

Dielectric Constant of Ionic Solutions: A Field-Theory Approach

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We study the variation of the dielectric response of a dielectric liquid (e.g. water) when a salt is added to the solution. Employing field-theoretical methods, we expand the Gibbs free energy to first order in a loop expansion and calculate self-consistently the dielectric constant. We predict analytically the dielectric decrement which depends on the ionic strength in a complex way. Furthermore, a qualitative description of the hydration shell is found and is characterized by a single length scale. Our prediction fits rather well a large range of concentrations for different salts using only one fit parameter related to the size of ions and dipoles.

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Electrostatic interactions in aqueous media between dipoles and charged objects such as ions, colloidal particles, and interfaces, play an important role in electrochemistry, biology, and materials science. The century-old Poisson-Boltzmann (PB) theory gives a simple and powerful description for numerous systems, taking into account only Coulombic interactions on a mean-field level, treating ions as pointlike particles and the aqueous solution as a continuous and homogeneous dielectric medium with a dielectric constant, ϵ_w . The PB theory succeeded over the years in capturing much of the underlying physics of electrolyte solutions, and, in particular, is successful when applied to monovalent ions and weak surface charges [1–4].

The PB theory has several limitations. It does not take into account the correlations between the charges, nor does it allow for any fluctuations beyond mean field. This leads to significant unaccounted corrections in cases of high charge density, especially near charged surfaces and interfaces [5]. In order to improve upon the PB theory, several extensions have been offered in recent years, and effects of correlations and fluctuations for charged interfaces were considered, for example, by using integral equation theories [6] and linearized hypernetted chain models [7,8]. In other approaches [9], the PB theory was modified in a simple and elegant way to include steric and other ionic-specific effects preventing ions from accumulating near a charged surface for very high ionic concentrations. Furthermore, in the well-known Deryagin-Landau-Verwey-Overbeek theory [10], van der Waals attractive interactions were added to the electrostatic repulsion in order to explain charged colloidal stability. More recently, Monte Carlo and molecular dynamics simulations were employed in order to study specific solvents and solutes and the interaction between them [11–16]. Some of these methods were also used to study the dielectric constant of ionic solutions [7,8,16].

The PB theory as well as other *primitive models* of ionic solutions [17] assume that the ions are immersed in a continuum dielectric background characterized by the dielectric constant of water, ϵ_w . Hence, in order to model the experimentally known dielectric decrement phenomenon [9,18–20], one needs to employ more refined theories, which take into account ion-dipole correlations and fluctuations. The electric decrement stems from the fact that the local electric field around each ion is greater than the external field, and orients the dipolar water molecules in its vicinity. This creates a *hydration shell* [21] that encircles the ions. The total response of dipoles to the external field is thus smaller and leads to a reduction in the dielectric constant. In dilute solutions, the dielectric constant depends linearly on c_s , the salt concentration, $\epsilon(c_s) = \epsilon_w - \gamma c_s$, where γ is the coefficient of the linear term. The value of γ/ϵ_0 is ion specific and ranges from 8 M^{-1} to 20 M^{-1} , for concentrations up to 1.5 M. At higher c_s values, noticeable deviations from linearity are observed and are due to ion-ion interactions [18–20].

In this Letter we go beyond the standard PB theory and investigate the microscopic origin of the dielectric decrement. We construct the field theory for a grand-canonical ensemble of pointlike ions and dipoles. On a mean-field level, we obtain an analytic description of the hydration shell around ions and calculate the average dielectric constant in the shell. Then, using a field-theoretical approach we examine the dielectric decrement by a one-loop calculation. A closed-form formula for the dielectric constant is obtained and depends on a single length scale, related to the typical size of ions and water molecules. Our results show a substantial contribution arising from the one-loop correction terms, and deviate from the linear relation, $\epsilon(c_s) = \epsilon_w - \gamma c_s$. We fit the calculated $\epsilon(c_s)$ and compare it with the experimental data for several monovalent ions. The results agree rather well for a

wide range of ionic concentrations, even in the nonlinear decrement regime.

