermore, increasing the salt concentration at the same surface charge density leads to the decrease of the effective dielectric constant close to the charged surfaces. This opposite trend to that from the DPB equation is due to the fact that the mean-field approach breaks down in such highly charged systems where the counterions are strongly attracted to the charged surfaces and form a quasi 2D layer. In this 2D layer, the ions are laterally correlated and surrounded by a large correlation hole. A measure of the applicability of the mean-field theories such as the PB, MPB, DPB and MDPB equations to charged systems is the so-called electrostatic coupling parameter $\Xi$, which is the ratio of Bjerrum length to Gouy–Chapman length. Strictly speaking, mean-field theories work well in the weak-coupling regime where $\Xi \ll 1$. In practice, mean-field theories should work in the regime where $\Xi < 1$, which is supported by our numerical results for the MDPB equation. In the regime where the surface charge density is so high that the coupling parameter $\Xi > 1$, the mean-field theories become invalid, as revealed by the inconsistency between the DPB and MDPB equations.

In the weak-coupling regime where the MDPB equation is valid, the dielectric permittivity is a constant across the two charged surfaces and there is no accumulation of dipoles near the charged surfaces. Therefore, in the weak-coupling regime where $\Xi < 1$, the nonlinear response of the dipolar interaction is extremely weak, and the effect of the dipolar interaction of the solvent dipoles amounts to the renormalisation of the dielectric constant of the medium which is the linear response of the dipolar interaction. Thus, there are no physical and computational advantages for the use of the MDPB equation over the MPB equation where the effect of the dipolar interaction of solvent dipoles is implicitly taken into account in the renormalised dielectric constant.

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