Although our formulation is very general, in this Letter we focus on the dielectric constant variation for ionic solutions. The solvent (water) is modeled as a liquid of pointlike permanent dipoles of dipolar moment \mathbf{p}_0 and the symmetric 1:1 monovalent salt as a liquid of pointlike charges, $\pm e$. Using the standard Hubbard-Stratonovich transformation [22], the grand-canonical partition function Z and free energy $F = -\beta^{-1} \log Z[\rho(\mathbf{r})]$ in the presence of an external charge distribution $\rho(\mathbf{r})$ can be written as a functional integral over the real field $\phi(\mathbf{r})$ that is conjugate to $\rho(\mathbf{r})$

$$Z[\rho(\mathbf{r})] = \int \mathcal{D}\phi(\mathbf{r}) \exp\left(-\beta \int d^3\mathbf{r} f(\phi(\mathbf{r})) - i\beta \int d^3\mathbf{r} \phi(\mathbf{r})\rho(\mathbf{r})\right), \quad (1)$$

with

$$\beta f(\phi(\mathbf{r})) = \frac{\beta\epsilon_0}{2} [\nabla\phi(\mathbf{r})]^2 - 2\lambda_s \cos[\beta e\phi(\mathbf{r})] - \lambda_d \frac{\sin(\beta p_0 |\nabla\phi(\mathbf{r})|)}{\beta p_0 |\nabla\phi(\mathbf{r})|}, \quad (2)$$

where $\beta = 1/k_B T$, and $k_B T$ is the thermal energy. The activity coefficients of the salt λ_s and water λ_d are determined by solving the implicit equations

$$\frac{\lambda_s}{V} \frac{\partial}{\partial \lambda_s} \log Z = c_s, \quad \frac{\lambda_d}{V} \frac{\partial}{\partial \lambda_d} \log Z = c_d, \quad (3)$$

where V is the volume and c_s and c_d are, respectively, the salt concentration and density of water molecules.

The electrostatic potential $\Psi(\mathbf{r})$ is given by

$$\Psi(\mathbf{r}) = -\frac{1}{\beta} \frac{\delta \log Z[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = i\langle \phi(\mathbf{r}) \rangle, \quad (4)$$

where the bracket $\langle \dots \rangle$ denotes the thermal average with the Boltzmann weight given in Eq. (1).

The Gibbs free energy G is a function of $\Psi(\mathbf{r})$ and is defined as the Legendre transform of $F[\rho(\mathbf{r})]$ with respect to $\rho(\mathbf{r})$ through the equations

$$G[\Psi(\mathbf{r})] = F[\rho(\mathbf{r})] - \int d^3\mathbf{r} \Psi(\mathbf{r})\rho(\mathbf{r}), \quad (5)$$

$$\Psi(\mathbf{r}) = \frac{\delta F[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})},$$

from which we deduce the Legendre relation

$$\rho(\mathbf{r}) = -\frac{\delta G[\Psi(\mathbf{r})]}{\delta \Psi(\mathbf{r})}, \quad (6)$$

The dielectric tensor $\epsilon_{\alpha\beta}$ is defined through the Fourier transform,

$$\epsilon_{\alpha\beta} = \frac{\partial^2}{\partial p_\alpha \partial p_\beta} \int d^3\mathbf{r} e^{i\mathbf{p}\cdot\mathbf{r}} \frac{\delta^2 G[\Psi(\mathbf{r})]}{\delta \Psi(\mathbf{r}) \delta \Psi(0)} \Big|_{\Psi=0, \mathbf{p}=0}. \quad (7)$$

In our present study, the dielectric tensor for isotropic aqueous solutions is diagonal $\epsilon_{\alpha\beta} = \epsilon \delta_{\alpha\beta}$, and our aim is to calculate its variation as a function of the salt concentration c_s . Following Eq. (7), we need only to calculate the coefficient of the $|\nabla\Psi(\mathbf{r})|^2$ terms in the Gibbs free energy $G[\Psi(\mathbf{r})]$.

On the mean-field level, the Gibbs free energy for the dipolar PB system, G_{DPB} , is

$$\beta G_{\text{DPB}}[\Psi] = -\frac{\beta\epsilon_0}{2} (\nabla\Psi)^2 - 2c_s \cosh(\beta e\Psi) - c_d g(u), \quad (8)$$

with $\mathbf{u} = \beta p_0 \nabla\Psi(\mathbf{r})$, $u = |\mathbf{u}|$, and $g(u) = \sinh u/u$. The dipolar Poisson-Boltzmann (DPB) equation is an extension of the standard PB equation, and can be derived via a variational principle from Eq. (8),

$$\epsilon_0 \nabla^2 \Psi = 2c_s e \sinh(\beta e\Psi) - c_d p_0 \nabla \cdot \left[\frac{\nabla\Psi}{|\nabla\Psi|} \mathcal{G}(\beta p_0 |\nabla\Psi|) \right], \quad (9)$$

where the function $\mathcal{G} = g'(u) = \cosh u/u - \sinh u/u^2$ is related to the Langevin function $L(u) = \coth(u) - 1/u$.

The dielectric constant ϵ_{DPB} is calculated by substituting G_{DPB} into Eq. (7). The result is the same as in Ref. [23],

$$\epsilon_{\text{DPB}} = \epsilon_0 + \beta p_0^2 c_d / 3. \quad (10)$$

As can be seen above, the dielectric response depends on the dipole (but not the ion) density c_d and, hence, cannot explain the dielectric decrement. At room temperature, $T = 300$ K, and for pure water with dipolar moment $p_0 = 1.8$ D and density $c_d = 55$ M, the obtained value of ϵ is $\epsilon_{\text{DPB}} \approx 11.1\epsilon_0$. Note that this value is much smaller than the measured water value $\epsilon_w \approx 80\epsilon_0$. This is not surprising [23] since Eq. (10) is a dilute gas approximation and does not capture the correlation effects in the case of dense liquid water as well as the finite size of water molecules.

It is still possible, however, to circumvent this drawback by solving the DPB equation, Eq. (9), around a fixed pointlike ion, and showing the existence of a hydration shell around it. Expanding \mathcal{G} in a Taylor series, the dielectric constant is extracted as a function of the distance r from the ion,

$$\epsilon(r) \approx \frac{\epsilon_{\text{DPB}}}{3h^2(l_h/r) + 1}, \quad (11)$$

where the function $h(u)$ is obtained by solving a cubic equation,

$$h(u) = \left[\sqrt{\frac{1}{27} + \frac{u}{4} + \frac{\sqrt{u}}{2}} \right]^{1/3} - \left[\sqrt{\frac{1}{27} + \frac{u}{4} - \frac{\sqrt{u}}{2}} \right]^{1/3}. \quad (12)$$

The length, $l_h^2 = l_B d / \sqrt{10}$ in Eq. (11), depends both on the dipole size $d = p_0/q$ and the Bjerrum length, $l_B = e^2/4\pi\epsilon_{\text{DPB}}k_B T$. It is the only length scale in the problem characterizing the hydration shell thickness as can be seen from the behavior of $\epsilon(r)$ [inset of Fig. 1]. In the vicinity of the ion ($r \leq l_h$), the dielectric response is very small and it smoothly rises to bulk values as the influence of the ion decreases, within distances of a few l_h .

By averaging ϵ of Eq. (11) over a sphere of radius R around each ion, and equating R with the typical distance between two ions, $(2c_s)^{-1/3}/2$, at concentration c_s , we obtain the expression of $\langle\epsilon(c_s)\rangle$. As can be seen in Fig. 1, the nonlinear dielectric decrement is reproduced and fits rather well the experimental data for RbCl and CsCl salts of Ref. [19]. For low salt concentration, the averaging of ϵ can be done analytically and results in a linear decrement with $\gamma \approx 110\epsilon_{\text{DPB}}l_h^3$, which is proportional to the hydration shell volume. Using parameter values as in Fig. 1, we get $\gamma/\epsilon_0 \approx 17 \text{ M}^{-1}$.

So far, in order to induce the necessary ion-dipole correlations, we had to rely on calculating the dielectric response around a single fixed ion, which gives the dielectric decrement in an approximated way. Moreover, the validity of the DPB theory can be justified only in the dilute limit, where the dipole-dipole fluctuations are not important.

To overcome this limitation a more complete treatment of the statistical mechanics of ionic and dipolar degrees of freedom (including their interactions) is developed.

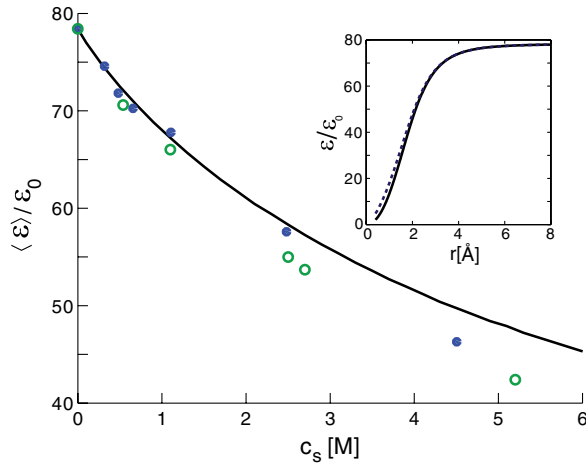


FIG. 1 (color online). The dielectric constant $\langle\epsilon\rangle$ averaged inside a specific volume around a single ion (solid line) as function of ionic concentration, c_s . The comparison is done with experimental values for RbCl (empty circles) and CsCl (full circles) [19]. In the inset, the exact (solid line) and approximated [dashed line, Eq. (11)] solutions of the DPB equation (9) are shown as a function of the distance r from a point charge (ion). Choosing as a fit parameter the dipole moment of water to be $p_0 = 4.8 \text{ D}$ (instead of the physical value $p_0 = 1.8 \text{ D}$) [23] allows us to obtain $\epsilon_{\text{DPB}} = 80\epsilon_0$ and $l_h \approx 1.5 \text{ \AA}$.

We generalize the Debye-Hückel approximation to dipolar systems in the presence of salt, via a loop expansion [24,25] of the Gibbs free energy, $G = G_{\text{DPB}} + \Delta G$. To one-loop order, the calculation of ΔG yields

$$\Delta G[\Psi(\mathbf{r})] = \frac{1}{2\beta} \text{Tr} \log[-\epsilon_0 \nabla^2 + 2\lambda_s \beta e^2 \cosh(\beta e \Psi(\mathbf{r})) + \lambda_d \beta p_0^2 (\partial_\alpha \Gamma_{\alpha\gamma}(\mathbf{r}) \partial_\gamma + \Gamma_{\alpha\gamma}(\mathbf{r}) \partial_\alpha \cdot \partial_\gamma)], \quad (13)$$

with

$$\Gamma_{\alpha\gamma}(\mathbf{r}) = \delta_{\alpha\gamma} \frac{g'(u)}{u} - \frac{u_\alpha u_\gamma}{u^2} \left(\frac{g'(u)}{u} - g''(u) \right). \quad (14)$$

To get a consistent expression for the dielectric constant we need to pay extra attention in the loop expansion to the expressions of the ion and dipole activities, λ_s and λ_d . While at mean-field level λ_s and λ_d are equal to the ion and dipole (water) densities, c_s and c_d , respectively, their corrections are derived by expanding Eq. (3) to one-loop order. To this order, only the correction to λ_d will affect the mean-field value of the dielectric constant, ϵ_{DPB} , and is written as

$$\lambda_d = c_d - \frac{2\pi}{3a^3} \frac{\epsilon_{\text{DPB}} - \epsilon_0}{\epsilon_{\text{DPB}}} \left[1 - \frac{3}{4\pi^2} (\kappa_D a)^2 + \frac{3}{8\pi^3} (\kappa_D a)^3 \tan^{-1} \frac{2\pi}{\kappa_D a} \right], \quad (15)$$

where a is a microscopic cutoff length and $\kappa_D = \sqrt{8\pi l_B c_s}$ is the inverse Debye length. The origin of the cutoff in our formulation is related to the fact that Coulombic interactions diverge at zero distance, while in reality such a divergence is avoided because of steric repulsion. An alternative elegant way of avoiding the divergence is to use the self-energy regulating technique [26]. However for the sake of simplicity, we use the cutoff length a , which is related to the minimal distance between adjacent dipoles and charges, and thus indirectly also to the size of dipoles and ions. By introducing a minimal distance, we also avoid unphysically high dipolar concentrations in the vicinity of the ions.

We can now calculate consistently the corrections to the dielectric constant up to one-loop order. The correction term can be split into water and salt contributions, $\epsilon - \epsilon_{\text{DPB}} = \Delta\epsilon_d + \Delta\epsilon_s$,

$$\Delta\epsilon_d = \frac{(\epsilon_{\text{DPB}} - \epsilon_0)^2}{\epsilon_{\text{DPB}}} \frac{4\pi}{3c_d a^3}, \quad (16)$$

$$\Delta\epsilon_s = -\frac{(\epsilon_{\text{DPB}} - \epsilon_0)^2}{\epsilon_{\text{DPB}}} \frac{\kappa_D^2}{\pi c_d a} \left(1 - \frac{\kappa_D a}{2\pi} \tan^{-1} \frac{2\pi}{\kappa_D a} \right).$$

The term $\Delta\epsilon_d$ represents the fluctuation effect of the water dipoles beyond the mean-field DPB level. It varies as $\sim 1/(c_d a^3)$. This pure water fluctuation term essentially adds a positive numerical prefactor of rather large magnitude

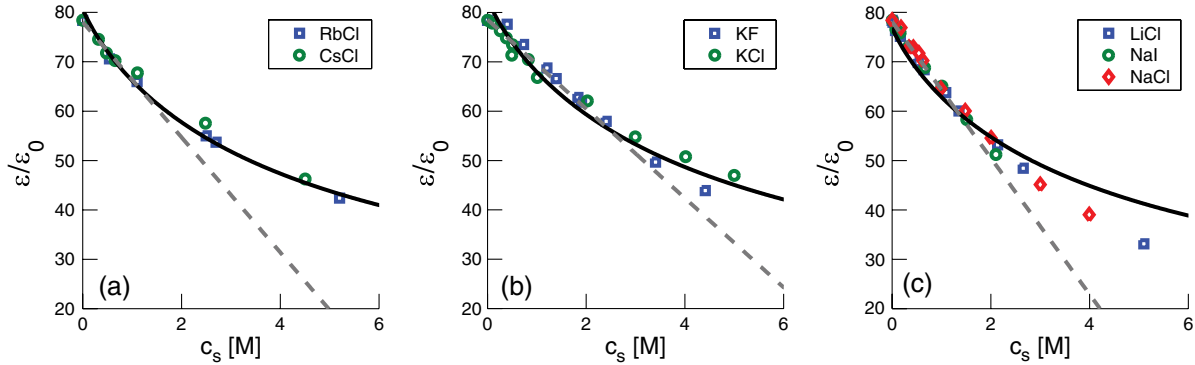


FIG. 2 (color online). Comparison of the predicted dielectric constant ε from Eq. (16), with experimental data from Ref. [19], as function of ionic concentration c_s for various salts. The theoretical prediction (solid line) was calculated using a as a fitting parameter. In (a) the fit is for RbCl and CsCl salts with $a = 2.66$ Å; in (b) the fit is for KF and KCl with $a = 2.64$ Å; while in (c) the fit is for LiCl, NaI, and NaCl with $a = 2.71$ Å. The dashed lines are the linear fit to the data in the low $c_s \leq 1$ M range. The slope of the linear fit is $\gamma/\varepsilon_0 = 11.7$ M $^{-1}$ in (a), 9.0 M $^{-1}$ in (b), and 13.8 M $^{-1}$ in (c). The value of γ for each salt varies by about 10–20% and the linear fit should be taken as representative of the low c_s behavior.

to the mean-field value of ε_{DPB} , meaning that the one-loop correction is important even for the pure water case.

The second term $\Delta\varepsilon_s$ has by itself two contributions. The leading term in the dilute solution limit, $\kappa_D a \ll 1$, depends linearly on the salt concentration, $\Delta\varepsilon_s = -\gamma c_s$, with

$$\gamma = \frac{(\varepsilon_{\text{DPB}} - \varepsilon_0)^2}{\varepsilon_{\text{DPB}}} \frac{8l_B}{c_d a}. \quad (17)$$

When the Debye length κ_D^{-1} is of the same order of magnitude as a (high salt limit), the last term in $\Delta\varepsilon_s$ becomes dominant and the dielectric decrement levels off until eventually it will reverse the trend and may even cause a *dielectric increment* as seen in some experiments in the very high salt limit [19].

We compare our prediction for the dielectric constant ε , Eq. (16), to experimental values [19] for seven different ionic solutions in concentration range of 0–6 M. We separate the seven salts into three subgroup according to the size of the alkaline cations as presented in the three parts of Fig. 2. In each of the figure parts the a parameter is fitted separately. We treat a as a free parameter and find its value by the best fit of our prediction, Eq. (16), to experimental data, while keeping the physical value of the water dipolar moment, $p_0 = 1.8$ D. The best fit to the data can be seen in Fig. 2(a) and corresponds to the largest ionic size of Cs $^+$ and Rb $^+$. In Fig. 2(b) the fit for K $^+$ ions is also quite good, while in Fig. 2(c) for the smallest ions, Na $^+$ and Li $^+$, and especially for the larger values of $c_s \geq 4$ M, the deviation is more pronounced.

Note that our formula takes into account only in a broad sense the finite size of ions (and the distance of closest approach between them) via the a parameter. It is beyond the level of the theory to give more specific ionic predictions. Hence, the obtained value of $a \approx 2.7$ Å is not very sensitive to the type of salt, but its main contribution comes

from the water dipoles themselves whose diameter [27] is about 2.75 Å. On the other hand, as can be clearly seen from Fig. 2, important cooperative effects of ions and dipoles are accounted for in our nonlinear expression for $\varepsilon(c_s)$. For small c_s , the dashed line represents the best linear fit [28] and works well only when $c_s \leq 1$ M, while the nonlinear prediction of Eq. (16) succeeds in fitting the large concentration range as well.

In conclusion, we are able to reproduce rather well the linear and nonlinear dielectric decrement behavior over a large range of ionic concentrations, and the obtained values of ε are in quantitative agreement with the data for several types of monovalent salts. In addition, we found a qualitative description of the hydration shell characterized by a single length scale, l_h . Note that our model does not contain any significant ionic-specific effects. To improve on the latter, we would need to include ionic finite size and specific nonelectrostatic short-range interactions. These modifications would affect the dielectric constant and viscosity of the solution as well as its surface tension.

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- [28] Note that from Eq. (17) we get $\gamma/\epsilon_0 \approx 26 \text{ M}^{-1}$ for $a = 2.7 \text{ \AA}$.